Acoustic Emulsions of Liquid, Near-Critical Carbon Dioxide and Water: Application to Synthetic Chemistry through Reaction Engineering

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ACOUSTIC EMULSIONS OF LIQUID, NEAR-CRITICAL CARBON DIOXIDE AND WATER: APPLICATION TO SYNTHETIC CHEMISTRY THROUGH REACTION ENGINEERING

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ABSTRACT

The need to eliminate hazardous solvents, such as methanol, toluene, and dichloromethane, in specialty and pharmaceutical chemical synthesis applications has motivated the development of alternative approaches. Because of its environmental compatibility, low cost, and favorable physicochemical properties, supercritical carbon dioxide (scCO₂) has been actively considered to replace conventional hydrocarbon solvents. Progress towards this objective has been impressive, for example scCO₂ is used as a selective extraction solvent in several commercial processes. By comparison, development of scCO₂ as a reaction solvent has been much less successful due to its limited solvation power. Furthermore, the rates of reactions conducted in scCO₂ tend to be slower than and their selectivities are comparable to those observed in hydrocarbon solvents.

This research focused on development of water/carbon dioxide biphasic reaction systems as an engineering solution to increase reaction rates and manipulate selectivity while preserving environmental compatibility of scCO₂. Emulsification by power ultrasound was selected as an additive-free means to bring near-critical liquid carbon dioxide and water into intimate contact and increase interphase transport. With this approach, the complementary solvation powers of the two solvents could be utilized to expand the range of potential chemical transformations. Carbon dioxide was envisioned as a delivery solvent, allowing access to the unique abilities of water to accelerate organic reactions while influencing their product spectrum.

First, the partitioning behavior of organic solutes was investigated with the objective of developing empirical correlations for estimating partition coefficients. The available literature database was limited primarily to substituted phenols. This study nearly doubled the number of compounds for which carbon dioxide/water partition coefficient data are known to include a wider range of aromatic, aliphatic, and heterocyclic compounds. Several existing correlation methods, including a comparison
to water solubility, estimation using octanol/water partition coefficients, and estimation using linear solvation energy relationships, were used. Good correlations were found using water solubility and octanol/water partition coefficients ($\pm 0.4 \log_{10}$ mole fraction units), provided that compounds with hydrogen bond donating ability were excluded from the analysis. A linear solvation energy relationship with optimized coefficients was found to accurately predict partition coefficients within $\pm 0.2 \log_{10}$ mole fraction units and was not limited to compounds that lack hydrogen bond donating ability. In general, such correlations should be useful for screening chemical reactions and for developing reactor designs.

Power ultrasound at a frequency of 20 kHz was used to generate emulsions containing liquid, near-critical carbon dioxide and water. Since no surfactants were used, sonication simultaneously generated emulsions with water and carbon dioxide continuous phases. Visual observation and turbidity measurements indicated that all types of emulsions broke spontaneously within 30 minutes. The short lifetimes of these surfactant-free emulsions is expected to be an advantage for commercial operation where phase entrainment is considered a contaminant. Pulsed ultrasound was found to maintain emulsions until sonication was terminated (i.e., up to several hours). Novel techniques were developed to characterize the emulsions. The concentration of water in the water/carbon dioxide emulsion was measured as 10% by volume, while that of carbon dioxide in the carbon dioxide/water emulsion was 5%. Increasing the sonic power monotonically increased the volume fractions of the dispersed phases, though the effect saturated at roughly 0.5 W cm$^{-3}$. A threshold power (equal to roughly 0.1 W cm$^{-3}$) was observed for formation of carbon dioxide/water emulsion but not the carbon dioxide/water emulsion. Video enhanced microscopy was used to image emulsion droplets using a high-pressure microreactor. The Sauter diameter (that is the volume-surface area average diameter) of water droplets was 10 $\mu$m, while that of carbon dioxide droplets was 15 $\mu$m. Droplet distributions were roughly log normal. Based on these measurements, the carbon dioxide/water interfacial area increased more than 1000-fold during sonication. Carbon dioxide/water emulsions broke primarily by settling while the water/carbon dioxide emulsions broke via a combination of coagulation and settling.

At low power densities (i.e., below 0.1 W cm$^{-3}$), ultrasound generates waves at the water/carbon dioxide interface which formed dilute dispersions of water droplets. At higher power densities, emulsification occurred by a cavitational mechanism. Since large hydrostatic pressures were expected to suppress cavitation, this result was somewhat surprising and merited further consideration. Image analysis clearly indicated cavity formation in water pressurized by carbon dioxide up to 120 bar. Carbon dioxide, on the other hand, cavitated only near its vapor pressure. Sonochemical oxidation of potassium iodide did not occur in water pressurized to 80 bar with carbon dioxide, indicating that the maximum temperature attained during bubble collapse was insufficient to produce hydroxyl radicals. Pitting on the tip of the sonic horn, indicative of the formation of cavitational microjets, was observed. In summary, cavitation appears to play a dominant role in the formation of water/carbon dioxide emulsions at power densities great than 0.1 W cm$^{-3}$.
The hydrolysis of benzoyl halides was used as a model reaction for investigating mass transport in the water/carbon dioxide systems. Benzoyl chloride hydrolysis was accelerated 100-fold by sonication, with the accelerative effect saturating at roughly 0.5 W cm\(^{-3}\). The observed reaction rate followed a trend with respect to power similar to that observed for emulsion concentrations. Hydrolysis rates of benzoyl halides representing a wide range of intrinsic reactivities were measured under both silent and sonicated conditions (0.5 W cm\(^{-3}\)). Two physical models were proposed to interpret the results. No fitting parameters were required in these models as the partition coefficients were estimated using the empirical correlations described previously and mass transport coefficients were measured directly using benzaldehyde as a test solute. For silent conditions, a simple reaction enhanced transport film model adequately described the experimental data set in terms of the water-film Hatta number. For halides more reactive than benzoyl chloride, the model underpredicted the observed reaction rate, and it seems likely that these compounds hydrolyzed in the bulk carbon dioxide prior to diffusion to the water phase. For sonicated conditions, a model was developed which accounted for diffusion of reactant from the carbon dioxide droplets and consumption of reactant in both in the bulk water phase and in the water droplets. The successes of the emulsion model indicate that acoustic acceleration was due to substantially increased interfacial area.

The Diels-Alder cycloaddition of cyclopentadiene to methylvinylketone was selected to demonstrate the utility of the acoustic technique for a commercially relevant reaction. It was shown that ultrasound could be used to allow operation at high conversions (greater than 90%) while maintaining selectivities of roughly 14:1. For comparison, the selectivity and conversion would be roughly 4:1 and 25% if the reaction were conducted in supercritical carbon dioxide. These results compare favorably with those obtained by homogeneous catalysis in pure supercritical carbon dioxide, without requiring the use of expensive or environmentally incompatible additives.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Solvent Use and the Chemical Process Industry

The Chemical Process Industry (CPI) is a vital part of the U.S. economy. Statistics from the American Chemical Council (ACC) indicate\(^1\) that the CPI is directly responsible for one million jobs and indirectly generated many more. The ACC also asserts that the business of chemistry is a $460 billion/year industry in the U.S. alone and that 27% of the world’s chemical shipments originate in the U.S. Additionally, many other industries (e.g. automotive, computer, aerospace, etc.) rely directly on products of the CPI, further underscoring the role of the chemical industry.

Unfortunately, the CPI is also a major contributor to environmental pollution. Much of this pollution is due to inefficient conversion of raw materials to final products. Greater chemical efficiency is desirable both from an economic and an environmental viewpoint. An ideal manufacturing process would convert raw materials with 100% atom efficiency to final products which could then be recycled to other useful products, energy, or restored to the original set of raw materials with 100% atom efficiency at the end of their useful lifetimes. Alternatively, an ideal process can be defined in terms of zero environmental emissions and an energy use equal to the net change in availability required to form products from raw materials. The advantage of this approach is its explicit consideration of energy flows which are of paramount importance for the CPI.

Of course, the ideals of 100% efficiency or zero emissions are not attainable, but they do provide ultimate goals. One step toward achieving these objectives is to reduce and eliminate the use of auxiliary chemicals, that is chemicals which do not become incorporated in final products, whenever possible. Solvents are one of the largest classes of auxiliary chemicals and large quantities are used each year by the CPI.
If solvents could be recovered and recycled with complete efficiency, the large amounts used by industry might not be problematic. In practice, completely efficient solvent recycling does not occur; accidental releases, fugitive emissions, and improper disposal contribute to large inputs of solvents into the environment each year. Table 1 lists annual releases of 4 common solvents for the year 2000 as estimated\(^2\) by the Environmental Protection Agency (EPA). The release of methanol alone was estimated to be greater than 200 million pounds, with emissions to the air accounting for roughly 80% of the total mass released. Although the effect of solvents on the environment and human health is difficult to estimate, the acute and chronic toxicity (e.g. carcinogenicity) of many common solvents and their environmental persistence suggests a severe impact. Perhaps less obvious, but of equal importance, solvent recovery and reuse are energy intensive and constitute an environmental problem of their own, as energy production also generates waste.

Great improvements have been made in containing industrial solvents with the annual release rate of toluene, for example, decreasing 75% in the years between 1988 and 2000 (EPA). Nonetheless, as is clear from the data in Table 1, the annual release of toluene and other solvents into the environment is still substantial. Although improvements in solvent recovery and end-of-pipe treatment of waste streams are the options most commonly implemented today, a fundamental change toward cleaner technologies would be a much better policy in the long term. One solution would be to eliminate the solvent. In instances where solvents cannot be eliminated, an attractive alternative is to replace the solvent with one which is inherently environmentally benign.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Air (lbs)</th>
<th>Surface Water (lbs)</th>
<th>Underground Injections (lbs)</th>
<th>Land (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>733,000</td>
<td>17,000</td>
<td>22,536,000</td>
<td>1,000</td>
</tr>
<tr>
<td>methanol</td>
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<td>3,754,000</td>
<td>18,353,000</td>
<td>1,828,000</td>
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<td>toluene</td>
<td>81,258,000</td>
<td>41,000</td>
<td>514,000</td>
<td>149,000</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>30,782,000</td>
<td>10,000</td>
<td>200,000</td>
<td>838,000</td>
</tr>
</tbody>
</table>

Table 1-1. Estimated annual release of solvents to various locations in the United States (2000 values) EPA.\(^2\)
1.2 Water and Carbon Dioxide as Benign Alternative Solvents

Industrial acceptance of environmentally benign replacement solvents is complicated by the fact that there are a wide variety of solvents in use (e.g., toluene, carbon disulfide, tetrahydrofuran, acetone, dichloromethane, methanol, etc.), with a considerable range of properties (e.g., polarity, capacity to hydrogen bond, etc.), which are used in many different applications (e.g., recrystallizations, extractions, cleaning, coating, etc.). For this reason, there is no one solvent that would be the perfect replacement for all possible applications. An underlying motivation in this research was to select a model, environmentally benign solvent system and investigate its use in a specific application, facilitating chemical reactions. This particular application was selected because it represents a large portion of overall solvent use and hence could have a substantial impact on the CPI.

Possibly the two most environmentally benign alternatives to conventional solvents are water and carbon dioxide. Both of these solvents are non-toxic, non-flammable, readily available (at least in most of the world), and cheap. Water has been proposed as the solvent for a number of chemical processes and has many unique properties due its ability to form strong hydrogen bonds which make it quite attractive. The unique properties of water have been exploited in a number of chemical reactions which, when carried out in water, proceed with markedly increased rates or selectivities when compared to conventional solvents.\(^3\) One of the most dramatic examples was reported by R. Breslow’s group at Columbia University.\(^4\) In this seminal work, the researchers reported that the selectivity to the endo product of the cycloaddition of 3-buten-2-one to cyclopentadiene:

\[
\text{Endo} + \text{Exo} \quad \rightarrow \quad \text{COCH}_3 + \text{COCH}_3
\]

was improved from 4:1 (in octane) to 21:1 when conducted in water. Despite such successes, a major drawback is that water at room temperature and pressure is a feeble solvent for many common organic chemicals. As an example, the solubility of cyclopentadiene in ambient water is roughly \(10 \times 10^3\) mol L\(^{-1}\). In its supercritical state
(\(T_c > 374 ^\circ\text{C}, P_c > 240\) bar), water is a good solvent for most organic chemicals and many permanent gases, though severe thermal conditions are required. These extreme conditions make supercritical water a poor choice for many reactions of synthetic interest, though supercritical water in conjunction with benign oxidants such as hydrogen peroxide, oxygen, or even air is an ideal choice for the destruction of toxic chemicals and wastes. More specifically, two major drawbacks to using water (either at room temperature or near the critical point) for chemical synthesis are: 1) many chemical processes cannot be carried out in a protic solvent such as water, and 2) many reagents of interest will hydrolyze rapidly in water solutions. At temperatures greater than the critical point of water, the rates of many hydrolysis reactions are actually relatively slow, though degradation during pre-heating may pose a significant problem.

Carbon dioxide at room temperature and pressure is a gas and is essentially a non-solvent. As the pressure is increased, carbon dioxide liquefies and its solvent properties improve dramatically. The solubilities of many compounds in carbon dioxide are increased if the solvent is heated beyond its critical point (\(T_c = 31.1 ^\circ\text{C}, P_c = 73.8\) bar). Besides being environmentally benign, there are other advantages to using compressed carbon dioxide as a solvent. Since the conditions at which carbon dioxide becomes supercritical are relatively mild, the large isothermal compressibility characteristic of a near-critical fluid can be exploited readily. A large isothermal compressibility means that small changes in pressure lead to large changes in fluid density, which indirectly allows tuning of a number of physicochemical properties such as solvent power, diffusivity, and viscosity. Many processes have been proposed which take advantage of this tunability, for instance selective dissolution of certain materials during solvent extraction. Operating above the critical point is particularly attractive for the cleaning of materials with micron-sized features such as those common in the microelectronics industry. Unlike conventional solvents, the supercritical fluid can be removed without introducing a vapor/liquid meniscus, thus preserving features that would otherwise be destroyed during the drying process.

Supercritical fluids offer distinct advantages in terms of product separations. Substances which are liquefied only at elevated pressures are more readily separated and recovered than a conventional liquid solvents as phase changes can be achieved through
pressure drop. Carbon dioxide is particularly attractive in the food and drug industries since residual amounts of the solvent (which should be low in any event) do not have any toxic or otherwise undesirable effects, unlike conventional solvents. Because of its many advantages, compressed carbon dioxide (both liquid, near critical- and supercritical carbon dioxide or scCO$_2$) has been used successfully in a number of industrial-scale processes, such as the extraction of caffeine from coffee beans.$^9$

There are two major drawbacks to scCO$_2$, the more important of which is its low solvation power for many reagents of interest even at high pressure.$^9$ As a rule of thumb, low-molecular weight hydrocarbons, many fluorocarbons$^{10}$ (though not highly crystalline fluorocarbons such as conventional Teflon®-type polymers), and many siloxane-based polymers$^{11}$ exhibit relatively high (greater than 1 wt%) solubility in scCO$_2$ at moderate conditions. Most other compounds, including high-molecular weight hydrocarbons and ionic salts exhibit extremely low solubilities. The example of benzene, naphthalene, and anthracene is instructive. Benzene is nearly completely miscible with scCO$_2$. The solubility of naphthalene is roughly 5 wt% at 35°C and 150 bar.$^{12}$ At the same conditions, the solubility of anthracene is less than 5 x 10$^{-3}$ wt%.$^{13}$ The second drawback to using scCO$_2$ as a solvent for reactions is that the rates and selectivities of most chemical reactions are similar or inferior to those characteristic of conventional solvents.$^{14,15}$

Without technological or economic advantages, environmental advantages are not sufficient to promote industrial use of scCO$_2$ as a solvent for reactions. One solution to the problems of using scCO$_2$ and water separately is to combine them. Near the critical point of CO$_2$, it is essentially immiscible$^{16,17,18,19}$ with water so that mixtures of the two solvents will naturally phase split in a manner quite similar to the phase splitting of water/hydrocarbon mixtures. The combination of the two solvents will, therefore, be biphasic. Though some limitations cannot be addressed with biphasic systems of carbon dioxide and water (for instance reactions requiring an aprotic solvent still are not feasible without protecting agents) and some new limitations are created (the pH of water in contact with high-pressure CO$_2$ is effectively buffered at ~3,$^{20}$ meaning that base-catalyzed reactions require extremely aggressive buffering), many of the limitations of the two solvents can be overcome by their combination. The solvation powers of CO$_2$
and water are complementary, allowing dissolution of a much wider range of reagents than is possible in either solvent alone. The unique properties related to hydrogen-bond formation in water which make it a desirable solvent from a chemical reactivity standpoint can be accessed more readily by using carbon dioxide to dissolve the primary reagents (which tend to be water insoluble). Finally, the combination could be used for more sophisticated chemical schemes involving homogeneous catalysts. Segregation of the catalyst in either one of the two phases would allow its reactivity to be accessed while allowing effective recovery of the catalyst.

For many reactions of interest, biphasic conditions will impose mass transport limitations. Whenever possible, mass transport limitations in chemically reacting systems should be removed. To achieve this goal, both emulsions\textsuperscript{21,22} and microemulsions\textsuperscript{23-28} of CO\textsubscript{2} and water have been investigated as a means to increase the contact area and facilitate chemical reactions.\textsuperscript{29} Overall, the results have been promising. In some instances the rates/selectivities of chemical reactions are improved when compared to systems based on conventional solvents. Previous efforts are limited by two major shortcomings: 1) engineering understanding of the interplay between mass transport, chemical kinetics, and thermodynamics is modest, 2) all examples of reactions conducted in carbon dioxide/water environments rely on surfactants which are typically specially designed for the carbon dioxide/water interface. The next section discusses the use of carbon dioxide/water systems to conduct chemical reactions, highlighting both the experimental achievements and the two shortcomings mentioned above.

1.3 Previous Studies of Reactions in Water/Carbon Dioxide Environments

The first example of conducting a chemical reaction in an environment containing both water and carbon dioxide was provided by K.P. Johnston and his co-workers at the University of Texas. They demonstrated the use of microemulsions\textsuperscript{23} for the synthesis of benzyl bromide from benzyl chloride and potassium bromide:

\[
\text{C}_6\text{H}_5\text{Cl} + \text{NaBr} \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{NaCl} \tag{2}
\]
A perfluorinated polyether surfactant (PFPE COO'NH₄⁺, MW = 740 g mol⁻¹) was used to stabilize the microemulsions. The authors reported that the yield of benzyl bromide in the water/carbon dioxide microemulsion was comparable to or greater than that reported for the same reaction in a conventional water/oil microemulsion and that much less surfactant was required in the carbon dioxide-based system.²³

Johnston and coworkers²¹ also studied the rate of reaction (1) in water/carbon dioxide emulsions. Three separate surfactants were used for the studies: 1) the perfluorinated ether, CF₃O(CF₂CF(CF₃)O)₃CF₂COO'NH₄⁺, 2) poly-(dimethyl siloxane)-g-poly(ethylene oxide), PDMS-g-PEO, and 3) poly(butenes oxide)-b-poly(ethylene oxide), PBO-b-PEO. The choice of surfactant affected the yield of benzyl bromide slightly; the yield in emulsions stabilized by PDMS-g-PEO was 20% after 2 hrs compared to a 40% yield after 2 hrs for emulsions stabilized by PBO-b-PEO block copolymers. Reaction yields were probably limited by slow intrinsic kinetics rather than competing pathways. The best results were obtained when PBO-b-PEO was used as the surfactant. For comparison, the reaction was conducted in a water/octane emulsion using the common surfactant AOT, bis(ethylhexyl) sodium sulfosuccinate. Yields of benzyl bromide in water/carbon dioxide emulsions were slightly greater than that for the same reaction in water/octane emulsions; after 2 hrs the measured yield in the carbon dioxide-based emulsions was roughly 40% while the yield in the octane-based emulsions was 30%. The authors attributed²¹ the increased yield in carbon dioxide-based emulsions to “the very low viscosity for this (water/carbon dioxide) interface and the high diffusion coefficients in the CO₂ phase...” No mention is made of the fact that different surfactants were used in the two emulsions (which presumably played some role) or that reagent partitioning between carbon dioxide and water is most likely very different from that between octane and water. A detailed model, including intrinsic kinetic information and partitioning data, was not proposed, thus limiting the strength of the authors’ assertion.

Several groups of researchers have investigated hydrogenation reactions in carbon dioxide/water systems. Carbon dioxide is used as the solvent for hydrogen while water soluble catalysts are delivered in the aqueous core of the reverse microemulsion droplets. For example, Tumas, Johnston and their coworkers²² investigated the hydrogenation of styrene to ethyl benzene:
in water/carbon dioxide emulsions and biphasic systems using a water-soluble rhodium-based catalyst. Fluorinated surfactants, including PFPE COO'NH$_4^+$ and the surfactant sold under the trade name “Lodyne 106A” (C$_6$F$_{13}$(CH$_2$)$_2$SCH(OH)CH$_2$N$^-$'(CH$_3$)$_3$Cl'), and one hydrocarbon surfactant (PBO-PEO) were used as stabilizers. The hydrogenation was slightly faster in biphasic (i.e. with no surfactant present) carbon dioxide/water systems than biphasic toluene/water systems, with the turnover frequency at 50% conversion increasing from 4 h$^{-1}$ to 26 h$^{-1}$. No explanation for the acceleration of the reaction in carbon dioxide-based systems was provided. In water/carbon dioxide emulsions, the turn-over frequency was further increased to greater than 150 h$^{-1}$, with the type of surfactant playing only a small role. The dramatic improvement between the biphasic system and the emulsions was attributed to the increased surface area. The hydrogenation of a series of n-alkenes was also studied. For the series 1-octene, 1-decene, 1-eicosene, the authors reported turnover frequencies of 140, 110, 30 h$^{-1}$, respectively. Since it is well known that the water solubility of n-alkenes decreases with chain length, the authors hypothesized that the carbon dioxide/water partition coefficient would decrease with chain length. The basis of this hypothesis was the assumption that the reaction occurred in the aqueous phase; reagent partitioning to the carbon dioxide phase would therefore retard the overall reaction dynamics. Consistent with this hypothesis, the observed reaction rate decreased with (predicted) increasing partition coefficient though no attempt to make a quantitative comparison was made since partition coefficient data were not available. It is not clear from the authors’ analysis whether partitioning is the controlling factor or one of several controlling factors.

Wai and his coworkers at the University of Idaho studied the hydrogenation of olefins using palladium$^{24}$ and arenes using rhodium nanoparticles.$^{25}$ In both studies catalytic nanoparticles were produced in situ; the respective metal cations were dissolved in the water core of a water/carbon dioxide microemulsion and subsequently reduced by
reaction with hydrogen. A combination of AOT and perfluoropolyether phosphate (PFPE-PO₄) surfactants were used to stabilize the microemulsions. Using this procedure, the rate of hydrogenation of 4-methoxyhydrocinammic acid catalyzed by palladium nanoparticles:

\[
\text{HOOC-} \underset{\text{Rh nanoparticle}}{\rightarrow} \text{OCH}_3 \quad \text{H}_2 \quad \text{HOOC-} \underset{\text{Rh nanoparticle}}{\rightarrow} \text{OCH}_3
\]  

was measured²⁴ and found to be a weak function of temperature. The pseudo-first order rate constants were estimated to be \(1.1 \times 10^{-2}\), \(6.9 \times 10^{-2}\), and \(9.4 \times 10^{-2} \text{ s}^{-1}\) at 20, 35, and 50 °C, respectively. The authors attributed the weak, non-Arrhenius temperature dependence of the rate to the variation of the diffusion coefficient of the reagent in the carbon dioxide phase (either liquid or supercritical), an explanation which implies that the rate limiting step of the reaction was diffusion of the reagent through the carbon dioxide. No attempt to verify this assumption was made, though for reactions with fast intrinsic kinetics (the reported half lives were less than 60 s) transport resistances would be expected to be important. In the second study, the hydrogenation rate of naphthalene catalyzed by rhodium particles:

\[
\text{C}_10\text{H}_{14} \quad \text{Rh nanoparticle} \quad \text{H}_2 \quad \text{C}_10\text{H}_{14}
\]  

was measured.²⁵ Interestingly, the hydrogenation rate depended on stirring with no reaction observed in unstirred systems. Presumably, without agitation the catalyst particles were not dispersed into the carbon dioxide, though the reason for complete loss of catalytic activity is not clear. Jessop and his coworkers²⁶ at the University of California, Davis tested rhodium particles in water/carbon dioxide microemulsions and found that they did not catalyze the hydrogenation of 2-methoxy-4-propylphenol:

\[
\text{HO-} \underset{\text{Rh nanoparticle}}{\rightarrow} \text{OCH}_3 \quad \text{H}_2 \quad \text{HO-} \underset{\text{Rh nanoparticle}}{\rightarrow} \text{OCH}_3
\]
Since the reaction proceeded smoothly with good conversion in water/supercritical ethane microemulsions, the authors attributed the poor results in the carbon dioxide-based systems to acidic buffering (pH~3) by bicarbonate ions. It is not clear why Jessop's\textsuperscript{26} rhodium particles did not catalyze hydrogenations whereas Wai's\textsuperscript{25} particles did, though the difference may be due to the researchers' choice of substrates; Jessop\textsuperscript{26} chose 2-methoxy-4-propylphenol because the substrate is notoriously difficult to hydrogenate. Leitner and his coworkers\textsuperscript{27} studied the hydroformylation of a hydrophilic alkene using a CO\textsubscript{2}-soluble rhodium-based catalyst:

\begin{equation}
\text{1} \quad \text{2a} \quad \text{2b}
\end{equation}

\begin{equation}
\text{Rh(CO)}_3[\text{P-Ph-CH}_2\text{C}_6\text{F}_{13}]_3
\end{equation}

Using a fluorocarbon-based CO\textsubscript{2}-philic ligand to solubilize the catalyst (formula indicated in reaction 7), good conversions of the reagent were obtained, though standard (i.e., hydrocarbon based) ligands were not effective. Post-reaction, separations were achieved by simply venting the liquid water at the bottom of the reactor through a needle valve. Using this technique, near quantitative recovery of the products was achieved and only trace (0.3 ppm) amounts of rhodium were found in the water phase. Various buffers were used to investigate the effect of pH on activity of the rhodium catalyst. Although rhodium catalyzed hydroformylation is generally carried out at neutral or basic pH, buffers greatly reduced the yield of 2. Instead, products of the hydrolysis of 1 were found in the reaction mixture. Presumably, at elevated pH the hydrolysis reaction of 1:

\begin{equation}
\text{1} \quad \text{3}
\end{equation}
occurs more readily than reaction (7). The authors\textsuperscript{27} hypothesize that 3 is even more water-soluble than 1 and does not enter the carbon dioxide phase. If so, then 3 does not encounter the rhodium catalyst and the hydroformylation indicated by reaction 7 does not occur. Unfortunately, no data for the partition coefficients of 1 and 3 or for the rates of reactions 7 or 8 are available to verify the authors’ hypothesis. A detailed understanding of the interplay between intrinsic kinetics, mass transport, and reagent partitioning is needed to fully analyze the complex behavior reported in this study.

The final example of a small-molecule chemical reaction conducted in a carbon dioxide/water environment is provided by D. Steytler’s research group.\textsuperscript{28} The researchers investigated the use of enzymes for two common bioconversions:

\[
\begin{align*}
\text{NO}_2^+ \quad \text{OOC(CH}_2\text{)}_2\text{CH}_3 & \xrightarrow{\text{Lipase}} \xrightarrow{\text{H}_2\text{O}} \text{NO}_2^+ \quad \text{CH}_3\text{(CH}_2\text{)}_2\text{CO}_2\text{H} \\
& + \quad \text{CH}_3\text{(CH}_2\text{)}_2\text{CO}_2\text{H} \\
\end{align*}
\]

(9)

\[
\begin{align*}
\text{(CH}_2\text{)}_7\text{CO}_2\text{H} & \xrightarrow{\text{Lipoxigenase}} \xrightarrow{\text{H}_2\text{O}} \text{(CH}_2\text{)}_7\text{CO}_2\text{H} \\
& + \quad \text{(CH}_2\text{)}_7\text{CO}_2\text{H} \\
\end{align*}
\]

(10)

The water-phase pH was buffered at \textasciitilde 5 (using a variety of bases) for all kinetic studies. The two reactions were studied both in water/carbon dioxide microemulsions and water/hexane microemulsions and the kinetics were analyzed within the Michaelis-Menten framework. The observed rates for both reactions were slightly faster in the carbon dioxide-based microemulsions than their hydrocarbon counterparts. The primary contribution of this study was to show that water/carbon dioxide microemulsions could be used for biological transformations. It is less clear if water/carbon dioxide microemulsions present any significant advantages for enzymatically catalyzed reactions, though this is an area for future research.
1.4 A Path Forward

Although there have been a number of investigations into the use of water/carbon dioxide systems for chemical synthesis, as stated previously, industrial implementation has been limited by two factors: 1) all prior work relies on the use of specialized surfactants, the most effective of which are based either on fluorocarbons or siloxanes and, 2) there has been little progress toward a firm understanding of the kinetics, transport, and thermodynamics of the chemical processes. Although some preliminary attempts have been made to interpret results from carbon dioxide/water systems, there has been extremely little quantitative analysis of rate data. A number of feasible explanations have been put forward to explain rates of reactions in the hybrid solvent, none of which have been verified by independent experiments or physical models. As long as the carbon dioxide/water solvent system is used for small scale synthesis, this approach is adequate. To become an industrial-scale technology, however, a detailed analysis of the interplay between thermodynamics, transport, and chemical kinetics is required.

The use of surfactants in the otherwise benign carbon dioxide/water medium is undesirable for several reasons. Most obviously, the use of surfactants makes the carbon dioxide/water system less environmentally friendly. Recently, fluorocarbon surfactants have come under intense scrutiny from the EPA\textsuperscript{30} as the Agency tries to confirm reports that perfluorooctanoic acid (a common perfluorinated surfactant) causes developmental toxicity in rats. Cost is also an issue. Surfactants are considerably more expensive than water and carbon dioxide. This is particularly true for the specialized surfactants needed to form microemulsions. Some recent developments may mitigate this cost somewhat as Beckman\textsuperscript{31} has recently developed a hydrocarbon-based surfactant for carbon dioxide-based microemulsions. Johnston\textsuperscript{32, 33} has demonstrated that carbon dioxide-based emulsions can be stabilized with carefully chosen hydrocarbon-based surfactants. Even if hydrocarbon surfactants can be found that stabilize the carbon dioxide-water interface as effectively as their fluorocarbon analogs, use of any surfactants will increase the cost of chemical processes since removal of such additives will require additional product purification steps.
In this thesis, we propose the use of power ultrasound as a novel method to bring carbon dioxide and water into intimate contact to facilitate chemical reactions. While previous efforts have relied upon surfactants, and could be described as "chemically based", the ultrasound method is best described as either a mechanical or physical approach that eliminates the need for surfactants. Furthermore, elimination of the surfactant simplifies the system, at least from a chemical standpoint. Since the presence of surfactants (which can affect chemical rates and selectivities in unusual ways) greatly complicates engineering analysis. Surfactant-free, ultrasonically generated emulsions may prove to be both easier to analyze quantitatively and more attractive economically.

1.5 References

(1) American Chemical Council, The U.S. Chemical Industry: Important to our Economy and to the Way that We Live, 2001.


(29) Note: The prefix “micro” does not strictly refer to the size of dispersed droplets. In fact, the droplets in emulsions have been known to be less than 1 μm, while droplets in microemulsions can be as small as 100 Å and as large as 1 μm. As an attempt at clarification, some authors use the terms “mini” and “macroemulsion” to distinguish between emulsions with different size droplets. The difference between
microemulsions and emulsions is that microemulsions are thermodynamically stable, while emulsions are kinetically stable. Furthermore, microemulsions require a stabilizing surfactant while emulsions do not (though their lifetimes can be extended with the use of stabilizers). The term “microemulsion” is primarily historic and “swollen micelles” (i.e., micelles in which the core has been expanded or swollen by solubilization of either water or an organic liquid) is sometimes used instead. Although the term “swollen micelles” is perhaps more clear, it is seldom used. For this reason the term “microemulsion” will be used in this document.


CHAPTER 2

OBJECTIVES AND APPROACH

This work is motivated by the goal of eliminating the significant disadvantages of near and supercritical carbon dioxide (as described in Chapter 1) while retaining its environmental and economic advantages. While previous efforts to address the limitations of carbon dioxide have relied on the use of additives (surfactants, cosolvents, catalysts), we propose a novel alternative: mechanical emulsification of carbon dioxide and water. The inherently environmentally benign combination of carbon dioxide and water has the potential to access aqueous acceleration of chemical reactions while solubilizing a much wider range of organic and inorganic reagents than either solvent independently. Because acoustic techniques have been shown to be an effective means of delivering power at the required length scales, power ultrasound is the agitation method of choice. This technology has the potential of forming short-lived, high-contact-area emulsions of carbon dioxide and water with minimal energy consumption.

2.1 OBJECTIVES

The overarching goal of this work was to determine principles for the design of chemical reactors for water/carbon dioxide emulsion systems. This overall research goal can be divided into four specific objectives:

1) The first objective was demonstration of the feasibility of using power ultrasound to generate emulsions consisting of carbon dioxide/water. Specifically, the ultrasonic power density required to generate emulsions was measured and mechanisms of emulsification were proposed. The time required for emulsions to break was determined via turbidity measurements and possible mechanisms of emulsion breaking were proposed. Also, the effect of power density on a carefully chosen chemical reaction was investigated. Conclusions drawn from this step of the
research served to motivate and guide subsequent efforts. These results are described in Chapters 4 (emulsion characterization) 5 (emulsion formation mechanisms) and 6 (reaction kinetics).

2) Detailed characterization of emulsions was necessary for rational selection of chemical reactions for acceleration with the ultrasound technique. Droplet sizes were measured directly by in situ optical microscopy in microfabricated reactors and carbon dioxide/water interfacial area was estimated based on the measured droplet diameters and measurements of the volume fraction of dispersed phase in the emulsions. Emulsion characterization is described in Chapter 4.

3) The acceleration of chemical reactions is complex, involving contributions from reaction kinetics, transport, and thermodynamics. Understanding how these issues influence observed kinetics is critical for rational selection of chemical reactions for the emulsion environment. The thermodynamics of reagent partitioning were investigated by measurement of the partition coefficients for a wide range of solutes. Existing empirical models were analyzed with the goal of developing predictive techniques for estimation of partition coefficients. This work is described in Chapter 3. Reaction kinetics and transport were investigated by studying the hydrolysis of 7 substituted benzoyl halides representing a wide range of chemical reactivity but a limited range of partitioning and diffusivity. Based on these results, quantitative mathematical models were proposed. Both the experimental measurements kinetic models of benzoyl halide hydrolysis are presented in Chapter 6.

4) The final objective was to use the emulsion system to promote a synthetically important chemical reaction, the Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene. The conversion and selectivity of the reaction were measured both under silent and sonicated conditions to demonstrate the usefulness of the acoustic technique. An additional goal of this work was to investigate the practical issue of reactor scale-up. This work is presented in Chapter 7.
2.2 Method of Approach

To accomplish the goals stated above, an intense experimental program was developed. The experimental plan consisted of the following sub-projects:

1) Measurement of carbon dioxide/water partition coefficients for a wide variety of solutes at a fixed temperature and pressure. These solutes were selected to expand the data base for which partition coefficient data were available and to provide the basis for evaluating empirical correlation methods.

2) Measurement of turbidity in the acoustic reactor. The time required for emulsion breaking was estimated based on turbidity measurements which allowed the positing of probably demulsification mechanisms.

3) Determination of the volume fractions of the dispersed phase(s) in acoustically generated emulsions. This information was used to interpret both emulsion breaking mechanisms and reaction dynamics in the two phase system.

4) Measurement of droplet diameters of the dispersed phase in the two emulsions. This work was conducted in microfabricated reactors with the assistance of E. Murphy, A. Günther, J. Kralj, and T. Inoue of K.F. Jensen’s research group.

5) Visualization of reactor contents during sonication at different power densities. These observations provided insight into the formation mechanism(s) of emulsions.

6) Determination of sonochemical effects. The oxidation of potassium iodide was studied as a model sonochemical reaction to investigate the nature of cavitation in high-pressure carbon dioxide/water systems and to determine if sonochemical acceleration of reactions was an important consideration for development of reactor models.

7) Measurement of the effect of acoustic power on a model phase-transfer reaction, hydrolysis of benzoyl chloride.

8) Study of the phase-transfer kinetics of 7 substituted benzoyl halides. This study was used to unravel the effects of intrinsic chemical reactivity, mass transport, and thermodynamics on observed rates of reactions in carbon dioxide/water emulsions.
9) Measurement of the conversion and selectivity of the well-known Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene to demonstrate the benefit of our novel approach for a commercially important reaction.

To interpret the data generated with this experimental approach, a modeling effort was also conducted. The measured partition coefficients were analyzed in conjunction with literature data to develop empirical methods for partition coefficient estimation. A useful contribution to the field in their own right, these models aided in the analysis of the kinetic data measured in experiments #7-9 above. Bubble dynamics were simulated with mathematical models to explore the nature of cavitation in systems containing carbon dioxide and water at elevated pressure. A physical mass-transport/reaction model was formulated to describe kinetic data of experiments #7-9. Taken together, the experimental data and theoretical models describe the process of emulsification, provide a strong foundation for the rational selection of reaction chemistries, and suggest possible modifications to the acoustic reactor design.
CHAPTER 3

PARTITION COEFFICIENTS OF ORGANIC SOLUTES BETWEEN SUPERCritical CARBON DIOXIDE AND WATER: EXPERIMENTAL MEASUREMENTS AND EMPIRICAL CORRELATIONS

3.1 Carbon Dioxide/ Water Reactor Design and the Importance of Partition Coefficients

Although supercritical carbon dioxide (scCO₂) is a non-toxic, readily available, benign alternative to traditional organic solvents, its adoption as a solvent for reactions on an industrial scale has been slower than for processes such as extraction. One of the primary reasons for this slow development is that few compounds show appreciable solubility in scCO₂ at modest temperatures and pressures. Attempts to increase the solubility of compounds often compromise the inherently environmentally benign nature of scCO₂. For instance, though addition of polar organic cosolvents can greatly increase the solubility of many non-volatile compounds in scCO₂, the resulting reaction mixture is generally less environmentally innocuous than pure carbon dioxide. Water, which would not significantly impact the green nature of carbon dioxide, is not appreciably soluble in the compressed fluid carbon dioxide at moderate conditions and cannot be used as a polar cosolvent. The combination of scCO₂ and water as a biphasic reaction solvent system, however, is receiving increasing attention. Not only do water and scCO₂ exhibit complementary solvation powers, but the biphasic system presents an ideal way of deploying phase-separable homogeneous catalysts.

Proper analysis of reaction rate data in water/carbon dioxide systems (and therefore accurate design of biphasic reactors) depends on a knowledge of the partitioning of organic solutes between the two phases. Despite the use of scCO₂ as an extraction solvent from highly aqueous media for some time, published data of partition
coefficients between water and carbon dioxide are sparse. Although partition coefficients have been reported for 29 compounds at 300 specific state points,\textsuperscript{12–22} nearly half of these compounds\textsuperscript{21} are substituted phenols. For these compounds, the influence of pressure, density and temperature on the partition coefficient have been thoroughly characterized and variables such as water–phase ionic strength and pH have been investigated to some degree.\textsuperscript{20} What is lacking is a broad spectrum of compounds for which partition coefficient data are available. As a result of the narrow data set, predictive models, which require a larger library of compounds in order to be sufficiently robust, are underdeveloped. Ideally, a semi–empirical model could be developed with the predictive capabilities necessary for engineering purposes. Though the studies discussed above presented equations–of–state (EOS) for data modeling, such methods are best suited to interpolation of existing temperature/pressure data for a given compound rather than for estimation of partition coefficients of new compounds. Alternatively, an empirical predictive approach would allow estimation of partition coefficient data based primarily on molecular structure and/or physicochemical properties which could be measured in separate, independent experiments. A general predictive method, with sufficient accuracy, would find applications in the design and development of biphasic CO\textsubscript{2}/H\textsubscript{2}O reaction systems (including reactions occurring in emulsions and microemulsions) and equipment for the extraction of organic species from aqueous streams using a dense CO\textsubscript{2} phase. In addition, such methods would potentially aid the rational design of CO\textsubscript{2}–philic ligands for chelation and subsequent extraction of transition metals from water or phase segregation of homogeneous catalysis in biphasic (CO\textsubscript{2}/H\textsubscript{2}O) systems. Robust estimation methods are particularly desirable because measurement of CO\textsubscript{2}/H\textsubscript{2}O partition coefficients requires specialized, high–pressure equipment.

3.2 Existing Correlation Methods for Carbon Dioxide/Water Partition Coefficients

Given that \textit{a priori} prediction of partition coefficients is such a tantalizing goal, it is not surprising that several researchers have already investigated the possibility. Karásek et al.\textsuperscript{21} showed that estimates of octanol–water partition coefficients ($K_{O/W}$) from group contribution methods did not accurately predict carbon dioxide–water
Chapter 3: Partition Coefficients

Partition coefficients \( (K_{C/W}) \) for the compounds in their study, with deviations between predictions and measurements as large as two orders of magnitude. Unfortunately, their analysis was limited primarily to substituted phenols.

Lagalante and Bruno\(^{23} \) demonstrated the use of Linear Solvation Energy Relationships (LSERs) to correlate \( CO_2/H_2O \) partition coefficient data. They based their approach on LSERs which had been developed for octanol/water partitioning to which they added a dipolarity/polarizability term with explicit dependence on the \( CO_2 \) density. The investigators reported less than 25% average absolute relative deviation (AARD) between the measured and LSER–predicted values of \( K_{C/W} \) for the 6 compounds considered. Although the results of this effort were promising, 6 compounds are insufficient to develop robust, general LSERs.

For the study described in this chapter, partition coefficients for 18 new compounds were measured at 300 K and 80 bar, corresponding to an estimated equivalent fluid density of 0.75 g cm\(^{-3} \). This estimate is based on an accurate EOS for pure \( CO_2 \)^\(^{24} \) as recommended by Ely.\(^{25} \) These new measurements significantly expand the database of partition coefficients to include aldehydes, ketones, esters, and halides. Because previous researchers have sufficiently investigated the effects of temperature and pressure/density on \( K_{C/W} \) (albeit for a narrow range of compounds), these effects were not investigated. These data, combined with the values previously reported in the literature, were then analyzed using three methods: 1) comparison to water solubility, 2) comparison to estimated values of \( K_{O/W} \), and 3) estimation using LSER.

3.3 Experimental Apparatus and Procedures

**Apparatus.** All measurements were made using a high–pressure cell (Jerguson, 19T–40) with a listed internal volume of 50 mL. The complete apparatus is shown in Figure 3–1. There was nearly complete optical access into the high–pressure cell so that 2–phase behavior could be confirmed visually for all experiments. The maximum operating pressure of the cell was rated at 340 bar at 40 °C. The high–pressure cell was immersed in a temperature–controlled (Omega, 9001CN) and heated/circulated (VWR, 1110) water
Figure 3-1. Experimental apparatus used for partition coefficient measurements; a) agitated water bath; b) high-pressure vessel (Jerguson sight gauge); c) water pump; d) water sampling valve; e) carbon dioxide pump; f) carbon dioxide sampling valve; g) water heater/circulator; h) PID controller.

bath. The temperature in the center of the high-pressure cell was measured to within ± 1.0 °C using a calibrated T-type thermocouple which was immersed directly in the fluid. Pressure was measured with a digital (piezo-type) pressure gauge (Omega, DPG5000L–5K) to within ± 1 bar. All experiments were performed at 300 ± 1 K and 80 ± 1 bar (p = 0.70 ± 0.03 g cm⁻³). A high-pressure pump (Eldex, BBB–4, rated for 100 mL min⁻¹) was used to recirculate the water phase through the CO₂ in order to provide good interfacial contact while the CO₂ phase was recirculated using a second high-pressure pump (Eldex, B–100–S, rated at 5 mL min⁻¹) to remove any dead spots in the CO₂ phase. The vigorous pumping also minimized temperature variations within the fluid to less than approximately 1.0 °C. Samples of the recirculating fluids (both water and CO₂) were taken with high-pressure sampling valves (Valco Instrument Company, Inc., uw–type) equipped with sample loops with volumes calibrated to within ±2.5% (Valco Instrument Company, Inc.). Samples withdrawn from the reactor were depressurized by slowly
bubbling the expanding gas through a small volume of acetone over several minutes. Both the volume of sample taken from the reactor \(25 \mu L \geq V_{S,C}, V_{S,W} \leq 500 \mu L\) and the volume of acetone used for depressurization/dilution \(5 mL \geq V_{D,C}, V_{D,W} \leq 50 mL\) were varied to confirm that solute collection efficiency was as close to 100% as possible. Chilled (-0 °C) acetone was used for volatile compounds such as the hydrocarbons to minimize evaporative losses. Samples drawn from the reactor were further diluted to standard volumes using acetone and analyzed using gas chromatography (GC, Agilent, 6890) equipped with a flame-ionization detector (FID) and a DB–Wax column (J&W Scientific). The GC was calibrated using standard solutions of defined molar concentrations and a linear relationship between peak area and molar concentration was observed in all instances. Dilution factors for the samples drawn from the reactor were chosen to ensure analysis of concentrations for which this linear relationship had been verified.

**Materials.** Grade 5.5 carbon dioxide (certified purity greater than 99.999%) was purchased from BOC Gases and used as received. Water was deionized (Barnstead, Nanopure) to a minimum resistivity of 18.0 MΩ–cm and used immediately. All other organic chemicals (including solutes for partitioning and acetone as a solvent) were purchased from Sigma–Aldrich at the highest available purity and used as received.

**Methods and Data Analysis.** The partition coefficient (denoted, in molar units, as \(K_{C/W}^C\)) of a given solute was calculated from the ratio of its molar concentration in the carbon dioxide phase \(C_i^{(C)}\) to that in the water phase \(C_i^{(W)}\). Molar concentrations of diluted samples were measured by GC \(C_i^{(C)}_{i,GC}\) and \(C_i^{(W)}_{i,GC}\) respectively) and corrected to the contactor concentrations by accounting for differences in sample dilution factors. Thus:

\[
K_{C/W}^C = \left( \frac{C_i^{(C)}}{C_i^{(W)}} \right) \left( \frac{V_{D,C} / V_{S,C}}{V_{D,W} / V_{S,W}} \right)
\] (3-1)

where \(V_{S,C}\) and \(V_{S,W}\) are the volumes of the samples taken using the high-pressure sample valve/sample loop, and \(V_{D,C}\) and \(V_{D,W}\) are the volumes after dilution with acetone. The conventional means of presenting data over a range of densities is to use a
mole-fraction-based partition coefficient, $K_{c/w}^x$. At low concentrations of the solute, the conversion between molar units and mole fraction units is:

$$K_{c/w}^x = K_{c/w}^c \frac{\rho_w}{\rho_c} \frac{MW_c}{MW_w}$$

(3.2)

Here, $MW_c$ and $MW_w$ are the molecular weights of carbon dioxide (44.01 g mol$^{-1}$) and water (18.01 g mol$^{-1}$) and $\rho_c$ and $\rho_w$ are the densities of the respective phases. The density of water was taken as 0.999 g cm$^{-3}$ and the density of carbon dioxide was calculated using the EOS of Span and Wagner$^{24}$ as explained previously. For both solvents, the concentration of the solutes was assumed to be low enough that pure component densities were accurate.

For each run, between 3 and 6 samples were taken from each phase over a period of 3 hours. No noticeable drift in GC peak area signal was apparent over the course of the measurements. Estimates of the relative standard deviations for these concentration measurements were generally less than 15% and were usually less than 10%. The only exceptions were the water-phase concentrations of water-insoluble reagents such as toluene and the alkanes/alkenes. In these instances, the GC peak area was small, leading to larger relative standard deviations (20-30%) within the replicate measurements.

To allow for equilibration, 3 hours elapsed between charging the reactor with the solute and taking the first sample. For several runs, we allowed 12 hours for equilibration and found that there was no statistical difference between these measurements and those made allowing 3 hours for equilibration. Initial solute concentration was varied between $4 \times 10^{-3}$ (wt/wt) and $8 \times 10^{-4}$ (wt/wt) with no statistically significant difference in measured values $K_{c/w}^x$. The ratio of the volumes of water/carbon dioxide charged to the reactor was varied from 0.5 to 2.0 with no apparent effect on $K_{c/w}^x$. In this fashion, between 2 and 6 separate measurements were made of each value for $K_{c/w}^x$ reported herein. Reported values of $K_{c/w}^x$ are the arithmetic average of the replicate measurements. The standard error for the mean for each reported value of $K_{c/w}^x$ based on these 2 to 6 replicate measurements was reported. For instances
where only 2 replicate measurements were made, the range of the data was reported as the error.

**Density Interpolation of Literature Data.** To analyze literature data taken over a range of conditions, it was necessary to interpolate the available data sets to a fixed carbon dioxide density of 0.75 g cm$^{-3}$. This interpolation was facilitated by the fact that $K_{c/w}^x$ is nearly a unique function of density for the combination of compounds and conditions for which data are available. Physically, the fact that $K_{c/w}^x$ is a function primarily of density, with temperature playing only a minor role, is analogous to the reported effect of density on the solubility of organic solutes in near- and supercritical carbon dioxide.\(^2\)

Thus, it seems that the correlation of $K_{c/w}^x$ with density is related to the solubility of the organic solute in the carbon dioxide phase. Figure 3-2a&b demonstrate the dependence of partition coefficients on density for phenol and 1,2-dichloroethane, two very different compounds. From examining plots of $K_{c/w}^x$ as a function of density, the error in the interpolation technique is estimated to be ±20%.

### 3.4 Experimental Observations

Values of $K_{c/w}^x$ (at a fixed scCO$_2$ density of 0.75 g cm$^{-3}$) for all compounds for which it has been measured are listed in Table 3-1 (this work) and Table 3-2 (all other sources). Literature data were interpolated to a scCO$_2$ density of 0.75 g cm$^{-3}$ as described above. When no data were available at or above a CO$_2$ density of 0.75 g cm$^{-3}$, no attempt to extrapolate existing data to that density was made. For the instances where the partition coefficient could not be interpolated to a density of 0.75 g cm$^{-3}$, the value of $K_{c/w}^x$ at the highest density for which data are available is listed instead. The large error reported for the partition coefficient of hexane is due to the low water solubility of this compound, as explained previously. Attempts to measure the partition coefficient of octane were made, but the concentration of octane in the water phase was less than the detection limit of the analytical method (roughly 1 ppm). The detection limit provides a lower bound estimate of approximately 100,000 for $K_{c/w}^x$ of octane.
Figure 3.2. $K_{C/W}^x$ - density interpolation plots for (a) phenol and (b) 1,2-dichloroethane. Data from reference [18] (phenol) and [16] (dichloroethane).
Table 3-1. Values of $K_{c/w}^x$ measured in this study. All data were measured at a fixed CO$_2$ density of 0.75 g cm$^{-3}$. Available literature data for compounds considered in this study are also listed for comparison.

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>$K_{c/w}^x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetophenone</td>
<td>48.5 ± 2.3</td>
</tr>
<tr>
<td>2</td>
<td>Benzaldehyde</td>
<td>39.1 ± 3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38$^a$</td>
</tr>
<tr>
<td>3</td>
<td>Bromobenzene</td>
<td>1090 ± 30</td>
</tr>
<tr>
<td>4</td>
<td>3–Buten–2–one</td>
<td>7.8 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>Chlorobenzene</td>
<td>1140 ± 70</td>
</tr>
<tr>
<td>6</td>
<td>Cyclohexane</td>
<td>4,900 ± 300</td>
</tr>
<tr>
<td>7</td>
<td>Cyclohexene</td>
<td>1,900 ± 300</td>
</tr>
<tr>
<td>8</td>
<td>Cyclopentene</td>
<td>1,400 ± 180</td>
</tr>
<tr>
<td>9</td>
<td>Ethyl benzoate</td>
<td>550 ± 100</td>
</tr>
<tr>
<td>10</td>
<td>Fluorobenzene</td>
<td>770 ± 150</td>
</tr>
<tr>
<td>11</td>
<td>Hexane</td>
<td>9,000 ± 2,500</td>
</tr>
<tr>
<td>12</td>
<td>2–Methoxyacetophenone</td>
<td>47.3 ± 1.1</td>
</tr>
<tr>
<td>13</td>
<td>3–Methoxyacetophenone</td>
<td>84.0 ± 0.9</td>
</tr>
<tr>
<td>14</td>
<td>Methyl benzoate</td>
<td>205 ± 21</td>
</tr>
<tr>
<td>15</td>
<td>Propiophenone</td>
<td>121 ± 13</td>
</tr>
<tr>
<td>16</td>
<td>Propyl benzoate</td>
<td>1,050 ± 220</td>
</tr>
<tr>
<td>17</td>
<td>Tetrahydrofuran</td>
<td>8.5 ± 1.0</td>
</tr>
<tr>
<td>18</td>
<td>Toluene</td>
<td>1,200 ± 250</td>
</tr>
</tbody>
</table>

$^a$ Value reported by Wagner et al., 1999$^{18}$

$^b$ Value reported by Yeo and Akgerman, 1990$^{12}$, value measured at 0.59 g cm$^{-3}$
Chapter 3: Partition Coefficients

Table 3-2. Compilation of all values for $K_{C/W}^x$ reported in the literature. All data were measured at (or interpolated to) a fixed CO$_2$ density of 0.75 g cm$^{-3}$, unless otherwise noted.

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>$K_{C/W}^x$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aniline</td>
<td>2.1</td>
<td>Wagner et al. 1999</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>2.756*</td>
<td>Yeo and Akgerman, 1990</td>
</tr>
<tr>
<td>3</td>
<td>Benzoic acid</td>
<td>1.3</td>
<td>Brudi et al. 1996</td>
</tr>
<tr>
<td>4</td>
<td>Benzyl alcohol</td>
<td>1.85</td>
<td>Brudi et al. 1996</td>
</tr>
<tr>
<td>5</td>
<td>Caffeine</td>
<td>0.15</td>
<td>Brudi et al. 1996</td>
</tr>
<tr>
<td>6</td>
<td>2-Chlorophenol</td>
<td>13</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>7</td>
<td>4-Chlorophenol</td>
<td>3</td>
<td>Ghonasgi et al., 1991</td>
</tr>
<tr>
<td>8</td>
<td>Cyclohexanone</td>
<td>41</td>
<td>Brudi et al., 1996</td>
</tr>
<tr>
<td>9</td>
<td>1,2-Dichloroethane</td>
<td>155</td>
<td>Sengupta et al., 1994</td>
</tr>
<tr>
<td>10</td>
<td>2,4-Dichlorophenol</td>
<td>70</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>11</td>
<td>2,4-Dichlorophenoxyacetic acid</td>
<td>0.1</td>
<td>Akgerman and Carter, 1994</td>
</tr>
<tr>
<td>12</td>
<td>2,4-Dimethylphenol</td>
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<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>13</td>
<td>2-Hexanone</td>
<td>118</td>
<td>Brudi et al., 1996</td>
</tr>
<tr>
<td>14</td>
<td>3-Methyl-4-chlorophenol</td>
<td>6</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>15</td>
<td>2-Methyl-4,6-dinitrophenol</td>
<td>55</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>16</td>
<td>2-Methyl-5-hexyloxydimethyl-8-qumolinol</td>
<td>490</td>
<td>Ohashi et al., 2000</td>
</tr>
<tr>
<td>17</td>
<td>3-Methylphenol</td>
<td>4</td>
<td>Ghonasgi et al., 1991</td>
</tr>
<tr>
<td>18</td>
<td>Naphthalene</td>
<td>347$^b$</td>
<td>Yeo and Akgerman, 1990</td>
</tr>
<tr>
<td>19</td>
<td>2-Nitrophenol</td>
<td>72</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>20</td>
<td>4-Nitrophenol</td>
<td>0.18</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>21</td>
<td>Parathion</td>
<td>18.3$^b$</td>
<td>Yeo and Akgerman, 1990</td>
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<td>22</td>
<td>Pentachlorophenol</td>
<td>80$^c$</td>
<td>Curren and Burk 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10$^d$</td>
<td>Curren and Burk 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8$^e$</td>
<td>Curren and Burk 2000</td>
</tr>
<tr>
<td>23</td>
<td>Phenol</td>
<td>1.0</td>
<td>Brudi et al., 1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45</td>
<td>Roop et al., 1989</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.50</td>
<td>Ghonasgi et al., 1991</td>
</tr>
<tr>
<td>24</td>
<td>Salicylic acid</td>
<td>0.21</td>
<td>Karásek et al. 2002</td>
</tr>
<tr>
<td>25</td>
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<td>80</td>
<td>Sengupta et al., 1994</td>
</tr>
<tr>
<td>26</td>
<td>2,3,4,5-Tetrachlorophenol</td>
<td>15</td>
<td>Curren and Burk 2000</td>
</tr>
</tbody>
</table>
Table 3-2. continued

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>$K_{C/W}^x$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>1,1,2-Trichloroethane</td>
<td>25</td>
<td>Sengupta et al., 1994</td>
</tr>
<tr>
<td>28</td>
<td>2,4,6-Trichlorophenol</td>
<td>150</td>
<td>Karásek et al., 2002</td>
</tr>
<tr>
<td>29</td>
<td>Vanillin</td>
<td>1.3</td>
<td>Brudi et al. 1996</td>
</tr>
</tbody>
</table>

a Data not available at 0.75 g cm$^{-3}$, value cited measured at 0.50 g cm$^{-3}$

b Data not available at 0.75 g cm$^{-3}$, value cited measured at 0.59 g cm$^{-3}$

c Reported value measured at a solute concentration of 11.6x10$^{-6}$ mass fraction (total solvent basis)

d Reported value measured at a solute concentration of 1.27x10$^{-6}$ mass fraction (total solvent basis)

e Reported value measured at a solute concentration of 1.9-4.3x10$^{-6}$ mass fraction (total solvent basis)

Some observations can be made regarding the data in Table 3-1. First, the measured partition coefficients span nearly 5 orders of magnitude (from 0.10 to almost 10,000) and include primarily carbon dioxide–philic compounds (i.e. compounds which prefer CO$_2$ to water). Salicylic acid, caffeine, and 4-nitrophenol are the only compounds with values of $K_{C/W}^x$ that are less than unity. For compounds for which multiple data points are available, there is reasonably good agreement; values of $K_{C/W}^x$ for the same compound reported by different research groups generally agree to within 50%. For example, there are 4 separate estimates of the partition coefficient for phenol$^{14,15,17,21}$ the values of which range from 0.45 to 1.6. Measurements for the partition coefficient of 2,4–dichlorophenol exhibit somewhat better agreement (42$^{13}$ to 70$^{21}$). Benzene measurements agreed better still (2,756$^{12}$ vs. 3,500$^{15}$). The value for toluene presented here does not agree well with the published value$^{12}$ but there is excellent agreement between our value and the literature value$^{18}$ for benzaldehyde. Although variations between research groups may be attributed in part to the density–interpolation technique used here, deviations greater than roughly 40% (± 20% for each data point) cannot be attributed to data handling procedures. The data of Curren and Burk$^{19}$ may provide insight into these discrepancies. For the partitioning of pentachlorophenol, these researchers found $K_{C/W}^x$ to have a strong dependence on the concentration of the solute.
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At the water saturation limit, a partition coefficient of approximately 80 was measured, while at 20% of the saturation limit the partition coefficient was found to be 10. Thus, some of the discrepancies between different researchers may be due to differences in the solute concentrations that were used in their experiments. Nonetheless, a strong dependence of solute partitioning on concentration was not found for the combination of compounds and conditions considered in this study.

Partition coefficient dependence on solute concentration notwithstanding, some generalizations regarding families of compounds can also be made. In the series including benzaldehyde, acetophenone, and propiophenone, the exchange of the hydrogen in benzaldehyde for the methyl group in acetophenone (simultaneously transforming an aldehyde into a ketone) has little effect on $K_{c/w}^*$. Exchanging the methyl group for the ethyl group of propiophenone has a larger effect. In the series, methyl−, ethyl−, propyl benzoate, however, the length of the alkyl chain has a much more regular effect, as the partition coefficients of the series are regularly distributed. Toluene is more water soluble than benzene, though the opposite behavior would be expected based on the hydrophobicity of the two compounds. As explained previously, for compounds with extremely large values of $K_{c/w}^*$, the experimental error tends to be rather large, possibly accounting for the surprising trend in the values measured for toluene and benzene. Fluorobenzene is more water soluble than chlorobenzene, but the partitioning behavior of the latter is comparable to bromobenzene.

Increasing the number of carbons in ring structures generally increases the partition coefficient (cyclopentene/cyclohexene). Cyclization increases the water solubility measurably (i.e., decreases the value of $K_{c/w}^*$) as illustrated by both cyclohexane/hexane and cyclohexanone/2–hexanone. Saturation of alkanes decreases their water solubility somewhat (cyclohexane/cyclohexene). Addition of the highly water–soluble hydroxyl– functional group decreases the $K_{c/w}^*$ of benzaldehyde dramatically from 40 to roughly unity (vanillin), but addition of the methoxy– functionality has a much smaller effect as illustrated by the comparison of acetophenone to the methoxyacetophenones. As successive chlorines are added to phenol (2–chlorophenol, 2,4–chlorophenol, 2,4,6–trichlorophenol, 2,3,4,5–tetrachlorophenol, and
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pentachlorophenol) the resulting compounds are generally less water soluble, though 2,3,4,5-tetrachlorophenol does not seem to follow this trend. This may indicate erroneous measurements of one or more of the chlorine-substituted phenols or it may be indicative of more complicated behavior perhaps related to comments made earlier regarding the effect of solute concentration on the measured partition coefficient. The position of substitution groups has a large and irregular effect on $K_{C/W}^x$; 2–nitrophenol is 400 times less water soluble than 4–nitrophenol, though 2–chlorophenol is 4–times more water soluble than 4–chlorophenol. Likewise, 2–methoxyacetophenone is roughly twice as water–soluble as 3–methoxyacetophenone. Although the strong effect of substitution group position was first noted by Karásek et al., the cause of this behavior is still not understood at this time.

3.5 Discussion of Empirical Correlation Methods

Three empirical methods for correlating data were examined in order to assess their abilities to extend the data set to include new compounds: comparison to water solubility; comparison to estimated values of $K_{O/W}^x$; and LSERs. Overall, water solubility correlation and $K_{O/W}^x$ provided relatively good estimates for non–acidic compounds, but failed for acidic compounds. The LSER approach was relatively robust ($\pm 0.20 \log_{10}$ units in the best case) for the majority of the available data. The remainder of this paper is a detailed discussion of these analyses.

Water Solubility and $K_{C/W}^x$. Given the wealth of water solubility data available, a method which relates $K_{C/W}^x$ directly to water solubility could be quite powerful. Thermodynamically, the partition coefficient is described by the inverse ratio of the activity coefficients ($\gamma_i$) of the solute $i$ in each of the corresponding phases:

$$K_{C/W}^x = \frac{x_i^{(C)}}{x_i^{(W)}} = \frac{\hat{f}_i^{(C)}}{\hat{f}_i^{(W)}} \frac{\gamma_i^{(W)}}{\gamma_i^{(C)}} = \frac{\gamma_i^{(W)}}{\gamma_i^{(C)}}$$  \hspace{1cm} (3-3)

where, $\hat{f}_i^{(P)}$ refers to the mixture fugacity of the solute $i$ in phase $P$ (either $C$ for carbon dioxide or $W$ for water). The two values, $\hat{f}_i^{(W)}$ and $\hat{f}_i^{(C)}$ must equal each other at
thermodynamic equilibrium. \( f_i^{(p)} \) is the reference fugacity of solute \( i \) in phase \( P \). The reference fugacity has been taken to be unity in the reference state (pure liquid at the same temperature and pressure).

If the logarithm (base 10) is taken of each side of equation (3-3), the resulting relationship is obtained:

\[
\log_{10} K_{C/W}^x = \log_{10} \gamma_i^{(W)} - \log_{10} \gamma_i^{(C)}
\]

(3-4)

The activity coefficient in the water phase is related to the saturation solubility (\( x_i^{(W), sat} \)), for liquids:

\[
\gamma_i^{(W), sat} = \frac{1}{x_i^{(W), sat}}
\]

(3-5a)

or solids\(,^{26}\)

\[
\gamma_i^{(W), sat} = \frac{1}{x_i^{(W), sat}} \frac{P_{\text{solid}}^*}{P_{\text{liquid}}^*}
\]

(3-5b)

where \( P^* \) refers to the vapor pressure of the pure solute, \( i \), at the temperature of the measurement and is used to correct for the reference state. The compounds under consideration here have limited water solubility (<1 wt\%, with the exceptions of tetrahydrofuran and 3–buten–2–one which are nearly completely miscible with water).

For compounds with low solubility the conventional assumption is to equate \( \gamma_i^{(W), sat} \) with the activity coefficient at infinite dilution (i.e., \( \gamma_i^{(W), \infty} \)). For dilute solutions, one can convert from mole fraction units to the more commonly used molarity units (\( C_i^{(W), sat} \)) using the molar volume of water \( V_w \):

\[
x_i^{(W), sat} = V_w C_i^{(W), sat}
\]

(3-6).

Substitution of this relationship into equation (3-5) yields:

\[
\log_{10} K_{C/W}^x = -\log_{10} C_i^{(W), sat} - \log_{10} V_w - \log_{10} \gamma_i^{(C), sat}
\]

(3-7).

If \( \gamma_i^{(C), sat} \) is a constant, then equation (3-7) predicts a linear relationship between \( \log_{10} C_i^{(W), sat} \) and \( \log_{10} K_{C/W}^x \) with a slope of \(-1\) and an intercept equal to the negative of
the sum of $\log_{10} V_w$ and $\log_{10} \gamma_i^{(C)}$. Figure 3-3 is a plot of the logarithm of $\log_{10} K_{c/w}^x$ versus $\log_{10} C_{i}^{(W),saturated}$ for the 30 compounds for which solubility measurements were available. Also shown are lines of equal carbon dioxide–phase activity coefficients. For a large subset of the compounds, mainly those with little or no hydrogen–bond acidity (with the exception of benzene which appears to be an outlier), a linear relationship exists between $\log_{10} C_{i}^{(W),saturated}$ and $\log_{10} K_{c/w}^x$. Benzene may not be a true outlier because, for highly water–insoluble compounds, calculated values of $K_{c/w}^x$ can be extremely sensitive to the measured water concentration as explained previously. The

![Graph showing correlation between logarithm of $K_{c/w}^x$ and logarithm of $C_{i}^{(W),saturated}$]([Image](image.png))

**Figure 3-3.** Correlation of measured CO$_2$/H$_2$O partition coefficients ($\log_{10} K_{c/w}^x$) to saturation water solubility ($\log_{10} C_{i}^{(W),saturated}$); ○, non–acidic solute; ●, acidic solute; ▲, benzene. Solid line is the best–fit line. Dashed lines denote lines of equal values of $\gamma_i^{(C)}$ ($\gamma_i^{(C)} = 1, 100, and 10,000$, respectively).
slope of the best-fit line of non-acidic compounds (excluding benzene) is equal to $-1.1 \pm 0.1$. Not surprisingly, both phases are quite non-ideal, and the activity coefficients of the dissolved solutes deviate significantly from unity. The carbon dioxide solutions yield an average value for the activity coefficient of $\gamma_i^{(c)} \sim 50$ to correlate the data, while the values of $\gamma_i^{(w)}$ range from 1 to 10,000. As it is derived directly from water solubility data, $\gamma_i^{(w)}$ has a firm basis. There is, however, no fundamental reason to expect $\gamma_i^{(c)}$ to be equal to 50 (or any other value) without further evidence. For this reason, equation (3-7) by itself is not particularly valuable as a predictive tool.

Since both the Hildebrand–Scatchard solubility parameter\textsuperscript{28, 29} and the Hansen solubility indexes\textsuperscript{29, 30} have been successful in correlating a variety of solvation phenomena, these approaches were also investigated. Not surprisingly, the single-parameter approach of Hildebrand–Scatchard failed to predict experimental values of $K_{c/w}^x$ (AARD $\gg$ 100%). Attempts to modify the inherently qualitative approach of Hansen, which incorporates three parameters to describe van der Waals, dipole–dipole, and hydrogen bonding interactions, to make quantitative predictions also failed (AARD $\sim$ 100%).

**Prediction of $K_{c/w}^x$ from $K_{o/w}^c$.** Although relatively few data are available for carbon dioxide/water partitioning, considerably more have been reported for the octanol/water system. This is because octanol has been recommended as the organic solvent for direct comparison to lipophilic biological fluids and environmental systems.\textsuperscript{31} Using the available partitioning data, a reliable molecular group contribution method has been developed by Leo and Hansch\textsuperscript{31} for estimation of $K_{o/w}^c$ (where the superscripts $C$ and $x$ have the same meanings as used for $K_{c/w}^x$). The general form of the model is shown in equation (3-8):

$$\log_{10} K_{o/w}^c = \sum_i f_i + \sum_j F_j$$

(3-8)

where $f_i$'s are referred to as “fragment constants” and are related to the constituent atoms of a molecule while the $F_j$'s are known as “structure factors” and are related to the manner in which the atoms are bonded. The values proposed by Leo and Hansch for $f_i$'s
and $F_j$'s were used for all estimates of the octanol/water partition coefficient, which is typically based on concentration units as indicated in equation (3-8). For internal consistency, values of $K_{O/W}^C$ were converted to $K_{O/W}^x$ by assuming a constant octanol density of 0.83 g cm$^{-3}$. It seems reasonable to expect that partitioning between octanol (a hydrophobic, low dielectric constant solvent) and water would be similar to partitioning between carbon dioxide (also a hydrophobic, low dielectric constant solvent) and water, though some deviation is expected in the case of hydrogen-bonding solutes since octanol can interact via hydrogen bonds whereas carbon dioxide cannot. Additionally, it is expected that $K_{O/W}^x$ would fail to predict the partitioning behavior of fluorinated compounds since this class of compounds is both hydrophobic and lyophobic but is readily soluble in CO$_2$ (as a rule). These differences notwithstanding, it was expected that $K_{C/W}^x$ and $K_{O/W}^x$ would be correlated for the hydrocarbon compounds studied here, though there is no reason to expect the two partition coefficients to be exactly equal.

Figure 3-4 is a plot of measured $\log_{10}K_{C/W}^x$ versus $\log_{10}K_{O/W}^x$ as estimated from equation (3-8). There are several striking features to Figure 3-4. First is the overall poor correlation of $K_{C/W}^x$ with $K_{O/W}^x$. Deviation between the octanol/water prediction and the carbon dioxide/water measurement ranges from as small as a factor of 1.6 to as large as 4 orders of magnitude. Interestingly, with the exceptions of tetrahydrofuran and 2-buten-3-one (both of which are highly water soluble), $K_{O/W}^x$ is greater than $K_{C/W}^x$.

A second notable feature in Figure 3-4 is that there is a much better correlation between $K_{O/W}^x$ and $K_{C/W}^x$ for a subset of compounds with no hydrogen–bond–donating capability (i.e., compounds with no Brønsted acidity). The correlation for this subset is depicted in Figure 3-5. The only non-acidic compound for which data are available and which does not belong to the highlighted subset is aniline which is a base. Most likely, aniline is an outlier due to the spontaneous reaction of amines with carbon dioxide to form carbamic acid.\textsuperscript{32} For the 24 non–acidic compounds considered, the correlation between $K_{O/W}^x$ and $K_{C/W}^x$ is adequate; the average absolute deviation (AAD) is 0.36 $\log_{10}$ units.
Figure 3-4. Correlation of $\log_{10} K_{\text{C}/\text{w}}^x$ (at a fixed CO$_2$ solvent density of 0.75 g cm$^{-3}$) to $\log_{10} K_{\text{O}/\text{w}}^x$ estimated by the methods of Leo and Hansch$^{30}$; o, non–acidic solute; •, acidic solute; solid line is the 45° line.

The largest outliers in Figure 3-5 are 2–methoxyacetophenone (absolute deviation = 0.88 log$_{10}$ units), 1,1,2,2–tetrachloroethane$^{16}$ (absolute deviation = 0.92 log$_{10}$ units) and benzene$^{15}$ (absolute deviation = 1.24 log$_{10}$ units). That an ortho–substituted compound is an outlier is not particularly surprising since partitioning behavior of such compounds is difficult to predict. Furthermore, the water solubility of 2–methoxyacetophenone may be influenced slightly by weak intermolecular hydrogen bonding between the methoxy hydrogen and the carbonyl oxygen. Failure of $K_{\text{O}/\text{w}}^x$ for 1,1,2,2–tetrachloroethane is more surprising given that polyhalogenation is included specifically by Leo and Hansch$^{31}$ as a structure factor contribution in an effort to capture the decrease in molecular polarity associated with opposing nearby dipoles. Benzene is an outlier for both the solubility correlation.
Figure 3-5. Correlation of $\log_{10} K_{C/W}^{x}$ (at a fixed CO$_2$ solvent density of 0.75 g cm$^{-3}$) to $\log_{10} K_{O/W}^{x}$ estimated by the methods of Leo and Hansch$^{30}$ including only non-acidic solutes; o, typical non-acidic solutes; •, benzene; ■, 2-methoxyacetophenone; ▲, 1,1,2,2-tetrachloroethane; solid line is the best-fit line; dashed lines indicate ±20%.

and the $K_{O/W}^{x}$ correlation. If these three compounds are neglected, the best-fit slope and intercept are 0.75±0.07 and 0.14±0.07, respectively, and the AAD reduces to 0.26 log$_{10}$ units. Including outliers in the correlation yields values of 0.71±0.10 and 0.23±0.10 respectively for the slope and intercept.

**Correlation of $K_{C/W}^{x}$ using LSERs.** Lagalante and Bruno$^{23}$ proposed the use of LSERs to correlate measured values of $K_{C/W}^{x}$. In general practice, the LSER method$^{33}$ assumes that the logarithm of some general thermodynamic or kinetic property ($\xi$) of a given solute ($i$) can be related empirically to its physicochemical properties (referred to as solute descriptors) in a linear fashion:

$$\log_{10} \xi = \log_{10} \xi_0 + \sum (\text{coefficient})_x (\text{solute descriptor})$$  \hspace{1cm} (3-9)
where $\zeta_0$ is a constant term. For a given thermodynamic property, the values of the various coefficients (as well as $\zeta_0$) must be determined by regression; however solute descriptors are typically measured independently by spectroscopic or chromatographic means. For their evaluation of LSERs for correlation of $K^x_{C/w}$, Lagalante and Bruno\textsuperscript{23} incorporated a solvent-dependent term to account for the compressibility of CO$_2$ near its critical point. Based on this approach, the researchers proposed several equations, the most successful of which was:

$$\log_{10} K^x_{C/w} = 2.175 - 1.578R_2 + 0.6323\pi_2^H - 2.254\alpha_2^H - 1.986\beta_2^H + 0.9221V_2 + 2.343\pi_1$$  \hspace{1cm} (3-10)

In equation (3-10), $R_2$ refers to the excess index of refraction, $\pi_2^H$ refers to dipolarity/polarizability, $\alpha_2^H$ refers to the hydrogen bond acidity, $\beta_2^H$ refers to the basicity, and $V_2$ is a measure of the molar volume as recommended by McGowan.\textsuperscript{34} $\pi_1$ refers to the solvent dipolarity/polarizability of carbon dioxide and was assumed to be a linear function of reduced density ($\rho_r$) as suggested by the spectroscopic measurements of Smith and his coworkers.\textsuperscript{35}

$$\pi_1 = 1.15\rho_r - 0.98 \quad (\rho_r < 0.7)$$  \hspace{1cm} (3-11a)

$$\pi_1 = 0.173\rho_r - 0.37 \quad (\rho_r > 0.7)$$  \hspace{1cm} (3-11b)

Lagalante and Bruno\textsuperscript{23} reported an AARD for 116 regressed data points of 21%. Unfortunately, their regression included data for only 6 compounds (phenol, benzyl alcohol, benzoic acid, 2-hexanone, cyclohexanone, caffeine), thus restricting the generalization of equation (3-10). With measurements of $K^x_{C/w}$ for many more compounds now available, equation (3-10) was tested at a fixed fluid density of CO$_2$ of 0.75 g cm$^{-3}$. Since solute descriptors for 33 of the compounds were available in the literature,\textsuperscript{36-38} a more robust test of the predictive power of equation (3-10) could be performed. Table 3-3 lists the values of solute descriptors used in this study. Figure 3-6 is a plot of the measured values of $\log_{10} K^x_{C/w}$ versus predictions using equation (3-10) for all of the compounds listed in Table 3-3 (except for naphthalene for which no $K^x_{C/w}$ data were available at a density of 0.75 g cm$^{-3}$). Although the majority of data
Table 3-3. LSER solute descriptors used in this study. Solute descriptors were based on data from references\textsuperscript{35-37} and appropriate physical descriptions are in the text.

<table>
<thead>
<tr>
<th>solute</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$V_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>0.818</td>
<td>1.01</td>
<td>0.0</td>
<td>0.49</td>
<td>1.0139</td>
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<td>Aniline</td>
<td>0.955</td>
<td>0.96</td>
<td>0.26</td>
<td>0.41</td>
<td>0.816</td>
</tr>
<tr>
<td>Benzaldehyde</td>
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<td>0.0</td>
<td>0.39</td>
<td>0.873</td>
</tr>
<tr>
<td>Benzene</td>
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<td>0.52</td>
<td>0.00</td>
<td>0.14</td>
<td>0.7164</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.73</td>
<td>0.9</td>
<td>0.59</td>
<td>0.4</td>
<td>0.932</td>
</tr>
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<td>Benzylic alcohol</td>
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<td>0.87</td>
<td>0.33</td>
<td>0.56</td>
<td>0.916</td>
</tr>
<tr>
<td>Bromobenzene</td>
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<td>0.73</td>
<td>0.00</td>
<td>0.09</td>
<td>0.8914</td>
</tr>
<tr>
<td>Caffeine</td>
<td>1.5</td>
<td>1.6</td>
<td>0.0</td>
<td>1.35</td>
<td>1.363</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.718</td>
<td>0.65</td>
<td>0.00</td>
<td>0.07</td>
<td>0.8388</td>
</tr>
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<td>2-Chlorophenol</td>
<td>0.853</td>
<td>0.88</td>
<td>0.32</td>
<td>0.31</td>
<td>0.8975</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>0.915</td>
<td>1.08</td>
<td>0.67</td>
<td>0.21</td>
<td>0.8975</td>
</tr>
<tr>
<td>Cyclohexane</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.8454</td>
</tr>
<tr>
<td>Cyclohexene</td>
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<td>0.20</td>
<td>0.00</td>
<td>0.10</td>
<td>0.8024</td>
</tr>
<tr>
<td>Cyclohexanone</td>
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<td>0.56</td>
<td>0.861</td>
</tr>
<tr>
<td>Cyclopentene</td>
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<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.6615</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.416</td>
<td>0.64</td>
<td>0.10</td>
<td>0.11</td>
<td>0.6352</td>
</tr>
<tr>
<td>2,4-Dimethylphenol</td>
<td>0.843</td>
<td>0.8</td>
<td>0.53</td>
<td>0.39</td>
<td>1.0569</td>
</tr>
<tr>
<td>Ethylbenzoate</td>
<td>0.689</td>
<td>0.85</td>
<td>0.0</td>
<td>0.46</td>
<td>1.2135</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>0.477</td>
<td>0.57</td>
<td>0.00</td>
<td>0.10</td>
<td>0.7341</td>
</tr>
<tr>
<td>Hexane</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.954</td>
</tr>
<tr>
<td>2-Hexanone</td>
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<td>0.68</td>
<td>0.0</td>
<td>0.51</td>
<td>0.97</td>
</tr>
<tr>
<td>Methylbenzoate</td>
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<td>0.85</td>
<td>0.0</td>
<td>0.48</td>
<td>1.0726</td>
</tr>
<tr>
<td>3-Methyl-4-chlorophenol</td>
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<td>1.02</td>
<td>0.65</td>
<td>0.22</td>
<td>1.038</td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>0.822</td>
<td>0.88</td>
<td>0.57</td>
<td>0.34</td>
<td>0.9160</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.340</td>
<td>0.92</td>
<td>0.0</td>
<td>0.20</td>
<td>1.085</td>
</tr>
<tr>
<td>2-Nitrophenol</td>
<td>1.015</td>
<td>1.05</td>
<td>0.05</td>
<td>0.37</td>
<td>0.949</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td>1.07</td>
<td>1.72</td>
<td>0.82</td>
<td>0.26</td>
<td>0.949</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.805</td>
<td>0.89</td>
<td>0.6</td>
<td>0.3</td>
<td>0.775</td>
</tr>
<tr>
<td>Propylbenzoate</td>
<td>0.675</td>
<td>0.8</td>
<td>0.0</td>
<td>0.46</td>
<td>1.354</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>0.595</td>
<td>0.76</td>
<td>0.16</td>
<td>0.12</td>
<td>0.8800</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>0.289</td>
<td>0.52</td>
<td>0.00</td>
<td>0.48</td>
<td>0.6223</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>0.499</td>
<td>0.68</td>
<td>0.13</td>
<td>0.08</td>
<td>0.7576</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.601</td>
<td>0.52</td>
<td>0.0</td>
<td>0.15</td>
<td>0.8573</td>
</tr>
</tbody>
</table>

points do not fall on the 1:1 line, there is a distinct correlation between the measurements and the predictions. All types of compounds (including hydrogen–bond forming species) followed the trend line reasonably well and there were no clear outliers (though there was significant scatter). The largest deviation was for benzene (absolute deviation = 1.9 log units).

Although these initial results are relatively encouraging, equation (3-10) clearly is not reliable as a predictive tool. Therefore, the coefficients of several LSERs of the form
Figure 3-6. Comparison of partition coefficients measured at a fixed CO\textsubscript{2} density of 0.75 g cm\textsuperscript{-3} to estimates based on the 7 parameter LSER recommended by Lagalante and Bruno.\textsuperscript{23} Parameter values are given in equation (3-10). The 45\textdegree line is shown for comparison.

suggested by equation (3-10) were regressed using the new data. Two approaches were taken: 1) only data at a fixed CO\textsubscript{2} solvent density of 0.75 g cm\textsuperscript{-3} were included and 2) data available at all densities were used for the regression.

At a fixed density, the number of adjustable parameters in equation (3-10) is reduced to 6 since the CO\textsubscript{2} polarizability (\(\pi_1\)) and the constant term are redundant. With this in mind, the performance of four equations with the general form of equation (3-10) was evaluated. Parameters were either removed based on statistical significance or combined in a process analogous to that used by Lagalante and Bruno.\textsuperscript{23} In one trial, the addition of the cross term corresponding to the product \(\pi_1 \times \pi_2\) was considered. Although the process of removing and combining parameters has a limited physical basis, the primary objective was to reduce the number of adjustable parameters needed for a satisfactory correlation.
Figure 3-7 compares predicted and measured values of $K_{c/w}^x$ on a log$_{10}$ scale at a fixed CO$_2$ density of 0.75 g cm$^{-3}$. Although the overall fit is reasonable ($r^2 \sim 0.88$, average absolute deviation (AAD) = 0.20 log$_{10}$ units, maximum deviation = 0.96 log$_{10}$ units), there are two outliers: benzene$^{15}$ and 1,1,2,2–tetrachloroethane.$^{16}$ Benzene is an outlier in all three analyses (water solubility, $K_{o/w}$, and LSER) and 1,1,2,2–tetrachloroethane is an outlier in both the $K_{o/w}$ and LSER analyses (solubility data were not available for this compound). The values and the errors of the regressed parameters of the 4 LSER correlations are listed in Table 3-4. Both benzene and 1,1,2,2–

**Figure 3-7.** Correlation of partition coefficients measured at a fixed CO$_2$ density of 0.75 g cm$^{-3}$ to partition coefficients predicted by a 6–parameter LSER (regressed values provided in Table 3-4, entry #1); ○, benzene; ■, 1,1,2,2–trichloroethane; O, all other compounds listed in Table 3 (except naphthalene for which only low density data were available). All 32 available data points included in regression.
Table 3-4. Regressed LSER Coefficients for LSERs describing partitioning at a fixed CO₂ density of 0.75 g cm⁻³; 32 compounds were considered in the regression (all compounds listed in Table 3-3 except naphthalene). Values for the correlation constant ($r^2$) and average absolute deviation (AAD) in log₁₀ units are also tabulated. Definitions for the solute descriptors are located in the text.

<table>
<thead>
<tr>
<th>#</th>
<th>AAD</th>
<th>$r^2$</th>
<th>(log₁₀)</th>
<th>$\xi_0$</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$V_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.20</td>
<td>0.95</td>
<td>0.000</td>
<td>-2.100</td>
<td>-0.973</td>
<td>-3.078</td>
<td>-3.319</td>
<td>2.780</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>±3.611</td>
<td>±0.380</td>
<td>±0.381</td>
<td>±0.306</td>
<td>±0.374</td>
<td>±0.234</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.32</td>
<td>0.88</td>
<td>3.300</td>
<td>NA</td>
<td>-0.779</td>
<td>-3.120</td>
<td>-2.472</td>
<td>0.362</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>±0.314</td>
<td>±0.427</td>
<td>±0.457</td>
<td>±0.513</td>
<td>±0.296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.37</td>
<td>0.86</td>
<td>3.100</td>
<td>NA</td>
<td>NA</td>
<td>-3.672</td>
<td>-3.143</td>
<td>0.259</td>
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<td></td>
<td></td>
<td></td>
<td>±0.307</td>
<td>±0.356</td>
<td>±0.372</td>
<td>±0.302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.38</td>
<td>0.86</td>
<td>3.400</td>
<td>NA</td>
<td>NA</td>
<td>-3.667</td>
<td>-3.073</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>±0.160</td>
<td>±0.354</td>
<td>±0.361</td>
<td></td>
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</tr>
</tbody>
</table>

tetrachloroethane were included in all regressions. Based on the magnitude of relative errors, the three most important parameters are $\alpha^H_2$, $\beta^H_2$, $V_2$. In their studies of partitioning between water and the near–critical refrigerants R143a³⁹ and R134a⁴⁰ Lagalante, Bruno and their coworkers found that the same parameters dominated. Quantitatively, the LSER parameter values presented here agree more closely with those reported for partitioning between water and hydrocarbon solvents.³⁸

The LSER method was used to analyze all available data for a set of 33 compounds (see Table 3-3); 332 data points, covering a range of CO₂ densities from 0.2–0.9 g cm⁻³, were utilized. Four separate forms of the LSER were tested. Regressed
parameters and their respective errors are listed in Table 3-5. Including all 7 parameters in the regression yielded acceptable correlations ($r^2 \sim 0.89$, AAD = 0.30 log$_{10}$ units, maximum deviation = 1.20 log$_{10}$ units). Figure 3-8 is a comparison between measured and LSER–predicted values (using the form suggested by equation (3-10) and the coefficient values listed as entry #1 in Table 3-5) of log$_{10} K^x_{C_{w}}$ for the entire data set.

Although there is considerable scatter, there are no clear outliers. In this particular LSER model, the most important parameters were $\alpha^H_2$, $\beta^H_2$, $V_2$ (as before) and $\pi_1$ (which accounts for the dependence of $K^x_{C_{w}}$ on CO$_2$ density). Consideration of all available density data leads to regressed LSER coefficients which agree rather closely with those reported by Lagalante and Bruno$^{39,40}$ to describe partitioning between water and the variable–density, near–critical refrigerants, R143a and R134a.

### Table 3-5. Regressed coefficients for LSERs based on data taken over a range of carbon dioxide densities. Values regressed for the entire data set (33 compounds, 332 data points). Values for the correlation constant ($r^2$) and average absolute deviation (AAD) in log$_{10}$ units are also tabulated. Definitions for the solute descriptors are located in the text.

<table>
<thead>
<tr>
<th>#</th>
<th>$r^2$</th>
<th>AAD (log$_{10}$)</th>
<th>Regressed coefficients for respective solute descriptors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terms</td>
<td>$r^2$</td>
<td>AAD</td>
<td>$\xi$</td>
</tr>
<tr>
<td>7</td>
<td>0.89</td>
<td>0.30</td>
<td>3.811</td>
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<tr>
<td>6</td>
<td>0.88</td>
<td>0.29</td>
<td>3.810</td>
</tr>
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<tr>
<td>5</td>
<td>0.87</td>
<td>0.30</td>
<td>3.150</td>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.87</td>
<td>0.32</td>
<td>3.180</td>
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</tr>
</tbody>
</table>
Figure 3-8. Correlation of measured partition coefficients to partition coefficients predicted by a 7-parameter LSER; all available data over a range of CO₂ densities from 0.2–0.9 g cm⁻³ were considered (332 data points, 33 compounds). Regressed parameters for the LSER are listed in Table 3-5 (entry #1).

The library of 33 compounds (and 332 separate data points) created by this study may be used to develop empirical correlations adequate at least for compound screening purposes or for and/or predicting trends. For compounds which are similar to those considered in this study, the LSER approach should provide estimates to within roughly ±0.30 log₁₀ units of log₁₀ \( K_{c/w}^* \). Although this error may seem large, values of \( K_{c/w}^* \) measured for a given compound at identical conditions may vary by as much as 50% between research groups. Given these errors in published data, use of the three correlation methods (correlation to water solubility, comparison to group contribution octanol/water partition coefficients, and LSER methods) presented here should provide estimates accurate enough for preliminary work, screening purposes, and evaluation of kinetic data. Since none of the methods has a firm basis in theory, there is no guarantee of the accuracy of any of the three methods for a compound not explicitly considered in
this study. To increase reliability, the three correlation methods should be used to
generate three separate partition coefficient estimates. If the three estimates agree to
within the correlation accuracy (within roughly 50%), the estimated value can be used
with reasonable confidence.

Since only the LSER approach successfully predicted the partitioning behavior of
acidic solutes, more work is needed to improve the current understanding of the behavior
of acidic compounds in biphasic CO₂/H₂O mixtures. At this point, it is not clear what
solvent properties contribute to the unusual partitioning behavior of acidic solutes and a
theoretical approach might be required to develop fundamental understanding.

3.6 Conclusions and Recommendations for the Usage of Correlation
Methods

Values of \( K_{C/W}^* \) for 18 new compounds have been measured at 300 K and 80 bar
at a fluid density of \( \rho = 0.75 \text{ g cm}^{-3} \) based on pure CO₂. This study nearly doubled the
database while focusing on aromatics, alkanes and alkenes, with one exception:
heterocyclic tetrahydrofuran. \( K_{C/W}^* \) correlated fairly well with solute solubility in water
except for the case of acidic compounds (Brønsted acidity). Use of \( K_{O/W}^* \) (estimated by
group contributions) as a correlant for \( K_{C/W}^* \) gave mixed results. The correlation is good
for non–acidic solutes, but the overall correlation (including both acidic and non–acidic
solutes) is extremely poor. There was, however, good correlation between LSER
predictions and experimental measurements (to within 0.30 \( \log_{10} \) units), with no
restrictions on the solute properties for the compounds considered in this study.
Regressed values for an LSER are recommended for compounds which are chemically
similar to those considered in this study. An LSER that was regressed at a fixed CO₂
density (0.75 g cm\(^{-3}\)) was presented along with an LSER for variable densities. In both
cases, reasonably good correlations were obtained with fixed density correlation
exhibiting less scatter. The most important LSER parameters were solute acidity, solute
basicity, and solute molecular volume. For non–acidic solutes, the three approaches
(correlation to water solubility, \( K_{O/W} \), and LSERs) are complementary and could be
used in conjunction to obtain estimates of \( K_{C/W}^* \) for which no prior data are available.
3.7 Acknowledgements

Undergraduates Ben F. Nicholson (now at Cornell University) and Christopher J. Russel made valuable contributions to the experimental measurements presented in this chapter.

3.8 Author's Note

This work has been submitted for publication in Journal of Chemical and Engineering Data under the title “Partition Coefficients of Organic Solutes between Supercritical Carbon Dioxide and Water: Experimental Measurements and Empirical Correlations”. Through the review process, this manuscript has been improved substantially relative to this thesis chapter.

3.9 References

(3) Schmitt, W.J.; Reid, R.C. The Use of Entrainers in Modifying the Solubility of Phenanthrene and Benzoic Acid in Supercritical Carbon Dioxide and Ethane, Fluid Phase Equil. 1986, 32, 77.


CHAPTER 4

CHARACTERIZATION OF ACOUSTICALLY GENERATED EMULSIONS AND EMULSION STABILITY

Reaction engineering of two-phase emulsified systems is considerably more difficult than design of one-phase systems. In addition to the effects of chemical kinetics, understanding the partitioning of reagents (Chapter 3) and mass transport effects is required for physical models of overall reaction dynamics in two phase systems. Estimates of mass transport rates invariably rely on accurate characterization of emulsion properties, especially droplet size, as it defines the length scale for intra-droplet diffusion. Furthermore, the interfacial area over which mass transport occurs in emulsions is determined directly from the combination of droplet size and the volume fraction of the dispersed phase. Additional complications arise if the rate of demulsification and reaction are similar. In these instances, insights regarding the process of demulsification are needed to help interpret kinetic data.

This chapter discusses the characterization and stability of emulsions consisting of dense carbon dioxide and water which are produced by using ultrasound. Although emulsions incorporating a dense carbon dioxide phase have been a topic of active research for only 5 years, the greater field of emulsion science is quite mature. There are definite parallels between the two sorts of emulsions and consideration of the well-known emulsions which contain oil and water can certainly guide analysis of emulsions containing a dense carbon dioxide phase. In this vein, the first three sections of this chapter provide some introductory material within the context of emulsions of oil and water generated at ambient pressure. The objective of this introduction is to provide sufficient background to permit an interpretation of data obtained with high pressure emulsions. Specifically, Section 4.1 describes general techniques for measuring emulsion characteristics that are especially relevant to reaction engineering applications and emulsion stability. The topic of emulsion stabilization is discussed in Section 4.2,
focusing on the effects of interdroplet forces. Important physical mechanisms of
demulsification are described in Section 4.3. Section 4.4 discusses previous work in the
relatively new field of carbon dioxide/water emulsions, a field which has been received
numerous contributions from Keith Johnston’s research group at the University of Texas,
Austin. Section 4.5 presents new experimental characterization techniques and
measurements of high-pressure carbon dioxide/water emulsions generated by ultrasound.
The process of emulsification is discussed separately in Chapter 5.

4.1 General Techniques for Characterization of Emulsions

Droplet size. The single most important characteristic of emulsions is the droplet size of
the dispersed phase. Flow properties, stability, and appearance are all directly influenced
by droplet size. The measurement of droplet sizes of emulsions containing dense carbon
dioxide is expected to be quite challenging due to the limited accessibility to the
pressurized environment. McClements¹ (1999) lists the most common droplet size
measurement techniques that could potentially be applied to our system:

1) Microscopy (either optical, confocal, or scanning/transmission electron)
whereby samples of the emulsion are analyzed directly by imaging. Light microscopy is
the most common method of droplet sizing, though it can be quite tedious since a large
number of images must be analyzed. Modern software expedites image analysis
somewhat, but microscopy remains more labor intensive than other more automated
means of determining droplet sizes. Provided that a suitable view cell can be constructed,
microscopy can be readily adapted to high-pressure applications. As compared to all
other methods, microscopy has the advantage that the droplet sizes obtained are model
independent. All other techniques require a model which includes droplet diameter as a
fit parameter. Due to approximations incorporated in the models and difficulties in
obtaining global fits of nonlinear equations, model-dependent measurements must always
be approached with a certain degree of skepticism. Viewed in this manner, fitting droplet
size distributions to experimental measurements is a classic poorly defined problem.

Of course, microscopy measurements are not error free. Most importantly, light
microscopy (the most common and easiest microscopy method) cannot resolve droplets
smaller than roughly 1 μm, and the initial development of emulsion science was greatly
hampered by this size limit. Higher resolution methods such as scanning/transmission
electron microscopy typically require that the sample be contained in an evacuated chamber and are not readily adapted to size analysis of emulsions. A further important limitation is that microscopy is a two-dimensional representation of a three-dimensional system. Depending on the depth of field, the volume of the sample, and differential sedimentation rates, droplet size measurements with microscopy can be subject to systematic errors. Some additional limitations of microscopy are discussed in Section 4.5.5.

2) Static light scattering by emulsion droplets can be used to determine their size. When light is transmitted through an emulsion, a certain percentage is scattered. The percentage of light that is scattered and the angle at which it is scattered can be analyzed to determine the droplet size. For droplets of the size range characteristic of most emulsions (i.e., 0.1 – 100 μm), scattering data is interpreted using Mie theory. This theory assumes that 1) there is no absorption of light by the emulsion droplets, and 2) light is scattered by only one spherical droplet. In concentrated emulsions, the second assumption is not valid and Mie theory cannot be used. For this reason, static light scattering is restricted to dilute emulsions. The book written by Heimenz and Rajagopalan 2 (1997) has an excellent description of the theories used to relate scattering to droplet size. Chapter 9 of van de Hulst’s 3 classic book on light scattering (1961) is dedicated to a description of Mie theory.

Static light scattering has been used previously in high pressure applications. Chapter 8 of F. Armellini’s 4 thesis (1993) describes his use of laser light scattering for in situ measurement of the micron-sized mean diameters of salt particles formed during supercritical water shock crystallization experiments. Mariot et al. 5 (2000) demonstrated the use of static light scattering at multiple wavelengths to determine particle sizes of TiO2, dimethyl sulfoxide, and dimethylformamide in supercritical carbon dioxide. K.P. Johnston’s group has also used static light scattering and related turbidity techniques to characterize emulsions of dense carbon dioxide and hydrocarbons 6 and water 7.

3) Dynamic light scattering (also referred to as photon correlation spectroscopy) can be used to size droplets in the range from 3 nm to 3 μm. Dynamic light scattering determines the diffusion coefficient of the droplets (due to Brownian motion) by
measuring fluctuations in the intensity of light transmitted by an emulsion over very short times. The diffusion coefficient, \( D \), is then related to the droplet radius, \( r \), using a suitable expression such as the Stokes-Einstein equation:

\[
D = \frac{k_B T}{6 \pi \mu r}
\]  

(4-1)

where \( k_B \) is Boltzmann’s constant \((1.38 \times 10^{-23} \text{ J K}^{-1})\), \( \mu \) is the viscosity of the continuous phase, and \( T \) is the absolute temperature. As with static light scattering, multiple scattering events are difficult to interpret. For this reason, dynamic light scattering is used only for dilute emulsions. Furthermore, given its sensitivity in the nanometer range, dynamic light scattering is the preferred method for analyzing colloids containing particles smaller than those characteristic of common emulsions. In supercritical carbon dioxide applications, dynamic light scattering has been used mainly to characterize micellar systems\(^8\) although the technique has been applied to dilute emulsions containing dense carbon dioxide.\(^9\) Chapter 10, volume 1, of T. Allen’s\(^10\) two volume series, Particle Size Measurement (1997), describes dynamic light scattering methods in more detail.

4) Electrical pulse counting is a technique commonly used in the food industry to measure droplet sizes.\(^1\) The concept is to flow the emulsion between two electrodes physically separated by a glass sheath containing a small orifice as depicted in Figure 4-1. When an oil droplet passes through this orifice, the current measured between the two electrodes decreases since the conductivity of typical oils is less than that of the aqueous phase. The decrease in current is related mathematically to the droplet size by physical models. Like many techniques, electrical pulse counting is also limited to dilute emulsions since interpretation of the current assumes that only one droplet passes through the orifice at a time. Furthermore, this technique is also limited to solutions which have sufficient electrolyte content to ensure conductivity of the aqueous phase. There are no accounts of using electrical pulse counting to characterize emulsions of dense carbon dioxide, though the technique could be adapted for high pressures reasonably easily.
Figure 4-1. Schematic of electrical pulse counting. The electrical current between the two electrodes is measured. The two electrodes are separated physically, with only a small orifice connecting them. The emulsion is sampled through this orifice. When an oil droplet passes through this orifice, the current decreases which can be related to droplet sizes.

5) *Sedimentation* rates are related to the droplet size. For the case of droplet sedimentation in a dilute medium (where droplet interactions can be neglected) under the influence of a gravitational field, the terminal velocity is given by:

\[
U_t = \frac{(2gr^2)(\rho_d - \rho)}{9\mu}
\]  

(4-2)

where \( g \) is the gravitational constant (~9.8 m s\(^{-2}\)), \( r \) is the droplet radius, \( \rho_d \) is the density of the droplet, \( \rho \) is the density of the surrounding fluid, and \( \mu \) is the viscosity of the surrounding fluid. Equation (4-2) applies when the droplet Reynold’s number (\( Re_d = 2\rho Ur_d \mu^{-1} \)) is less than roughly 2, a criterion which is generally met. By measuring the time required for a droplet to fall (or rise) a known distance, its diameter can be
determined using equation (4-2). For droplets smaller than roughly 2 μm, centrifugation
techniques are used to increase the terminal velocity by subjecting the emulsion to an
acceleration which is many times greater than gravity.

6) Ultrasonic spectrometry in its most common form, is a measurement of the
attenuation and/or velocity of a sound wave propagating through an emulsion as a
function of the frequency of the wave.\textsuperscript{11} The primary mechanism of attenuation is the
differential pulsation of the emulsion droplets when subjected to an acoustic field. For
emulsions, the useful frequencies of the sound wave range from 1-100 MHz,
corresponding to wavelengths from 1 to 15 μm. The primary advantage of acoustic
techniques is that theoretical interpretation of experimental data is possible for
concentrated emulsions containing up to 40% dispersed phase.\textsuperscript{12,13} The drawback to
acoustic techniques is that a large amount of thermophysical data (including adiabatic
compressibility, density, specific heat capacity, thermal conductivity, and sometimes
viscosity of the component phases) is needed to interpret the results. In practice, this
information is not always available. Ultrasonic spectroscopy is an intriguing option for
the characterization of dense carbon dioxide/water emulsions given that the
thermophysical properties of both components are readily available.\textsuperscript{14,15} A.S. Duhkin’s
and P.J. Goetz’s\textsuperscript{16} (2002) book on ultrasonic characterization of colloids is a good source
of additional information on ultrasonic methods for particle size determination.

7) Nuclear magnetic resonance (NMR) is used to measure the restriction in the
diffusion length of an emulsion component due to its presence in discrete droplets rather
than a continuum.\textsuperscript{17} The basis of this technique is to excite the free protons of a sample
using a strong magnetic field and to monitor their decay at some later time. For un-
confined systems, the NMR technique can be used to measure diffusion coefficients. For
confined systems, such as emulsions, the probe molecules are unable to diffuse freely.
As a result, their decay signal is attenuated to a lesser extent than it would be in an un-
confined system. For the confinement effect to be important, the delay time must be
large compared to the diffusion length. The time delay between proton excitation and
decay signal measurement can be varied continuously from several milliseconds to a few
seconds, so that the NMR technique is applicable to a wide range of droplet sizes.
The technique, which is not restricted to dilute emulsions, has been applied to both oil in
water and water in oil emulsions. Adapting NMR techniques to the high pressures required for dense carbon dioxide emulsions is possible though not trivial since most of the materials of pressure vessel construction (e.g., stainless steels, titanium, high-nickel alloys) are not compatible with strong magnetic fields. There is a significant literature that describes the use of sapphire and engineering polymers as materials of construction for pressure vessels that can be used for NMR studies.

8) Neutron scattering has been applied to measure droplet sizes in emulsions, though the technique is used most frequently for smaller size ranges (i.e., for particles with characteristic lengths less than 100 nm). As with dynamic light scattering, neutron scattering studies of systems containing dense carbon dioxide have generally involved micellar and microemulsion systems.

9) Dielectric spectroscopy involves measurement of the impedance spectrum, that is the combined capacitive and resistive response, of an emulsion as a function of the frequency of an applied alternating electrical current. These data are used to determine the dielectric constant of the emulsion at different frequencies. The dependence of the dielectric constant on frequency can be analyzed to determine the droplet distribution. The technique is most sensitive for emulsions containing charged particles because such particles respond most strongly to an imposed electrical field. There are no reports of using dielectric spectroscopy in systems containing dense carbon dioxide though the technique could be adapted for high-pressure studies.

10) Electroacoustic techniques rely on the observation that emulsions respond to electrical radiation by producing acoustic radiation and vice versa. The method involves either a) the generation of a potential difference when a sound wave passes through an emulsion or b) the generation of a sound wave when an alternating electrical field is applied to an emulsion. The size range which can be analyzed is relatively narrow, 0.1-10 μm, but the technique is not limited to dilute emulsions. The emulsion droplets must possess a surface potential for this technique to be effective. Chapter 5 and 7 of A.S. Duhkin's and P.J. Goetz's book (2002) on ultrasonic characterization of colloids are devoted to electroacoustic methods. Electroacoustic techniques have not been used to characterize emulsions containing dense carbon dioxide, but might be useful given that the technique applies to concentrated emulsions.
Microscopy is the most common means of sizing emulsion droplets and was selected as the experimental technique for determining droplet size distributions in this work for two reasons: 1) it avoids the difficulties associated with fitting an unknown droplet size distribution to an experimental data set and 2) it was expected that the droplets in this study would be larger than 1 micron so that they would be easily resolvable using light microscopy. The relevant experimental protocols and results are presented in Section 4.5.5.

Because microscopy is a labor intensive operation, only a limited number of measurements were conducted. Specifically, droplet sizes were determined at one power density, at one position in the pressure vessel, and only immediately after termination of sonic irradiation. Future work should build on the results obtained with this technique, extending the measurements to cover a range of power densities, locations, and times during demulsification. Several of the techniques listed above could be used for such purposes. Since the standard α-Al₂O₃ sapphire windows commonly used in supercritical fluid studies can also be used for static light scattering measurements, it is an easy technique to convert to high-pressure conditions, though the limitation of light scattering to dilute emulsions may pose a significant problem. Ultrasonic spectroscopy is a promising technique, since it is not restricted to dilute emulsions and the required thermophysical data are available for carbon dioxide and water. Light scattering and diagnostic ultrasound are recommended for further consideration for obtaining a more complete data set of emulsion droplet sizes. It is noted that only a brief sampling of the most important droplet size measurement techniques has been provided here. Additional discussions of particle size measurement techniques are contained in C. Orr's²⁵ chapter in the Encyclopedia of Emulsion Technology series (1988) and T. Allen's¹⁰ (1997) book on particle size measurements.

**Volume fraction of the disperse phase.** The second important characteristic which defines emulsions is the volume fraction of the dispersed phase. The importance of measuring this characteristic is often ignored since, in a typical application, a surfactant (or combination of surfactants) is used to ensure complete dispersal of a known volume of one liquid phase into a known volume of a second liquid phase. The identity of the continuous phase can be dictated by the relative initial volumes (the smaller volume
typically becomes the dispersed phase) and the characteristics of the surfactant(s). The properties of the surfactants which influence the identity of the continuous phase (either water or oil, in typical circumstances) are summarized by the so-called hydrophilic-lyophilic balance (HLB). The HLB of a surfactant can be estimated by the ratio of its solubilities in aqueous and oil phases. In general, a surfactant with a low HLB will favor an oil continuous phase, while high values of HLB will favor an aqueous continuous phase. By convention, emulsions of water dispersed in a continuous oil phase are referred to as water/oil or sometimes w/o. Conversely, emulsions of oil dispersed in an aqueous continuous phase are referred to as oil/water or o/w. Lee et al.\cite{26} uses a metric similar to HLB, which he has termed "HCB" for hydrophilic-carbon dioxide-philic balance, for emulsions containing water and dense carbon dioxide.

In instances where more of the phase to be dispersed is present than can be emulsified into the continuous phase, the volume fraction of the dispersed phase will not be known. Since our approach is aimed at eliminating the use of surfactants, dispersed phase volume fraction measurements are required. Fortunately, there are several methods in common use for measuring the dispersed-phase volume fractions of emulsions:

1) *Chemical analysis* can be used in many instances. The emulsion to be analyzed is solubilized using a suitable mutual solvent and the resulting solution is analyzed via conventional analytical methods. The method used in this project was based on standard chemical analysis techniques.

2) *Density measurements* of the emulsion can be used if the densities of the two component phases are known. The volume fraction of the dispersed phase ($\phi_d$) is related to the measured density of the emulsion ($\rho_e$), the known density of the dispersed phase ($\rho_d$) and the known density of the continuous phase ($\rho_c$) by the simple relationship:

$$\phi_d = \frac{\rho_e - \rho_c}{\rho_d - \rho_c}$$

(4-3)

This method has been used successfully to determine $\phi_d$ for emulsions with a difference between $\rho_d$ and $\rho_c$ of less than 100 kg m$^{-3}$\cite{1}. Adapting this technique for supercritical fluid applications would be possible using a high-pressure density meter such as that available from Anton-Paar (DMA512P) which has an operating pressure range of 0-680 bar and 0-90 °C. In fact, since the density difference between carbon dioxide and water
is generally greater than 100 kg m\(^{-3}\), density measurements might prove to be a very accurate technique for investigating emulsions containing dense carbon dioxide.

3) Electrical conductivity measurements can be used to measure \(\phi_d\). The dielectric constant of water, \(\varepsilon_r\), is much greater than that of oil phases. Therefore an emulsion containing oil and water will have a bulk dielectric constant that lies somewhere between the two extremes. Measurements of the dielectric constant of the emulsion, \(\varepsilon_e\), can be used to calculate \(\phi_d\):

\[
\phi_d = \left( \frac{\varepsilon_e - \varepsilon_c}{\varepsilon_e + 2\varepsilon_c} \right) \left( \frac{\varepsilon_d + 2\varepsilon_c}{\varepsilon_d - 2\varepsilon_c} \right)
\]  

(4-4)

where the subscripts have the same meanings as in equation (4-3). \(\varepsilon_e, \varepsilon_d, \varepsilon_c\) can be measured using standard electrochemical procedures.\(^{27}\) Lee et al. have used a similar technique to determine what type of emulsion (CO\(_2\)/H\(_2\)O or H\(_2\)O/CO\(_2\)) is stable under a given set of conditions,\(^{26}\) but have not published any accounts of determining \(\phi_d\) from \(\varepsilon_e\).

**Surface area and droplet distributions.** For applications of reaction engineering, surface area (per unit volume or unit mass) is a critical characteristic for describing emulsions. The most direct means of determining surface area is from independent measurements of droplet radius and volume fraction of the dispersed phase. In an emulsion consisting of spherical droplets of one discrete radius (i.e., a monodisperse emulsion), the surface area per unit volume of emulsion, \(a\), is given by the geometric expression:

\[
a = \frac{3\phi_d}{r}
\]  

(4-5)

In practice, emulsions almost always contain a distribution of droplet sizes and equation (4-5) needs to be modified somewhat. It is often convenient to represent the size distribution in terms of an “average” diameter. The simplest means of averaging the distribution is to use the number of droplets, \(N_i\), with a certain radius, \(d_i\):

\[
\langle d_n \rangle = \frac{\sum_i N_i d_i}{\sum_i N_i}
\]  

(4-6)

where the denominator is simply the total number of droplets. Alternatively, the average radius could be defined by surface area:
\[ \langle d_s \rangle = \left( \frac{\sum_i N_i d_i^2}{\sum_i N_i} \right)^{1/2} \]  

(4-7)

or volume

\[ \langle d_v \rangle = \left( \frac{\sum_i N_i d_i^3}{\sum_i N_i} \right)^{1/3} \]  

(4-8)

The so-called Sauter diameter, \( \langle d_{32} \rangle \), is also often used:

\[ \langle d_{32} \rangle = \left( \frac{\sum_i N_i d_i^3}{\sum_i N_i d_i^2} \right) \]  

(4-9)

For a polydisperse emulsion, \( r \) is substituted in equation (4-5) with \( \langle d_{32} \rangle / 2 \) (the Sauter radius, \( \langle r_{32} \rangle \)). This expression can be derived formally, or considered in terms of dimensional analysis. The units of volume fraction are volume of dispersed phase divided by total emulsion volume. The units of \( \langle d_{32} \rangle \) are volume of dispersed phase divided by its surface area. Taking the ratio of \( \phi_d \) to \( \langle d_{32} \rangle \) results in units of surface area of dispersed phase per unit volume of emulsion, as desired. It is noted that similar definitions apply for continuous distributions of the droplet size, in which event integral operators are substituted for the summations in equations (4-7) – (4-9).

### 4.2 Emulsion Stability and Interdroplet Potential

In the absence of stabilizing interdroplet forces, emulsions break rather rapidly by the processes of coagulation and sedimentation. Many emulsions persist indefinitely, the result of repulsive droplet-droplet interactions. It is instructive to consider these forces so that conclusions regarding stabilization of emulsions containing dense carbon dioxide can be drawn. The description of the theory of these inter-droplet forces presented here is quite brief and has been adapted from a number of more elegant treatises on the subject including those of Claeson et al., Friberg and Yang, Tadros and Vincent, Melik and Fogler, McClements, and Heimenz and Rajagopalan.

The primary theory for describing droplet-droplet interactions was developed independently in the early 1940’s by Derjaguin and Landau and Verwey and
Overbeek.\textsuperscript{33} It is commonly referred to as “D.L.V.O.” in recognition of these authors. D.L.V.O. theory is based on the balance between the \textit{van der Waals attractive} potential ($V_{\text{vdW}}$) and the \textit{electrostatic repulsive} potential ($V_{\text{electro}}$). These two contributions will be discussed separately in the following sections.

\textbf{Attractive forces between droplets.} The theory describing the attractive forces between droplets is based on London’s concept of dispersion interactions between atoms or molecules. Hamaker\textsuperscript{34} first integrated the individual van der Waals interactions between all of the molecules contained in two discrete droplets. His expression for the van der Waals potential, $V_{\text{vdW}}$, between two droplets separated by a distance, $R-2r$, can be written as:

$$V_{\text{vdW}} = -\frac{\pi^2 (\rho_d N_A / M_w)^2 \beta_1}{6} \left\{ \frac{2r^2}{R^2 - 4r^2} + \frac{2r^2}{R^2} + \ln \left( \frac{R^2 - 4r^2}{R^2} \right) \right\}$$

(4-10)

Where $\rho_d$ is the density of the material in the particles, $N_A$ is Avogadro’s number ($6.022 \times 10^{23}$ molecules mol$^{-1}$) and $M_w$ is the molecular weight of the material. The term $\beta_1$ is the interaction of a pair of the molecules which compose the particle.

Conventionally, the constants in equation (4-10) are lumped together and referred to as Hamaker’s constant:

$$A = \frac{\pi^2 (\rho N_A / M_w)^2 \beta_1}{6}$$

(4-11)

Experimental and theoretical estimates of $A$ indicate that it takes a value of roughly $5 \times 10^{-19}$ J when the particles interact through a vacuum.\textsuperscript{35} Embedding the particles in a solvent decreases the value of $A$ to roughly $5 \times 10^{-20}$ J.\textsuperscript{1} For a given value of $A$, equation (4-10) predicts that $V_{\text{vdW}}$ decays to zero as $R$ becomes large and approaches negative infinity as $R-2r$ becomes small. This, of course, is analogous to the van der Waals attraction between atoms or molecules. The analogy should come as no surprise given that equation (4-10) was derived with this picture in mind. An important difference between the interaction between particles and that between molecules is that, for the latter system, the van der Waals attraction scales with $R^6$ while in the former it scales with $R^2$ (to first order).\textsuperscript{35} This implies that the van der Waals attraction between droplets is a much longer range attraction than it is between molecules.
Despite many refinements, the magnitude of the attraction predicted by equation (4-10) is approximately correct in a quantitative sense and its behavior with regards to particle separation is qualitatively accurate. For these reasons, equation (4-10) is adequate for the current discussion.

**Repulsive forces between droplets.** The origin of electrostatic repulsion is the presence of charged species near the droplet interface. Interfacial charged species are often associated with the presence of ionic surfactants (i.e., surfactants that carry a charge) which have been added intentionally to confer emulsion stability, but might also result from accumulation of ions naturally present in the solution at the droplet surface. For instance, there is some evidence that OH\(^{-}\) is effectively adsorbed to the surface of oil droplets in an aqueous continuous phase, though the physical basis for this behavior remains elusive.\(^{36}\) The presence of small amounts of contaminants may also play a role in some instances. The analytical expression for predicting electrostatic repulsion between charged spheres is generally attributed to Hogg et al.\(^{37}\) (1966). Although the full analytical solution is somewhat complicated, a useful approximation for the electrostatic repulsion, \(V_{\text{electro}}\), valid at small droplet separations was formulated by Hunter:\(^{38}\)

\[
V_{\text{electro}} = 2\pi\varepsilon_0\varepsilon r \psi_d^2 \ln \left[1 - \exp[-\kappa (R - 2r)]\right]
\]

(4-12)

where \(\varepsilon_0\) is the permittivity of a vacuum (8.85410\(\times\)10\(^{-12}\) \(\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}\)), \(\varepsilon\) is the dielectric constant of the continuous phase relative to vacuum (e.g., 78.54 for water or roughly 1-5 for a nonpolar oil), \(\psi_d\) is the surface potential, and \(\kappa\) is the inverse of the Debye screening length (m\(^{-1}\)). \(\kappa\) can be calculated using the following equation:

\[
\kappa = \left(\frac{2N_A \rho e^2 \sum_i z_i^2 C_i}{\varepsilon_0 \varepsilon k_B T}\right)^{1/2} = \left(\frac{2N_A \rho e^2}{\varepsilon_0 \varepsilon k_B T}\right)^{1/2} \left(\sum_i z_i^2 C_i\right)^{1/2} = \alpha I^{1/2}
\]

(4-13)

where \(C_i\) is the molal concentration of electrolyte \(i\) in the bulk solution (typically reported in units of mol kg\(^{-1}\)), \(z_i\) is the valency of the same electrolyte, \(e\) is the electron charge (1.602\(\times\)10\(^{-19}\) \(\text{C}\) electron\(^{-1}\)), \(k_B\) is Boltzmann's constant (1.381 \(\times\) 10\(^{-23}\) J K\(^{-1}\)), \(N_A\) is Avogadro’s number (6.022 \(\times\) 10\(^{23}\) mol\(^{-1}\)), \(\rho\) is the density of the continuous phase (997 kg m\(^{-3}\) for water at 298 K), and \(T\) is the absolute temperature. Equation (4-13) also shows that \(\kappa\) can be defined in terms of the ionic strength, \(I\), of the solution. The combination of
constants defined by \( \alpha \) takes a value of \( 3.282 \times 10^9 \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ m}^{-1} \) in aqueous solution at 298 K.

The surface potential, \( \psi_d \), merits further discussion. \( \psi_d \) is influenced by a number of factors including the surface coverage of surfactants and their charge as well as the specific adsorption of counter-ions. In practice, \( \psi_d \) is often approximated by the zeta potential, \( \zeta \), a quantity which can be estimated by measurements of droplet velocity in an electric field. The substitution of the zeta potential for the surface potential is questionable but necessary, since \( \psi_d \) cannot be measured directly. Setting \( \psi_d \) equal to \( \zeta \) has been the convention since at least the 1960's and no suitable alternative has yet been determined.

The total interaction potential. The combination of equations (4-10) and (4-12) results in the total particle-particle interaction potential, i.e., \( V_{\text{tot}} (R) \):

\[
V_{\text{tot}} (R) = V_{\text{diss}} (R) + V_{\text{electro}} (R)
\]

(4-14)

Figure 4-2 is a set of plots for \( V_{\text{tot}} (R-2r) \) with \( A = 5 \times 10^{-20} \text{ J} \) and for \( \psi_d \) ranging from 0-55 mV. For the purposes of demonstration, \( r = 1 \text{ \mu m} \) and the continuous phase is water with \( l = 0.1 \text{ mol kg}^{-1} \). For \( \psi_d \) less than about 45 mV, the interaction is completely attractive and there is no barrier for particle collisions. As \( \psi_d \) is increased to 45 mV and beyond, a distinct activation barrier forms. For \( \psi_d = 55 \text{ mV} \), the barrier is several times larger than \( k_B T \). For particles to collide, this activation barrier must first be surmounted. Since the barrier is significantly greater than \( k_B T \), the effect of \( \psi_d \) is to retard droplet agglomeration. In actual practice, it has been found that the zeta potential must be greater than 30 mV for "stable" emulsions which persist for periods of days or more. The fact that the critical value of \( \psi_d \) reported in Figure 4-2 is somewhat larger than the experimental observation is most likely due to the approximations made in equations (4-10) and (4-12) and the error associated with assuming that \( \psi_d = \zeta \). At small separations, \( V_{\text{tot}} \) approaches negative infinity for all realistic values of \( \psi_d \). Because of this so-called "primary minimum", which might be better termed a singularity, emulsions are never thermodynamically stable since the configuration of lowest energy occurs for complete coagulation of the emulsion droplets.
Figure 4-2. Plot of $V_{\text{tot}}$ (scaled by $k_B T$) calculated from equation (4-14) as a function of the separation between two spherical droplets with radius, $r$, for various values of $\psi_d$, as listed in the figure. $V_{\text{tot}} / k_B T = 0$ is shown as the solid horizontal line for reference. All conditions other than surface potential are listed in the text.

In addition to the primary minimum in $V_{\text{tot}}$, for $\psi_d > 50 \text{ mV}$ there is a secondary minimum at somewhat larger droplet separations. The presence of this minimum suggests that droplets first "stick" (or flocculate) for finite periods without coalescing, separated only by a thin film of the continuous phase which is roughly 10 Å thick. For droplets to fully coalesce, this film must first drain. Depending upon the rate of drainage of this thin film and the height of the energy barrier, the agglomerated particles can either proceed to coalesce or may eventually re-separate into distinct droplets. Coalescence and flocculation are discussed in more detail in Section 4.3.

Equation (4-13) also predicts the effect of solvent polarity (as it is reflected in $\varepsilon$) on $V_{\text{tot}}$. Figure 4-3 is a plot of $V_{\text{tot}}$ as a function of droplet separation for $\varepsilon$ ranging from 78.54 (e.g., water) to 2 (e.g., alkanes and dense carbon dioxide). The surface potential is constant and equal to 55 mV. As the dielectric constant of the continuous phase decreases, the barrier height for droplet collisions decreases rapidly. In fact, for a dielectric constant characteristic of dense carbon dioxide, a surface potential greater than 500 mV is needed for electrostatic repulsion. Since such a large value for the surface potential is never encountered in practical systems, electrostatic repulsion via ionic
Figure 4-3. Plot of $V_{tot}$ (scaled by $k_B T$) calculated from equation (4-14) as a function of the separation between two spherical droplets with radius, $r$, for various values of the dielectric constant of the continuous phase, $\varepsilon$, as listed in the figure. $V_{tot} / k_B T = 0$ is shown as the solid horizontal line for reference. All other conditions are listed in the text.

Surfactants cannot be used to confer stability of emulsions with a nonpolar continuous phase. Instead, long-chain surfactants such as block copolymers are used. These bulky surfactants interact *sterically* with one another, thus stabilizing the emulsion droplets.

Steric stabilization is a rich field in its own right and will not be discussed in great detail here. Hiemenz and Rajagopalan,\(^2\) D.J. McClements,\(^1\) P. Walstra,\(^3\) Friberg, S.E.,\(^4\) and R.J. Hunter\(^5\) all describe this topic more thoroughly. Steric stabilization of emulsion droplets requires that the continuous phase be a good solvent for the polymer surfactant so that the solvophobic “tails” extend into the continuous phase, thereby producing an osmotic pressure which prevents droplet flocculation. Steric stabilization of emulsions with a carbon dioxide continuous phase is mentioned in Section 4.3 in the context of K.P. Johnston’s research.

### 4.3 Mechanisms of Demulsification

Breaking of emulsions occurs by the combined processes of coalescence, flocculation (also referred to as “agglomeration”), and sedimentation (or creaming if the dispersed phase is less dense). Figure 4-3 is a schematic of these processes. For a given
emulsion, one or all of these processes may be important. The processes of coalescence and flocculation are sometimes referred to collectively as “coagulation.” For instance, for emulsions which resist coalescence, demulsification results from flocculation followed by sedimentation and eventual (slow) coalescence. To determine which mechanism(s) contribute to demulsification, therefore, it is necessary to know the rates of the various processes. The remainder of this section briefly describes physical models for predicting the rates of coalescence, agglomeration, and sedimentation, in three categories: 1) fast coagulation in which the droplets do not resist coalescence, the dynamics of which were described first by Smoluchowski,\textsuperscript{41} 2) slow coagulation in which interdroplet potential inhibits droplet coalescence, the dynamics of which were first described by Fuchs,\textsuperscript{42} and 3) the process of sedimentation/creaming. Ostwald ripening is a fourth demulsification mechanism, but since ripening is important only in rare cases in which the emulsion is stabilized against flocculation and settling it will not be discussed here.

**Fast Coagulation: Smoluchowski Theory.** In the absence of electrostatic and steric stabilization, droplets coalesce immediately upon contact. As depicted in Figure 4-4, the product of the coalescence of two distinct droplets is one droplet of larger radius. The kinetic expression for the disappearance of droplets in the regime of fast coagulation was given by Smoluchowski\textsuperscript{41} who considered collisions due to Brownian diffusion of droplets in a continuum sufficiently dilute such that only 2-body collisions occurred. Within this context, Smoluchowski derived the following expression for the rate of disappearance of the number of droplets per unit volume of the emulsion, $N$:

$$\frac{dN}{dt} = -k_c N^2 = -\frac{4k_BT}{3\mu} N^2$$ (4-14)

The rate constant for fast coagulation, $k_c$ (which has units of length$^3$ time$^{-1}$), is based on the collision frequency of mutually diffusing spheres, assuming Stokes-Einstein diffusivity, equation (4-1). Integrating equation (4-14), using the initial condition that the emulsion consists of $N_0$ droplets per unit volume, yields:

$$N = \frac{N_0}{1 + k_c N_0 t}$$ (4-15)

The time required for coalescence of exactly 50% of the emulsion droplets, $\tau_{1/2}$, is given by:
Figure 4-4. Schematic representation of three of the primary mechanisms of demulsification. Coalescence is the merging of two droplets into one indistinguishable drop. Flocculation is the attachment of two droplets. The identities of the two droplets remain distinct during flocculation. Sedimentation/creaming is the falling/rising of droplets due to a density difference in the presence of a gravitational acceleration.

\[ \tau_{1/2} = \frac{1}{k_{\gamma N_0}} = \left( \frac{\pi \mu}{k_B T} \right) \frac{r^3}{\phi_d} \]  

(4-16)

Equation (4-16) predicts that, for an emulsion consisting of 1 μm droplets in water at a volume fraction of \( \phi_d = 0.10 \), about 10 s would be required for half of the droplets to coalesce. The short half-lives predicted by Smoluchowsky's equation are the basis for the term "fast coagulation".

**Slow Coagulation:** Fuchs’ Theory. In the presence of electrostatic and/or steric stabilization, the collision efficiency is less than unity and not all collisions lead to coalescence. In these instances, equation (4-16) underpredicts the half-life for droplet coagulation. For droplets stabilized only by an electrostatic force, the barrier depicted in Figure 4-2 is the activation energy which must be overcome prior to droplet coagulation.
Fuchs\textsuperscript{42} provided the first analytic solution for this problem, relating the rate constant for fast coagulation ($k_f$, given above) to the rate constant for slow coagulation ($k_s$):

$$k_s = \frac{k_f}{W} = \frac{k_f}{2r \int_{2r}^{\infty} \frac{\exp(V_{\text{max}}/RT)}{R} dR} \quad (4-17)$$

Where $R$ is the center-center separation between droplets and $V_{\text{max}}$ is given by the maximum in the $V_{\text{tot}}$ curves of Figure 4-2. For instances where a distinct maximum is present, $W$ is always greater than unity and $k_s < k_f$. It should be clear that Fuchs' theory does not incorporate considerations of the secondary minima depicted in Figure 4-2, since only the maximum in the potential energy curve is incorporated in equation (4-17).

In the presence of an activation barrier and a secondary minimum (as depicted in Figure 4-2), the collision of two droplets will not immediately result in the formation of one larger droplet. In these instances, collisions typically result first in flocculation (see Figure 4-4). Depending on the interdroplet forces/separation, viscosity of the continuous phase, and shear stresses on the droplets, the droplets will either coalesce into one droplet or separate. Since droplet flocculation was not observed in the carbon dioxide/water system, only a cursory treatment is provided here. More detailed discussions of droplet coalescence in the presence of stabilizing interactions can be found in the monographs by McClements,\textsuperscript{1} B.P. Binks,\textsuperscript{43} Kabalnov\textsuperscript{44} and especially P. Walstra.\textsuperscript{39}

**Sedimentation and Creaming.** The processes of coagulation and ripening refer only to droplet growth and do not explain the removal of droplets from the emulsion. Droplet removal occurs by the processes of settling (sedimentation) or rising (creaming), depending on whether the droplets are more or less dense than the continuous phase. For droplets initially small enough that simple Brownian motion allows them to resist sedimentation/creaming, they must first grow through the processes of coagulation and ripening. An estimate of the droplet size which is resistant to sedimentation/creaming can be obtained by balancing the rate of sedimentation/creaming with that of Brownian motion as described by Probstein\textsuperscript{45} (1994). When sedimentation/creaming and Brownian motion are balanced, the number of droplets per unit volume ($N$) is a function of height in the vessel containing the emulsion, $h$, and is given by the expression:
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\[ N(h) = N(h = 0) \exp \left( \frac{-4\pi r^3 \Delta \rho g h}{3k_B T} \right) \]  \hspace{1cm} (4-18)

where the definitions of all other variables are retained. Brownian motion alone is able to stabilize only very small droplets against settling. For a vessel that is 10 cm in height and for \( \Delta \rho = 200 \text{ kg m}^{-3} \), the equilibrium value of \( N(h=10 \text{ cm})/N(h=0 \text{ cm}) \) is roughly 0.02% for \( r \sim 40 \text{ nm} \). For \( r > 40 \text{ nm} \), the equilibrated state is complete settling of the dispersed droplets. Since an initial radius of 40 nm is extremely small for an emulsion, sedimentation/creaming represents a major barrier to emulsion stability and generally occurs during all stages of demulsification. Of course, equation (4-18) does not include dynamic information so that droplets larger than 40 nm may settle at rates which are essentially zero for all practical purposes.

For dilute emulsions of monodisperse spheres, equation (4-2) applies directly and can be used to estimate the time required for sedimentation in a vessel of height, \( h \). If the droplets are initially evenly distributed throughout the vessel, the sedimentation half life, \( \tau_{1/2} \), is given by:

\[ \tau_{1/2} = \frac{9 \mu h}{4gr^2 \Delta \rho} \]  \hspace{1cm} (4-19)

where \( \Delta \rho \) is the absolute difference between the densities of the droplet and the continuous phase.

If the assumptions of a dilute emulsion of monodisperse droplets are not valid, equations (4-2) and (4-19) must be corrected to account for distributions of droplet diameters and droplet-droplet interactions. The problem of settling in dilute, disperse emulsions is generally handled by substituting the Sauter radius, \( <r_{32}> \). Correcting equation (4-2) for the case of concentrated emulsions is more complicated. When a droplet settles, it displaces the surrounding fluid, thereby causing a flow which is opposite in direction to that of particle motion. For dilute emulsions, this secondary flow can be ignored. In concentrated emulsions, the flow of continuous phase can significantly retard or "hinder" the motion of the droplets. Batchelor\(^{46} \) (1972) derived a rigorous expression for hindered settling valid for \( \phi_d \ll 0.1 \) to relate the terminal velocity in a concentrated emulsion (\( U_{\text{hindered}} \)) to that predicted by equation (4-2):
\[
\frac{U_{\text{hindered}}}{U_t} = 1 - 6.55\phi_d
\]

Using equation (4-20), a 1% deviation from the Stokes settling velocity, equation (4-2), is predicted for \( \phi_d \sim 0.0015 \). For more concentrated emulsions, equation (4-2) cannot be used. Based on experimental data for settling in concentrated emulsions, equation (4-20) is adequate for values of \( \phi_d \) up to roughly 0.05 provided that the acceleration is due to gravity alone. To extend Batchelor’s analysis to more concentrated emulsions, a variety of empirical and semi-empirical expressions for \( U_{\text{hindered}} \) have been proposed.\(^{39}\) The topic of hindered settling in polydisperse emulsions continues to be an area of interest.\(^{47}\)

### 4.4 Existing Literature on Carbon Dioxide/Water Emulsions

Characterizing emulsions which are formed and exist only at high pressures is more challenging than the characterization of emulsions at ambient pressure. Nonetheless, considerable progress in high-pressure emulsion formation/characterization techniques has been made in the past 5-10 years. Probably the single most important breakthrough in this field was the discovery by Beckman and his coworkers\(^{48}\) that certain fluorinated surfactants are soluble in dense carbon dioxide. Without carbon dioxide-soluble surfactants it was impossible to form stable colloids with a supercritical carbon dioxide component. In the mid 1990’s K.P. Johnston\(^{48-51}\) significantly expanded Beckman’s discovery by successfully demonstrating that the fluorinated surfactants stabilized carbon dioxide/water interfaces. Based on these advances, progress has been rapid in fields as diverse as dispersion polymerization as pioneered by DeSimone’s research group at the University of North Carolina,\(^{52}\) stabilization of inorganic colloids demonstrated by both Beckman’s and Johnston’s research groups,\(^{53,54}\) solubilization of metals for catalysis\(^{55,56}\) and extraction, a field dominated by C. Wai’s research group at the University of Idaho\(^{57}\) and reviewed recently by C. Erkey,\(^{58}\) and formation of both carbon dioxide-based microemulsions\(^{59-61}\) and emulsions (see below). This section presents only those results that are most salient to carbon dioxide-based emulsions. The 1999 monograph on supercritical fluids edited by W. Leitner and P.G. Jessop\(^{62}\) provides considerable background information.

Johnston’s group at the University of Texas, Austin has focused on the field of water/carbon dioxide emulsions having published 9 reports\(^{7,26,63-69}\) on the development
of rules for the rational design of surfactants. As was discussed in Section 4.2, the primary stabilization force in carbon dioxide continuous emulsions is steric hindrance. To be effective and prevent flocculation, steric hindrance requires that the surfactant be well solubilized in the continuous phase. Given the limited solvation power of dense carbon dioxide, emulsion stabilization by steric hindrance mechanisms is quite challenging. Not surprisingly, based on their unusually high solubility, fluorinated surfactants have been the most effective, though there have been some encouraging results using hydrocarbon surfactants for stabilizing dilute emulsions.

The first reported study on the formation of water/carbon dioxide emulsions by Lee et al.\textsuperscript{26} will be discussed in some detail since it establishes the primary methods. The researchers examined the use of poly(perfluoroether) COO$^-$NH$_4^+$ surfactants with molecular weights ranging from 672-7,500 g mol$^{-1}$ to stabilize emulsions containing 50% water. The emulsions were formed by shearing the solution through an Aveston homogenizer. The effects of temperature (15-70 °C), pressure (50-275 bar), salt content of the aqueous phase (0.01-1 mol L$^{-1}$ NaCl), and ethanol coemulsifier (up to 5 wt%) were all investigated. The measured variables were 1) stability, determined visually, 2) droplet sizes, measured using \textit{in situ} microscopy of the emulsions contained within capillary tubing, and 3) the identity of the continuous phase (sometimes referred to as "emulsion morphology"), investigated using conductivity measurements.

Microscopy studies revealed that the emulsion droplet diameters were 3-10 μm, though a high degree of flocculation was observed in most systems. Emulsion breaking times (time required for 25% of the emulsion to settle after cessation of agitation) of up to several days were reported. Based on these observations, Johnston’s group postulates that the mechanism of demulsification was rapid flocculation (based on the formation of "flocs" in the first minutes after emulsification) followed by slow creaming and sedimentation and eventual coalescence. It is likely that initial flocculation led to a dramatic increase in the effective solution viscosity, greatly retarding the settling process so that the emulsions were much more stable than would be predicted from the viscosities of pure carbon dioxide or water.

A number of additional investigations have been reported by Johnston’s group which build on the initial study and use many of the same methods. The primary
innovations of next-generation studies were adjustments to the chemical composition of the surfactant(s) used. Table 4-1, adapted from Dixon et al.\textsuperscript{68} which appeared in 2003, is a compilation of the most pertinent results. Although the conditions of the measurements are not listed, they were generally made in the range 30-60 °C and 100-200 bar. Apparent in Table 4-1 is that a wide range of surfactants has been tested and found to stabilize water/carbon dioxide emulsions to some degree. In all studies, average droplet diameters smaller than 10 μm are reported though droplet size distributions have been reported only once.\textsuperscript{65} Measurements and predictions of droplet distributions (particularly within the context of formation technique, see Chapter 5 for discussion) in carbon dioxide-based emulsions is an area where further research is needed.

An important finding that may eliminate the need for fluorinated substitution (thus improving process economics and having environmental impacts) was the discovery\textsuperscript{7} that a hydrocarbon surfactant, sodium bis(3,5,5-trimethyl-1-hexyl)sulfosuccinate, could stabilize water/carbon dioxide emulsions. The average droplet sizes (measured using a combination of static and dynamic light scattering) were as small as 0.2 μm and did not appear to flocculate. The only drawback is the fact that the emulsions contained only 1 wt% water. Nonetheless, this result makes the goal of developing completely hydrocarbon-based surfactants for carbon dioxide applications seem attainable.

In addition to K.P. Johnston’s work in the field of water/carbon dioxide emulsions, Marioth et al.\textsuperscript{5} demonstrated the use of static light scattering to determine particle sizes of TiO\textsubscript{2}, dimethyl sulfoxide, and dimethylformamide in supercritical carbon dioxide. Heath and Cochran\textsuperscript{70,71} used an electrospray technique to disperse micron-sized droplets of water in carbon dioxide. Since the researchers gave more attention to the dispersion technique than to the properties of the final emulsion, the electrospray technique will be discussed in more detail in Section 5.5.1 which deals with emulsion formation.
Table 4-1. Properties of water/carbon dioxide emulsions as reported in the literature, adapted from Dixon et al.\textsuperscript{68}

<table>
<thead>
<tr>
<th>surfactant\textsuperscript{a}</th>
<th>surfactant wt%</th>
<th>water wt%</th>
<th>droplet size\textsuperscript{b} ((\mu\text{m}))</th>
<th>stability\textsuperscript{c} (hr)</th>
<th>flocculation observed?</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPE COO-NH(_4)</td>
<td>0.36</td>
<td>50</td>
<td>3-10</td>
<td>278</td>
<td>yes</td>
<td>Lee, 1999</td>
</tr>
<tr>
<td>PFPE COO-NH(_4)</td>
<td>0.36</td>
<td>5</td>
<td>3-10</td>
<td>0.03</td>
<td>yes</td>
<td>Lee, 1999</td>
</tr>
<tr>
<td>PDMS-b-PMA</td>
<td>1</td>
<td>50</td>
<td>2-5</td>
<td>&gt;24</td>
<td>yes</td>
<td>Psathas, 2000</td>
</tr>
<tr>
<td>PDMS-g-EO</td>
<td>0.1</td>
<td>9.5</td>
<td>3.5</td>
<td>0.01</td>
<td>yes</td>
<td>da Rocha, 1999</td>
</tr>
<tr>
<td>AOT-TMH</td>
<td>1</td>
<td>1</td>
<td>0.05-4\textsuperscript{d}</td>
<td>&lt;1</td>
<td>yes</td>
<td>Johnston, 2001</td>
</tr>
<tr>
<td>Trisiloxane-g-EO</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0.03</td>
<td>yes</td>
<td>da Rocha, 2003</td>
</tr>
<tr>
<td>Trisiloxane-g-EO</td>
<td>1</td>
<td>3</td>
<td>NA\textsuperscript{e}</td>
<td>0.0003</td>
<td>yes</td>
<td>da Rocha, 2003</td>
</tr>
<tr>
<td>PFOMA-b-PEO</td>
<td>1</td>
<td>2</td>
<td>0.07\textsuperscript{f}</td>
<td>&gt;24</td>
<td>no</td>
<td>Dickson, 2003</td>
</tr>
<tr>
<td>PFOMA-b-PEO</td>
<td>1</td>
<td>3</td>
<td>0.07\textsuperscript{c}</td>
<td>&gt;24</td>
<td>no</td>
<td>Dickson, 2003</td>
</tr>
<tr>
<td>PEO-b-PDMS-b-PEO</td>
<td>1</td>
<td>50</td>
<td>0.7\textsuperscript{d,g,h}</td>
<td>2\textsuperscript{f}</td>
<td>NA\textsuperscript{e}</td>
<td>Psathas, 2002</td>
</tr>
<tr>
<td>PDMS-g-EO-PO</td>
<td>0.1</td>
<td>3.8</td>
<td>3.1</td>
<td>&gt;30</td>
<td>yes</td>
<td>da Rocha, 1999</td>
</tr>
</tbody>
</table>

Notes:
\textsuperscript{a} surfactant abbreviations:
PFPE COO-NH\(_4\) poly(perfluorooctyle) ammonium carboxylate
PDMS-b-PMA polydimethylsiloxane-b-poly(methacrylic acid)
PDMS-g-EO polydimethylsiloxane-g-ethylene oxide
AOT-TMH sodium bis(3,5,5-trimethyl-1-hexyl)sulfosuccinate
Trisiloxane-g-EO ((CH\(_3\))\(_2\)SiO\(_2\)Si(CH\(_3\))\(_2\)(CH\(_2\)\(_2\)O\(_n\))\(_2\)OH
PFOMA-b-PEO perfluorooctylacrylate-b-polyethylene oxide
PEO-b-PDMS-b-PEO polyethylene oxide-b-polydimethylsiloxane-b-polyethylene oxide
PDMS-g-EO-PO polydimethylsiloxane-g-ethylene oxide propylene oxide

\textsuperscript{b} presumably all reported diameters are number average
\textsuperscript{c} time required for 25% of the emulsion to become clear
\textsuperscript{d} measured by static light scattering, if not specified optical microscopy was used
\textsuperscript{e} NA - not reported
\textsuperscript{f} emulsion formed using phase-inversion-temperature method (see Chapter 5)
\textsuperscript{g} emulsion formed using isothermal high-shear recirculation method
\textsuperscript{h} emulsion diluted before light scattering measurements
4.5 Characterization of Emulsions Containing Dense Carbon Dioxide Generated by Ultrasound

This section describes experiments which were performed to characterize acoustically generated emulsions of carbon dioxide and water. The principles discussed in Sections 4.1 and 4.4 were considered before selection of a set of techniques which a) were readily adapted for the characterization of high-pressure and b) provided a maximum of high quality information regarding droplet size distributions and volume fractions of the dispersed phase. The simplest means of emulsion characterization was visual observation. Turbidity measurements were made to quantify the time required for demulsification. Volume fractions of the dispersed phase were measured by chemical tracer technique. Microfabricated channels were modified for improved visualization and measurement of droplet diameters (and droplet diameter distributions) using video-enhanced, in situ optical microscopy. Surface areas were calculated from measured volume fractions and droplet diameters using the approach described in Section 4.1. These results are analyzed using the theories of fast coagulation and sedimentation (as described in Section 4.3) and some conclusions are drawn regarding probable emulsion-breaking mechanisms.

4.5.1 General experimental techniques

Many experimental techniques were developed for the purpose of ultrasonic emulsion characterization and were then used throughout this study. Specifically, a novel high-pressure view-cell reactor was developed which could accommodate the sonic probe. The experiments described here as well as those detailed in Chapters 5, 6, and 7 were performed in this reactor.

**High-pressure reactor and peripheral equipment.** A high-pressure reactor, consisting of two intersecting cylindrical chambers (i.d. = 1.9 cm) bored in a slab (18.8 cm x 15.3 cm x 5.1 cm) of 316-stainless steel, was designed and built for the studies of high-pressure ultrasonic emulsification. 316-stainless steel was selected as the material of construction because of its high strength and good resistance to corrosion. Three of the four apertures in the reactor contained $\alpha$-Al$_2$O$_3$ sapphire windows sealed with stainless steel glands. Figure 4-5 contains a schematic rendering and a digital photograph of the reactor. The
pressure seal was made using a Teflon gasket and the sapphire itself was protected from damage during tightening by a buna-N rubber gasket (90 durometer, Shore A, ordered from New England Die Cutting, Inc.). The fourth aperture contains a titanium sonic probe (o.d. = 0.80 cm, Sonics and Materials, Inc.) sealed with a stainless steel gland. The pressure seal was made using a combination of a Teflon and buna-N gasket similar to that used for the seals for the windows. The sonic probe is described in greater detail in the next section. All glands were tightened to 80-110 ft lbs using a standard torque wrench. After stripping a number of threads on the glands during tightening, a small amount of anti-seize (Loctite, Silver Grade) was applied to the threads. This seemed to reduce stripping, most likely because cross threading was more easily identified before the equipment was damaged with the low friction surface. Alternate designs for the pressure seals that used a collar/multiple bolt assembly were tested, but did not seal reliably at pressures greater than 10 bar.

![Figure 4-5. Schematic of the custom-build high-pressure reactor used for sonic experiments. A: stainless steel gland; B: buna-N gasket; C: sapphire window; D: Teflon gasket; E: \( \frac{1}{4} \)" apertures for machined NPT fittings; F: sonic probe. Pictured on the right is a digital photograph of the reactor.](image)
The internal volume of the reactor was measured as $87.2 \pm 0.4 \text{ cm}^3$ using two measurement techniques. A schematic of the apparatus used for the first procedure is shown in Figure 4-6. Here $V_{\text{reactor}}$ is the volume of the reactor and $V_{\text{gauge}}$ is the volume of the pressure gauge and associated tubing. The sum of these two volumes is $V_{\text{tot}}$. The following procedure refers to this notation and Figure 4-6:

1) The reactor (and any peripheral valves or recirculation equipment) was pressurized to a known, initial pressure ($P_i$) using Grade V helium gas (99.999% purity, BOC). Helium gas at pressures less than 1 bar (gage) was used to ensure the validity of the ideal gas law. The initial pressure was varied over a range as a double check on the ideal gas assumption. Pressure was measured using a digital pressure gauge (Omega, DPG1000B-15G) with a readability of $\pm 0.00068 \text{ bar} \ (\pm 0.01 \text{ psi})$ and reported accuracy of $\pm 0.0375 \text{ psi}$.

2) The reactor was connected to a 2-position 6-port HPLC valve (Valco Instrument Company, Inc., uW-type) which was equipped with a sample loop with a manufacturer-certified volume, $V_{\text{loop}}$. Although the sample loop volume was varied, it was found that the most accurate results were obtained using $V_{\text{loop}} = 10.00$
cm$^3$, the largest loop volume available from the manufacturer. The loop was initially at atmospheric pressure and filled with helium.

3) After a brief equilibration period, the gas in the reactor (still at $P_i$) was evacuated into the loop (still at atmospheric pressure) by opening the Valco valve and the final pressure of the entire system ($P_f$) system was recorded. The unknown volume was determined from these measurements using the formula:

$$V_{unknown} = \frac{P_i}{(P_i - P_f)} V_{loop}$$  \hspace{1cm} (4-21)

where all pressures are listed as gauge.

4) Two separate sets of measurements were conducted, both with valve A (see Figure 4-6) open (which allowed determination of $V_{total}$) and with valve A closed (which allowed determination of $V_{gauge}$). $V_{reactor}$ was determined by the difference of these two quantities.

The second method of determining the reactor volume involved injecting a known mass of an organic tracer (such as octane) directly into the reactor using either a syringe or pipette. The reactor was pressurized with carbon dioxide to 80-85 bar to ensure that the reactor was completely filled with liquid. After a period of equilibration and mixing (using a combination of a Teflon-coated magnetically coupled stir bar and a recirculation pump), a sample of known volume was taken using an HPLC sample valve. The sample of carbon dioxide was slowly released to atmospheric pressure by bubbling through a chilled organic solvent. The organic solvent was diluted to a standard volume and the solution was analyzed with a gas chromatograph (Agilent, 6890) equipped with a flame-ionization detector (FID). A DB-Wax column (J&W Scientific) was used for the analysis and the FID peak area was calibrated to the injected mass of organic tracer. From this calibration and the known dilution factor, the concentration of tracer in the reactor was determined. $V_{reactor}$ was determined from the ratio of this concentration to the mass of tracer added to the reactor.

$V_{reactor}$ determined using the two methods (pressure expansion and concentration dilution) agreed to within ± 0.2 cm$^3$. The error was conservatively estimated as twice this uncertainty to arrive at the figure reported previously (± 0.4 cm$^3$).
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The maximum design operating pressure of the reactor was 250 bar (at 25 °C), approximately 25% of the yield pressure ($P_y$) of the vessel. The yield pressure was calculated from the maximum yield strength of 316-stainless steel ($Y_0 = 2,600$ bar$^{22}$) using the standard formula:

$$P_y = Y_0 \left( \frac{r_o - 1}{r_i} \right)^{\frac{3}{2}} \left( \frac{r_o}{r_i} \right)$$

(4-22)

where $r_o$ is the outer radius and $r_i$ is the inner radius. Equation (4-22) applies strictly to an annulus, rather than a cylinder drilled through a rectangular slab. This means that the ratio $r_o / r_i$ takes a range of values for the acoustic reactor. The smallest value of $r_o / r_i$ was used to calculate $P_y$ since this provided the most conservative estimate. Using $r_o / r_i \sim 1.8$ in equation (4-22) results in $P_y \approx 930$ bar.

In addition to the 4 apertures previously described, 5 1/4" openings were bored into the reactor. National pipe thread (NPT) was machined into these fittings so that they could accept standard NPT fittings. Teflon tape was used to ensure the pressure seal. As is often the case, the NPT fittings were found to leak after repeated use. To eliminate this problem, HiP fittings could be used instead of the NPT variety though, in all experiments described in this study, the NPT fittings did not leak appreciably. Operating the reactor overnight typically resulted in less than a 2 bar drop in pressure (out of a total of 80+ bar).

The reactor was equipped with a piezoelectric pressure transducer (Dynisco, 832) with an accuracy specified as ± 1 bar and a maximum operating pressure of 680 bar. The voltage output of the transducer was converted into a pressure reading using a digital pressure indicator (Dynisco, 1290). The readability of the pressure indicator was ±0.7 bar. The fluid temperature within the reactor was measured using an immersed T-type thermocouple (Omega) with a listed accuracy of ± 0.5 °C. Reactor temperature was maintained to within ±0.1 °C using a PID controller (Omega, 9001CN)/thermal tape (100 W output/Barnstead).

Thermocouples sheathed in 304-stainless steel were used for all measurements. In preliminary experiments the location of the thermocouple probe was varied.
systematically to ensure that the reactor was reasonably isothermal (to within roughly $\pm 1.0 \, ^\circ C$) during sonication. Both 1/8" and 1/16" sheaths were tested, though the 1/16" sheath was damaged during high-intensity sonication when placed within several centimeters of the tip of the sonic horn.

Figure 4-7 is a schematic of the reactor depicting several options for injection, sampling, and recirculation. The critical piece of equipment was the Milton Roy/LDC Analytical minipump (p/n 92014903). This dual-piston reciprocating pump, which had a maximum design pressure of 400 bar and a maximum flow rate of 25 cm$^3$ min$^{-1}$, was used to recirculate the contents of the vessel to provide agitation. At its maximum flow rate, the reactor volume was completely recirculated in less than 4 min. Different positions for withdrawal and re-injection were used in different experiments and will be specified as appropriate. As shown in Figure 4-7, the recirculation loop (which had a measured volume of roughly 3.0 cm$^3$) was equipped with two in-line filters and one HPLC sampling valve. A 15 $\mu$m filter was positioned on the inlet side of the pump and was designed to prevent large particles from entering the pump and damaging the piston seals. A second 2 $\mu$m filter was positioned on the outlet side of the pump to prevent the

![Figure 4-7. Schematic of the generic setup for reactor recirculation and sample injection/withdrawal. A: high-pressure reactor; B: recirculating pump; C: ball valve used to isolate the reactor; D: HPLC valve which was used for sample injection during reactor pressurization with carbon dioxide; E: HPLC sampling valves; F: 15 $\mu$m filter; G: 2 $\mu$m filter; H: withdrawal point; I: re-injection point.](image-url)
accumulation of small particles in the recirculating fluid. The 2 μm filter could not be located on the inlet side of the pump as the suction head was not great enough to maintain flow in this configuration.

HPLC valves (Valco Instruments Company, Inc. uw-type) were positioned in the recirculation loop for sample injection and withdrawal. Alternatively, samples could be injected either directly into the reactor using a syringe/pipette when the reactor was depressurized and open to the atmosphere or through an HPLC valve located at the reactor inlet. If the second option were used, the flow of pressurized carbon dioxide into the reactor ensured injection of the sample through the loop. The exact method of sample injection used in a particular experiment is specified where appropriate.

Although recirculation was used to mix the reactor contents, independent agitation was possible using a Teflon-coated magnetically coupled stir bar. The stir bar rested on the tip of the sonic horn (see the next section). The stir bar was used only in a handful of experiments since it was anticipated that it would interfere with the sonic field.

No substantial changes were made to the peripheral equipment described by Randy Weinstein\textsuperscript{72} in his thesis (1998). The essential elements of the setup include: 1) a cylinder of grade 5.5 (99.99+% pure) liquid carbon dioxide equipped with a dip tube, 2) a heat exchanger system supplied with cold water from a refrigerated circulator (Cole-Parmer, Polystat model), the purpose of which was to condense the carbon dioxide before pumping to higher pressures, 3) a high-pressure pump (Eldex, BBB-4) to deliver carbon dioxide to the vessel, 4) a piezoelectric pressure gauge (Dynisco, 833)/pressure indicator (Dynisco, uPR 690) assembly to measure system pressure. As a safety precaution, the system was also equipped with pressure relief valves rated at 300 bar and positioned directly after the pump. The peripheral equipment was isolated from the ultrasonic reactor by an Autoclave Engineering needle valve and a Whitey ball valve in series.

**Ultrasound technique.** There are two basic methods that are used for laboratory sonication applications: 1) ultrasonic baths, 2) ultrasonic immersion horns. In general, ultrasonic baths are low power devices designed primarily for degassing and cleaning purposes. Ultrasonic immersion horns deliver much larger power densities to the processing fluid and are typically used for sonochemical applications. Manufacturers of ultrasonic immersion horns claim that ultrasonic baths are inferior because the sound
field in such devices is non-uniform. In fact, both products generate non-uniform sound fields in the processing fluid. Sound field non-uniformity is discussed in a section on practical aspects of ultrasonic engineering and reactor scale-up in Section 7.6.3. In the end, an ultrasonic immersion horn system was selected, primarily for the higher power densities which could be delivered directly to the reactor. An attempt to use an ultrasonic bath (E/MC, model # 250) to emulsify dense carbon dioxide and water (contained within a high-pressure, stainless steel reactor) failed though toluene/water (contained within a glass beaker) was emulsified successfully.

The ultrasound system required for an immersion horn consists of three components: 1) a sonic processor which converts a 60 Hz electrical signal to an ultrasonic frequency (20 kHz for all experiments in this project), 2) a piezoelectric crystal which converts the electrical signal to a mechanical signal, 3) a titanium probe (also referred to as horn) which vibrates to generate the actual sound wave within the processing fluid. The same piezoelectric converter, supplied by Sonics and Materials, Inc., was used in all experiments and will not be discussed further here.

A titanium-alloy (90% Ti/6% Al/4% V) horn, custom built by Sonics and Materials, Inc., was used in all experiments (see Figure 4-8). The diameter at the tip of the horn was 1.0 cm, resulting in an active area of 0.785 cm$^2$. The horn's distinct catenoidal design was selected to ensure high intensity sonication at its tip.

Titanium-alloy is the preferred material of construction for sonic horns due to its: 1) good acoustical properties, including low acoustic impedance, that is the product of solid density and sound speed, and 2) its good mechanical strength and resistance to chemical corrosion. It was found that the probe could withstand immersion in a liquid carbon dioxide/water environment at 80 bar and 30 $^\circ$C indefinitely, provided that the horn was not in operation. No traces of chloride-induced pitting were observed after 24 hours of operation in acidic solution containing 1 x $10^{-3}$ mol L$^{-1}$ chloride ion. Physical erosion of the tip was observed after sustained sonication (10+ hrs) as is discussed in greater detail in Section 5.3.1. Immersion of the tip in acidic water (pH ~ 3) with 1.0 mol L$^{-1}$ KF caused widespread pitting and general corrosion. Immersion in solutions containing salts such as KNO$_3$ and KI did not result in any observable corrosion, though the concentrations of the salts in these studies was considerably less than 1.0 mol L$^{-1}$. 
Figure 4-8. Digital photograph of the solid titanium sonic probe and stainless steel sealing gland. The scale bar is 2 cm.

Two separate ultrasonic processors were used. For the initial experiments a Vibra-cell VCX-750 manufactured by Sonics and Materials was employed. This unit, which is rated at a maximum sustained power output of 750 W, was selected to provide a flexible user interface and high power output. Unfortunately, the Sonics and Materials unit stalled when operated at pressures greater than 75 bar. Dr. Mike Donaty, a senior engineer at Sonics and Materials, suggested that the stalling was due to a small (less than 2%) drift in the resonant frequency of the sonic horn due to the resistance of the high pressure fluid. The VCX-750 corrects for deviations in the operation frequency in a process referred to as “auto-tuning”, but the ultimate safety guard against operating at an unknown frequency is instrument shut down. In their studies of ultrasonic treatment of acetic acid in near-critical water, Aymonier et al.\textsuperscript{74} reported a similar failure with the Branson PGB240A sonifier at temperatures between 150-200 °C at 250 bar. These researchers also attributed the failure to drift in the resonance frequency (which was measured directly using a hydrophone) from the design frequency.
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Faced with the shut down of the Sonics and Materials processor at pressures greater than 75 bar, a more basic unit, the Branson 400, was used for the majority of the experiments. This analog unit was capable of most of the functions of the Sonics and Materials digital processor but did not auto-tune the operating frequency. In this research, the Branson sonifier has been used successfully at pressures up to 150 bar at 30 °C. One drawback to using the Branson sonifier is that the actual frequency of operation was unknown. Based on the hydrophone measurements of Aymonier et al., the deviation from the 20 kHz set point is expected to be roughly 2%.

In addition to operating frequency, power output of the sonic equipment was also considered. Like most commercially available sonic processors, both the units used in this study allowed the amplitude of the horn vibration to be varied. The amplitude of vibration, which is on the order of several microns, is related to the power output of the instrument, which is the physically relevant metric. Unfortunately, the power delivered by the instrument for a given amplitude setting depends upon the fluid environment. The power output rating provided by the manufacturer is the maximum power that the instrument can supply and cannot be used to determine the actual power output by the sonic horn. Although both sonic processors used in this study were equipped with internal watt meters, the power draw of the sonic processor is not necessarily equal to the power delivered to the fluid since some of the energy is lost to the environment. An independent calibration was required to relate the operator-determined vibration amplitude to the experimentally relevant power delivered to the fluid.

Calibrating the energy output of sonic equipment has been a challenge to sonochemists for some time. T.J. Mason's 1991 book on the subject describes the problem in detail. Proper calibration of ultrasonic equipment is important for two reasons: 1) sonochemical enhancement can be quite sensitive to applied power density and sonochemical yield does not always increase monotonically with applied power and 2) calibration of power delivery is required for standardization of ultrasonic experiments.

The primary method for calibrating the power output of ultrasonic probes is based on temperature rise. The accuracy of this calorimetric technique relies on the fact that the overwhelming majority (99%) of sound which enters the reactor is dissipated as heat. The usual protocol for the calorimetric technique is to sonicate the reactor/process fluid
for a known amount of time while measuring the temperature. Assuming adiabatic conditions, the temperature rise during sonication, $\Delta T$ (°C or K) for a given time, $t$ (s), is converted to power output, $P$ (J s$^{-1}$ or W), using the standard formula:

$$P = \frac{\Delta T}{t}(c_p M)$$  \hspace{1cm} (4-23)  

where $c_p$ is the heat capacity (J kg$^{-1}$ K$^{-1}$) and $M$ is the mass of the fluid (kg). There are two problems with this approach: 1) adiabatic conditions are difficult to achieve and 2) the heat capacity of the reactor is not easily treated. To minimize heat losses, several layers of kaoline wool and fiber glass tape insulation was applied to the reactor. The heat leak was measured after heating the reactor to roughly 35 °C using thermal tape. At this temperature there was a measurable heat loss, corresponding to a leak rate of $4.3 \times 10^{-4}$ °C s$^{-1}$ in the absence of external heating from either sonication or thermal tape. This slow heat leak rate was negligible so that the reactor could be considered as nearly adiabatic.

Because a large, stainless steel reactor was used, properly accounting for the heat capacity of the vessel was extremely important. The procedure that was used is as follows. First, the reactor was sonicated for a known period of time (90-120 s, depending on the run) and the temperature was recorded every 20 s. A maximum temperature was observed and recorded directly after sonication was terminated. This temperature spike corresponded to heating of the vessel contents and partial heating of the vessel itself. In the first minutes after termination of the ultrasound, the temperature rapidly dropped before achieving a steady value. During the initial time interval, heat was transferred from the reactor contents to the vessel. The temperature of the reactor increased and that of the contents decreased. Once the steady temperature was reached, the reactor was assumed to be isothermal as it had equilibrated with the reactor contents. The isothermal assumption was confirmed by taking temperature measurements at various locations in the reactor and at its surface. The steady value was used in equation (4-23) to determine the power delivered to the reactor. The total heat capacity, $c_pM$, for the reactor and its contents was estimated to be 4370 J °C$^{-1}$ based on the masses and heat capacities of water, carbon dioxide, and 316-stainless steel.

Figure 4-9 shows representative time/temperature profiles recorded during sonication with the Branson 400 sonifier for a range of amplitude settings. The
Figure 4-9. Temperature rise during calibration of the sonic probe. ▲ 50% vibration of the tip; ○ 25% vibration of the tip; ● 10% vibration of tip; Full scale is 5 μm. The system was sonicated for 90 s and then the ultrasound was terminated. The reactor reached a maximum temperature after 90 s and rapidly cooled to the steady temperature at 200 s.

maximum temperature and the steady temperature are quite distinct. A number of calibration experiments for the Branson sonifier were conducted at 80 bar, 30 °C, and water fractions ranging from 0.2-0.8. At a given set of conditions, the amplitude of the sonication was varied systematically from 10-60% full range. The results of the calibration experiments are plotted in Figure 4-10. The percentage of water did not greatly affect the power output at a given amplitude of vibration and so data sets for a number of volume fractions are combined in Figure 4-10.

The data were fit to a second-order polynomial and this calibration was used to relate the experimentally set amplitude to the power delivered to the processing fluid. Also plotted in Figure 4-10 is the power drawn by the sonic processor as measured by the internal watt meter. As expected, the power drawn by the sonic processor is slightly greater than the power delivered to the reactor as determined by the calorimetric calibration. The two measures agree well at low power vibration amplitude and begin to diverge only at amplitudes greater than 40%. The agreement between the two measurements at low amplitudes lends credence to the calorimetric calibration method.
**Figure 4-10.** Calibration plot for the power delivered by the Branson sonifier to the high-pressure reactor. The ordinate is the power delivered to the reactor as determined by equation (4-23). The black line is the best fit $2^{\text{nd}}$ order polynomial while the dashed curve represents the power drawn as indicated by the watt meter of the sonicator.

The divergence at higher amplitudes reflects an increasing loss in energy to the ambient environment associated with higher amplitude vibration of the piezoelectric converter.

The most common metric for reporting power input is simply the absolute power, $P_{\text{abs}}$, such as is depicted in Figure 4-10. Absolute power is not particularly useful for purposes of scale up or analysis since it contains no information regarding the vessel geometry or volume. Power intensity, which is defined as the ratio of $P_{\text{abs}}$ to the surface area of the sonic horn and goes by the symbol $P_{\text{int}}$, is also frequently used in the literature to specify the acoustic conditions. $P_{\text{int}}$ is useful because it can be related directly to the pressure amplitude, $P_A$, of the ultrasonic sound wave using the relationship:

$$P_A = (2 \rho c P_{\text{int}})$$  \hspace{1cm} (4-24)

where $\rho$ is the density of and $c$ is the speed of sound in the fluid through which the sound wave propagates. $P_A$ is convenient since the minimum power required to cavitate a fluid is most easily understood in terms of pressure amplitude (see Chapter 5). The final means of reporting power conditions is the power density, $P_{\text{density}}$. The ratio of $P_{\text{abs}}$ to the total fluid volume is equal to $P_{\text{density}}$. This metric is useful for purposes of scale up,
though the relationship is somewhat misleading since the ultrasonic power is not
dissipated evenly throughout the reactor. In this thesis, the ultrasonic power density is
reported with the knowledge that the other power metrics can be recovered using the
surface area of the ultrasonic horn (0.785 cm$^2$) and the volume of the reactor (87.2 ± 0.4
cm$^3$).

4.5.2 Appearance of carbon dioxide/water emulsions

The stability of ultrasonically formed emulsions was determined visually by
recording the time required for the emulsion to clear after termination of agitation. The
process of demulsification was imaged using a video camera (Sanyo, VCB 3524)
equipped with telescopic lenses (Tiffen). The camera was focused on the center of the
reactor which corresponded to a working distance of roughly 7 cm. Indirect illumination
was provided using a fiber optic light source (Fostec, 8375) with a maximum power
output of 150 W. The light from the optical fiber was directed onto a Teflon sheet placed
10 cm behind the reactor to provide indirect lighting. Better images were obtained using
indirect lighting with the fiber optic operating at maximum power output than with direct
lighting at a lower power setting. A standard video recorder was used to archive
demulsification. The video tape was digitized using commercial software (FinalCut,
available at MIT's New Media Center) and still images were extracted from the digitized
movies.

In a typical experiment, the reactor contents were sonicated continuously for 2
min at the desired power density. In the first 10 s, the emulsions became quite turbid and
did not appear to change significantly over the remainder of the agitation period. The
prolonged sonication time was used to ensure that the emulsions had indeed reached
steady state in terms of emulsification and demulsification. In the presence of intense
agitation, the process of droplet formation initially dominates. As the density of
dispersed droplets increases, agitation actually increases the rate of droplet coagulation.
Two minutes were provided for the processes of droplet formation and coagulation to
reach steady state. Sonication for longer times did not lead to more stable emulsions. In
the presence of pulsed ultrasound (0.5 seconds ON/2.0 seconds OFF i.e. 20% duty of a
2.5 second cycle) at time-averaged pulsed power densities greater than 0.15 W cm$^3$,
emulsions persisted with no apparent change for as long as the ultrasound was applied (i.e., for as long as several hours).

Visually, the emulsions were turbid and gray. Surfactant-stabilized water/carbon dioxide emulsions\textsuperscript{66,68} have been described primarily as "white" or "milky white". White emulsions were never observed in this study. R.S. Farinato and R.L. Rowell\textsuperscript{77} indicate that the appearance of emulsions containing oil and water can be roughly related to the droplet size of the dispersed phase. According to these authors, pure white emulsions consists of droplets of diameters greater than 0.5 μm while the droplets in gray emulsions have diameters that are in the submicron range. This would lead to the conclusion that the droplets formed acoustically were smaller than 1 μm which is substantially smaller than the droplets present in surfactant-stabilized carbon dioxide emulsions. Although quite encouraging, this inference should not be taken as quantitative or unequivocal proof. In addition to droplet diameters, a number of factors, including the volume fraction of the dispersed phase, degree of flocculation, and the optical properties of the pure components, play a major role in determining the optical appearance of emulsions. In particular, the water/carbon dioxide emulsions described in the literature tend to exist in a highly flocculated state due to the limited solubility of the polymeric surfactants. In the absence of surfactants, flocculation without droplet coalescence is not expected. Thus the difference in the appearance of the ultrasonic emulsions and the surfactant-stabilized emulsions may be primarily a consequence of their corresponding degrees of flocculation.

Table 4-2 lists the experimental conditions and observed demulsification times for ultrasonically generated emulsions containing dense carbon dioxide. Figure 4-11 provides still images of the gradual clearing of the reactor without a clearly defined demulsification front. To the unaided eye, unstabilized emulsions appeared to break completely in 5-15 minutes. Although not apparent in Figure 4-11, turbidity persisted longest near the carbon dioxide/water interface.

No emulsification was possible below a power density of roughly 0.05 W cm\textsuperscript{-3}. Increases in $P_{\text{density}}$ beyond this threshold did not significantly increase the lifetime of the emulsions at least as could be determined visually. The significance of the threshold power density is considered in Chapter 5.
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Table 4-2. Visual observations of demulsification times, $\tau$, for ultrasonically generated (2 min continuous ultrasound) emulsions containing dense carbon dioxide as determined visually. $T = 298$ K in all experiments while pressure was varied between 60 and 76 bar. Emulsions were formed by application of 2 min of continuous ultrasound at 20 kHz at the power density indicated.

<table>
<thead>
<tr>
<th>Continuous Phase</th>
<th>$P$ (bar)</th>
<th>Power Density (W cm$^{-3}$)</th>
<th>$\tau$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>60</td>
<td>0.05</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>60</td>
<td>0.20</td>
<td>7</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>60</td>
<td>0.30</td>
<td>9</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>76</td>
<td>0.05</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>76</td>
<td>0.20</td>
<td>7</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>76</td>
<td>0.30</td>
<td>9</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>60</td>
<td>0.05</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>60</td>
<td>0.20</td>
<td>4</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>60</td>
<td>0.30</td>
<td>6</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>76</td>
<td>0.05</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>76</td>
<td>0.20</td>
<td>15</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>76</td>
<td>0.30</td>
<td>15</td>
</tr>
</tbody>
</table>

NA denotes “not applicable” and applies for demulsification times, $\tau$, when no emulsion was formed.

Figure 4-11. Still images of the reactor contents during demulsification. (a) 30 s after termination of ultrasound; (b) 3 min after termination of ultrasound; (c) 10 min after termination of ultrasound; (d) schematic. The two emulsions are clearly visible in (b) and (c), though not so in image (a). In all cases the water/carbon dioxide emulsion is the upper phase. The conditions were 80 bar, 30 °C and the reactor was initially 50% filled with water (by volume).

Increases in the pressure did not affect the stability of the carbon dioxide continuous emulsions but did seem to stabilize the water continuous emulsions. Since the properties of water that directly influence emulsion stability (primarily density and
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viscosity) are weak functions of pressure at these temperatures, the greater emulsion
stability must be due to changes in the properties of carbon dioxide. That carbon
dioxide/water emulsions are stabilized by increasing density while water/carbon dioxide
emulsions are not is an important observation that is considered in the more quantitative
treatment of demulsification presented in Section 4.6.

4.5.3 Turbidity of carbon dioxide/water emulsions

Turbidity was used to quantify the demulsification times listed in Table 4-2. In
these experiments, light from a fiber optic source (Fostec, 8375) was passed directly
through the reactor. The transmitted light was detected using a detector (Newport,
818SL) and an optical power meter (Newport, 835). The signal was digitized using an
analog/digital converter (National Instruments, BNC 1110) and sent to a standard
personal computer which was running Virtual Bench. A data point was taken every 0.5 s.
Before emulsification, the intensity of light transmitted through the reactor ($I_0$) was
measured. Following standard practice, transmittance was defined as the ratio of the
intensity of light transmitted through the reactor at a given instant ($I$) relative to $I_0$.
Turbidity was then calculated as the percent transmittance per unit length, assuming a
path length equal to 10 cm.

Figure 4-12 is a plot of turbidity measurements taken during demulsification of
emulsions formed after 2 min of continuous ultrasound. For greater clarity, data points
are shown at an interval of 30 s even though data points were collected every 0.5 s. Just
as in Table 4-2, a threshold power, below which emulsification does not occur, is
apparent. For the three data sets representing sonication at power densities greater than
or equal to 0.16 W cm$^{-3}$, the turbidity is initially high and slowly diminishes over a period
of 30 minutes. The data set representing sonication at 0.05 W cm$^{-3}$ exhibits high initial
turbidity, but the incremental attenuation of light rapidly decays to nearly zero. The
presence of some turbidity after termination of the ultrasound at 0.05 W cm$^{-3}$ is from two
sources: 1) the formation of surface waves at the carbon dioxide/water interface which
scatter incident light themselves and lead to the formation of large droplets which also
scatter light and 2) the deposition of large (1 mm) droplets of water on the sapphire
Figure 4-12. Turbidity plots for demulsification. The reactor contents were sonicated for 2 min (pulsed ultrasound with 25% duty cycle) and then agitation was terminated. Time $t = 0$ s corresponds to time at which sonication was terminated. The light transmitted by the emulsions was recorded as a function of time after sonication. Turbidity is transmittance divided by path length (10 cm). Sonication was applied over a range of power densities. Conditions: 80 bar, 30 °C, 20 kHz.

windows of the vessel. The surface waves rapidly relax and the turbidity diminishes substantially within 2-3 minutes. The large droplets detach more slowly, resulting in slight attenuation of the incident light for approximately 10 minutes. At power densities of 0.15 W cm$^{-3}$ and greater, the carbon-dioxide-water system becomes extremely turbid following sonication. The persistence of extreme turbidity for several minutes following termination of sonication is indicative of the formation of tiny droplets of the two phases which have been dispersed throughout the reactor. The discrepancy in demulsification times determined visually and with turbidity is due to the greater sensitivity of the latter.

An interesting feature of ultrasonic emulsification that is depicted in Figure 4-12 is that increasing the power density beyond the threshold required for emulsification has little benefit; emulsions formed at power densities greater than 0.15 W cm$^{-3}$ are neither significantly more turbid (immediately after termination of sonication) nor more stable (i.e., they take no longer to break, within the limits of experimental reproducibility) than those formed at lower power density. This observation (also noted in Table 4-2) is discussed in more detail later in this section. Both carbon dioxide/water and
water/carbon dioxide emulsions broke completely within 30 minutes after termination of the ultrasonic irradiation, as demonstrated by the turbidity plots in Figure 4-12.

4.5.4 Volume fractions of the dispersed phase

Volume fractions of the dispersed phase were measured with a technique similar to the chemical analysis approach described in Section 4.1 for characterization of emulsions of oil and water. The difference was that instead of analyzing water or carbon dioxide content directly, tracer compounds were used. The tracer technique was used because analytical methods for quantification of carbon dioxide/water concentrations were not readily available. Tracer compound selection was based on the following criteria:

1) The partition coefficient of the tracer must be known accurately. Preferably, the tracer would partition (99.9±%) into only one of the two phases.
2) The tracer must be soluble in concentrations sufficient to ensure easy quantification.
3) The tracer must be chemically inert and surface inactive.
4) Suitable analytical techniques were required for the quantification of the tracer.
5) The best tracers would be readily available and non-toxic.

Based on these criteria, octane was selected as a tracer for the dense carbon dioxide phase and KNO₃ was selected for the water phase tracer. Previous studies had shown that the partition coefficient of octane was greater than 100,000:1 in preference to carbon dioxide over water. Since it is strictly hydrophobic and not dipolar, octane was not expected to lower the carbon dioxide/water interfacial tension. Finally, octane can be quantified readily using gas chromatography and its solubility in carbon dioxide, which is on the order of 1 x 10⁻³ mol L⁻¹ at these conditions, is sufficient for detection purposes.

KNO₃ is effectively insoluble in carbon dioxide but its solubility in water is greater than 1.0 mol L⁻¹. Therefore, it will partition completely into the water phase. Although large concentrations of salt can raise water/air surface tension, small amounts, less than 1 wt%, have little effect. Therefore, ppm levels of KNO₃ can be quantified
readily using ion chromatography, a technique which was available. Both octane and KNO₃ are relatively non-toxic in small quantities.

Once suitable tracers had been selected, the task of developing a sampling method remained. The primary challenge was to develop a sampling probe to be inserted into the reactor. The recirculation pump could then use the probe as the inlet. Emulsion would be sampled from the reactor through the probe, and forced through a sample loop to isolate it from the reactor contents.

Proper design of a sample probe and development of a viable sampling procedure were both important. Initial attempts to use 1/16” tubing in conjunction with 1/16” HPLC valves failed as no tracer was ever detected in the sample loops. Most likely, severe restrictions in the 1/16” tubing or valve prevented flow of emulsion droplets into the sample loop. The inner diameter of the tubing was 1/64” (400 µm). Since the droplets were expected to be much smaller than 400 µm, the 1/16” tubing was most likely not the source of the problem. The 1/16” HPLC valve has internal restrictions on the order of 10 µm which probably accounted for most of the difficulties of emulsion sampling with this probe system.

The second-generation probe was a straight piece of 1/8” tubing placed 0.5 cm away from the carbon dioxide/water interface. Although the probe itself was not implicated by previous attempts, it was obvious that increasing the inner diameter of the probe could only help obtain representative samples. More importantly, the HPLC sample loop was replaced by a piece of 1/8” tubing (internal volume = 0.45 cm³). Instead of the HPLC valve, two 3-way valves (Swagelok) were used to isolate the sample loop from the reactor contents. The inner diameters of the 3-way valves were roughly 1/4” so that they did not represent any restriction to the flow of micron-sized droplets. Using this probe system, tracer compounds were reproducibly detected after depressurization of the sample loop contents into cold acetone at 0 °C.

Having developed a technique which could sample some emulsion droplets, it was necessary to optimize the protocol and perform control experiments. Initially, the contents of the reactor were recirculated during sonication. It was quickly realized that the surface waves which accompanied ultrasound would sometimes bring the carbon dioxide/water interface below the position of the sample probe. By recirculating during
sonication, both the water/carbon dioxide emulsion and the carbon dioxide/water emulsion were sampled in some unknown ratio. Obviously, this was neither reproducible nor accurate. Instead of recirculating continuously, the pump was not operated during sonication. Several seconds were allowed after termination of the ultrasound so that the carbon dioxide/water interface could stabilize. The sapphire windows were used to monitor the intensity of the surface waves and decide when to begin sampling. This small modification to the sampling protocol greatly improved reproducibility.

The protocol selected for volume fraction measurements was as follows:

1) The reactor was filled half-way with 44 cm$^3$ of deionized water. For measuring the volume fraction of water in the carbon dioxide emulsion, an aqueous solution containing either 2,500 or 5,000 ppm of KNO$_3$ was used. Otherwise, pure, deionized water was used and either 50 or 100 µL of octane was delivered separately to the reactor using a pipette.

2) The reactor was sealed, pressurized to 80 bar with carbon dioxide, and heated to 30 °C.

3) The phase to be sampled (either carbon dioxide or water) was recirculated for more than one hour to ensure phase equilibration.

4) The recirculation flow was discontinued and the contents of the reactor were sonicated for 2 min under pulsed operation (0.25 s ON and 0.75 s OFF) at the desired power. During this time, visual observation (coupled with previous turbidity measurements) indicated that the emulsification/demulsification processes had reached steady state.

5) Between 5-10 s were allowed for the surface waves to lose intensity. The recirculation was restarted at a flow rate of 5 cm$^3$ min$^{-1}$ (see below) for 20-25 s.

6) The sample loop was isolated from the reactor and slowly depressurized into either cold acetone (for measuring the volume fraction of carbon dioxide in water) or deionized water (for measuring the volume fraction of water in carbon dioxide).

7) The sample was diluted to a standard volume and analyzed. Samples of octane in acetone (for measuring the volume fraction of carbon dioxide in water) were
analyzed by gas chromatography (GC) using the procedure described in Section 3.3. Samples of KNO₃ in water (for measuring the volume fraction of water in carbon dioxide) were analyzed by ion chromatography (IC). The IC unit consisted of a low-pulse isocratic pump (Dionex, IP25), an anion exchange column (Dionex, Ionpac), an ion suppressor (Dynisco, AMMS-ICCE), used to improve signal-to-noise ratio, and an electrochemical detector (Dionex, ED40). A standard HPLC valve (Rheodyne) equipped with a 20 μL sample loop was used for all IC measurements. The mobile phase was deionized water containing 21 × 10⁻³ mol L⁻¹ NaOH and the flow rate was 1 cm³ min⁻¹. Emulsion samples were analyzed directly for NO₃⁻ and the detection limit was estimated to be roughly 1 ppm. The elution time of NO₃⁻ was 3.1 min. Both the IC and the GC were calibrated using standards of known concentration prior to actual experiments.

10) The volume fraction, φₐ, was calculated from the concentration measured by the analytical instrument, Cₛ, the known concentration of the analyte in the reactor, Cₑ, and the volume dilution factor, DF, using the formula:

\[
φₐ = DF \frac{Cₛ}{Cₑ}
\]  
(4-25)

Before conducting the full set of volume fraction experiments, several control experiments were conducted. The rate of the recirculation flow during emulsion sampling was varied between 5-15 cm³ min⁻¹ and no statistical difference in the measured volume fraction was observed. This set of experiments was conducted to ensure isokinetic sampling of the emulsions so that the measurement was not biased by droplet size. The position of the probe was varied from 0.5-1.5 cm from the carbon dioxide/water interface and no statistically significant difference was observed in the results. The 1/8” o.d. (1.65 mm i.d.) sample probe was replaced with a 1/4” o.d. (3.5 mm i.d.) sample probe for several experiments to verify that the largest emulsion droplets were sampled. Null experiments were performed in which reactor samples were withdrawn prior to emulsification to ensure that no tracer compounds were found in the absence of an emulsion.
Measurements of the volume fractions of the dispersed phase in each of the emulsions were made using the protocol described above. The conditions of the experiments were: 80 bar, 30 °C, 20 kHz, 25% duty cycle and 50% water by volume. The power density was varied systematically from 0-1.5 W cm$^{-3}$. Power densities greater than 1.5 W cm$^{-3}$ led to rapid heating of the vessel contents and were not included in this study. Figure 4-13a,b contains plots of the dispersed phase fractions ($\phi_d$) that were measured in the two emulsions as functions of applied power density. Error bars are estimated from the accuracy of the analytical techniques and uncertainty in the sample loop volume. Figure 4-13a exhibits a distinct threshold with respect to power density, below which emulsification does not occur. Above the threshold, increasing the power density had little effect. The slight decrease in the amount of dispersed carbon dioxide shown in Figure 4-13a is probably not statistically significant. At power densities greater than 0.15 W cm$^{-3}$, the volume fraction of carbon dioxide in the water phase was relatively constant at 0.05. Figure 4-13b does not exhibit a sharp threshold power density. Instead, a small amount of water is dispersed into the carbon dioxide even at power densities less than the threshold. The volume fraction of water increases monotonically with applied power density and does not quite reach a maximum in the range of power densities studied here. Nonetheless, the volume fraction of water in the carbon dioxide emulsion is not a strong function of power density above 0.2 W cm$^{-3}$ and $\phi_d$ is always less than 0.10.

Combined with turbidity data, the volume fraction data begin to provide some information regarding the processes of emulsification and demulsification. For now, it will be noted that carbon dioxide/water emulsions appear to require a threshold power density while water/carbon dioxide emulsions do not. Significantly more concentrated water/carbon dioxide emulsions are formed at power densities greater than 0.15 W cm$^{-3}$, at which point the effect of increasing power density begins to saturate. Emulsification is the subject of Chapter 5.

Visual observations provide a final consistency check on the relative amounts of dispersed water and carbon dioxide. Since the position of the water/carbon dioxide interface is unchanged by sonication, it would be expected that roughly equal amounts of the two phases were dispersed as is observed.
Figure 4-13. Measured values of $\phi_d$ for (a) carbon dioxide/water emulsions and (b) water/carbon dioxide emulsions. The smooth lines are meant only to highlight the data trends. Conditions: 80 bar, 30 °C, 20 kHz, 25% duty cycle and 50% water by volume.
4.5.5 Droplet sizes via in situ video-enhanced microscopy

**Experimental Protocol.** A number of techniques were considered for droplet sizing before selecting video-enhanced microscopy. This technique was selected because droplet diameters measured with microscopy are model independent. All other methods assume some physical relationship between the measurements (for instance scattering of light) and the droplet diameter. A further limitation of the most common methods for sizing droplets is that they cannot be used in concentrated emulsions. The extreme turbidity measured during and immediately after sonication suggests that the emulsions were too concentrated for standard static light scattering techniques without sample dilution.

Although microscopy has some distinct advantages, it has its own set of limitations. The most obvious limitation is that microscopy is a tedious technique requiring many hundreds of droplets to be counted to ensure a statistically significant sample size. Modern software automates this process somewhat. A second limitation of microscopy is the size of droplets which can be resolved. The smallest feature size which can be imaged using optical microscopy is given by the following formula:

\[ d = f \frac{\lambda}{NA} \]

(4-26)

where \( \lambda \) is the wavelength of the illumination and \( NA \) is the numerical aperture. \( NA \) is determined from the following formula:

\[ NA = n \sin \theta \]

(4-27)

where \( n \) is the index of refraction for the immersion medium and \( \theta \) is the angular aperture of the objective. For \( \lambda = 600 \) nm (representative of white light) and \( NA = 1.4 \) (the best possible with an oil-immersed objective), the smallest resolvable diameter, \( d_{\text{min}} \), is 0.4 \( \mu \text{m} \). T. Allen\(^{10}\) conservatively recommends \( d_{\text{min}} \sim 0.8 \mu \text{m} \), despite the fact that many researchers report microscopically determined feature sizes significantly smaller than this. The smallest droplets reported in K.P. Johnston's work (Table 4-1) could not be resolved using optical microscopy. Furthermore, for droplets which are of a size comparable to \( d_{\text{min}} \), the perceived image is larger than the actual image. J.G. Santiago et al. (1998)\(^{82}\) and C.D. Meinhart et al. (1999)\(^{83}\) describe this effect in greater detail within the context of micro-particle image velocimetry (PIV).
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Droplet sizing via microscopy of carbon dioxide/water emulsions has a distinct set of obstacles related to pressure sealing of a vessel which is suitable for imaging. Working in K.P. Johnston’s research group, C.T. Lee\textsuperscript{26} described one solution to this problem. In this work, a piece of fused silica microcapillary tubing (360 µm o.d. x 150 µm i.d.) with a polyimide coating was used for high-pressure imaging vessel. A portion of this coating was removed by first heating it and then wiping it clean. The microcapillary was connected to the high pressure vessel using standard PEEK tubing. The microcapillary technique was investigated by the author and rejected on two grounds: 1) after flame treatment, the tube became quite fragile and easily broke, 2) there was concern that the highly curved surface would magnify the droplets, thus leading to errors in the measured droplet diameters.

Thick-walled glass can withstand high pressure and is optically transparent. Glass tubing (6.5 mm o.d. x 0.65 mm i.d.) was obtained for the purpose of sizing emulsion droplets. It was connected to the reactor using 1/16” 316-stainless steel tubing and the pressure seal was made using standard 316-stainless steel ferrules. The glass tube held static pressures up to 80 bar, but shattered immediately once the sonication of the reactor was begun. Failure appeared to originate at the point of contact between the steel ferrule and the glass tube.

Sapphire tubes were also considered for the pressurizable view cell. To this end, single-crystal sapphire tubes (3.1 mm o.d. x 1 mm i.d.) were purchased (Rubikon). The outer diameter was optically polished, but the inner diameter was much rougher so that the tubes were not fully optically transparent. Based on experience from the glass tube experiment, vesopule graphite was used as the ferrule material for the pressure seals. Vesopule graphite is a much softer material than steel and was expected to be more forgiving. Furthermore, PEEK tubing was used to connect the sapphire view cell to the reactor, to reduce vibration of the sapphire cell during sonication rendering it less likely to burst during sonication. It was found that the sapphire tubes withstood static pressure up to 100 bar and sonication at all power densities. Despite this breakthrough, the sapphire tubes were rejected for three reasons: 1) the poor polish of the inner diameter limited optical access to the tube; 2) the index of refraction of sapphire (1.7) is much higher than liquid water (1.4) or carbon dioxide (1.0), which presents a challenge to
imaging; 3) although the tubes were quite robust to static pressure, they were extremely fragile to handle. All three sapphire tubes purchased from Rubikon were broken during routine handling within weeks. Diamond paste containing micron-sized particles was used to polish the inner diameter, but did not greatly improve their transparency.

A successful view-cell strategy was formulated after conversations with members of K.F. Jensen’s research group. In their microreactor studies, E. Murphy and T. Inoue designed a microchannel with optical access that could be interfaced to a high-pressure reactor and withstand pressures up to 120 bar (at 25 °C). The device, which was microfabricated using standard techniques at the Microsystems Technology Laboratory (MTL) at MIT, was based on a 31.5 mm (length) x 10.3 mm (width) x 1 mm (thick) silicon chip cut from a 4 inch diameter silicon wafer (Silicon Quest). A 200 mm (length) x 0.625 mm (width) x 0.250 mm (depth) trench was etched (Deep Reactive Ion Etch, Surface Technology Systems) into the surface of the silicon using SF₆ etchant. The silicon chip was sealed with an anodically bonded pyrex window (dimensions identical to the silicon chip). The novel feature of the device was its pressure connection. To achieve the pressure seal, the silicon was wetted using a 1,000 Å layer of titanium applied by electron beam evaporation. A 5,000 Å layer of copper was deposited on top of the titanium also using electron beam evaporation. The copper layer was then soldered directly to a 1/16” stainless steel tube fit with brass ferrules. The microdevice was attached with epoxy to an aluminum chuck for better stability.

The microdevice was attached to the sonic reactor using standard 1/8” and 1/16” stainless steel tubing and three-way valves (Swagelok). The sample probe system was identical to that used for measuring volume fractions. The only difference between the setups for the two experiments was that the droplet size measurements used a system of 4 three-way valves instead of the 2 three-way valves used in the volume fraction experiments. Four valves were required because the microdevice was taken to Jensen’s laboratory (66-125) for microscopy (see below). Two of the valves were used to pressure seal the reactor during microscopy and two of the valves were used to pressure seal the microdevice. Figure 4-14 is a digital photograph of the device and the two valves which were used to contain the pressure during imaging. Figure 4-15 is a schematic of the microdevice/reactor which highlights the most pertinent features.
Figure 4-14. Digital photograph of the (a) microfabricated device used as the high-pressure view cell, (b) the aluminum chuck that stabilized the view cell; (c) the outlet 3-way valve; (d) the inlet 3-way valve.

Figure 4-15. Schematic drawing of the microfabricated device used as the high-pressure view cell. (a) the pyrex window; (b) the silicon chip; (c) the 625 mm wide channel etched in the chip, (d) the inlet/outlets of the channel, (e) 1/16" tubing to the peripheral equipment. Prior to service, the pyrex window (a) was irreversibly bonded to the silicon.
Microscopy of the emulsions was conducted in K.F. Jensen's laboratory with the assistance of E. Murphy, A. Günther, and D. Coleman. A Zeiss Axiovert 200 microscope with a resolution of 0.29 μm/pixel (at a magnification of 20x) was used. The smallest feature that could be quantitatively resolved at this magnification was about 1 μm. Submicron features in the silicon surface that resulted from the etching process were visible, but not resolvable. A higher power objective lens (40x) was available on the microscope, but did not have sufficient depth of field to image droplets in the microchannel. It is conceivable that features as small as 500 nm could be resolved using the more powerful objective lens, and further improvements could be made using fluorescent dyes. If these techniques are used in the future, corrections due to optical diffraction will be required. C.D. Meinhart\textsuperscript{82,83} describes these calculations in several recent papers.

For image recording, the microscope was attached to a digital video camera and the entire unit was interfaced with a standard personal computer. Individual frames were extracted from the digital video using standard software. The microscope was calibrated with 4 μm (imaged as 3.95 ± 0.21 mm, by hand) and 20 μm (imaged as 19.3 ± 1.1 μm, by hand) polystyrene latex bead standards (Duke Scientific). Images of emulsion droplets were analyzed by hand using Adobe Photoshop and automatically using ImageJ software (available as freeware on the internet). Droplet sizes obtained via the two methods agreed to within better than 10%. Images were edited as little as possible prior to running the software, but more consistent results were obtained with background subtractions. Occasionally, images were edited by hand using Adobe Photoshop software to remove noise or to ensure that droplets in close proximity to one another were counted separately. Otherwise, ImageJ occasionally incorrectly counted two or more droplets that were closer than ~3 pixels as one droplet.

During a run, emulsions were generated at an applied acoustic power density of 0.60 W cm\textsuperscript{-3} and duty cycle of 25% at 80 bar and 30 °C. This power density was selected based on the results from the turbidity (Section 4.5.3) and volume fraction measurements (Section 4.5.4). Since each run was rather tedious (including both the experiment time and image analysis time), power density was not varied in these experiments. The reactor was loaded with 50% water by volume for all runs. The protocol used for droplet
imaging was similar to that used for volume fraction measurements. The reactor contents were sonicated for 2 min with pulsed ultrasound (0.25 s ON and 0.75 s OFF), during which time the emulsion reached steady state. Following termination of sonication, 5-10 s were allowed for the carbon dioxide/water interface to stabilize. The fluid was then recirculated through the microdevice at a flow rate of 5 cm$^3$ min$^{-1}$ for 20-30 s, and was completely flushed roughly 20 times. Once a representative sample had been obtained, the microdevice was isolated from the reactor using the first set of 3-way valves. The second set of 3-way valves was closed to maintain pressure in the sonic reactor. The microdevice was then removed from the reactor and transported to K.F. Jensen's laboratory for image analysis.

In a typical run, 3 min elapsed between taking the emulsion sample and microscope imaging. During this time, it was found that the majority (≥90%) of the water droplets in water/carbon dioxide emulsions settled to the silicon surface. The remainder adhered to the glass surface or the silicon walls. That the water droplets settled during the 3 minutes of transportation time is not surprising. Twenty seconds are required for a 10 μm carbon dioxide droplet to fall 250 μm (the entire channel depth) in water at 80 bar and 30 °C (assuming Stokes’ law). Non-settled droplets could be imaged only with a continuous flow, and the flow rate requirement for imaging of suspended droplets can be calculated from the settling time of an individual droplet. Considering droplets which fall only 10% of the entire 250 μm as truly suspended in the flow, leads to an estimate of the maximum residence time in the channel of 2 s for droplets 10 μm in diameter. The total cross-sectional area of the channel was 0.156 cm$^2$, implying that a volumetric flow rate of approximately 1.5 cm$^3$ min$^{-1}$ would be sufficient to ensure that the droplets did not settle significantly in the channel. The flow rate of 5 cm$^3$ min$^{-1}$ used in this study would have been sufficient to ensure that dispersed droplets could be imaged. To perform experiments with continuous flow, the entire reactor assembly would need to be transported to the microscopy laboratory. It was decided that moving the reactor was not justified for this improvement in droplet diameter measurements.

Water droplets found on the silicon surface were used exclusively for particle sizing. Since the droplets adhered to the surface, there was no coagulation during imaging which was a definite advantage. Since the droplets were essentially static, there
was no time limit for microscopic analysis. A disadvantage was that the droplets did spread on the silica surface. Corrections for droplet spreading, and the resultant distortion of the perceived droplet diameter, were made using a geometric procedure which will be discussed later.

The situation for carbon dioxide droplets in carbon dioxide/water emulsions was somewhat different. It was found that the carbon dioxide droplets adhered equally to the pyrex and silicon surfaces. Carbon dioxide droplet wetting of the surfaces was therefore treated somewhat differently than water droplet wetting of the silicon surface. This procedure will also be discussed below.

**Droplet diameters measured using optical microscopy.** Using the protocol described above, 7 separate runs (4 for water/carbon dioxide and 3 for carbon dioxide/water) were performed to measure droplet diameters. Over 500 droplets were counted for carbon dioxide/water emulsions and over 1,500 droplet were counted for water/carbon dioxide emulsions. Figures 4-16 and 4-17 are representative digital photographs of water droplets in carbon dioxide and carbon dioxide droplets in water, respectively. In all instances, droplets were essentially spherical and there was no evidence of flocculation without complete coalescence.

The raw droplet size data were binned to determine size distributions. Figure 4-18 contains plots of the distributions for the two emulsions. In this figure, the carbon dioxide droplets are binned every 3 μm, while the water droplets are binned every 1 μm. These bin sizes were selected primarily for appearance; the effect of bin size on derived statistics such as average diameters and surface areas is discussed later in this section. It is also noted that the droplet distributions in Figure 4-18 have been divided by the total number of droplets to yield probability distributions. This operation was performed primarily so that the two distributions could be depicted meaningfully in one figure. No correction for droplet spreading has been made in Figure 4-18. Both types of emulsions consisted of a unimodal distribution of droplet diameters which was roughly log normal:
Figure 4-16. Representative micrograph of water/carbon dioxide droplets. Image taken using a Zeiss 200 Axiovert microscope. Emulsification conditions: 80 bar, 30 °C, 2 min pulsed (25% duty cycle) ultrasound at 0.6 W cm\(^{-3}\) and 20 kHz.

Figure 4-17. Representative micrograph of carbon dioxide/water droplets. Image taken using a Zeiss 200 Axiovert microscope. Emulsification conditions: 80 bar, 30 °C, 2 min pulsed (25% duty cycle) ultrasound at 0.6 W cm\(^{-3}\) and 20 kHz.
Figure 4-18. Droplet diameters measured via microscopy (Zeiss, Axiovert 200) for ○ water droplets in a carbon dioxide emulsion and for ● carbon dioxide droplets in a water emulsion. Over 2,000 droplets were imaged and counted for this figure. Emulsification conditions: 80 bar, 30 °C, 2 min pulsed (25% duty cycle) ultrasound at 0.6 W cm$^{-3}$ and 20 kHz. The solid lines are best fit log normal curves.

\[ f(d_p) = a \exp \left[ -0.5 \left( \ln \left( \frac{d_p}{d_{p,0}} \right) / b \right)^2 \right] \]  \hspace{1cm} (4-28)

where $d_{p,0}$, $a$, and $b$ are fit parameters. The best-fit parameters for the two distributions are given in Table 4-3.

Table 4-3. Best-fit parameters for the log-normal functions, as presented in equation (4-28), describing the droplet probability distribution for both carbon dioxide and water droplets. Raw data are plotted in Figure 4-18.

<table>
<thead>
<tr>
<th>Droplet Type</th>
<th>$a$</th>
<th>$b$</th>
<th>$d_{p,0}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water/carbon dioxide</td>
<td>0.38</td>
<td>0.45</td>
<td>3.68</td>
</tr>
<tr>
<td>carbon dioxide/water</td>
<td>0.27</td>
<td>0.36</td>
<td>11.7</td>
</tr>
</tbody>
</table>

*no correction applied*
Since water droplets were sized while adhered to a silicon surface, the droplet diameters determined directly from microscopy were larger than the true diameter. A correction for spreading was required to correct the “imaged diameters” to the “true diameters”. In the absence of additional information, interfacial tension data (for water/silicon, carbon dioxide/silicon, and water/carbon dioxide) could be used to determine the contact angle and shape of the droplet and correct for spreading. This approach is actually not viable without additional experiments because no interfacial tension data are available for carbon dioxide/silicon. Fortunately, the rigorous contact angle approach was not needed because a certain fraction of the water droplets adhered to the sides of the microchannel. This allowed the profile of the droplet to be photographed so that spreading on a silicon surface could be estimated. Figure 4-19 is an example of the profile of a water droplet attached to the silicon wall of the microchannel.

**Figure 4-19.** Micrograph (Zeiss, Axiovert 200) of water droplets on the silicon sides of the microchannel. “A” denotes the silicon wall while “B” denotes bulk carbon dioxide. The dimensions (2a and b) of the largest water droplet are shown. The scale is provided by 2a, which is 10 μm. Images such as this one were used to correct for spreading of water droplets on the silicon surface. Emulsification conditions: 80 bar, 30 °C, 2 min pulsed (25% duty cycle) ultrasound at 0.6 W cm⁻³ and 20 kHz.
There are several sources of error when profile images of the droplets on the wall are used to correct for droplet spreading on the channel floor. The first of these has to do with the nature of the silicon surface. When a silicon wafer is etched in different directions, different crystal planes are revealed. Thus, the floor of the channel (where the majority of the droplets were imaged) and the walls of the channel (where droplets were imaged in profile) corresponded to different crystal planes of the silicon. Since the surface energies of the different crystal planes are not quite equal, droplet wetting is expected to be slightly different on the two surfaces. This effect was assumed to be negligible. More importantly, submicron roughness in the silicon surface is clearly visible in images of the droplets. The roughness is an artifact of the etching process. Undoubtedly, these surface defects contribute and may even dominate droplet wetting. It is not clear if the surface roughnesses on the walls and floor of the channel were the same. Differences in roughness between these two surfaces is a large source of uncertainty in the wetting correction calculation.

The surface roughness of the silicon walls was investigated further using SEM. Figure 4-20 is an SEM micrograph of the channel walls courtesy of E. Murphy. Scalloping of the walls, with a relevant length scale of roughly 10 μm, is clearly visible in this image. These grooves undoubtedly influence droplet spreading. It is entirely possible that the droplets in Figure 4-19 spread to fill the reservoirs revealed in the SEM. Conversely, SEM images of the channel floor reveal the presence of submicron defects which are expected to have a much different, and more subtle, effect on droplet spreading. This called into question the use of droplet profiles on the device walls to correct for droplet spreading on the device floor.

A series of experiments was conducted with the assistance of B. Cicciairelli to image droplet spreading on a silicon substrate similar to that used to fabricate the microchannel. Since the experiments were conducted at room pressure, perfluorohexane was used to simulate dense carbon dioxide as the two fluids were expected to have similar physicochemical properties. In separate work, we have studied the molecular solvation effects of supercritical carbon dioxide on chemical kinetics and demonstrated the analogy between carbon dioxide and fluorinated solvents. Images of water droplets surrounded by a perfluorohexane continuum (Figure 4-21a) and perfluorohexane droplets
Figure 4-20. SEM image (supplied by E. Murphy) of the walls of a microfabricated silicon channel. Grooves with a characteristic length of roughly 10 \( \mu \text{m} \) are clearly visible along the device walls as are a series of ridges with a characteristic length of roughly 0.5 \( \mu \text{m} \).

surrounded by a water continuum (Figure 4-21b) were obtained and are shown in Figure 4-21. In a perfluorohexane solvent, the water droplets spread considerably on the silicon surface with a corresponding contact angle of roughly 45 \( \pm \) 5\(^\circ\). More importantly, the droplets in Figure 4-21a appear qualitatively similar to the profiles depicted in Figure 4-19. This lends support for the use of Figure 4-19 to correct for droplet spreading on the silicon surface. In contrast, the perfluorohexane drops did not wet the silicon substrate, suggesting that no correction was necessary for the carbon dioxide droplets.

It is somewhat surprising that the silicon surface is hydrophilic as the experience of the Jensen research group indicates that freshly made silicon devices are hydrophobic. Presumably, under normal atmospheric conditions the silicon surface oxidizes to silica, which is expected to be hydrophilic. The oxidation rate is not certain, but several weeks elapsed between device fabrication and the actual experiments. This provides ample
Figure 4-21. Images obtained from contact angle measurements on a silicon surface of (a) water droplets in a perfluorohexane solvent and (b) perfluorohexane droplets in a water solvent. The contact angle was measured as $45 \pm 5^\circ$ and $115 \pm 10^\circ$, respectively. The scale bar in each micrograph corresponds to 500 \( \mu \text{m} \). Conditions: 1 bar, 10 \( ^\circ \text{C} \).

Time for significant oxidation. The state of the silicon surface during microscopy measurements is therefore an unknown. One method of standardizing the silicon surface would be to coat it with a suitable material. This concept was tested by coating a silicon substrate with a thin layer of Cytop, an optically transparent amorphous fluoropolymer available commercially from Bellex International Corporation. Cytop was applied to the silicon substrate from the solution and baked overnight at 80 \( ^\circ \text{C} \). After this treatment, the air/water contact angle was measured to be roughly $110^\circ$. The coating appeared to be resistant to a supercritical carbon dioxide environment; the contact angle of water was not changed by pre-treating the coated silicon wafer in carbon dioxide at 100 bar and 30 \( ^\circ \text{C} \) for 3 hours. These experiments proved the feasibility of using Cytop to render the silicon surface hydrophobic and the treatment is recommended for future work.
The final potential source of error in the wetting correction is the effect of gravity on the shape of the droplets. If gravity forces dominate, the shape of droplets suspended on the wall would be drastically different from those adhered to the floor of the device. The ratio of the gravity force to the surface tension force is given by the Bond number, \( Bo \):

\[
Bo = \frac{gr^2 \Delta \rho}{\sigma}
\]

(4-29)

where \( \sigma \) is the interfacial tension. For representative values of \( \Delta \rho \) (300 kg \( \text{m}^{-3} \)) and \( \sigma \) (25 x \( 10^{-3} \) N \( \text{m}^{-1} \)), \( Bo \sim 1 \) for \( r \sim 0.4 \) cm. \( Bo \) for the droplets in this study was less than 1 x \( 10^{-5} \) and the effect of gravity on droplet shape was insignificant.

At this point it was decided to pursue spreading correction using the profile images obtained from the sides of the microchannel. Over 20 water droplet profiles were imaged similar to those depicted in Figure 4-19. These images were analyzed as spherical caps with a height, \( b \), and a base radius, \( a \), as shown in Figure 4-19. From Figure 4-19 it is clear that the droplet diameters presented in Figure 4-16, 4-17, and 4-18 are equal to 2\( a \). From the available images, the average value of \( b/2a \approx 0.36 \). The volume of the spread droplet, \( V_{\text{cap}} \), was calculated using the geometric formula:

\[
V_{\text{cap}} = \frac{1}{6} \pi b (3a^2 + b^2)
\]

(4-30)

Since mass, and hence volume in a constant density system, is conserved, \( V_{\text{cap}} \) must equal the droplet volume if it were a true sphere, \( V_{\text{sphere}} \). Setting \( V_{\text{cap}} = V_{\text{sphere}} \) allows calculation of the equivalent radius, \( r_{\text{equiv}} \). The ratio of \( a \) to \( r_{\text{equiv}} \) was calculated for all available droplet profiles resulting in a value of 0.25. To correct for droplet wetting, observed diameters, 2\( a \), were multiplied by 0.25. The effect of this transformation was to shift the number average droplet diameter from 5.2 \( \mu \text{m} \) to 1.3 \( \mu \text{m} \) (see below). After the wetting correction, the water droplets formed using ultrasound compare favorably to the higher end of those reported by K.P. Johnston’s group (Table 4-1). That no surfactant was required in the current study is a clear advantage.

For carbon dioxide droplets in carbon dioxide/water emulsions, no useful profile images could be obtained. The lack of profile images necessitated a new strategy for dealing with the possibility of carbon dioxide wetting. It was clear from the contact angle
from images of water droplet profiles that the silicon surface was hydrophilic. Dense carbon dioxide is hydrophobic. Since the silicon surface cannot be simultaneously hydrophilic and hydrophobic, it was expected that the carbon dioxide would not wet the silicon surface. Unlike the water droplets in the carbon dioxide emulsions, the carbon dioxide droplets were distributed roughly evenly between the silicon and pyrex surfaces. Since pyrex is also a hydrophilic surface, it seems reasonable to assume that carbon dioxide would not wet the pyrex appreciably. As added evidence, the diameters of droplets adhered to the two surfaces were essentially the same, though slightly more small droplets had adhered to the pyrex (which was the top of the channel) than to the silica (which was the bottom). Unless the pyrex and silicon surface energies were identical, there would be a statistical bias between the diameters determined from the two droplet populations. Based on these observations and arguments, it was reasoned that wetting of carbon dioxide of both the silica and the pyrex was insignificant and no correction was made. Further support for this decision is provided in Figure 4-21b which shows that air-oxidized silicon is a fluorophobic (and hence probably CO$_2$-phobic) surface.

Correcting the droplet diameters to reflect wetting of the silicon (or air-oxidized silicon) surface was somewhat of an ad hoc procedure. As such the droplet diameters reported in this thesis are open to interpretation. Future work should be conducted to measure droplet diameters more accurately. In the meantime, we will see in Section 4.6 that the spreading correction probably provides a lower estimate of the actual water droplet diameters, while the diameters as imaged are an upper estimate. Only the upper estimate is used for analyzing reaction/transport as presented in Section 6.6.

Equations (4-6)-(4-9) were used to calculate average diameters as listed in Table 4-4. Diameters of water droplets before and after wetting corrections are listed separately. The raw droplet distribution data, binned as shown in Figure 4-18, was used to determine the average diameters. It was found that the calculated average diameters were not particularly sensitive (less than ± 0.1 μm) to bin size provided that the bin sizes were no larger than 2 μm. Without correction, the water droplets were roughly the same size as the carbon dioxide droplets, at least in terms of Sauter diameters. The fact that $<d_{32}>$ for the carbon dioxide/water droplets is nearly the same as that for water/carbon
dioxide droplets (before wetting correction), despite the fact that the two droplet populations have much different values of \( \langle d_N \rangle \), is a consequence of the fact that the carbon dioxide droplets were more nearly monodisperse (see Figure 4-18). After spread correction, the water droplets were 5-fold smaller than the carbon dioxide droplets.

**Table 4-4.** Various averages of droplet distributions given in microns. Calculated from data in Figures 4-16 and 4-17 and equations (4-6)-(4-9). Spreading corrected using images in Figure 4-19 and equation (4-30).

<table>
<thead>
<tr>
<th>Droplet Type</th>
<th>( \langle d_N \rangle )</th>
<th>( \langle d_S \rangle )</th>
<th>( \langle d_V \rangle )</th>
<th>( \langle d_{92} \rangle = d_{92}^3 / d_s^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water/carbon dioxide</td>
<td>5.2</td>
<td>6.0</td>
<td>6.8</td>
<td>9.1</td>
</tr>
<tr>
<td>no correction applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water/carbon dioxide</td>
<td>1.3</td>
<td>1.4</td>
<td>1.7</td>
<td>2.1</td>
</tr>
<tr>
<td>corrected for wetting</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon dioxide/water</td>
<td>12.3</td>
<td>13.2</td>
<td>13.8</td>
<td>15.1</td>
</tr>
<tr>
<td>no correction applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 4.5.6 Interfacial area estimation

Interfacial area can be calculated directly from the droplet size distributions and volume fraction measurements. As suggest in Section 4.5.3, \( \phi_d \) was assumed to be 0.1 for water/carbon dioxide emulsions and 0.05 for carbon dioxide/water emulsions. Equation (4-5) and the Sauter diameters (Table 4-4) were used for the calculation. The resulting values of \( \alpha \) were \( \sim 600 \) and \( \sim 2800 \text{ cm}^{-1} \) (or 100 and 500 m² kg⁻¹) for the water/carbon dioxide emulsion with and without wetting correction. For the carbon dioxide/water emulsion, \( \alpha \) is equal to roughly 200 cm⁻¹ (or 20 m² kg⁻¹). These estimates of surface area are used in Section 5.6.1 for estimating the emulsification energy efficiency and in Section 6.5 when mass transport and reaction kinetics are analyzed.

### 4.6 Comments on Emulsion Stability and the Process of Demulsification

Some statements can be made regarding the process of demulsification based on the combination of turbidity data, volume fraction measurements, and droplet diameters. To make quantitative statements, information regarding volume fractions and droplets sizes as a function of demulsification time would be needed and only a qualitative analysis is performed here. The strategy in this section will be to use the equations presented in Sections 4.1-4.3 and the emulsion measurements described in Section 4.5 to
Chapter 4: Emulsion Characterization

predict half lives for Smoluchowski coagulation and settling. Calculated half lives are compared to the known demulsification times as measured by turbidity to determine the most important demulsification processes. Additionally, calculated emulsion breaking times will prove useful as a reality check for the spreading corrections discussed in Section 4.5.

Before any calculations were made, estimates of the density and viscosity of the two fluids were required. The Span-Wagner\textsuperscript{85} equation of state recommended by NIST predicts a carbon dioxide density of 700 kg m\textsuperscript{-3} at 30 °C/80 bar. The density of water at these conditions is 997 kg m\textsuperscript{-3} (NIST Steam Tables\textsuperscript{14}) so that the density difference between the two phases is approximately 300 kg m\textsuperscript{-3}. At these same conditions, the viscosity of water is 7.992 × 10\textsuperscript{-4} kg m\textsuperscript{-1} s\textsuperscript{-1} (NIST Steam Tables\textsuperscript{14}). Based on a thorough consideration of the available literature sources, K. Stephen and K. Lucas\textsuperscript{86} recommend a value for the viscosity of carbon dioxide of roughly 6 × 10\textsuperscript{-5} kg m\textsuperscript{-1} s\textsuperscript{-1} at 30 °C and 80 bar. The effect of mutual solubility of the two fluids on the density and viscosity of the pure fluids was assumed to be negligible.

Using these property values and an estimate for the total settling distance of 10 cm, the unhindered, $\tau_{unhindered}$, and hindered settling times, $\tau_{hindered}$, of the two emulsions were calculated using equations (4-2), (4-19) and (4-20). The results are presented in Table 4-5. Settling times are presented for water droplets both with and without the spreading correction. Similarly, Smoluchowski coagulation times were calculated using equation (4-16) and are reported in Table 4-5. It is clear from the time constants presented in Table 4-5 that the carbon dioxide/water emulsion breaks by a process of settling as the coagulation rate is too slow to be important. The predicted settling times are comparable to, though somewhat longer than, the observed demulsification times for the carbon dioxide/water emulsions. Corrections to the simple theories used in Table 4-5, which may resolve this discrepancy, are discussed later in this section.

Analysis of the breaking mechanism of water/carbon dioxide emulsions depends on whether or not the spread correction is used. If the uncorrected droplet diameters are used, the water/carbon dioxide emulsions appear to break by a combined process of coagulation and settling as the rates of these two processes are similar. When the spread correction is applied, the coagulation rate is much faster than settling with a time constant
Table 4-5. Time constants, $\tau$, for the breaking of acoustically generated emulsions. Equations (4-2), (4-19) and (4-20) were used for calculating the settling times assuming a settling distance of 10 cm. Equation (4-16) was used to calculate Smoluchowski coagulation times. Other parameter values are provided in the text.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>$&lt;d_{32}&gt; = d_v^3 / d_s^2$ (µm)</th>
<th>lifetime (min)</th>
<th>$\tau_{\text{unhindered}}$ (min)</th>
<th>$\tau_{\text{hindered}}$ (min)</th>
<th>$\tau_{\text{coagulation}}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water/carbon dioxide</td>
<td>9.1</td>
<td>10</td>
<td>19</td>
<td>20</td>
<td>93</td>
</tr>
<tr>
<td>no correction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water/carbon dioxide</td>
<td>2.1</td>
<td>10</td>
<td>140</td>
<td>200</td>
<td>0.5 s</td>
</tr>
<tr>
<td>spread corrected</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon dioxide/water</td>
<td>8.8</td>
<td>15</td>
<td>55</td>
<td>82</td>
<td>20</td>
</tr>
</tbody>
</table>

of less than 1 s. In actuality, this coagulation rate is unrealistically fast. This is because, although roughly 10-20 s elapsed between termination of the ultrasound and emulsion sampling, similar droplet distributions were obtained in 3 separate runs. The only way that such a procedure could yield reproducible results is if this delay time were exactly the same in each measurement so that the same “snap shot” in time was sampled. The fact that the measurement was reproducible even though the time interval varied from 10-20 s suggests a coagulation time on the order of 10 s, corresponding more closely to the diameters obtained without correction.

An attempt was made to reconcile the discrepancy between the spreading correction and the calculated coagulation times. While some spreading correction was deemed necessary, coagulation times indicated that the correction applied in Section 4.5 was possibly too aggressive. Additionally, the surface features depicted in Figure 4-20 cast suspicion on the quantitative use of the spreading correction. Nonetheless, some spreading of the water droplets is inevitable. While spread-corrected droplets coagulated at an unrealistically fast rate, the uncorrected droplet diameter resulted in a coagulation time scale roughly 5 times longer than the requirement for “snap shot” measurement. This implies the existence of a critical droplet diameter of an intermediate size for which the coagulation time scale and the delay time were roughly equal. Figure 4-22 contains a plot of predicted coagulation times, calculated from equation (4-16), in terms of the percentage of the full correction factor (in terms of droplet diameter). In this plot, 100%
Figure 4-22. Coagulation times predicted using equation (4-16) as a function of the percentage of the spreading correction factor applied. Use of the full correction factor is denoted as “100 %” and corresponds to a droplet diameter of 2.1 μm. No correction factor is “0 %” and the corresponding droplet diameter is 9.1 μm.

correction corresponds to a diameter of 2.1 μm, while 0% correction is a 9.1 μm droplet. Also shown is a horizontal line corresponding to the “delay time” of 20 s. Provided that the experiment was conducted near or above this operating line, the “snap shot” assumption of droplet sampling is valid. Otherwise, it would be expected that experiments conducted with differing delay times would result in widely different observed diameters. It is important to remember that each Smoluchowski lifetime results in a diameter increase of only 2\(^{1/3}\) (a factor of 1.26), so that several coagulation lifetimes could have elapsed between termination of ultrasound and droplet sampling with only a small change in the observed diameter.

We have quite a lot of information at our disposal for determining the best estimate of water droplet diameters. Droplet profile images suggest a correction factor to apply to the water droplet diameters, while water/perfluorohexane spreading qualitatively supports such a correction procedure. On the other hand, the full spreading correction leads to estimated coagulation times which are not physically possible based on the sampling technique. Images of the surfaces of the microchannel device introduce an
additional degree of uncertainty. In the final analysis, the full correction factor probably overcorrects for spreading, while the droplet sizes determined directly from the images are almost certainly too large. Figure 4-22 suggests droplets with an average diameter of roughly 6 μm. This crude estimate will prove sufficient for reaction/transport analysis, but the uncertainties introduced by the analysis clearly demonstrate the need for in situ, real time monitoring of the emulsified droplets. The techniques discussed in Section 4.1 are expected to provide a spring board for future work in this area.

Taking into account uncertainties in the diameters introduced by spreading corrections, predicted demulsification times correspond reasonably well with observed demulsification times. This agreement is encouraging, but the theoretical interpretation can be refined in two ways. First, droplet distributions have been dealt with in a very rudimentary manner, by means of the Sauter diameter. A more sophisticated analysis would consider the actual distributions. Qualitatively, real treatment of droplet distributions would lower predictions of emulsion stability since the largest droplets are expected to settle at rates faster than that predicted for the Sauter diameter. As these large drops settle, they would encounter smaller droplets which are settling at slower rates. Such collisions are not accounted for in Smoluchowski theory and would increase the actual coagulation rates. Future work should address the effects of droplet size distributions in a more quantitative manner; however, it is difficult to justify a detailed analysis without data regarding droplet diameters and dispersed phase concentrations as a function of time during demulsification. In this respect, on-line diagnostics are expected to provide an important opportunity for advancing our understanding of emulsion breaking.

Second, coagulation has been assumed to be 100% efficient. This is clearly a limiting case as the droplets may be stabilized against coagulation by the presence of impurities or naturally occurring species such as OH⁻. Potential stabilization is expected to be more important for water/carbon dioxide emulsions since, for these emulsions, droplet coagulation is a step in the demulsification process. On the other hand, we saw in Sections 4.2 and 4.3 that stabilizing colloidal particles in a nonpolar solvent requires surfactants with high solubility in the continuous phase, a considerable obstacle to stabilization of such particles in supercritical carbon dioxide. Preliminary experiments
conducted with the addition of conventional hydrocarbon surfactants such as sodium
dodecyl sulfate and bis(ethylhexyl) sulfosuccinate indicate that relatively large
concentrations of impurities (on the order of $1 \times 10^2$ mol L$^{-1}$) are required before any
change in emulsion stability is noticed. Isopropanol at a concentration of 1.0 mol L$^{-1}$ was
also added to otherwise pure carbon dioxide/water systems and only a small change in
emulsion stability was observed. These results suggest that deviation from the
Smoluchowski limit due to the presence of trace impurities is not important. Consistent
with this conclusion is that, for the 2,000 droplets imaged, flocculation without
coalescence was never observed.

4.7 Conclusions

Using a novel, high pressure reactor, emulsions of dense carbon dioxide and water
were generated using power ultrasound at 20 kHz. Typical experimental conditions were
30 °C, 80 bar, and 50% water by volume. Both carbon dioxide/water and water/carbon
dioxide emulsions were formed. Visually, the emulsions were stable for roughly 10 min.
Turbidity measurements indicated that the emulsions were somewhat more stable than
visual observation indicated, with complete breaking in 20-30 min. Most likely, the
turbidity measurement is slightly more sensitive than visual inspection. Using a tracer
technique, volume fractions of the dispersed phase were measured to be 0.05 and 0.10 for
the carbon dioxide/water and water/carbon dioxide emulsions, respectively. For both the
volume fraction and turbidity measurements, both threshold and saturation power
densities were observed. At power densities above the saturation level, there was little to
gain by increasing the applied power in terms of phase dispersion or greater emulsion
stability.

Droplet diameters in acoustically formed emulsions (at 30 °C and 80 bar using
0.60 W cm$^{-3}$, 20 kHz, 2 min pulsed ultrasound at 25% duty cycle), were measured in a
microfabricated silicon/pyrex device using digitally enhanced microscopy. In both cases,
the droplet distributions were roughly log-normal. For water droplets in carbon dioxide,
the Sauter diameter was 9.1 μm (uncorrected for spreading) while for carbon dioxide
droplets in water the diameter was 15.1 μm. All images were obtained after the droplets
had settled to either a pyrex or silicon surface and attempts to correct for subsequent
spreading were discussed. Spreading of the carbon dioxide droplets was expected to be
small so that the image diameter was a reliable estimate of the actual diameter. The water droplets probably spread significantly on the partially oxidized silicon surface. Based on all of the available evidence, which included raw droplet images, images of droplets in profile, spreading behavior of macroscopic water droplets on silicon surfaces, and coagulation time scales, it was determined that a droplet size of roughly 6 μm was the most realistic. Water droplet size estimates ranged from 2.1 to 9.1 μm, providing a measure of the uncertainty.

Comparison of demulsification times with theoretical demulsification rates suggested that both types of emulsions broke via a combination of settling and coagulation. Continuous measurements of the droplet diameters/volume fractions during demulsification are recommended to advance our current level of understanding. Real time measurements would also remove the uncertainties associated with emulsion sampling and droplet spreading. Nonetheless, all other methods of droplet sizing suffer from their own inherent limitations, and the results presented in this chapter provide a strong basis for future work.

4.8 References


Chapter 4: Emulsion Characterization


CHAPTER 5

On the Mechanisms of Ultrasonic Emulsification of Liquid, Near-Critical Carbon Dioxide and Water

5.1 Introduction

Emulsions are not at thermodynamic equilibrium, and their properties are determined both by their composition and by the process by which they were formed. Therefore, emulsion characterization and emulsion formation mechanism are closely related topics which, for reasons of clarity, are frequently described separately in texts describing emulsion science. Beyond determining emulsion properties, understanding the relevant emulsification mechanisms important to a particular process is particularly critical for purposes of reactor design and scale-up. This is especially true for a novel application such as is described in this thesis.

This chapter describes the process of emulsification of near-critical carbon dioxide/water systems and investigates probable emulsification mechanisms. Visual observations, bolstered by comparisons with existing theories and by additional experiments, provide the most important clues into emulsification mechanisms. Experimentally measured droplet size distributions and dispersed phase volume fractions, described in Chapter 4, are also rationalized with respect to emulsification mechanisms. Some ramifications of these mechanisms on process design are considered separately in Section 7.6.4 within the context of synthetic chemistry.

5.2 Visual Observations

Visual observations conducted in the acoustic reactor (see Section 4.5) constitute the bulk of the investigations of emulsification mechanisms. Imaging of hydrodynamic behavior during sonication was performed using a video camera (Sanyo, VCB 3524) equipped with telescopic lenses (Tiffen) making use of the α-Al₂O₃ windows of the reactor. A standard video recorder with a recording rate of 33 frames s⁻¹ was used to
capture dynamic behavior. The analog output was digitized using Final Cut Pro (available at the New Media Center of MIT) so that individual frames could be extracted. Although care was taken to preserve image integrity, it was found that still images extracted from action video seldom did justice to the observed behavior. For this reason, schematic renderings are always presented along side still images. Unless otherwise noted, all observations were made at 30 °C, 80 bar, 50% water loading by volume.

Although this is the first published use of ultrasound to emulsify near-critical carbon dioxide and water, there is a significant body of literature describing ultrasonic emulsification of oil and water systems\textsuperscript{1-16} which guided much of the work presented in this chapter. After much debate, it is now widely\textsuperscript{5,9,10} believed that acoustic emulsification occurs by a two-step process: 1) formation of large, “primary” droplets, with characteristic diameters on the order of 100 μm, as a result of the action of capillary waves at the oil/water interface; 2) cavitational disruption of the primary droplets into the micron-sized droplets characteristic of the final emulsion. A third mechanism is also conceivable, but less frequently mentioned, that being the action of acoustic streaming. Visual observations revealed that all three of these phenomena (i.e., interfacial waves, cavitation, and acoustic streaming) occurred during sonication of high-pressure mixtures of carbon dioxide and water.

5.2.1 Observation of interfacial waves

Interfacial waves were clearly visible during emulsification at power densities less than roughly 0.05 W cm\textsuperscript{-3}. A representative result is depicted in Figure 5-1a (actual image) and b (schematic rendering). From Figure 5-1a, the characteristic wavelength can be estimated as 0.5 cm. Most likely, there are waves smaller than this dimension which are not resolvable in the available images. Also, interfacial waves may have been present at power densities greater than roughly 0.05 W cm\textsuperscript{-3}, but were obscured by acoustic streaming and cavitation (Section 5.2.2 and 5.2.3).

The formation of water droplets at low power densities (see Section 4.5.4) can be ascribed to the action of interfacial waves since this was the only hydrodynamic phenomenon observed under these conditions. Theories of ultrasonic atomization, that is
Figure 5-1. The carbon dioxide/water interface during sonication at a power density of 0.05 W cm\(^{-3}\). (a) digitized still image of the interface taken with a time resolution of 0.03 s showing the formation of large interfacial waves; (b) schematic of the interface. Water is the bottom phase in both images. The diameter of the viewing area is 2 cm and the horn is offset from the lower edge of the image by roughly 5 mm. Although it is difficult to reconcile the still image with the schematic, real time observation is more conclusive. Conditions: 80 bar, 30 °C, 50% overall loading with water. The viewing area is roughly 2 cm in diameter.

dispersion of a liquid into a vapor, provide an analogy for the role of interfacial waves on formation of liquid/liquid emulsions. Waves with a spectrum of wavelengths are produced when a film of water is subjected to a sinusoidally varying acceleration such as that caused by an acoustic horn. Some of these waves are unstable and their amplitudes grow over time. Droplet formation occurs when waves with a critical wavelength break off into the continuous phase. This critical wavelength therefore provides a useful scale for correlating droplet diameters. Peskin and Raco\(^{17}\) performed a linear stability analysis of the system to determine that, to first order, the Rayleigh-Taylor capillary-wave theory could be used to determine the critically unstable wavelength, \(\lambda\):

\[
\frac{1}{\lambda} = \frac{1}{\pi} \left( \frac{\Delta \rho \omega^2}{4 \gamma} \right)^{\frac{1}{3}}
\]

(5-1)

where \(\Delta \rho\) is the density difference, \(\gamma\) is the interfacial tension, and \(\omega\) is the driving frequency (always 20,000 x 2\(\pi\) in these experiments). For the carbon dioxide/water system at 30 °C, 80 bar, \(\Delta \rho\) is 300 kg m\(^{-3}\), \(\gamma\) is 25 x 10\(^{-3}\) N m\(^{-1}\).\(^{18}\) It is agreed\(^{19,20}\) that
droplets formed by breakup of the interfacial waves have diameters which are on the order of \( \lambda/2 \), leading to an estimated diameter of 40 µm for droplets formed by waves at the carbon dioxide/water interface. Though this is much larger than the droplet diameters presented in Section 4.5.5, these measurements were made only at power densities of 0.60 W cm\(^{-3}\). The 40 µm droplets predicted by equation (5-1) are consistent with the observation that sonication at 0.05 W cm\(^{-3}\) produced emulsions which broke within minutes after termination of sonic irradiation.

The wave mechanism is consistent with the fact that only water was dispersed at low power densities. Though the physical situation at the liquid/liquid interface is too complex for a mathematical stability analysis of the processes occurring during continuous ultrasonic vibration, Gopal\(^20\) has performed a stability analysis of a liquid/liquid interface which has received an impulse acceleration. Gopal\(^20\) indicates that the denser phase (water, in this case) forms a narrow spike as it penetrates the less dense phase. The peak subsequently breaks off into droplets. The less dense phase becomes blunted as it penetrates and is therefore less likely to form droplets. This is consistent with the fact that only water/carbon dioxide emulsions were formed at power densities of 0.05 W cm\(^{-3}\). The accumulation of experimental evidence suggests that, at the very least, interfacial waves may be responsible for water droplet formation at low applied power densities. Dynamic, \textit{in situ} measurement of droplet sizes formed at low ultrasonic power densities is the best means to confirm this theory.

\textbf{5.2.2 Acoustic jets and acoustic streaming}

At power densities greater than approximately 0.05 W cm\(^{-3}\), the subtle action of wave formation is no longer apparent as it is obscured by the much more striking formation of an “acoustic jet”. Such behavior is well known and has been described theoretically by J. Lighthill\(^21\) and explored experimentally by a number of researchers.\(^{22-24}\) Figure 5-2 contains images of acoustic jet formation during the first 0.03 s after initiation of ultrasound. After several frames (i.e., less than roughly 0.1 s), it is no longer possible to discern the hydrodynamic behavior in the vessel due to the extreme turbidity resulting from droplet formation. Visual observation suggested that the applied power density did not affect the intensity of the acoustic jet at least under the conditions explored in this study (0.1-1.0 W cm\(^{-3}\) at 20 kHz).
Figure 5-2. The carbon dioxide/water interface during sonication at a power density of 0.1 W cm$^{-3}$ or greater. The undisturbed carbon dioxide/water interface is shown at 0 s, just before ultrasound is applied. After 0.03 s, the acoustic jet has formed as evidenced by the deflection of the carbon dioxide/water interface. After 0.06 s, the image is no longer clear. The diameter of the viewing area is 2 cm and the horn is offset from the upper edge of the image by roughly 5 mm (i.e., the horn is vertically aligned relative to the image and is positioned down). Although it is difficult to reconcile the still image with the schematic, real-time observation is more conclusive. Conditions: 80 bar, 30 °C, 50% overall loading with water.

The velocity of the acoustic jet can be estimated crudely based on digital images. The front of the jet travels roughly 1 cm in 5 frames, corresponding to a velocity of 6 cm s$^{-1}$, comparable to jet velocities reported in the literature.\textsuperscript{22-24} Assuming a jet diameter equal to 1 cm (based on the diameter of the sonic horn), the Reynolds number is 10,000. The jet appears to be turbulent, consistent with a transition Reynolds number of 8,000-10,000 for free jets.\textsuperscript{19} The analysis by Davies\textsuperscript{25} suggests that this turbulent jet sheds droplets with an average diameter, $d_p$, given by:

$$d_p = \frac{3100}{U} \left( \frac{\mu_D}{\rho_D} \right)^{1/4} \left( \frac{\mu_C}{\rho_C} \right)^{3/4}$$

(5-2)

where $\mu$ and $\rho$ are the fluid viscosity and density and the subscripts D and C refer to the dispersed and continuous phases. For disruption of a turbulent water jet with $\mu_D = 6$ x
$10^{-5}$ kg m$^{-1}$ s$^{-1}$, $\mu_c = 6 \times 10^{-5}$ kg m$^{-1}$ s$^{-1}$, $\rho_o = 1000$ kg m$^{-3}$, and $\rho_c = 700$ kg m$^{-3}$, equation (5-2) predicts $d_p \approx 10$ mm. For disruption of a carbon dioxide jet (which corresponds to an emulsification geometry in which the horn is inserted in the carbon dioxide phase), $d_p \approx 30$ mm. This is three orders of magnitude greater than the diameters observed experimentally, implying that the acoustic jet is not responsible for formation of the micron-sized droplets present in the acoustic reactor. In fact, the diameter of the acoustic jet is actually larger than these droplet size predictions. Clearly, the kinetic energy in the acoustic jet is not sufficient to generate micron-sized droplets.

In addition to forming large primary droplets, acoustic streaming provides bulk mixing to the reactor contents. Vichare et al.$^{26}$ have shown that mixing in the presence of high intensity ultrasound is comparable to that observed in jet loop reactors. Thus, acoustic streaming in the carbon dioxide/water biphasic system may be sufficient for mixing of the bulk fluids, reducing the need for an impeller.

5.2.3 Cavitation

Cavitation is generally considered$^{4,9,10}$ to be the principal mechanism for the formation of micron-sized droplets during acoustic emulsification. The process of cavitation involves the formation of a vapor-filled cavity during a rarefaction phase of the pressure wave which subsequently collapses violently during a compression phase. The final stages of the violent collapse of vapor-filled cavities is nearly adiabatic, so that high temperatures and high pressures are attained, at least locally. It is generally agreed$^{27-31}$ that the pressures during the final stages of cavitation are on the order of 1,000 bar. The maximum temperature attained during cavitation is still the subject of debate,$^{27-31}$ though it is certainly greater than 1,000 K.

As is depicted in Figure 5-3, bubble collapse in the vicinity of a solid surface or other heterogeneity produces a microjet of liquid which is directed toward the solid surface. These microjets attain velocities on the order of 100 m s$^{-1}$ or more$^{32}$ and are the primary mechanism of cavitation damage.$^{33,34}$ If the heterogeneity is a second fluid phase, the microjets penetrate this second phase where they are disrupted to form small droplets. The radius of the resulting droplets roughly equals that of the microjet, which in turn can be estimated from photographs as roughly 10% that of the radius of the collapsing bubble. From analyzing images such as those in Figure 5-3, the radius of the
Figure 5-3. Photograph of non-spherical distortion and microjet formation during collapse of a gas cavity in the vicinity of a solid surface taken by Benjamin and Ellis. The liquid microjet is visible in the interior of the gas bubble and the beginning stages of droplet formation are evident at the tip of the microjet. The scale of the photograph is not given by the authors, but it can be estimated to be 100 µm as indicated above.

collapsing bubble is roughly 100 µm when the jet begins to form, so that cavitation is expected to account for droplets on the order of 10 µm in diameter. This agrees quantitatively with the diameters observed experimentally implying that cavitation may be the primary cause of acoustic emulsification. The same conclusion could be reached by a process of elimination, since the other two possible mechanisms (i.e., interfacial waves and acoustic streaming) have been shown to produce droplets much larger than those observed. A cavitational mechanism is also consistent with the observation of a distinct threshold power density for formation of carbon dioxide/water emulsions since cavitation generally occurs only above some threshold power density. The absence of such a threshold for formation of water/carbon dioxide emulsions can be attributed to the breakup of interfacial waves at low applied power densities.

Cavitation occurs when the local pressure falls below the vapor pressure of the fluid, provided that the effects of surface tension are negligible. The local pressure is simply the sum of the applied hydrostatic pressure and the instantaneous acoustic pressure. Increasing the hydrostatic pressure beyond 1 bar (the pressure at which most reported experiments are conducted) would be anticipated to suppress cavitation once it was greater than the difference between the acoustic pressure and the vapor pressure of the fluid. Incorporating surface tension effects into this analysis leads to the so-called Blake threshold pressure, $P_B$: 
where $P_H$ is the hydrostatic pressure, $P_{vap}$ is the vapor pressure of the liquid undergoing sonication, $\sigma$ is the surface tension of the fluid undergoing cavitation, and $R_0$ is the “equilibrium bubble radius” that undergoes stable oscillations.

Equation (5-3) can be derived from consideration of a bubble of radius, $R_0$, which is in mechanical equilibrium with its surroundings such that:

$$P_{vap} - P_H + P_{bubble} - \frac{2\sigma}{R_0} = 0$$ (5-4)

where $P_{bubble}$ is the pressure inside the bubble. If the bubble shrinks or expands isothermally due to the action of an external applied pressure such as an acoustic field, mechanical equilibrium is re-defined as:

$$\left( \frac{P_H + \frac{2\sigma}{R_0}}{R_0} \right)^3 = P_H - P_A - P_{vap} + \frac{2\sigma}{R}$$ (5-5)

where $P_A$ is the pressure amplitude of the disturbance. The left-hand side of equation (5-5) is the pressure of gas inside the bubble due to isothermal expansion or contraction. Equation (5-5) can be solved for $P_A - P_H$ and differentiated with respect to $R$ to find the minimum external pressure for which explosive bubble expansion is predicted, thus yielding equation (5-3).

Equation (5-3) relates the minimum acoustic pressure necessary for explosive expansion of a bubble with an arbitrary radius. Without knowledge of the likely radii of bubbles in a particular liquid, equation (5-3) has no predictive power. Brennan indicates that the radii of gas bubbles is governed by the solubility of the gas contained within bubble and the rates of mass transport to and from the bubble. Experimentally, $R_0$ is observed to be on the order of 5 $\mu$m, at least for aqueous systems, which allows equation (5-3) to be used in a semi-predictive manner to estimate $P_B$.

Cavitation is expected to occur when the acoustic pressure is greater than the Blake threshold. As expected, to first order, equation (5-3) predicts that the Blake threshold pressure is simply the difference between the hydrostatic pressure and the vapor pressure. The vapor pressure of water is roughly 0.025 bar at 300 K while that of carbon
dioxide is roughly 65 bar. Thus, the Blake threshold pressure of water is significantly higher than that of carbon dioxide. For instance, at a hydrostatic pressure of 70 bar, the Blake threshold for carbon dioxide is roughly 5 bar, while that for water is nearly 70 bar. This leads to the expectation that carbon dioxide would cavitate far more readily than would water.

**Cavitation of water with a carbon dioxide head pressure.** A set of experiments was conducted to detect cavitation in liquid water and carbon dioxide at different pressures. For cavitation of the aqueous phase, 90% of the reactor volume was filled with de-ionized water, sealed, and pressurized using carbon dioxide. Air was displaced from the vessel prior to each experiment using a flow of low-pressure carbon dioxide. At this water loading, the carbon dioxide/water interface did not obscure the viewing area so that the turbulent acoustic jet did not prevent visual detection of cavitation. The power density of ultrasound was 1.0 W cm\(^{-3}\) in all experiments. Power intensity (that is, total power input divided by the surface area of the sonic horn) is sometimes a more convenient metric than power density. Based on a reactor volume of 87 cm\(^3\) and a horn surface area of 0.785 cm\(^2\), a power density of 1.0 W cm\(^{-3}\) corresponds to an intensity of 115 W cm\(^{-2}\). Equation (5-6) can be used to convert this power intensity to a pressure amplitude, \(P_A\):

\[
\text{Power Intensity} = \frac{P_A^2}{2\rho c}
\]  

(5-6)

where \(c\) is the speed of sound and is equal to 1,500 m s\(^{-1}\) in pure water. Assuming that \(c\) is not influenced by dissolved carbonic acid or hydrostatic pressure, \(P_A\) is roughly 20 bar in the current set of experiments.

Figure 5-4 contains photographs of water cavitation in carbon dioxide environments at 1 and 80 bar of hydrostatic pressure. Though not obvious from still images, a dense cloud of cavitation bubbles forms at 1 bar under the influence of ultrasound. This cloud of bubbles conforms qualitatively to descriptions of ultrasonic cavitation in the literature\(^{37,39}\) as the bubbles are confined to a region within several cm of the horn. At 80 bar, however, sonication at 1.0 W cm\(^{-3}\) forms much larger bubbles which are distributed more or less homogeneously throughout the viewing area. The largest
bubbles attain diameters of roughly 1 cm, much larger than those observed during sonication at 1 bar. The character of cavitation is strikingly different than at 1 bar.

Although no measurements of the cavitation bubble contents were made, it seems reasonable to assume that they contained primarily carbon dioxide as the vapor pressure of water is on the order of 0.025 bar at these conditions. No experiments were conducted in which the water phase was pressurized without a vapor head space. Under these conditions cavitation would be completely suppressed unless the acoustic pressure exceeded the Blake threshold pressure.

Experiments were also conducted at 20 bar, 50, and 120 bar. At 20 and 50 bar, no cavitation was evident, only acoustic streaming. Surprisingly, cavitation was possible at 120 bar (which is roughly 50 bar greater than the vapor pressure of carbon dioxide at 30 °C) while a carbon dioxide pressure of either 20 or 50 bar appeared to suppress cavitation, at least at a power density of 1.0 W cm\(^{-3}\). The behavior at 120 bar was indistinguishable from that at 80 bar, with cavitation occurring throughout the viewing area. Water cavitation at 80 bar will be revisited once the carbon dioxide cavitation experiments have been discussed.
Although these results are difficult to interpret, it is undeniable that, in the presence of liquid, near-critical carbon dioxide, ultrasound leads to some sort of cavitation phenomenon of water even at acoustic pressures much less than its Blake threshold pressure. There is a literature report\textsuperscript{40} of the effects of static carbon dioxide pressure on the cavitation threshold of liquid water. Goldfarb et al.\textsuperscript{40} measured the diffusion-limited current for the reduction of Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} in aqueous solutions subjected to head pressures of either argon or carbon dioxide. The authors monitored this current as they increased the acoustic power density, assuming that the observation of a sudden jump in the diffusion-limited current was the result of acoustic cavitation. Their experimental data of threshold pressures are reproduced in Figure 5-5. As expected from a simple consideration of the Blake threshold pressure, increasing the pressure of argon monotonically increased the threshold power intensity required for cavitation. The threshold power also increased with carbon dioxide pressures up to roughly 30 bar, and then, surprisingly, sharply decreased. The highest pressure that was studied was 45 bar, which is roughly 25 bar less than the vapor pressure of carbon dioxide at 20 °C. The threshold power was always less in carbon dioxide atmospheres than in argon.

![Graph showing threshold power intensities for cavitation of liquid water in carbon dioxide and argon environments at gas over-pressures greater than 1 bar. These data were adapted from Goldfarb et al.\textsuperscript{40}]({"figure":true,"caption":"Figure 5-5. Threshold power intensities for cavitation of liquid water in carbon dioxide and argon environments at gas over-pressures greater than 1 bar. These data were adapted from Goldfarb et al.\textsuperscript{40} The threshold power intensity is always greater with argon than carbon dioxide. The threshold power intensity for water in a carbon dioxide environment goes through a maximum at roughly 30 bar."}}
Goldfarb et al.\textsuperscript{40} offered three explanations for the reduction in cavitation threshold power density with increasing carbon dioxide pressure, none of which are particularly satisfying:

1) reduction in carbon dioxide/water interfacial tension with pressure,\textsuperscript{18} resulting in a lower acoustic threshold required for cavity inception. Although there is a reduction in carbon dioxide/water interfacial tension in the vicinity of 50 bar at 20 °C, this effect is negligible compared to that of increased hydrostatic pressure, at least for cavitation of water. To quantify this effect, for a reduction in the interfacial tension from 72 x 10\textsuperscript{-3} N m\textsuperscript{-1} (the value for an air/water interface) to 15 x 10\textsuperscript{-3} N m\textsuperscript{-1} (for a carbon dioxide/water interface\textsuperscript{18} at 20 °C, 50 bar), the Blake threshold pressure changes by less than 0.01 bar. Cavitation of near critical carbon dioxide might be enhanced by the fact that the surface tension of a liquid in contact with its vapor goes to zero at its critical point, but this cannot explain the results of Goldfarb et al.\textsuperscript{40}

2) higher water solubility of carbon dioxide than argon, thus facilitating cavity inception. Although carbon dioxide is roughly 15 times more water soluble than argon,\textsuperscript{41} the solubility of both gases in water increases smoothly as their head space pressure increases. Therefore, solubility considerations provide no reason to expect a maximum in the power threshold as pressure is increased. The higher water solubility of carbon dioxide compared to argon does account for the lower threshold of the former as shown in Figure 5-5.

3) formation of a transient liquid carbon dioxide phase during the compressive cycle of the ultrasound. This small droplet of liquid carbon dioxide later experiences a rarefaction cycle and readily cavitates.

Of these three explanations, only the third cannot be refuted readily for the conditions that Goldfarb et al.\textsuperscript{40} investigated, because it is difficult to quantify. Formation of a transient liquid carbon dioxide phase at the conditions studied here (30 °C, 80 bar) is nonsensical since carbon dioxide is a stable liquid under these conditions.

**Cavitation of carbon dioxide.** A second set of experiments were conducted in pure carbon dioxide at pressures of 65, 80, and 120 bar at 25 °C. The pressure was maintained at or above the vapor pressure of carbon dioxide since it is not possible to cavitate a vapor. The ultrasonic power density was 1.0 W cm\textsuperscript{-3} and the frequency was 20 kHz, as in
the water cavitation studies. Cavitation bubbles were detected only when the Blake threshold pressure was exceeded (i.e., at 65 and 80 bar). As with water cavitation in high pressure carbon dioxide environments, sonication of liquid carbon dioxide has a literature precedent. In their studies of sonochemical initiation of the radical polymerization of methyl methacrylate, Kuijpers et al. found that cavitation of carbon dioxide was possible at pressures comparable to the vapor pressure of pure carbon dioxide. The authors concluded that cavitation was impossible above the critical point since the density of the supercritical fluid varies continuously with pressure. The current results are consistent with those of Kuijpers et al. in that cavitation was not possible at hydrostatic pressures much greater than the vapor pressure of carbon dioxide.

Cavitation of carbon dioxide at 80 bar suggests a possible mechanism for water cavitation at the same hydrostatic pressure. The small vapor pressure of water precludes its cavitation provided that the hydrostatic pressure is greater than the acoustic pressure. As we have seen, however, the high vapor pressure of carbon dioxide effectively lowers its Blake threshold pressure. It seems reasonable that what has thus far been described as "cavitation of water" is actually cavitation of carbon dioxide. Since the water and carbon dioxide phases are in equilibrium, the fugacity of liquid carbon dioxide and dissolved carbon dioxide are equal. Moreover, their fugacities, but not their fugacity coefficients, must have the same pressure functionality. Therefore, the Blake threshold pressure of carbon dioxide dissolved in the water phase may be equal to that of the liquid carbon dioxide. If so, cavitation of liquid water at 80 bar can be interpreted as "cavitation" of dissolved carbon dioxide. The observation of water cavitation at 120 bar is not so neatly described in this fashion and is an area for further research.

5.3 Further Consideration of Cavitation

For applied power densities greater than 0.05 W cm⁻³, cavitation of liquid water under a pressurized carbon dioxide environment appears to be the dominant mechanism for formation of fine emulsions containing carbon dioxide and water. The nature of this cavitation and even its mechanism were less clear. A series of studies, including pitting of the ultrasonic horn, sonochemical oxidation of potassium iodide, and mathematical modeling of bubble dynamics, were conducted to further explore the nature of cavitation at high pressures under a carbon dioxide environment.
5.3.1 *Pitting of the sonic horn*

Formation of microjets is the primary mechanism of both cavitation emulsification and damage. Therefore, if microjetting were occurring in the acoustic reactor, it would be expected that the horn would become pitted during use. Figure 5-6 shows the horn at 10x magnification after polishing and after roughly 50 hours of pulsed (25% duty cycle) use at an average power density of 0.5 W cm\(^{-3}\) and 80 bar of hydrostatic pressure. The only features apparent in the polished specimen are the scratches imparted by the polishing process, while after operation the horn is quite pitted. Apparent in Figure 5-6b are both a number of small pits, with characteristic diameters on the order of 10 µm, and a large crevice running along the center line of the horn. The width of this crevice is roughly 0.5 mm and it runs nearly the entire diameter of the specimen, which is 1.0 cm. The pitting damage is greatest along circles concentric with the center of the horn, though this geometry may reflect the fabrication process. The horn was not operated at ambient pressure before the photographs in Figure 5-6 were taken so that this damage must have occurred during high pressure operation. The images in Figure 5-7 are reproduced from several literature sources\(^{43-45}\) and are characteristic of cavitation damage under typical operation at 1 bar.

Figure 5-4 clearly demonstrates that cavitation occurs in the acoustic reactor under 80 bar of hydrostatic pressure in a carbon dioxide environment. Furthermore, though cavitation at elevated pressures was different visually from that at ambient pressure (as shown in Figure 5-4), the presence of cavitation damage to the horn pictured in Figure 5-6 is consistent with the formation of the microjets required for ultrasonic emulsification. Thus, while cavitation at elevated pressures may differ qualitatively from standard cavitation in other ways, increasing the pressure does not suppress cavitational microjet formation.
Figure 5-6. Digital images of the sonic horn: a) after polishing; b) after 50 hours of operation at 80 bar (at a duty cycle of 25%). The scratches apparent in (a) are the result of the polishing process. The diameter of the horn is 1 cm.

Figure 5-7. Photographs of cavitational corrosion of metal specimens after exposure to ultrasound. (a) Bofors B14 steel exposed to 20 kHz ultrasound for 2 hours at a power intensity of 60 W cm\(^{-2}\) in an aqueous solution of pH = 4;\(^{43}\) (b) Zinc-precoated steel exposed to 500 kHz ultrasound in an aqueous solution containing Cl\(^{-}\), SO\(_4\)^{2-}, HCO\(_3\)^{-}, and H\(_2\)O\(_2\) for 1 hour – the power intensity was not listed;\(^{44}\) (c) nickel-aluminum bronze exposed to 20 kHz ultrasound in a sea water environment for 40 hours – the power intensity was not listed.\(^{45}\) In all cases, the diameter of the sample is roughly 1 cm.
5.3.2 Sonochemistry

Many chemical reactions are influenced by ultrasound, and the "sonochemical yield" is often used as a metric for cavitation. The accepted mechanism of the sonochemical effect, termed the "hot spot" theory, is that the violent collapse of the cavity attains such high temperatures that vaporized species can react in ways not normally possible at ambient conditions. Based on this theory, a distinction is sometimes drawn between "true sonochemistry", that is chemical effects brought about by acoustic cavitation, and the physical effects of ultrasound which include increased mass transport rates. One success of the hot spot theory is that it correctly predicts that radical reactions, including both polymerizations\(^ {46} \) and oxidations,\(^ {47} \) which would normally occur only at elevated temperatures, are possible in room temperature solutions under the influence of ultrasound. At least in the case of oxidative decomposition, it is postulated that the role of ultrasound is to form hydroxyl radicals during bubble collapse which subsequently react with either vaporized or dissolved organic compounds.\(^ {48} \) The high pressure in collapsing bubble may play a role as well.

Oxidation of potassium iodide is a commonly selected\(^ {49-52} \) reaction for measuring the degree of cavitation in sonochemical reactors. The overall mechanism of potassium iodide oxidation is postulated as:\(^ {52} \)

\[
2\text{KI} + 2 \cdot \text{OH} \rightarrow 2 \text{KOH} + \text{I}_2 \\
2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \\
2 \text{HO}_2^- + 2\text{KI} \rightarrow 2 \text{KOH} + \text{I}_2 + \text{O}_2 \\
2 \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
2\text{O}^\cdot + 2\Gamma + 2\text{K}^+ + 2\text{H}_2\text{O} \rightarrow \text{I}_2 + \text{O}_2 + 2 \text{KOH} + \text{H}_2
\]

So that the primary products are I\(_2\) and H\(_2\)O\(_2\), along with O\(_2\) and H\(_2\). The only source of the radical species (\(\cdot\)OH, \(\text{HO}_2^-\), and \(\text{O}^\cdot\)) is cavitation, and the oxidation rate of potassium iodide is a good metric for the rate of radical production via acoustic cavitation. Consequently, it was selected for our measurements.

Experiments were conducted in the acoustic reactor under both nitrogen and carbon dioxide atmospheres. In a typical experiment, the reactor was filled with 60 cm\(^3\) of an aqueous solution containing 0.5 mol L\(^{-1}\) (8 wt%) of potassium iodide. The head space of the reactor was purged of atmospheric gas either by nitrogen or carbon dioxide. The reactor was then pressurized and heated to the desired conditions. Samples were
withdrawn at known time intervals using a HPLC valve (Valco Instrument Company, Inc. uw-type) and analyzed for iodine with visible absorption spectroscopy (Varian, Cary 50) using its 354 nm peak. At this wavelength, the molar extinction coefficient for iodide was determined to be $6,000 \text{ mol L}^{-1} \text{ cm}^{-1}$ based on standard solutions of aqueous iodine.

Using this procedure, the generation rate of iodine was measured at 1 bar under nitrogen and carbon dioxide atmospheres at an acoustic power density of $1.0 \text{ W cm}^{-3}$. Measured iodine concentrations are plotted as functions of time in Figure 5-8 for the 5 experimental runs. Under a nitrogen environment, the initial production rate was measured as roughly $1 \times 10^{-7} \text{ mol hr}^{-1} \text{ W}^{-1}$. This is comparable to, but somewhat less than, reported iodine production rates in glass beakers and other sonochemical reactors.\textsuperscript{49-52} The lower measured production rate indicates that the acoustic reactor geometry is not optimized for sonochemical reactivity.

At 1 bar under a carbon dioxide atmosphere, the production rate of iodine is reduced by roughly 80% relative to that observed in a nitrogen environment to $2 \times 10^{-8} \text{ mol hr}^{-1} \text{ W}^{-1}$. Suppression of iodine formation under a carbon dioxide environment can be attributed to two factors. First, the temperature rise of gaseous carbon dioxide during

![Graph](image)

**Figure 5-8.** Sonochemical oxidation of KI to I$_2$ in water under nitrogen and carbon dioxide atmospheres. Ultrasound conditions: 20 kHz, 1.0 W cm$^{-3}$. The reaction was suppressed in a carbon dioxide atmosphere at 80 bar.
compression is less than that expected for nitrogen due to differences in the heat capacities of the two gases.\textsuperscript{50,53} Second, carbon dioxide forms bicarbonate in solution, which is an effective hydroxyl radical quencher. Beckett and Hua\textsuperscript{53} report a 70\% decrease in sonochemical yield in the presence of 0.05 mol L\textsuperscript{-1} of bicarbonate. Since the concentration of bicarbonate is only about 1 x 10\textsuperscript{-5} mol L\textsuperscript{-1} in water subjected to a carbon dioxide environment at 1 bar, this second effect may be relatively small.

At 80 bar, no iodine was produced, indicating that the maximum temperature attained during cavitation under these conditions was insufficient to produce hydroxyl radicals. Radical scavenging by bicarbonate is not sufficient to explain this result since the bicarbonate concentration is roughly 1 x 10\textsuperscript{-3} mol L\textsuperscript{-1} in water in contact with carbon dioxide at 80 bar. Goldfarb et al.\textsuperscript{40} termed the cavitation of liquid water at high carbon dioxide pressure “soft”, thinking that the large amount of carbon dioxide in the cavitation bubbles would liquefy during compression, thus cushioning the collapse and reducing the amount of energy released during cavity implosion. Our results support the “soft cavitation” hypothesis forwarded by Goldfarb et al.\textsuperscript{40} since the conditions in the cavitating bubbles in the high pressure environment seem to be much less energetic than those formed at 1 bar. As a consequence, this study suggests that sonochemical effects are not important when the acoustic reactor is operated at 80 bar in a carbon dioxide environment. The formation of microjets does not require intense local heating during cavitation so that the results from these sonochemical results do not contradict the observation of pitting damage.

\textbf{5.3.3 Rayleigh-Plesset analysis}

The final study aimed at further understanding of cavitation at elevated pressures was a mathematical analysis of bubble dynamics. Although there are many methods for treating the problem of bubble dynamics,\textsuperscript{55} the most commonly used\textsuperscript{56} is the Rayleigh-Plesset equation:

$$\rho_L \left( R \ddot{R} + \frac{3}{2} \dot{R}^2 \right) = P_{\text{gas}}(R,t) - P_A(t) - P_H + \frac{R}{\rho_L} \frac{d}{dt} \left[ P_{\text{gas}}(R,t) - 4 \mu_L \frac{\dot{R}}{R} - \frac{2\sigma}{R} \right]$$

(5-7)

where $\rho_L$ is the density of liquid water (999 kg m\textsuperscript{-3}), $R$ is the bubble radius at time $t$, $\dot{R}$ is the velocity and $\ddot{R}$ the acceleration of the bubble wall, $c_L$ is the velocity of sound in the fluid (1,500 m s\textsuperscript{-1} in water at 25 °C), $\mu_L$ is the viscosity of liquid water (9 x 10\textsuperscript{-4} kg m\textsuperscript{-1}}
s⁻¹), σ is the surface tension (0.072 N m⁻¹ for an air/water interface at 25 °C), \( P_{\text{gas}} \) is the pressure of gas inside the bubble, and \( P_{\text{H}} \) is the hydrostatic pressure far from the gas bubble. \( P_A \) is the time-varying acoustic pressure, which can be modeled as:

\[
P_A(t) = P_{\text{amplitude}} \sin(\omega t)
\]

where \( \omega \) is the frequency of the sound wave (20 kHz for these experiments) and \( P_{\text{amplitude}} \) is its amplitude. Due to the mathematical complexity of equation (5-6), \( P_{\text{gas}} \) is usually assumed to follow a simple polytropic gas law:

\[
P_{\text{gas}}(R, t) = P_{\text{gas}}(R(t)) = \left( P_{\text{H}} + \frac{2\sigma}{R} \left( \frac{R_0}{R(t)} \right)^\kappa \right)
\]

where \( \kappa \) is the polytropic index (commonly assumed to be equal to unity), and \( R_0 \) is the initial bubble radius. The first equality shows that formally \( P_{\text{gas}} \) is a function of both \( R \) and \( t \), but its time functionality only appears indirectly through \( R(t) \).

Equations (5-7) through (5-9) can be derived directly from the Navier-Stokes equations with the following assumptions:

1) incompressible fluid
2) isothermal bubble – infinitely fast heat transport
3) constant mass of bubble contents – infinitely slow mass transport
4) negligible vapor pressure of the solvent so that the bubble is filled with carbon dioxide

Although these assumptions are not strictly correct, equations (5-7) through (5-9) can be used to gain qualitative insight into cavitation at elevated hydrostatic pressures. The formulation of the Rayleigh-Plesset equation described by equation (5-7) through (5-9) cannot predict the extreme temperatures observed during cavitation as the bubble contents are assumed to be isothermal. From theoretical considerations, Flynn⁵⁷ has shown that heat transfer from the surrounding liquid to the bubble contents is sufficient that isothermal conditions are approached for the majority of the compression. During the final moments of collapse, compressive heating is fast enough that adiabatic conditions are approached, thus accounting for the high temperatures actually observed. Additionally, equation (5-7) would need to be modified to account for the significant
vapor pressure and compressibility of carbon dioxide, if it were desired to model
cavitation of this fluid.

The system of equations (5-7) through (5-9) was solved numerically using an
implicit Runge-Kutta, 4-5 method for constant \( P_{\text{amplitude}} = 10 \) bar over a range of \( P_H \) from
1 to 100 bar. Preliminary simulations were performed to determine that the equilibrium
bubble radius was 4 \( \mu \)m; this bubble radius was completely stable at its initial value when
\( P_{\text{amplitude}} \) was set equal to 0 bar while all other initial bubble radii quickly equilibrated to
4 \( \mu \)m. The equilibrium bubble radius was independent of hydrostatic pressure. The
values of all other parameters used in this analysis are listed in Table 5-1.

In Figure 5-9, typical results for the bubble radius as a function of time are shown
for \( P_H = 1 \) bar and \( P_H / P_{\text{amplitude}} = 0.5 \) or 2. Figure 5-9a depicts bubble dynamics for \( P_H / P_{\text{amplitude}} = 2 \) showing that the bubble radius merely oscillates over time. Figure 5-9b, in
which \( P_H / P_{\text{amplitude}} = 0.5 \), depicts the slow growth of the bubble beginning at \( 2 \times 10^{-4} \) s
and its sudden collapse after slightly less than \( 5 \times 10^{-4} \) s.

Table 5-1. Parameter values used in bubble simulations using the Rayleigh-Plesset
equation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0 ) (initial bubble radius)</td>
<td>( 4 \times 10^{-5} ) m</td>
</tr>
<tr>
<td>( P_H ) (hydrostatic pressure)</td>
<td>1 – 100 bar</td>
</tr>
<tr>
<td>( \sigma ) (surface tension)</td>
<td>( 72 \times 10^{-3} ) N m(^{-1})</td>
</tr>
<tr>
<td>( \mu ) (viscosity of water)</td>
<td>( 9 \times 10^{-5} ) kg m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( \kappa ) (polytropic index)</td>
<td>1</td>
</tr>
<tr>
<td>( \omega ) (frequency of the pressure wave)</td>
<td>( 2\pi \times 20 ) kHz</td>
</tr>
<tr>
<td>( P_{\text{amplitude}} ) (amplitude of the pressure wave)</td>
<td>10 bar</td>
</tr>
<tr>
<td>( T ) (temperature)</td>
<td>300</td>
</tr>
<tr>
<td>( \rho_L ) (density of liquid water)</td>
<td>( 1000 ) kg m(^{-3})</td>
</tr>
<tr>
<td>( c_L ) (speed of sound in liquid water)</td>
<td>( 1500 ) m s(^{-1})</td>
</tr>
</tbody>
</table>
Figure 5-9. Response of a bubble (with an initial radius of 4 μm) to an acoustic pressure field with a frequency of 20 kHz predicted by equation (5-6). Hydrostatic pressure is 1 bar, (a) $P_H/P_{\text{amplitude}} = 2$, collapse is not possible and the bubble oscillates around an equilibrium value with a period equal to $5 \times 10^{-5}$ s; (b) $P_H/P_{\text{amplitude}} = 0.5$, collapse occurs after approximately $5 \times 10^{-5}$ s.
Figure 5-10 is a compilation of the maximum pressure (non-dimensionalized using the hydrostatic pressure) attained during a complete time cycle for all of the runs. Collapse is most dramatic at $P_H / P_{\text{amplitude}} = 1$, and is not possible for $P_H / P_{\text{amplitude}} > 1$. For $P_H / P_{\text{amplitude}} < 1$, increases in $P_H$ further squeeze the contents of the bubble and raise the maximum pressure attained during collapse. This simple mathematical analysis suggests that collapse is not possible for $P_H / P_{\text{amplitude}} > 1$, in agreement with the Blake threshold pressure for a liquid with negligible vapor pressure (such as water). This analysis also ignores the effect of dissolved carbon dioxide which is present in water that is equilibrated with a liquid carbon dioxide phase.

\[ P_{\text{max}} / P_H \]

\[ 10^{13} \quad 10^{11} \quad 10^{9} \quad 10^{7} \quad 10^{5} \quad 10^{3} \quad 10^{1} \quad 10^{-1} \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \]

\[ P_H / P_{\text{amplitude}} \]

**Figure 5-10.** Maximum bubble pressure (normalized by the hydrostatic pressure) as a function of hydrostatic pressure (normalized by acoustic pressure amplitude). Bubble dynamics simulated for $5 \times 10^{-4}$ s using equation (5-6). The acoustic pressure is constant at 10 bar, while the hydrostatic pressure is increased from 1 to 100 bar. At these conditions, the Blake threshold pressure is nearly equal the hydrostatic pressure. Collapse is possible only for acoustic pressure greater than hydrostatic pressure. The predictions presented in this plot are intended only for trends since the simplified gas law indicated by equation (5-9) is not valid at pressures greater than roughly 10 bar.

### 5.3.4 Summary of cavitation studies

The results of these three studies (pitting, sonochemical oxidation, mathematical analysis) combined with the actual observations of cavitation in liquid water subjected to high pressure carbon dioxide environments are somewhat inconsistent. While some
cavitation phenomenon was observed experimentally, its nature is qualitatively different from that observed under ambient pressure. Pitting of the ultrasonic horn indicates that cavitation at elevated pressures results in formation of microjets qualitatively similar to those observed at ambient conditions. Sonochemical experiments indicate that the maximum temperatures attained during cavitation at 80 bar are less than that required to form hydroxyl radicals. Mathematical analysis of bubble dynamics using the Rayleigh-Plesset equation confirms that cavitation is not theoretically possible for acoustic pressures less than the Blake threshold (which for water is roughly equal to the hydrostatic pressure). Cavitation of dissolved carbon dioxide is suggested as a possible explanation for the seemingly contradictory behavior observed in liquid water (in contact with a liquid carbon dioxide phase) at least at a hydrostatic pressure of 80 bar.

5.4 Combined Action of Cavitation and Acoustic Streaming

From volume fraction measurements reported in Section 4.5.4, the cavitation threshold for formation of water/carbon dioxide emulsions can be estimated as 0.1 W cm\(^{-3}\), corresponding to an acoustic pressure of roughly 6 bar. Assuming that cavitation of liquid water is due to dissolved carbon dioxide leads to an estimate of the Blake threshold equal to roughly 15 bar, much greater than the actual acoustic threshold observed for emulsification. Experiments conducted with the carbon dioxide/water interface removed from the sonication zone revealed a cavitation threshold of 20 bar, consistent at least with that expected for carbon dioxide. The phenomenon of acoustic self concentration may resolve the discrepancy between emulsification experiments (where the interface is positioned in the sonication zone) and cavitation experiments (where the interface is far from the sonication zone). Acoustic self concentration occurs at an interface when the action of sound causes its deformation, as in acoustic streaming. Figure 5-11 is a schematic of acoustic self concentration reproduced from Leighton.\(^{58}\) While the self-concentration effect is difficult to quantify, it is clear that, within the acoustic fountain, the local acoustic pressure may be somewhat greater than at its source. Thus, an apparent emulsification threshold of 6 bar is somewhat misleading since the local acoustic pressure may actually be greater than this.
Figure 5-11. Schematic of acoustic self-concentration adapted from Leighton.\textsuperscript{58} Sound waves may be focused due to reflections of the sound wave off the liquid/liquid interface formed by acoustic streaming. The focusing process increases the local acoustic pressure.

5.5 Comparison to Literature Data

Although there are no published studies of acoustic emulsification of carbon dioxide and water mixtures, there are two related sets of data that can be used for validation and comparison: 1) formation of carbon dioxide/water emulsions using mechanical techniques other than ultrasound and 2) formation of oil/water (and water/oil) emulsions using ultrasound.

5.5.1 Formation of H$_2$O/CO$_2$ emulsions by use of surfactants

Section 4.4 detailed progress in the field of surfactant design and water/carbon dioxide emulsion stabilization. The purpose of this brief review is to outline the influence of the emulsification mechanism on emulsion properties.

The literature contains reports of water/carbon dioxide emulsions formed by shear through a capillary tube,\textsuperscript{59-64} by expansion through a high-pressure homogenizing valve operating at 10,000-15,000 psi,\textsuperscript{65,66} or by phase inversion.\textsuperscript{67} A recent investigation explores the influence of surface tension and shear rates on emulsion droplet diameters.\textsuperscript{65} In this study, emulsions with a water content of 2 wt\% were formed using 1 wt\% of the
surfactant, poly(1,1-dihydroperfluorooctyl methacrylate)-b-polyethylene oxide. Emulsification conditions were either “high” or “low” shear high-pressure homogenization or magnetically coupled stir bar (very low shear). At high shear (corresponding to a 700 bar pressure drop across the homogenizer valve), droplets with an average size of 70 nm were formed. Low shear homogenization (a 34 bar pressure drop across the homogenizing valve) formed droplets with an average size of 110 nm. Simple agitation with a stir bar formed emulsions with diameters estimated as roughly 1 μm. The authors proposed the following expression to correlate droplet diameters to shear rate:

\[
\frac{d_{\text{High Shear}}}{d_{\text{Low Shear}}} = \left(\frac{\Delta P_{\text{Low Shear}}}{\Delta P_{\text{High Shear}}}\right)^{3/5}
\]

(5-10)

which can be derived from considerations of the energy dissipation rate.\(^6\) Equation (5-10) indicates that droplets formed at the high shear rate should be six-fold smaller than those formed at the low shear rate, rather than the 50% difference actually observed. The authors attribute the failure of equation (5-10) on the compressibility of the carbon dioxide phase claiming that compression of the supercritical fluid in the homogenizing valve dissipates much of the energy which would otherwise be directed toward shear. Nonetheless, the authors did observe a clear relationship between shear rates and droplet sizes, as expected. Surfactants lead to formation of much finer emulsions (significantly less than 1 μm in some instances) than are possible using surfactant-free sonication (on the order of 5 μm), even though the shear rates exerted by sonication may be greater than those of other sorts of mechanical agitation.

Dickson et al.\(^6\) also report on the effect of surface tensions of water droplets formed at constant shear rates by a 700 bar pressure drop across a homogenizing valve. By changing temperature and surfactant properties, the authors were able to systematically vary carbon dioxide/water interfacial tension over the range from 0.2 to 1.4 x 10\(^{-3}\) N m\(^{-1}\). Over this range of interfacial tensions, water droplets increased in size from roughly 70 to nearly 140 nm, though the effect of increasing surface tension appeared to begin to saturate at the higher end. This study nicely demonstrates the importance of interfacial tension for obtaining fine emulsions, at least using standard
homogenization techniques and suggests that it is not reasonable to form submicron
droplets in the absence of surfactants.

From the above discussion, it is apparent that formation of extremely fine
water/carbon dioxide emulsions is possible even using simple techniques such as shear
through capillaries, provided that a suitable surfactant is used. It would be instructive to
quantify the effects of surface tension and power density on droplet formation so that the
literature results might be compared to ours. For droplet disruption in turbulent flow
(such as in high-pressure homogenizers) Walstra\textsuperscript{19} suggests the following formula for
predicting droplet diameters:

\begin{equation}
    d_p = C \varepsilon^{-2/5} \gamma^{3/5} \rho_C^{-1/5}
\end{equation}

where \( \varepsilon \) is the energy density (W m\(^{-3}\)) within the homogenizing valve, \( \gamma \) is the interfacial
tension (N m\(^{-1}\)), \( \rho_C \) is the continuous phase density (kg m\(^{-3}\)), and \( C \) is a constant of order
one. In the presence of surfactants, the carbon dioxide/water interface can be lowered to
less than 1 \times 10\(^{-3}\) N m\(^{-1}\)\textsuperscript{59-67} from about 25 \times 10\(^{-3}\) N m\(^{-1}\).\textsuperscript{18} Since the droplets formed by
ultrasound were roughly 1 order of magnitude larger than the smallest droplets reported
in the literature, equation (5-11) predicts an energy density three-fold higher in the high-
pressure homogenizers as compared to the acoustic system. This estimate does not make
sense given the high energy densities used in this study. This analysis may be faulty
since it assumes equal efficiencies for the two emulsification methods and droplet
diameters which are determined primarily by consideration of droplet breakup rather than
droplet coalescence. If droplet re-coalescence is accelerated during ultrasonic agitation
(as it almost definitely is), equation (5-11) does not apply.

Chun and Wilkinson\textsuperscript{69} describe the operation of a countercurrent liquid/liquid
extraction column containing water and droplets of supercritical carbon dioxide. In this
study, carbon dioxide droplets were formed by forcing the fluid through holes with a
diameter of 1.6 mm. No surfactant was used, though ethanol and iso-propanol were
present as cosolvents, thus lowering the interfacial tension to roughly 15 \times 10\(^{-3}\) N m\(^{-1}\).\textsuperscript{18}
Using this approach, droplets with an average diameter of roughly 0.4 mm were formed
at conditions near 35 °C and 100 bar. Carbon dioxide holdup was well described using a
standard correlation derived for low pressure systems containing incompressible,
immiscible fluids with density differences comparable to that between carbon dioxide
and water at the conditions of interest. A similar approach was tested for predicting the carbon dioxide droplet sizes, but the range of the experimental data was too small (from 0.3 to 0.5 mm) to provide a good test for the correlation. The low power densities associated with the dispersion method used in Chun and Wilkinson's study\textsuperscript{69} make it difficult to compare directly to our results, though it is noted that bubble columns may be an efficient means of promoting carbon dioxide/water contact when micron-sized droplets are not required.

Heath and Cochran\textsuperscript{70,71} have reported the use of electrospay to disperse fine droplets of water in carbon dioxide. The electrospay technique involves spraying a mist of conductive solution through a standard valve. The mist is subjected to an intense electrical field, on the order of 1,000 V cm\textsuperscript{-1} which causes the mist to break into micron-sized droplets. Since the electrospay method does not rely on the use of surfactants, it is technologically comparable to the ultrasonic method described here. Heath and Cochran\textsuperscript{70} report the formation of droplets with average diameters of roughly 1 \( \mu \text{m} \) over a relatively wide range of operating conditions. The authors indicate that the resulting emulsions were unstable, and were found to break instantly upon contact with a wire mesh electrode. The authors were not able to measure water-phase holdup with their experimental setup so that the total interfacial area was unknown. Nonetheless, electrospay could prove to be a useful means of dispersing water in carbon dioxide which does not rely on surfactants. Quantitative comparison of ultrasonic emulsification with electrospaying is limited since Heath and Cochran\textsuperscript{70,71} did not report a current draw or power density in their experiments.

5.5.2 Emulsions Containing Oil and Water from Power Ultrasound

While power ultrasound has not been used to emulsify liquid near-critical or supercritical carbon dioxide and water, it is a useful technique for dispersing systems containing oil and water.\textsuperscript{1-16} Ultrasonic emulsification of oil/water systems is the subject of several reviews.\textsuperscript{1,5,20} E.S.R. Gopal\textsuperscript{20} asserts that ultrasonic emulsification yields emulsions comparable to those formed by other techniques, though the amount of surfactant required for stability is frequently reduced. In fact, Reddy and Fogler\textsuperscript{8} formed kinetically stable, surfactant-free emulsions containing 0.1 vol\% of \( \text{C}_{36}\text{H}_{74} \) in water using ultrasound. The authors conjectured that droplet stabilization may have been the result of
preferential adsorption of \( \text{OH}^- \) to the surface, though why ultrasound should promote such behavior process is not at all clear. It is equally likely that the droplets were stabilized by the small metal particles generated by pitting of the ultrasonic horn. Formation of stable, surfactant-free emulsions has never been reported by other research groups, despite efforts\(^3\) to reproduce Reddy and Fogler's\(^8\) results.

The acoustic power threshold observed in the current study has also been observed for emulsification of oil and water. Nedhuzii\(^72\) reported a minimum power intensity of 0.5 W cm\(^{-2}\) to form oil/water emulsions and 1.5 W cm\(^{-2}\) to form water/oil emulsions. These threshold power intensities are comparable to, but somewhat less than, those found in our study as the 0.1 W cm\(^{-3}\) threshold density reported here corresponds to an intensity of roughly 10 W cm\(^{-2}\).

Behrend and Schubert\(^13\) report that ultrasound achieves higher power densities and smaller droplet sizes at a given power density as compared to colloid mills and most high-pressure homogenizers. In their compilation of emulsification data, Walstra and Smulders\(^68\) indicate that ultrasound is capable of higher energy dissipation rates than mechanical emulsification methods (including colloid mills, high-pressure homogenizers, and the "Ultra Torrex") and is more energy efficient at a given energy density. The emulsification conditions presented by Walstra and Smulders\(^68\) vary depending on the emulsification method so that this conclusion may be misleading. In contrast, Maa and Hsu\(^11\) found that ultrasound is inferior to microfluidization, whereby high-pressure is used to force the emulsion components through specially designed microchannels, but slightly superior to high-pressure homogenization.

In their studies of kerosene/water systems stabilized by polyethoxylated sorbitan monostearate, Abismaïl et al.\(^3\) were not able to produce kinetically stable emulsions with ultrasound in the absence of surfactant, though for a given amount of surfactant smaller droplets were formed using the acoustic technique (0.1 to 2.0 \(\mu\)m) as compared to mechanical agitation using the Ultra-Torrex (2 to 6 \(\mu\)m). In a second study, Abismaïl et al.\(^4\) found that the kerosene/water/polyethoxylated sorbitan monostearate system was fully emulsified in less than 10 min of continuous ultrasound at a power rating of more than 60 W in a pump-around system. The minimum droplet sizes achieved in this study were on the order of 0.4 \(\mu\)m, with smaller droplets resulting from sonication at higher
power inputs. These findings are difficult to evaluate quantitatively as the volume of the emulsion and the recirculation rate are not reported.

Li and Fogler\textsuperscript{9,10} first described ultrasonic emulsification as the two-step process introduced in Section 5.2.3. To support their hypothesis, the authors prepared emulsions of styrene/water, octacosane/water, and hexatriacontane/water, achieving minimum droplet diameters of 0.15, 0.22, and 0.25 $\mu$m, respectively. These limiting droplet diameters were approached over a sonication time of several minutes. The authors do not report the total volume of the emulsion or the power density. Perhaps more usefully, Abismaïl et al.\textsuperscript{4} suggest that equation (5-11) applies to ultrasonic droplet formation, though the value of the proportionality constant differs depending on the mechanism of emulsification. The analysis of Abismaïl et al.\textsuperscript{4} suggest equation (5-11) as a tool for correlating droplet diameters obtained in acoustic systems.

The observation of a gradual approach to a limiting droplet size has been frequently reported in studies of ultrasonic emulsification. For example, in addition to Li and Fogler,\textsuperscript{9,10} Merry and Eberth\textsuperscript{6,7} found that emulsions containing pharmaceutical components tended toward limiting diameters of roughly 0.2 $\mu$m with sonication times greater than 5 min, though diameters as small as 0.5 $\mu$m were observed after 30 s. Maa and Hsu\textsuperscript{11} report reaching droplet sizes as small as 1 $\mu$m in emulsions of methylene chloride and water after 15 s of continuous ultrasound in a batch system. The minimum achievable size depended on sonication power, though the authors reported their findings in terms of the amplitude of the vibration rather than the more convenient energy density. Abismaïl et al.\textsuperscript{3} also reported reaching a minimum droplet size (diameters measured as 0.5 $\mu$m) after roughly 10 s of continuous emulsification. These results will be used to support estimates of the time required to form carbon dioxide/water emulsions using ultrasound presented in Section 6.5.2.

5.6 Practical Implications

The analysis presented thus far provides some insight into practical emulsification of systems containing carbon dioxide and water. This section describes some of these implications beginning with the power efficiency of ultrasonic emulsification.
5.6.1 Power efficiency

The efficiency of energy dissipation during emulsification with power ultrasound can be estimated starting based on the value for the ideal emulsification energy: \( \gamma \Delta a \), where \( \gamma \) is the interfacial tension and \( \Delta a \) is change in the total interfacial area during emulsification. From Section 4.5.5, the total interfacial area generated during sonication is 3.9 m\(^2\), assuming a water droplet diameter of 9.1 \( \mu \)m and a carbon dioxide droplet diameter of 15.1 \( \mu \)m. This leads to an ideal emulsification energy of 0.1 J, assuming that \( \gamma \approx 25 \times 10^{-3} \) N m\(^{-1}\) for a carbon dioxide/water interface at 30 °C and 80 bar as suggested by Chun and Wilkinson.\(^{18}\) The energy density required to form this emulsion was approximately 0.5 W cm\(^{-3}\), corresponding to a power input of 45 W. Based on visual observation, it seems that emulsification was complete after 10 s of sonication at a duty cycle of 25\%, a figure consistent with that reported for formation of oil/water emulsions.\(^{3,6,7,9,10,11}\) This indicates that a total of 110 J were dissipated by the system prior to reaching steady state. Thus, the energy efficiency of ultrasonic emulsification was approximately 0.09 \%, which is consistent of 0.1 \% quoted by Walstra and Smulders\(^{66}\) as a typical efficiency of emulsification. Regardless of the emulsification process, the majority of the energy (i.e., 99.9 \%) goes toward bulk heating. The agreement between our figure and that found in the literature is remarkable considering the uncertainty in the time required to form the emulsion.

5.6.2 Particle contamination

As described in Section 5.3.1, the acoustic horn becomes pitted during formation of carbon dioxide/water emulsions. The result is that small amounts of titanium are ejected into the emulsion where they are a contaminant. These particles were removed from the emulsion by filtering the recirculating fluids with 15 and 2 \( \mu \)m sintered metal filters. Over time, the 15 \( \mu \)m filter collected a thin film of particles, indicating that a large fraction of the titanium particles were larger than 15 \( \mu \)m. Fewer particles were observed on the 2 \( \mu \)m filter; however, visual detection of such small particles is difficult. It may be necessary to actively remove the cavitationally produced particles for some applications. It is also possible to use acoustic horns made of glass if it is desired to exclude metal particles specifically from the emulsions. Finally, it may be possible to
sonicate the reactor contents indirectly, using an external piezoelectric agitator cemented to the reactor walls by epoxy or an acoustic horn coupled to the reactor using a suitable fluid. This final solution is appealing since the temperature of the coupling fluid can be maintained independently of the reactor contents, thus allowing operation at elevated temperatures while extending horn lifetimes. Indirect systems do suffer from the inherent loss of energy associated with penetrating the reactor walls. Additionally, it is not fully clear if material erosion would be transferred from the horn to the reactor walls. Given these uncertainties, some experiments are needed to determine the exact limitations of externally mounted transducers.

5.6.3 Scale-Up

Cavitation (or streaming-enhanced cavitation) seems to be the primary mechanism of ultrasonic emulsification of near-critical carbon dioxide and water. This presents a challenge to reactor scale-up since it is well known that penetration of the cavitation zone beyond several centimeters is generally not possible.\textsuperscript{15,37-39}

Several metrics for acoustic power dissipation have been presented in this study that have different uses in terms of design variables. Though average power density is useful because it contains information regarding the size of the vessel, it can also be misleading since the power is not dissipated uniformly throughout the entire reactor. Thus, the actual local power density is generally less than the reported average power density, except in a small region in close proximity to the acoustic horn where it is much greater. Power intensity, on the other hand, contains no information regarding vessel geometry, considering only the region close to the acoustic source. Power intensity is useful due to its relationship with the acoustic pressure. Given the role of cavitation in the formation of emulsions of carbon dioxide and water, acoustic pressure is an important design variable, particularly in relationship to the Blake threshold pressure. Finally, it seems plausible that acoustic self-concentration plays an important role, highlighting the interaction between streaming and cavitation. The issue of reactor scale-up is addressed more thoroughly in Section 7.6.4.

5.7 Conclusions

At power densities less than 0.05 W cm\textsuperscript{-3} breakup of interfacial waves leads to formation of coarse water/carbon dioxide emulsions consisting of droplets with diameters
on the order of 40 μm. This result is completely consistent with the turbidity results presented in Chapter 4. Above the threshold power density, sonication leads to both acoustic streaming and cavitation. The kinetic energy dissipated by acoustic streaming is insufficient to account for the micron-sized droplets actually observed in the emulsion, implying that cavitation is a dominant emulsification mechanism. Carbon dioxide cavitation was observed only when the acoustic pressure exceeded the Blake threshold pressure. Cavitation was observed in liquid water subjected to pressures of 80 and 120 bar in a carbon dioxide environment, even though the acoustic pressure was less than the Blake threshold pressure of pure water. What was taken as cavitation of liquid water may have actually been cavitation of carbon dioxide which was dissolved in the water phase. The appearance of cavitation in high-pressure water systems was qualitatively different from that observed at 1 bar, as the resulting cavitation cloud was much more turbid and appeared to extend deeper into the fluid. Observation of acoustic horn pitting suggested that high-pressure cavitation produced the microjets required for ultrasonic emulsification. Sonochemical oxidation of potassium iodide was suppressed at carbon dioxide pressures of 80 bar, indicating that the cavitation bubbles did not attain temperatures required for formation of hydroxyl radicals.

The experimental results were compared to literature reports describing the surfactant-assisted emulsification of carbon dioxide/water using simple shear and oil/water systems using ultrasound. In both cases, the final droplet diameters were much smaller in the literature reports, a direct consequence of the presence of emulsifiers. The time required to achieve a steady state between droplet formation and coalescence rates was estimated as 10 s, leading to an approximate energy efficiency of 0.02%.

Chapter 8 contains recommendations based on the results in presented in this chapter.

5.8 References


Chapter 5: Emulsification Mechanisms


CHAPTER 6


6.1 Supercritical Carbon Dioxide/Water Systems for Chemical Reactions

Background and motivation. In the vicinity of its critical point, carbon dioxide has high diffusivity, low viscosity, and high compressibility which results in tunable density and solvation power. These properties make carbon dioxide a potentially attractive solvent for industrial scale chemical synthesis. Additional advantages of carbon dioxide over conventional solvents are that it is inexpensive, non-toxic, and non-flammable. It is not surprising, therefore, that both near- and supercritical carbon dioxide (scCO₂), have been used for a number of industrial processes, most notably separations involving multi-phase extractions.¹ Despite this success, relatively little progress has been made toward using carbon dioxide as a solvent for chemical reactions. There are two primary reasons for this. First, carbon dioxide exhibits poor solvent power for many reagents of interest¹ including most hydrophilic compounds and high-molecular weight hydrocarbons. Second, only modest improvements of reaction rates and/or selectivity²⁻¹¹ have been observed in carbon dioxide as compared to traditional hydrocarbon solvents. Without significant technological advantages, industrial implementation of “greener” technologies including replacement of organic solvents with dense carbon dioxide has been slow.

In an effort to improve either selectivities or rates of certain reactions in scCO₂, a number of researchers have investigated the use of heterogeneous and homogeneous catalysts in supercritical fluids. Initial development of homogeneous catalysis was delayed by the low solvent power of carbon dioxide for common catalysts, but the discovery that the addition of CO₂-philic ligands (primarily fluorinated alkanes and ethers or siloxane-based molecules) could increase the solubility of many transition-metal-based
organometallic compounds, has opened the field of supercritical-fluid-based homogeneous catalysis.\textsuperscript{12-20} Unfortunately, the otherwise promising catalysts are more expensive than their lipophilic analogs. Additionally, like all homogeneous catalysts, carbon dioxide-based homogeneous catalysts must be separated from the post-reaction mixture, which can be difficult or expensive. Heterogeneous catalysts, on the other hand, can be easily recovered and recycled; but their lower specificity as compared to homogeneous catalysts and inherent mass-transport limitations (either in the bulk fluid or within the catalyst support structure) reduces their attractiveness.

Because of these limitations, techniques that exploit the advantages of reactivity inherent to homogeneous catalysts while retaining the ease of separation of heterogeneous catalysts are of interest. One approach has been to employ a homogeneous catalyst which is phase-separated from the reactants and products,\textsuperscript{21-23} either by immobilization on a solid support or dissolution in a second, CO\textsubscript{2}-immiscible, liquid phase. Although supporting homogeneous catalysts on heterogeneous supports is a viable approach, this solution does not address the solubility issues associated with scCO\textsubscript{2}. Use of CO\textsubscript{2} in combination with a second solvent could improve solubilization. Biphasic mixtures of liquid water and scCO\textsubscript{2}, which are essentially immiscible close to the critical point of pure CO\textsubscript{2} at 31.1 °C and 73.8 bar, are particularly attractive. Since the two solvents have complementary solvent powers, their combination in a biphasic system increases effective solubility for a wider range of reagents and should facilitate liquid-liquid phase segregation of reactants and products from homogeneous catalysts. Furthermore, this approach preserves the environmental advantages of carbon dioxide since the only additives are water and an easily recoverable catalyst.

One disadvantage of a phase segregated system is that it increases mass-transport resistances, as the reagents need to enter the phase containing the catalyst prior to reacting. These transport limitations can be offset by using high-surface-area emulsions and microemulsions of carbon dioxide and water.\textsuperscript{24-29} The use of microemulsion/emulsions shows promise, but stabilization of water/carbon dioxide interfaces generally requires specially fluorinated surfactants. The use of these surfactants has economic and environmental impacts, which may prohibit some commercial applications. Furthermore, addition of any surfactant (fluorinated or not) to pure carbon dioxide/water systems
necessarily detracts from their chemically benign natures and complicates otherwise simple chemistry and post-reaction separations. Practical implementation of water/carbon dioxide microemulsion systems would be accelerated greatly by a surfactant-free means of emulsification.

Earlier studies of chemical reactions in water/carbon dioxide systems, including biphasic (i.e., non-dispersed) systems, emulsions, and microemulsions were reviewed in Chapter 1. Previous researchers have demonstrated that many reactions proceed at reasonable rates in the biphasic environment, albeit with reliance on costly surfactants. A second recurring theme in the literature is the lack of quantitative interpretation. Probable mechanisms and rate limiting steps are sometimes inferred from experimental data, but there have been no attempts to develop rigorous physical models. The location of reactions in carbon dioxide/water systems (e.g., bulk water, bulk carbon dioxide, or the interface) is not known. Analysis of existing rate data is greatly complicated by the presence of surfactants which frequently influence reagent partitioning and reaction rates in addition to their intended physical effects. As discussed in Chapter 1, the effect of surfactants on chemical reactivity is difficult, if not impossible, to predict _a priori._

The lack of theoretical analysis and basic mechanistic understanding of reactions in carbon dioxide/water systems greatly hinders selection of model reactions. In some instances, it is possible that unfavorable reagent partitioning and reaction dynamics might combine to render biphasic conditions prohibitively slow. Mechanistic models of reaction dynamics in two-phase systems containing carbon dioxide/water would enlighten efforts to increase reaction rates in biphasic systems. Furthermore, no rational basis is available for determining which reactions might benefit from phase dispersion as emulsions or microemulsions. For a given reaction, it is not even clear which type of dispersion (i.e., water/carbon dioxide or carbon dioxide/water, emulsion or microemulsion) is preferred. Without physical models characterizing reaction/transport dynamics in carbon dioxide/water systems, progress in this promising field will continue to be slow.

_The use of ultrasound to accelerate reactions in carbon dioxide/water systems._ This chapter builds on the findings presented in Chapters 4 and 5 to demonstrate that ultrasound can be used as a an efficient means of accelerating chemical reactions by
increasing the interfacial area of the carbon dioxide and water phases. Replacing surfactants with ultrasound offers a means to generate emulsions which are more amenable to mathematical analysis. This is because ultrasound exerts physical effects which are much easier to model or estimate than the chemical effects associated with surfactants. Though acoustically formed emulsions remain a complicated system, the characteristics of primary importance (droplet size distribution and volume fractions of the dispersed phase) for the purposes of kinetic analysis were measured previously. Based on the results presented in Chapter 5, the sonochemical effects that have been observed in low pressure systems do not arise to complicate the analysis of high pressure carbon dioxide/water systems. This facilitates first-principles modeling of the emulsions since rate constants measured in the pure phases (carbon dioxide or water) can be used directly. Pure phase rate constants (available in the literature for many reactions of interest) and reagent partition coefficients (which can be estimated using the empirical methods presented in Chapter 3) are available for use in conjunction with first principles models of reaction/transport dynamics in surfactant-free emulsions. Acoustically generated emulsions present a means to validate rigorous physical models which do not rely on any fit parameters.

The short lifetimes of additive-free emulsions are a distinct technological advantage over those that are stabilized by surfactants. Although emulsions stable for greater than several hours might be desired in certain applications (for instance applications of coatings), they are of limited utility for chemical reactions. Pulsed ultrasound can be used to maintain large interfacial contact area between the carbon dioxide/water phases for as long as is required. Following completion of reaction, surfactant-free emulsions will break spontaneously within 30 min, facilitating post-reaction separation. Breaking surfactant-stabilized emulsions requires either a change in conditions (which may result in precipitation of products from the carbon dioxide phase prior to its separation from the aqueous layer) or additional demulsification processes.

The two primary objectives of the research presented in this chapter are: 1) quantification of ultrasonic acceleration for reactions which are mass transport limited in carbon dioxide/water systems and 2) development of first principles models to predict the overall observed rate under both emulsified and non-emulsified cases. The first objective
is intended to verify that ultrasound can have beneficial effects on chemical reactions while the second objective provides basic understanding of reaction/transport in carbon dioxide/water systems. The goal of the second objective is to provide the basic understanding necessary for rational selection of model reactions for carbon dioxide/water systems and to predict the accelerative effects of emulsification.

The structure of Chapter 6 is as follows. Section 6.2 reviews previous studies of ultrasound in supercritical fluid media. Experimental methods and measurements of mass transport coefficients for non-emulsified carbon dioxide/water systems are presented in Section 6.3. These data were incorporated into first principles models of reaction/transport in the silent (e.g., non-emulsified) case. Benzoyl halide hydrolysis is discussed as a model reaction for studying chemical reactivity in carbon dioxide/water emulsions in Section 6.4. The reactivity, partitioning, and diffusivity of benzoyl halides are briefly reviewed within this context. Section 6.5 presents kinetic rate data for the hydrolysis of benzoyl halides both in the silent (i.e., non-emulsified) and sonicated (i.e., emulsified) cases. Theoretical interpretation, including mathematical models, is discussed in Section 6.6. The final section presents conclusions.

6.2 Previous Studies Combining Ultrasound with Supercritical Fluids

Ultrasound and supercritical fluids have both received attention independently as environmentally benign processing tools, and it is not entirely surprising that researchers have already investigated the combination of the two. Although there have been no reports of acoustic emulsification of water and carbon dioxide which would be of direct relevance to this work, it is useful to review investigations involving both ultrasound and supercritical fluids. The contributions of Goldfarb et al.\(^{30}\) and Kuijpers et al.\(^{31}\) to the nascent field of high-pressure cavitation were introduced in Chapter 5. Aymonier et al.\(^{32}\) used ultrasound to reduce plugging in supercritical water oxidation reactors. The authors also reported an increase in the oxidation of acetic acid when ultrasound was used close to the critical point of water, though whether this was a sonochemical or physical phenomenon was unclear.

In the past three years, C.M. Wai’s research group at the University of Idaho has shown that ultrasound can accelerate dissolution of solids into supercritical carbon dioxide.\(^{33,34}\) The acoustic field in these studies was generated outside of the reactor via a
sonic bath, limiting the opportunity for quantitative analysis, as the power intensity of the sound field is unknown in the entire working volume in such experiments. Phenomenologically, dissolution rates were accelerated by 100%\textsuperscript{,34} a result which may be useful in applications such as extraction. Park et al.\textsuperscript{35} reported similar results for the dissolution of copper compounds into supercritical carbon dioxide under ultrasonic stimulation, a phenomenon that was attributed to acoustic streaming.

Finally, P. Chattopadhyay and R.B. Gupta have demonstrated\textsuperscript{36,37} the use of ultrasound in conjunction with supercritical fluid anti-solvent (SAS) crystallization. SAS utilizes supercritical carbon dioxide as an anti-solvent to effect precipitation of a solute dissolved in an organic solvent. The organic solvent is sprayed as small droplets into the carbon dioxide, and precipitation of the solute occurs as the organic solvent dissolves into the carbon dioxide phase. The authors modified this process,\textsuperscript{38} positioning an ultrasonic horn at the position at which the carbon dioxide and organic solvent mix. P. Chattopadhyay and R.B. Gupta report formation of smaller (average diameters of 0.2 compared to 2 \(\mu\)m), slightly more uniform (diameters ranging from 0.2-0.8 \(\mu\)m compared to 0.5-5 \(\mu\)m) particles\textsuperscript{36} when crystallization was accompanied by sonication, effects that were attributed to formation of smaller droplets of the organic solvent and more intense mixing of the spray.

### 6.3 Mass Transport Experiments

**Objective.** The objective of this portion of the study was to determine values of mass transport coefficients (\(k_c\) and \(k_w\) for carbon dioxide and water, respectively) for quantitatively characterizing the transport rate of a hydrophobic species from the carbon dioxide phase to the water phase in the absence of a chemical reaction.

**Theory.** Two-film theory was used to describe mass transport in the biphasic carbon dioxide/water system. It should be noted that more complicated alternatives exist such as penetration and surface renewal theories. The film model was selected over these alternatives because it is mathematically and physically simple yet gives results comparable to the more complicated theories. For the relevant case of mass transport coupled with first order reaction, Sherwood et al.\textsuperscript{39} report that predictions based on the film, penetration, and surface renewal models are nearly identical.
Figure 6-1 is a schematic representation of film theory. The concentration of $A$ in the bulk carbon dioxide phase is referred to as $[A]_c$ and that at the carbon dioxide side of the interface is $[A]_{c,\text{int}}$. The terms $[A]_w$ and $[A]_{w,\text{int}}$ then refer to the bulk concentration of $A$ in the water and the concentration of $A$ on the water side of the interface, respectively.

The flux of $A$, $N_A$, out of the carbon dioxide phase is equal to:

$$N_A = k_c (\text{\Large []} - [A]_{c,\text{int}}) \quad (6-1)$$

$N_A$ can also be related to the water phase concentrations:

$$N_A = -k_w ([A]_w - [A]_{w,\text{int}}) \quad (6-2)$$

where $k_c$ and $k_w$ are the mass transport coefficients in carbon dioxide and water, respectively, and take units of cm s$^{-1}$. In the absence of interfacial resistance, the interfacial concentrations are related by the equilibrium partition coefficient:

![Diagram]

Figure 6-1. Schematic representation of the two film model for mass transfer. $[A]_c$ is the concentration in the bulk carbon dioxide phase and $[A]_w$ is the bulk concentration in the water phase. $[A]_{c,\text{int}}$ and $[A]_{w,\text{int}}$ are the concentrations on the carbon dioxide and water sides of the interface. In the absence of interfacial resistance, the interfacial concentrations are related by the partition coefficient at all times as suggested by equation (6-3).
\[ K_{CW} = \frac{[A]_{c,\text{int}}}{[A]_{w,\text{int}}} \]  
(6-3)

For hydrophobic species, \( K_{cw} \) will be greater than unity. Combining equations (6-1), (6-2), and (6-3) allows the flux to be written in terms of known or measurable quantities:

\[
N_A = \frac{1}{1 + \frac{K_{CW}}{k_c}} ([A]_c - K_{CW} [A]_w)  \tag{6-4}
\]

Equation (6-4) can be re-written using an overall mass transport coefficient defined as:

\[
k_{mt, CO2} = \frac{1}{1 + \frac{K_{CW}}{k_c}} \frac{k_{mt, H2O}}{K_{CW}} \tag{6-4a}
\]

The overall mass transport coefficients can be written in terms of either \([A]_c\), in which case \( k_{mt, CO2} \) is used, or \([A]_w\), in which case \( k_{mt, H2O} \) is used. The two overall mass transport coefficients are related by the partition coefficient, \( k_{mt, CO2} = K_{CW} k_{mt, H2O} \).

Experimentally, concentration measurements are more accessible than flux measurements. Since the volumes of the two phases are constant to within 1% over the course of an experiment, concentration balances and mass balances are equivalent, which facilitates the analysis. Only the flux in equation (6-4) is required to formulate a transient mass balance on \([A]_w\):

\[
\frac{d[A]_w}{dt} = k_{mt, CO2} \frac{a}{V_w} ([A]_c - K_{CW} [A]_w) \tag{6-5}
\]

where \( V_w \) is the total volume of the water phase and \( a \) is the total interfacial area. The underbars are used to denote extensive properties. Equation (6-5) implicitly assumes that the hold up of solute in the film region is negligible compared to that in the bulk.

Since any \( A \) that disappears from the carbon dioxide phase must appear in the water phase, the following mass balance applies at all times:

\[ [A]_c = [A]_c (t = 0) \frac{V_w}{V_c} [A]_w \]  
(6-6)

where \([A]_c (t = 0)\) is the initial concentration of \( A \) in the carbon dioxide and \( V_c \) is the volume of the carbon dioxide phase, both of which are experimentally known. In
equation (6-6) it has been assumed that the initial concentration of the solute in the water phase is zero. Assuming that $K_{CW}$ is independent of concentration (valid for dilute solutions based on the measurements made in Chapter 3), equation (6-6) allows integration of equation (6-5). The result is:

$$\ln\left\{\frac{[A]_C(t = 0) - (V_w/V_c + K_{CW})[A]_W}{[A]_C(t = 0)} \right\} = -k_{mt,CO_2} \frac{a}{V_w} (V_w/V_c + K_{CW}) t \quad \text{(6-7)}$$

A plot of the left hand side of equation (6-7) as a function of time will be linear with a slope composed of known quantities and the mass transport coefficients.

**Experimental.** The acoustic reactor described in Chapter 4 was used for all mass transport experiments. The reactor was partially filled with 50 cm$^3$ of deionized water and pressurized to 65 bar at 30 °C under a carbon dioxide atmosphere. Several hours were allowed for the two phases to equilibrate. During this time, agitation was applied directly to the water phase using the recirculation pump (LDC Analytical) operating at a flow rate of 20 cm$^3$ min$^{-1}$. The sample point within the reactor was 5 cm removed from the interface, and the re-injection point was 1 cm from the interface. The recirculating stream was directed through an HPLC valve (Valco Instrument Company, Inc. uW-type) from which samples were taken of the water phase.

Benzaldehyde was selected as the tracer compound for mass transport studies. This compound was selected for two reasons: 1) its partition coefficient had been measured previously (see Section 3.3) and 2) the molecular structure of benzaldehyde is similar to that of the benzoyl halides which were used in studies investigating chemical reactions, suggesting that their physicochemical properties are likely to be similar. The experiment was initiated by injection of a known volume of benzaldehyde (either 20 or 100 μL) through a second HPLC valve as the reactor was pressurized to 80 bar using carbon dioxide. Two phase conditions were verified visually through the $\alpha$-Al$_2$O$_3$ windows. The progress of mass transport was followed by withdrawing samples from the recirculation loop at known times. Each sample was diluted to a standard volume and the concentration of benzaldehyde was measured using gas chromatography (Agilent, 6890)
as described in Section 3.2. The GC was calibrated using known standards, and the response was linear in the concentration range of interest.

**Mass Transport Results.** The transport of benzaldehyde from carbon dioxide to water at 80 bar and 30 °C was monitored by measuring the concentration of the benzaldehyde in the aqueous phase over time. Equilibrium partitioning was reached within an hour, and the partition coefficient measured in this fashion agreed with that reported in Chapter 3 to within 10%. The left-hand side of equation (6-7) is plotted as a function of time in Figure 6-2. The slope of the resulting straight line is $0.0545 \pm 0.006 \text{ s}^{-1}$. Substitution of the known values of $K_{cw}$ (12, from Chapter 3), $a$ (20 cm$^2$), $V_w$ (50 cm$^3$), and $V_c$ (37 cm$^3$) into equation (6-7) yields $k_{ml,CO_2} = 2.2 \pm 0.2 \times 10^{-5} \text{ cm s}^{-1}$.

It is desirable to break $k_{ml,CO_2}$ into its components, $k_c$ and $k_w$. To do so, the hydrodynamic conditions in the films need to be modeled using a suitable theory. One
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...
\[
\frac{k_c}{U_c} Sc_c^{2/3} = \text{constant} \left( \frac{U_c L}{\mu_c / \rho_c} \right)^{-1/2}
\] (6-9)

where \(\mu_c\) is the viscosity of carbon dioxide, \(\rho_c\) is the density of carbon dioxide, and \(Sc_c\) is the Schmidt number for carbon dioxide. \(Sc\) is defined as follows:

\[
Sc = \frac{\mu}{\rho D_{ab}}
\] (6-10)

An expression similar to equation (6-9) can be written for \(k_w\). Assuming still that \(U_c \approx U_w\) and that the same proportionality constant applies for both fluids, the ratio of the boundary-layer expressions for \(k_c\) and \(k_w\) is given by:

\[
\frac{k_c}{k_w} = \left( \frac{\mu w \rho_c}{\mu_c \rho_w} \right)^{1/6} \left( \frac{D_{AC}}{D_{AW}} \right)^{2/3}
\] (6-11)

which implies that the ratio of mass transport coefficients is determined primarily by the ratio of the molecular diffusivities in the two phases, roughly 15:1 at 30 °C and 80 bar.\(^{41,44}\) The selection of representative values for diffusion coefficients in water and carbon dioxide is covered in detail in Section 6.4. Insertion of characteristic values for the other transport properties that appear in equation (6-11) yields \(k_c / k_w \approx 9:1\). Thus, for transport of a hydrophobic species (i.e., for \(K_{cw} \gg 1\), the water film resistance will always dominate. From the data presented in Figure 6-2, \(k_w \approx 3 \times 10^{-4} \text{ cm s}^{-1}\) and \(k_c \approx 2 \times 10^{-3} \text{ cm s}^{-1}\) for the specific case of benzaldehyde transfer. Based on the uncertainties in the parameters in equation (6-7) and the error in the slope of Figure 6-2, the estimated error in \(k_w\) is roughly ± 30%.

Because the overall flux is not appreciably affected by mass transport resistance in the carbon dioxide film, equation (6-4a) is less sensitive to \(k_c\) than \(k_w\). For this reason, the value for \(k_c\) given above is reliable only as an order of magnitude estimate. \(k_c\) could be determined with greater accuracy from transport measurements of hydrophilic species. Since the focus of this study is the transport of hydrophobic species, the exact value of \(k_c\) is not particularly important, as it will not appear in any of the final transport/reaction expressions.

It is also useful to reconsider the validity of equation (6-11). If this were to be quite erroneous, the overall conclusion that \(k_w\) dominates mass transport is not altered,
provided that both $K_{cw} \gg 1$, as it is in this case, and $k_c$ is at least roughly equal to $k_w$.

Furthermore, even if the characteristic velocity of the carbon dioxide phase is appreciably less than that of the water phase, say $U_C = 0.1 \ U_W$, the value of $k_w$ estimated from the above analysis remains roughly $3 \times 10^{-4}$ cm s$^{-1}$ since $K_{cw} = 12$. This analysis suggests that the results of the mass transport study can be used with some confidence in conjunction with models describing transport/reaction in biphasic systems.

**Comparison to the literature.** Supercritical fluid extraction (SFE) of natural components from solid matrices is commonly used in practice and has been the subject of several reviews.\textsuperscript{45-47} SFE of ethanol from aqueous streams using *countercurrent extraction columns*\textsuperscript{48-50} is also the focus of many studies. In another body of literature, waste water treatment with supercritical carbon dioxide focuses on equilibrium partitioning\textsuperscript{51} rather than dynamic behavior. Unfortunately, literature reports of SFE and water treatment applications are not directly relevant to our work.

There have been several recent reports of static mixers\textsuperscript{52,53} and electrosprayers\textsuperscript{54,55} to improve interfacial contact during mass transport processes. It has been reported that static mixers can increase carbon dioxide/water mass transport rates by as much as 3-fold,\textsuperscript{52} but little analysis of the experimental data was presented.

In a relevant study, Tai et al.\textsuperscript{56} examined the dynamics of Zn$^{2+}$ extraction from water using scCO$_2$ and an extraction ligand (Cyanex 302) in an impeller-stirred vessel. The chelation reaction between the zinc ion and the extraction ligand was assumed to be instantaneous so that the extraction of the Zn-ligand complex was modeled as a purely physical process. Using a treatment identical to that described above, $(k_{mt,water \ a} \ \nu_W^{-1})$ was found to be equal to $2 \times 10^{-4}$ s$^{-1}$ at 40 °C, 83 bar, and a stirring rate of 420 rpm.

Unfortunately, the authors do not provide a value for $a$. A value could be estimated from the dimensions of the vessel, but the authors suggest partial dispersion of the two phases making the nominal surface area irrelevant. The value of $(k_{mt,water \ a} \ \nu_W^{-1})$ reported by Tai et al.\textsuperscript{56} is comparable but slightly faster than that reported here ($1 \times 10^{-4}$ s$^{-1}$). Given that mixing in the experiments of Tai et al.\textsuperscript{56} was much more effective than in this study (rotating impeller as opposed to gentle recirculation) and that the value of $a$ in the literature study is unknown, it is fortuitous that the two values agree this closely. The overall mass transport coefficient reported by Tai et al.\textsuperscript{56} increased by an order of
magnitude when the impeller speed increased from 420 to 1000 rpm, highlighting the role of agitation on observed mass transport rates.

A second comparison, albeit for incompressible fluids, is provided by the study of diffusion in Lewis cells.\textsuperscript{57-59} These studies involve measurement of the transport rate of a solute from an organic solvent to water. Typically, each phase is stirred independently by separate impellers. In the original study, Lewis\textsuperscript{57} measured $k_{\text{mt,organic}} \approx 5 \times 10^{-4}$ cm s\textsuperscript{-1} for the transport of acetone from water to toluene. This value is roughly one order of magnitude larger than reported here which is reasonable given that Lewis’ experiments were conducted under conditions of high Reynolds number (>10,000) mixing. Agitation in the current carbon dioxide/water experiments was achieved by gentle recirculation and resulted in lower mass transport rates. In related studies, McManamey\textsuperscript{58,59} proposed that for transport between an organic and aqueous phase, the ratio of the mass transport coefficients was proportional to the square root of the inverse ratio of the diffusion coefficients. This is nearly identical to equation (6-11), supporting the use of this correlation to separate the overall mass transport coefficient into its components.

### 6.4 Approach: Benzoyl Halide Hydrolysis as a Model Reaction

The primary objective here was to develop a model which separated the effects of intrinsic reactivity, partitioning, and transport on overall observed reaction kinetics in carbon dioxide/water systems. Rate data for a reaction were required to validate this model. Benzoyl halide hydrolysis:

\[
\begin{align*}
X & \quad \text{Z} + \text{H}_2\text{O} \quad \rightarrow \quad \text{HO} & \quad \text{Z} + \text{HX}
\end{align*}
\]

\text{Reaction A}

$X =$ leaving group, \textit{e.g.} F, Cl, Br
$Z =$ substitution group, \textit{e.g.} \textit{para-OCH}_3

was chosen for several reasons. First, benzoyl halides are virtually water-insoluble but are highly CO\textsubscript{2}-soluble. Conversely, benzoic acids are preferentially solubilized by water (roughly 10:1 in molar units at experimental conditions\textsuperscript{60} for benzoic acid). Second,
hydrolysis of benzyol halides is irreversible, greatly facilitating interpretation of kinetic data. Third, hydrolysis of benzyol halides in water can be treated as a first-order reaction.

Earlier research indicates that benzyol halide hydrolysis is confined primarily to the water phase. The reported intrinsic rate constant for benzyol chloride hydrolysis in pure water \( (k_{\text{rxn}}) \) is approximately \( 1.4 \pm 0.3 \, \text{s}^{-1} \) (25 °C, 1 bar).\(^{61-66}\) Although no data are available for the hydrolysis of benzyol halides in dense carbon dioxide, some measurements have been reported in nonpolar solvents. The reported apparent second-order rate constant in dioxane/water mixtures is approximately \( 2 \times 10^{-5} \, \text{L mol}^{-1} \, \text{s}^{-1} \).\(^{67}\) If one accounts for differences in the water concentration (i.e., 55.6 mol L\(^{-1}\) as compared to 0.1 mol L\(^{-1}\)), the true second-order rate constant for benzyol chloride hydrolysis in the non-polar dioxane mixture is roughly 700x smaller than in pure water. Based on its dielectric constant\(^{68}\) of approximately at 1 room temperature and 100 bar, CO\(_2\) should also be an extremely poor solvent for this hydrolysis. Thus, to a good approximation, the hydrolysis reaction occurs only in the water phase, after transport of the benzyol chloride through the CO\(_2\) phase. Presumably, a similar ratio of hydrolysis rates in water to those in nonpolar solvents is observed for benzyol halides other than benzyol chloride (see Section 6.5.1 for further discussion).

The rapid hydrolysis of benzyol chloride in the water phase ensures that, under most circumstances, transport of the benzyol chloride (in either the carbon dioxide or water phase) will in fact be the rate-limiting step. The importance of mass-transport barriers to biphasic benzyol halide hydrolysis makes it a useful choice as a model for more complicated schemes involving homogeneous catalysis for which extremely fast chemical kinetics might be expected. A final, though quite important, reason for selecting this model reaction is that an earlier study of hydrolysis of benzyol chloride in a water/carbon dioxide microemulsion\(^{28}\) can be used for bench-marking our measurements.

Hydrolysis measurements of a series of benzyol halides can further unravel the contributions of intrinsic kinetics, thermodynamics (in particular the effect of partition coefficient, \( K_{\text{E/W}} \)), and mass transport to the apparent overall rate constants. The reaction rate constant in pure water, \( k_{\text{rxn}} \), can be varied substantially by changing the halide leaving group (\( \mathcal{X} \), in equation A) and/or the substitution group (\( \mathcal{Z} \), in reaction A), but the effect of \( \mathcal{X} \) and \( \mathcal{Z} \) on both the partition coefficient and diffusion coefficient is
much less dramatic. Thus, in principle, it should be possible to vary X and Z in a systematic way such that the effects of intrinsic kinetics and mass transport can be separated quantitatively. To see how this might be done, it is helpful to consider the effect of X and Z on the three physical parameters ($k_{rxn}$, $D_{AB}$, and $K_{C/W}^C$).

**Effect of leaving group (X) and substitution group (Z) on $k_{rxn}$**. Hydrolysis rates of benzoyl halides have been measured for a number of compounds (with various X's and Z's) in pure water. $k_{rxn}$ for these reactions varies over several orders of magnitude. A list of reported values of $k_{rxn}$ for the hydrolysis of benzoyl halides is presented in Table 6-1. The single most important feature of the data in Table 6-1 is that a 5-order of magnitude change in $k_{rxn}$ can be achieved simply by changing X and Z. Values of $k_{rxn}$ vary relatively continuously from $3 \times 10^{-4}$ ($p$-anisoylbenzoyl fluoride) to roughly $10$ s$^{-1}$ ($p$-anisoyl chloride). In general, benzoyl fluorides react more slowly than benzoyl chlorides.

Reproducibility of rate constant measurements can be quantified by examining benzoyl chloride. Six measurements of $k_{rxn}$ have been reported for this compound, the values of which vary from 0.86 to 1.8 s$^{-1}$. The average of these 6 values is $1.4$ s$^{-1}$ and the calculated standard deviation is $0.3$ s$^{-1}$. All reported data fall within 50% of this average value. Reported rate constants for less reactive compounds (i.e., benzoyl fluoride, $p$-nitrobenzoyl chloride) are more reproducible than those for benzoyl chloride. The kinetics of liquid phase reactions with half lives faster than 1 s are subject to errors associated with finite mixing times. For reactions with half-lives slower than 10 s (i.e., $k_{rxn} < 0.1$ s$^{-1}$), mixing times are not a significant source of error in stop-flow kinetic experiments and rate constant measurements are more reproducible and reliable.

**Effect of X and Z on Diffusion Coefficients**. Although the binary molecular diffusion coefficients of benzoyl halides have not been measured in either water or carbon dioxide, infinite dilution diffusion coefficients for a number of similar organic compounds are reported in the literature. Table 6-2a is a list of infinite dilution diffusion coefficients of organic solutes in water at 25 °C and 1 bar. Most of the compounds presented in Table 6-2a (and Table 6-2b, below) are substituted benzenes, selected on the basis of their molecular similarity to the benzoyl halides. Data for acetone and naphthalene are also
Table 6-1. Reported values of $k_{\text{rxn}}$ for benzoyl halides for a variety of $X$s and $Z$s measured at 25 °C and 1 bar.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$X$</th>
<th>$Z$</th>
<th>$k_{\text{rxn}}$ (s$^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-anisoylbenzoyl fluoride</td>
<td>F</td>
<td>$p$-OCH$_3$</td>
<td>2.90$x10^{-4}$</td>
<td>[62]</td>
</tr>
<tr>
<td>$p$-methylbenzoyl fluoride</td>
<td>F</td>
<td>$p$-CH$_3$</td>
<td>7.9$x10^{-4}$</td>
<td>[69]</td>
</tr>
<tr>
<td>$p$-fluorobenzoyl fluoride</td>
<td>F</td>
<td>$p$-F</td>
<td>1.7$x10^{-3}$</td>
<td>[69]</td>
</tr>
<tr>
<td>benzyol fluoride</td>
<td>F</td>
<td>H</td>
<td>1.80$x10^{-3}$</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.0$x10^{-3}$</td>
<td>[69]</td>
</tr>
<tr>
<td>$p$-dimethylamine benzoyl fluoride</td>
<td>F</td>
<td>$p$-N(CH$_3$)$_2$</td>
<td>3.50$x10^{-3}$</td>
<td>[62]</td>
</tr>
<tr>
<td>$m$-chlorobenzoyl fluoride</td>
<td>F</td>
<td>$m$-Cl</td>
<td>9.00$x10^{-3}$</td>
<td>[62]</td>
</tr>
<tr>
<td>$m$-trifluoromethyl benzoyl chloride</td>
<td>Cl</td>
<td>$m$-CF$_3$</td>
<td>0.034</td>
<td>[62]</td>
</tr>
<tr>
<td>$p$-nitrobenzoyl fluoride</td>
<td>F</td>
<td>$p$-NO$_2$</td>
<td>0.051</td>
<td>[62]</td>
</tr>
<tr>
<td>$m$-chlorobenzoyl chloride</td>
<td>Cl</td>
<td>$m$-Cl</td>
<td>0.056</td>
<td>[62]</td>
</tr>
<tr>
<td>$p$-nitrobenzoyl chloride</td>
<td>Cl</td>
<td>$p$-NO$_2$</td>
<td>0.0575</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.053</td>
<td>[63]</td>
</tr>
<tr>
<td>$p$-bromobenzoyl chloride</td>
<td>Cl</td>
<td>$p$-Br</td>
<td>0.190</td>
<td>[63]</td>
</tr>
<tr>
<td>3,5-dinitrobenzoyl chloride</td>
<td>Cl</td>
<td>3,5-NO$_2$</td>
<td>0.20</td>
<td>[63]</td>
</tr>
<tr>
<td>$p$-chlorobenzoyl chloride</td>
<td>Cl</td>
<td>$p$-Cl</td>
<td>0.214</td>
<td>[63]</td>
</tr>
<tr>
<td>$m$-anisoyl chloride</td>
<td>Cl</td>
<td>$m$-OCH$_3$</td>
<td>0.6</td>
<td>[62]</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>Cl</td>
<td>H</td>
<td>0.86$^a$</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.41</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.4</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.67</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.8$^b$</td>
<td>[66]</td>
</tr>
<tr>
<td>$p$-methylbenzoyl chloride</td>
<td>Cl</td>
<td>$p$-CH$_3$</td>
<td>5</td>
<td>[63]</td>
</tr>
<tr>
<td>$p$-anisoyl chloride</td>
<td>Cl</td>
<td>$p$-OCH$_3$</td>
<td>11$^c$</td>
<td>[63]</td>
</tr>
</tbody>
</table>

$^a$ The original reference contains a decimal point error, the value reported here is correct.

$^b$ Conducted in CO$_2$-free water.

$^c$ Value reported is an estimate; the reaction was too fast for accurate measurement.

presented for comparison. The measured diffusivities for all of these compounds are tightly distributed around $1 \times 10^{-5}$ cm$^2$ s$^{-1}$, within the variability in the measurements of the diffusion coefficient of benzoic acid.
Table 6-2a. Literature values of infinite dilution diffusion coefficients of organic solutes in liquid water at 25 °C and 1 bar.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D_{aw}^{*}$ (10$^5$ cm$^2$ s$^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>1.28</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>1.17</td>
<td>[71]</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>1.30</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>1.11</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>1.005</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td>0.935</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>0.928</td>
<td>[79]</td>
</tr>
<tr>
<td>benzene</td>
<td>1.09</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>[72]</td>
</tr>
<tr>
<td>aniline</td>
<td>1.05</td>
<td>[82]</td>
</tr>
<tr>
<td>benzyl alcohol</td>
<td>0.93</td>
<td>[83]</td>
</tr>
<tr>
<td>toluene</td>
<td>0.93</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>0.915</td>
<td>[83]</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>0.90</td>
<td>[83]</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.749</td>
<td>[83]</td>
</tr>
</tbody>
</table>

Table 6-2b lists literature values for infinite dilution diffusion coefficients of organic solutes in carbon dioxide at conditions near 30 °C and 100 bar. The values of $D_{ac}$ presented in Table 6-2b are centered around roughly 1.5 x 10$^{-4}$ cm$^2$ s$^{-1}$, more than 10-fold greater than in water at the same temperature. Diffusion is faster in carbon dioxide than water, behavior which is attributed to the lower viscosity$^{42}$ of the dense gas. Both pressure and temperature influence diffusion coefficients in dense carbon dioxide, as expected. $D_{ac}$ varies by only 50% for the diverse group of compounds presented in Table 6-2b. Comparing the data presented in Table 6-1 with that in Table 6-2a,b strongly suggests that reactivity can be varied independently of the diffusion coefficient.
Table 6-2b. Literature values of infinite dilution diffusion coefficients of organic solutes in dense liquid carbon dioxide at conditions near 30 °C and 100 bar.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D_{Ac}$ (10^8 cm^2 s^-1)</th>
<th>$T$ (°C)</th>
<th>$P$ (bar)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>12.6</td>
<td>40</td>
<td>160</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>13.8 ± 0.3</td>
<td>30</td>
<td>115</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>14.1</td>
<td>30</td>
<td>160</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>12.99</td>
<td>40</td>
<td>150</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>16.131</td>
<td>40</td>
<td>120</td>
<td>[88]</td>
</tr>
<tr>
<td>toluene</td>
<td>12.35</td>
<td>40</td>
<td>160</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>30</td>
<td>160</td>
<td>[86]</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>12.06</td>
<td>40</td>
<td>160</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>12.15</td>
<td>40</td>
<td>160</td>
<td>[87]</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>12.3 ± 0.8</td>
<td>25</td>
<td>71</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>13 ± 1</td>
<td>35</td>
<td>75</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>13.4 ± 1.9</td>
<td>25</td>
<td>71</td>
<td>[90]</td>
</tr>
<tr>
<td>acetone</td>
<td>14 ± 0.5</td>
<td>30</td>
<td>115</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>13.8</td>
<td>30</td>
<td>160</td>
<td>[87]</td>
</tr>
<tr>
<td>naphthalene</td>
<td>11.3 ± 0.2</td>
<td>30</td>
<td>115</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>11.3 ± 1.1</td>
<td>45</td>
<td>160</td>
<td>[90]</td>
</tr>
</tbody>
</table>

Effect of X and Z on Partition Coefficients. Since benzyol halides react rapidly with water, direct measurement of water/carbon dioxide partition coefficients is not possible. Instead, the correlations from Chapter 3 were used to predict the effect of $X$ and $Z$ on reagent partitioning at 30 °C and 80 bar (which corresponds to a fluid density of 0.75 g cm^-3). LSERs were the most accurate and robust estimation method presented in Chapter 3 and are the best method available for estimating unknown partition coefficients. The necessary solute descriptors were available for benzyol fluoride, chloride, and bromide, so that the LSER method could be used to estimate these $K_{cw}$ values directly. Then, using the LSER estimates of benzyol fluoride, chloride and bromide as starting points, the group contribution method was used to determine perturbations from the base value arising from the substitution groups. In this fashion, LSER estimates of $K_{cw}$ for the three parent compounds could be extended to a wide array of substituted benzyol halides.

The LSER/group contribution method estimates of $K_{cw}$ are presented in Table 6-3. Both Table 6-1 and 6-3 contain the same set of compounds, with the exceptions of $p$-trifluoromethylbenzyol fluoride and $p$-dimethylaminebenzyol fluoride which appear in
Table 6-1 only. These two compounds contain functional groups not considered in Chapter 3 and the estimated values of $K_{cw}$ are not reliable. For all other compounds, errors were estimated based on $\pm 0.13 \log_{10}$ unit accuracy of the predictions, which assumes that all of the error is contained within the LSER correlation itself. This is a reasonable assumption since the group contribution method corrections constitute small perturbations from the LSER base estimates. In mole fraction units, $\log_{10} K_{cw}$ for the parent compounds is approximately 2.5, while the contribution of functional groups is generally less than $\pm 0.5 \log_{10}$ units, except for the halogenated and methylated compounds which appear at the end of Table 6-3.

In Section 3.5, it was suggested that multiple methods should be used to estimate $K_{cw}$. Unfortunately, the only method which could be used for benzoil halides was the LSER. This is because the other two methods (i.e., octanol/water partitioning and correlation to water solubility) require water-phase data which is not accessible for the highly reactive benzoil halides.

One important note regarding the units of partition coefficients is necessary. In Section 3.2, a distinction was made between mole-fraction based ($K'_{cw}$) and molarity

<table>
<thead>
<tr>
<th>Compound</th>
<th>$X$</th>
<th>$Y$</th>
<th>$K_{cw}$ (molar units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-nitrobenzoyl fluoride</td>
<td>F</td>
<td>$p$-NO$_2$</td>
<td>110 $\pm$ 30</td>
</tr>
<tr>
<td>benzoyl fluoride</td>
<td>F</td>
<td>H</td>
<td>120 $\pm$ 30 (LSER)</td>
</tr>
<tr>
<td>3,5-dinitrobenzoyl chloride</td>
<td>Cl</td>
<td>3,5-NO$_2$</td>
<td>120 $\pm$ 40</td>
</tr>
<tr>
<td>$p$-nitrobenzoyl chloride</td>
<td>Cl</td>
<td>p-NO$_2$</td>
<td>130 $\pm$ 40</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>Cl</td>
<td>H</td>
<td>140 $\pm$ 40 (LSER)</td>
</tr>
<tr>
<td>benzoil bromide</td>
<td>Br</td>
<td>H</td>
<td>160 $\pm$ 50 (LSER)</td>
</tr>
<tr>
<td>$p$-anisoyl fluoride</td>
<td>F</td>
<td>$p$-OCH$_3$</td>
<td>190 $\pm$ 60</td>
</tr>
<tr>
<td>$m$-anisoyl chloride</td>
<td>Cl</td>
<td>m-OCH$_3$</td>
<td>220 $\pm$ 70</td>
</tr>
<tr>
<td>$p$-anisoyl chloride</td>
<td>Cl</td>
<td>$p$-OCH$_3$</td>
<td>220 $\pm$ 70</td>
</tr>
<tr>
<td>$p$-fluorobenzoyl fluoride</td>
<td>F</td>
<td>$p$-F</td>
<td>230 $\pm$ 70</td>
</tr>
<tr>
<td>$p$-methyl benzoyl fluoride</td>
<td>F</td>
<td>$p$-CH$_3$</td>
<td>600 $\pm$ 200</td>
</tr>
<tr>
<td>$p$-methyl benzoyl chloride</td>
<td>Cl</td>
<td>$p$-CH$_3$</td>
<td>600 $\pm$ 200</td>
</tr>
<tr>
<td>$m$-chlorobenzoyl chloride</td>
<td>Cl</td>
<td>$m$-Cl</td>
<td>700 $\pm$ 200</td>
</tr>
<tr>
<td>$p$-chlorobenzoyl chloride</td>
<td>Cl</td>
<td>$p$-Cl</td>
<td>700 $\pm$ 200</td>
</tr>
<tr>
<td>$p$-bromobenzoyl chloride</td>
<td>Cl</td>
<td>$p$-Br</td>
<td>900 $\pm$ 300</td>
</tr>
</tbody>
</table>
Based ($K_{cw}^*\,\text{partition coefficients}$. For the analysis of reaction dynamics, $K_{cw}^*$ is more useful and will be used exclusively in the analysis presented later in this chapter. From this point on, all partition coefficients will be referred to as $K_{cw}$ with the understanding that molar units are in use.

The values of $K_{cw}$ presented in Table 6-3 vary by roughly one order of magnitude. For a large subset of the compounds (from $p$-nitrobenzoyl chloride to $p$-fluorobenzoyl fluoride in Table 6-3), the variation is a factor of two. It is possible to select compounds with a large variation in intrinsic reactivity (based on Table 6-1), with only small variations of $K_{cw}$ (from Table 6-3). This result, combined with the narrow ranges of diffusion coefficients in Table 6-2a and 6-2b, shows that benzoyl halide reactivity can be varied widely (over as many as 5 orders of magnitude) while the other relevant physical parameters remain constant (within a multiple of 2).

6.5 Hydrolysis of Benzoyl Halides: Experimental Procedures and Results

**Experimental Protocol.** The acoustic reactor/sonication system described in Section 4.5.1 was used for these experiments. Agitation was supplied either as described in Section 6.3 or using a Teflon-coated, magnetically-coupled stir bar. The sonic probe was inserted directly in the aqueous phase. The distance between the tip of the horn and the carbon dioxide/water interface was kept constant at 2 cm. It was shown in Section 4.5.2 that pulsed ultrasound (at an acoustic frequency of 20 kHz and a duty cycle of 20% on a 2.5 s cycle or 25% on a 1.0 s cycle) could be used to maintain turbid emulsions until sonication was terminated. Pulsed ultrasound minimizes total power input to the system, reducing sonic heating of the reaction mixture. For these reasons, pulsing was used for all sonicated experiments, typically with a duty cycle of either 20 (2.5 s cycle) or 25% (1.0 s cycle). The ultrasound power density was varied between 0-0.8 W cm$^{-3}$ for the hydrolysis of benzoyl chloride. For all other halides (see below), the power density was maintained at a value of 0.6 W cm$^{-3}$.

All experiments were conducted at 30 °C and 80 bar. This temperature and pressure were selected for two reasons: 1) pure phase kinetic data are generally available at or near 30 °C, 2) 30 °C is a low enough temperature that carbon dioxide attains a liquid-like density and good solvation power at pressures below 100 bar. Initially, it was
hypothesized that emulsification would be most efficient close to the vapor pressure of carbon dioxide, though this assumption was challenged by the results presented in Chapter 5. Nonetheless, effective emulsification was observed at 30 °C and 80 bar as described in Chapters 4 and 5, making these conditions convenient choices for the operating temperature and pressure.

Table 6-4 lists the benzoyl halides which were selected for these experiments, along with estimated partition coefficients, and hydrolysis rate constants in pure water (if available). These compounds represent a wide range of reactivities and were available commercially in purities greater than 98% (Sigma Aldrich). Commercial availability was important because laboratory synthesis of pure benzoyl halides is complicated by acid contamination. Benzoyl bromide and o-anisoyl chloride were included in this study even though no accurate measurements of their hydrolysis rates are available. In fact, these compounds react so quickly with water that accurate measurement of $k_{\text{rxn}}$ is a challenge even for a conventional stop-flow apparatus.\(^2\) Crude estimation of $k_{\text{rxn}}$ using a combined computational chemistry/Evans-Polanyi analysis suggests that the hydrolysis rates of benzoyl bromide and o-anisoyl chloride are between 1-100 s\(^{-1}\). This uncertainty notwithstanding, carbon dioxide/water data for these two compounds are qualitatively useful for isolating the effects of extremely fast reaction kinetics.

**Table 6-4.** Benzoyl halides selected for carbon dioxide/water hydrolysis experiments. Sources for literature values of $k_{\text{rxn}}$ are the same as Table 6-1.

<table>
<thead>
<tr>
<th>Halide</th>
<th>$k_{\text{rxn}}$ (s(^{-1}))</th>
<th>$K_{\text{CW}}$ (estimated, molar units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoyl fluoride</td>
<td>$2 \times 10^{-3}$</td>
<td>120 ± 30</td>
</tr>
<tr>
<td>p-nitrobenzoyl chloride</td>
<td>0.05</td>
<td>130 ± 40</td>
</tr>
<tr>
<td>m-anisoyl chloride</td>
<td>0.5</td>
<td>220 ± 70</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>1.3(^a)</td>
<td>140 ± 40</td>
</tr>
<tr>
<td>p-anisoyl chloride</td>
<td>11</td>
<td>220 ± 70</td>
</tr>
<tr>
<td>benzoyl bromide</td>
<td>fast(^b)</td>
<td>160 ± 50</td>
</tr>
<tr>
<td>o-anisoyl chloride</td>
<td>fast(^b)</td>
<td>220(^c) ± 70</td>
</tr>
</tbody>
</table>

\(^a\) The average value from Table 6-1 is used here.

\(^b\) Reactions too fast to be accurately measured in pure water, see text for more discussion.

\(^c\) $K_{\text{CW}}$ for o-anisoyl chloride is assumed to be equal to that of the para and meta substituted analogs, though the group contribution method in Chapter 3 is not reliable for ortho substituted solutes.
The experimental procedure was identical to that described in Section 6.3 except that the water loading was 40 cm$^3$. Different quantities of the halide reactant (between $5 \times 10^{-6}$ and $1 \times 10^{-4}$ mol) were injected into the reactor. Under these conditions, benzoyl halide is the limiting reagent. The corresponding initial concentrations of halide in the carbon dioxide phase ranged between 0.1 and $10 \times 10^{-3}$ mol L$^{-1}$, and the initial concentration had no effect on observed kinetics. This observation indicates that the halide was always completely dissolved in the carbon dioxide phase, otherwise, it would form a separate, third phase. Given that the density of the benzoyl halides is greater than water, this halide-rich phase would sink to the bottom of the vessel and promptly react. The volume of the halide-rich phase would vary with the amount of injected halide leading to a strong dependence of the observed kinetic rate constant on initial halide concentration. Because we never observed such dependence, it is reasonable to assume that the halides were completely dissolved in the carbon dioxide. Visual inspection through the windows of the reactor supported this conclusion.

Samples withdrawn from the aqueous phase were analyzed for organic acid. The analysis was conducted by either GC (Agilent, 6890), equipped with a SPB-5 column (Supelco) and flame-ionization detector (FID), or by UV absorption at roughly 280 nm (Varian, Cary 50). The exact wavelength of maximum sensitivity varied with the compound to be analyzed and was determined prior to kinetic experiments. The GC was used to analyze samples from experiments with benzoyl fluoride, chloride, and bromide. The GC separates the acid product from the unreacted halide and any potential byproducts prior to quantification, which is a distinct advantage for analyzing mixtures. In practice, only trace amounts of benzoyl fluoride (the most stable reagent) were detected in reactor samples with the GC. Efforts to quench the reaction upon sampling were made to ensure that unreacted halide present in the reactor water phase survived until analysis. Specifically, samples were immediately diluted (roughly 1:10) using cold tetrahydrofuran (0 °C) and the analysis was performed within minutes of dilution. The fact that halides more reactive than benzoyl fluoride were not detected by this quenching procedure is not surprising given their extremely short half-lives. No byproducts were detected by GC, meaning that samples from the reactor contained only acid and solvent and did not require separation prior to quantification. This simplified the chemical analysis.
UV absorption was used for quantification of samples from experiments using benzoyl chloride, the anisoyl chlorides, and \(p\)-nitrobenzoyl chloride. The detection limit for UV absorption was roughly 0.1 ppm, which is 10-fold lower than the detection limit of the GC technique. The greater sensitivity of the analytical technique allowed lower concentrations of halides to be used than otherwise would have been possible, which served to increase the accessible range of initial concentrations of halide reactant for better confirmation of two-phase behavior. Rates measured for benzoyl chloride hydrolysis based on parallel chemical analysis by the GC and UV techniques agreed with one another to within the limits of experimental reproducibility (± 5%).

The measured concentration of acid in the water phase was used to determine the concentration of unreacted halide by a mole balance:

\[
n_{\text{Halide, CO}_2}(t) = n_{\text{Halide, CO}_2}(t = 0) - n_{\text{acid, water}}\tag{6-12}
\]

Equation (6-12) assumes that the concentration of acid in the carbon dioxide phase and the concentration of benzoyl halide in the water phase are both negligible. Based on the literature values for the partition coefficient of benzoic acid,\(^5\) the former assumption is true to within ±10% while the estimated partition coefficient of benzoyl halides indicates that the latter is true to within ±1%. The remaining moles of halide at any given time were used to determine the disappearance rate of the reactant. After each experiment, the contents of the reactor were collected, mixed with water to complete the reaction, and analyzed for the acid product. Mass balance closure was complete to within ±5% on average and within 15% in the worst case.

**Effect of mixing and sample position on observed hydrolysis rates.** Experiments were conducted to determine the effects of mixing and sample position on measured hydrolysis rates. The hydrolysis of benzoyl chloride under silent conditions was used as the test case. Hydrolysis experiments were conducted either quiescently or with mixing provided by the recirculation pump or the Teflon-coated stir bar. Within the limits of experimental reproducibility (± 5%), there was no effect of mixing on the observed disappearance rates or hydrolysis rate constants. Furthermore, different sampling positions (either 1 or 5 cm from the carbon dioxide/water interface) were tested with no apparent difference in observed hydrolysis rate constants within the limits of experimental reproducibility.
These experiments verified that, at least in the bulk, the two phases were well-mixed, supporting the use of the film theory for mass transport.

**Effect of power on hydrolysis rates.** Hydrolysis kinetics of benzoyl chloride were measured without ultrasound (i.e., under silent conditions) and under conditions of pulsed ultrasound (20% duty of a 2.5 s cycle at 20 kHz) from 0.05 to 0.77 W cm\(^{-3}\). Under all conditions, the rate of disappearance of benzoyl chloride was described adequately by apparent first-order kinetics, as depicted in Figure 6-3. The slopes of the first-order plots of Figure 6-3 are interpreted as the apparent first-order rate constant \(k^*\). An alternative means of confirming first order kinetics is to determine the dependence of the rate on the initial concentrations of reactants. Varying the initial concentration of the limiting reagent from 0.1-10 \(\times 10^{-3}\) L\(^{-1}\) at a fixed power density had no effect on \(k^*\), further evidence of first order dependence with respect to the benzoyl halide. Kinetic data from the silent hydrolysis of benzoyl bromide demonstrates the invariance of the rate constant with initial reactant concentration. In a set of 3 runs, performed at an initial concentration

![Graph showing first-order plots for benzoyl chloride hydrolysis](image)

**Figure 6-3.** Representative assumed first order plots for benzoyl chloride hydrolysis in carbon dioxide/water mixtures as a function of power. \([A]_C\) is the instantaneous and \([A]_{C0}\) is the initial concentration of benzoyl halide in the carbon dioxide phase. Conditions: 30 °C, 80 bar, pulsed ultrasound at 25% of a 2.5 s cycle, 20 kHz, 45% water by volume. The slopes of these plots were taken as \(k^*\) and are plotted in Figure 6-4 as a function of power.
of halide equal to $9 \times 10^{-3}$ mol L$^{-1}$, the apparent first order rate constant was measured as $1.74 \pm 0.1 \times 10^{-4}$ s$^{-1}$, while in a second set of 2 runs, with an initial reactant concentration of $5 \times 10^{-3}$ mol L$^{-1}$, the measured rate constant was $1.69 \pm 0.1 \times 10^{-4}$ s$^{-1}$.

Figure 6-4 is a plot of $k^*$ as a function of applied power density. The magnitude of $k^*$ increased very significantly from its silent value of about $1 \times 10^{-5}$ s$^{-1}$ with application of even low intensity power ultrasound (less than 0.11 W cm$^{-3}$). Above about 0.50 W/cm$^3$, the ultrasonic effect saturates at a value of roughly $1 \times 10^{-3}$ s$^{-1}$, i.e., two orders of magnitude greater than its silent value. The value of $k^*$ at saturation is also much greater than the largest reported rate constant for hydrolysis of benzoyl chloride in a water/carbon dioxide microemulsion,$^{29} 5 \times 10^{-5}$ s$^{-1}$.

![Figure 6-4](image.png)

**Figure 6-4.** First order rate constant ($k^*$) as a function of applied power density. The rate at zero applied power (i.e., silent conditions) is $1 \times 10^{-5}$ s$^{-1}$. Conditions: 30 °C, 80 bar, pulsed ultrasound at 25% of a 2.5 s cycle, 20 kHz, 45% water by volume.
Chapter 6: Hydrolysis of Benzoyl Halides

Although the sigmoidal shape of $k^*$ with respect to power density is familiar to sonochemists, the experimental observations of KI oxidation presented in Chapter 5 suggest that sonochemical considerations are not important in the high-pressure carbon dioxide/water system. A more likely explanation, based solely on the physical effects of ultrasound, is presented in Section 6.5.3.

**Effect of X and Z on $k^*$**. The effects of leaving group and substitution groups on $k^*$ was determined for all of the compounds listed in Table 6-4. Experiments were conducted both silently (to determine $k^*_{\text{silent}}$) and acoustically (to determine $k^*_{\text{sonic}}$). Pulsed ultrasound (25% of a 1 s cycle at 20 kHz) at a power density equal to 0.6 W cm$^{-3}$ was used for all sonicated experiments. This power density was selected based on both the saturation value observed for benzoyl chloride hydrolysis and the maximum amount of emulsification possible in our acoustic reactor (Chapter 4).

Representative first-order plots are presented in Figure 6-5a (silent cases) and 6-5b (sonicated cases). At least two separate runs were performed for the hydrolysis of each compound and between 3 and 6 samples were taken in each run. Data points from all available runs were pooled for a given compound and set of conditions (i.e., silent or sonicated) and used to determine an overall value for $k^*$. Table 6-5 lists the best-fit values of $k^*$ and the ratios of $k^*_{\text{sonic}}$ to $k^*_{\text{silent}}$ (i.e., sonic enhancement). The numbers of separate runs ($r$) that were conducted and samples ($n$) that were collected for each value of $k^*$ are also listed in Table 6-5. Statistically based errors in the best-fit slopes are reported in Table 6-5 at the 95% level of confidence.

From Table 6-5, both $k^*_{\text{silent}}$ and $k^*_{\text{sonic}}$ are functions of $k_{\text{rxn}}$ over its entire range. This indicates that the chemical reaction is involved in the rate determining step. In all cases, $k^*_{\text{silent}}$ is less than $k^*_{\text{sonic}}$ and the ultrasonic effect is accelerative. The least reactive halides (e.g., benzoyl fluoride) are accelerated only modestly (less than 10-fold), while more reactive halides (e.g., benzoyl chloride) are accelerated more than 100-fold. Interestingly, the most reactive halides (e.g., benzoyl bromide) are accelerated modestly as well (roughly 20 fold). Furthermore, $k^*_{\text{sonic}}$ is always smaller than $k_{\text{rxn}}$, which is simply a consequence of basing the rate constant on the concentration in the carbon
Figure 6-5. Representative assumed first order plots for benzoyl halide hydrolysis in carbon dioxide/water mixtures under (a) silent conditions and (b) sonicated conditions. $[A]_c$ is the instantaneous and $[A]_{C0}$ is the initial concentration of benzoyl halide in the carbon dioxide phase. Conditions: 30 °C, 80 bar, 45% water by volume. Ultrasound pulsed at 25% of a 1 s cycle, 20 kHz frequency, 0.60 W cm$^{-3}$ power density. The slopes of these plots were taken to be $k^*$ and are listed in Table 6-5.
Table 6-5. Observed hydrolysis rate constants of benzoyl halides under silent ($k_{\text{s} silent}$) and sonicated ($k_{\text{sonic}}$) conditions. The number of runs ($r$) and the total number of data points ($n$) is listed. The sonic enhancement factor, the ratio of $k_{\text{sonic}}$ to $k_{\text{s} silent}$, is calculated. Data collected at 30°C and 80 bar. Errors are absolute, based on the 95% confidence intervals of the best-fit slopes in assumed first-order plots.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$k_{\text{rxn}}$ (s$^{-1}$)</th>
<th>$k_{\text{s} silent}$ (s$^{-1}$)</th>
<th>$r$</th>
<th>$n$</th>
<th>$k_{\text{sonic}}$ (s$^{-1}$)</th>
<th>$r$</th>
<th>$n$</th>
<th>$k_{\text{sonic}} / k_{\text{s} silent}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoyl fluoride</td>
<td>2.0x10$^{-3}$</td>
<td>1.7 ± 0.1 x 10$^{-6}$</td>
<td>2</td>
<td>7</td>
<td>7.7 ± 0.2 x 10$^{-6}$</td>
<td>2</td>
<td>9</td>
<td>4.6</td>
</tr>
<tr>
<td>p-nitrobenzoyl chloride</td>
<td>0.05</td>
<td>1.7 ± 0.1 x 10$^{-5}$</td>
<td>2</td>
<td>7</td>
<td>4.6 ± 0.2 x 10$^{-4}$</td>
<td>2</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>m-anisoyl chloride</td>
<td>0.5</td>
<td>3.3 ± 0.3 x 10$^{-6}$</td>
<td>3</td>
<td>12</td>
<td>7.0 ± 0.4 x 10$^{-4}$</td>
<td>4</td>
<td>19</td>
<td>210</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>1.3$^b$</td>
<td>1.10±0.04x10$^{-5}$</td>
<td>4</td>
<td>18</td>
<td>1.8 ± 0.2 x 10$^{-3}$</td>
<td>5</td>
<td>18</td>
<td>160</td>
</tr>
<tr>
<td>p-anisoyl chloride</td>
<td>11</td>
<td>6.5 ± 0.1 x 10$^{-5}$</td>
<td>2</td>
<td>11</td>
<td>3.6 ± 0.3 x 10$^{-3}$</td>
<td>3</td>
<td>12</td>
<td>60</td>
</tr>
<tr>
<td>benzoyl bromide</td>
<td>fast$^c$</td>
<td>1.7 ± 0.1 x 10$^{-4}$</td>
<td>4</td>
<td>16</td>
<td>3.3 ± 0.2 x 10$^{-3}$</td>
<td>3</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>o-anisoyl chloride</td>
<td>fast$^c$</td>
<td>1.05±0.05x10$^{-3}$</td>
<td>3</td>
<td>17</td>
<td>0.027 ± 0.002</td>
<td>4</td>
<td>10</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Defined as the pseudo-first order rate constant for hydrolysis as measured in pure water (see Table 6-1).
$^b$ The average value from Table 6-1 is used here.
$^c$ Reactions too fast to be measured accurately in pure water, see text for more discussion.

dioxide phase. Presumably the hydrolysis rate in the water phase remains $k_{\text{rxn}}$ and the discrepancy between the measurements and this rate constant is due to reagent partitioning and finite transport rates.

6.6 Theoretical Interpretation of Benzoyl Halide Hydrolysis

At this point it was possible to derive mathematical models for transport/reaction in the biphasic system, using the data in Table 6-5 as validation. The objective was development of physical expressions which were independent of any fitting parameters. The structure of this section is as follows. First, the case of reaction/transport in the silent, un-emulsified system is considered. A mathematical model is formulated and its
predictions are compared to the available data set. The model accurately predicts the observed trends in $k^*_{\text{silent}}$ with $k_{\text{rxn}}$ but underpredicts $k^*_{\text{silent}}$ for $k_{\text{rxn}} > 10 \text{ s}^{-1}$. Hydrolysis of halide in the carbon dioxide phase is suggested to explain the discrepancy. Second, the sonicated, emulsified case is considered. A mathematical model is proposed which is based on three contributions: 1) the carbon dioxide/water emulsion, 2) the water/carbon dioxide emulsion and 3) the film model used for the un-emulsified system. Inclusion of hydrolysis in the carbon dioxide phase has little effect on the combined emulsion model and predictions of $k^*_{\text{sonic}}$ are reasonably good (nearly within the limits of experimental error) for the entire range of $k_{\text{rxn}}$.

6.6.1 Silent case

The modeling strategy for silent case was to develop a dynamic mass balance on the concentration of halide in the carbon dioxide phase, $[A]_C$, using an expression for the flux of reactant to the water phase. The film theory of mass transport presented in Section 6.3 will be used as the basis for modeling this flux. Introduction of reaction to the film model potentially accelerates the flux of reagent through the water film, and to properly account for this, reaction/transport in the film must be modeled accurately. Figure 6-6 is a qualitative schematic of the water film which will be used throughout this analysis. Section 6.3 suggests that the carbon dioxide phase should be well mixed, but this assumption will be verified in the presence of reaction once an expression for the reaction enhanced flux through the water film has been formulated. In Figure 6-6, the concentration of reagent decreases from that at the interface (i.e., $[A]_m$) to that in the bulk (i.e., $[A]_W$) over the thickness of the film. $[A]_W$ does not necessarily equal zero in the general case.

It is necessary to determine the concentration of reagent, $A$, as a function of the distance $y$, within the film. Assuming that a steady state exists within the film yields the following governing equation applicable for a first-order rate law:

$$D_{AW} \frac{d^2[A]}{dy^2} = k_{\text{rxn}} [A]$$  \(6-13a\)

The boundary conditions are:
Figure 6-6. Film model for mass transport/chemical reaction. $[A]_{\text{int}}$ is the concentration of reactant on the water side of the interface, $[A]_{\text{w}}$ is the concentration of reactant in the bulk water phase. $y_L$ is the thickness of the film, defined in the text. Qualitatively, chemical reaction depletes the reactant in the film and enhances mass transport. The carbon dioxide phase has been assumed to be well mixed, an assumption which will be verified

$$[A](y = 0) = [A]_{\text{w, int}} \quad (6-13\text{b})$$

$$[A](y = y_L) = [A]_{\text{w}} \quad (6-13\text{c})$$

where $y_L$ is the thickness of the reaction zone in the absence of reaction and is defined as:

$$y_L = \frac{D_{\text{AW}}}{k_w} \quad (6-14)$$

For fast reactions, the reaction zone will be compressed, but this behavior must be captured by the physics of the situation and cannot be artificially imposed. In equation (6-14), $k_w$ is the mass transport coefficient in the absence of chemical reaction. $k_w$ was measured as roughly $3 \times 10^{-4} \text{ cm s}^{-1}$ for this reactor geometry under silent conditions.

The solution to equation (6-13) which satisfies the boundary conditions is:

$$[A] = \frac{[A]_{\text{w, int}} \sinh \left( \gamma \left( 1 - \frac{y}{y_L} \right) \right) + [A]_{\text{w}} \sinh \left( \gamma \frac{y}{y_L} \right)}{\sinh(\gamma)} \quad (6-15)$$
where $\gamma$ is sometimes referred to as the Hatta number and is defined as:

$$\gamma = \frac{\sqrt{D_{AW}k_{\text{rxn}}}}{k_w}$$

(6-16)

We note that $\gamma^2$ is also sometimes used as the Hatta number so that care should be exercised when consulting the literature on this subject.

Equation (6-13a) assumes that reaction takes place in a region with the properties of bulk water so that $k_{\text{rxn}}$ is the appropriate rate constant for reaction. At the molecular level, there is a region at the phase boundary which is neither bulk water nor bulk carbon dioxide. The thickness of this interfacial region is on the order of several nanometers. The assumption of bulk phase kinetics in the film is valid provided that the reaction zone is much larger than the interfacial region. In the limit as $k_{\text{rxn}}$ and $\gamma$ approach zero, the estimated reaction zone is roughly 0.03 cm, a full 5 orders of magnitude larger than the hypothetical “interfacial” region. Equation (6-15), with $[A]_W = 0$, can be used to evaluate the thickness of the reaction zone for $\gamma \neq 0$. For $k_{\text{rxn}} \approx 100$ s$^{-1}$ (and $\gamma \approx 100$, incidentally), the concentration falls to 10% of its interfacial value in $6 \times 10^{-4}$ cm. The reaction film is still 1000x thicker than the interfacial region. Thus, the contribution of interfacial reactions, where $k_{\text{rxn}}$ differs from its value in bulk water, is likely negligible to within 0.1%.

To determine the flux from the carbon dioxide phase into the film, it is necessary to differentiate equation (6-14) and evaluate it at $y = 0$:

$$N_A = -D_{AW} \frac{d[A]}{dy} \bigg|_{y=0} = \frac{\gamma}{\tanh(\gamma)} \left( 1 - \frac{[A]_W}{[A]_{W \text{ int}}} \frac{1}{\cosh(\gamma)} \right) k_w [A]_{\text{int}}$$

(6-17).

The flux through the carbon dioxide film and the flux in equation (6-16) are strictly in series and are therefore equal. Equation (6-1) can thus be used to eliminate $[A]_{W \text{ int}}$ and introduce $K_{CW}$ and $k_C$:

$$N_A = \frac{[A]_C - \frac{K_{CW}[A]_W}{\cosh(\gamma)}}{1 + \frac{K_{CW}}{k_C} \frac{\tanh(\gamma)}{k_w \gamma}}$$

(6-18)

When there is no reaction, $\gamma \to 0$, $\tanh(\gamma)/\gamma \to 1$, and $\cosh(\gamma) \to 1$ so that equation (6-4) is recovered, as it must be.
Equation (6-18) includes resistances from both the water and carbon dioxide films. In Section 6.4 it was concluded that for mass transport of hydrophobic solutes in the absence of reaction, the carbon dioxide resistance is always small compared to that of the water film resistance suggesting that $k_C >> k_W K_{CW}^{-1}$. Chemical reaction in the water film decreases the resistance in the water film so that it may not be valid to ignore the carbon dioxide resistance for all cases of interest. To test the validity of ignoring the carbon dioxide film resistance, the two terms in the denominator of equation (6-18) must be evaluated for large values of $k_{xn}$. From Table 6-5, the largest $k_{xn}$ which is accurately known is 11 s$^{-1}$ (for p-anisoyl chloride). Substituting this value and characteristic values of $K_{CW} = 150$, $k_W = 3 \times 10^{-4}$ cm s$^{-1}$, and $D_{AW} = 1 \times 10^{-5}$ cm$^2$ s$^{-1}$ into the expression for the water film resistance with reaction:

$$\frac{water \hspace{1cm} film \hspace{1cm} resistance \hspace{1cm} with \hspace{1cm} reaction}{k_w} = \frac{K_{CW}}{k_w} \frac{tanh(\gamma)}{\gamma}$$

(6-19)

leads to a water film resistance of 15,000 s cm$^{-1}$. The carbon dioxide film resistance (which is equal to the reciprocal of $k_C$ assuming that reaction has no effect on transport in the carbon dioxide film and is equal to 2 x 10$^{-3}$ cm s$^{-1}$) remains 500 s cm$^{-1}$ so that the water film resistance dominates equation (6-18) even in the presence of a “fast” reaction. In fact, at least for the case of transport of the hydrophobic benzyol halides, the water film resistance is 10-fold greater than the carbon dioxide film resistance provided that $k_{xn} < 1,000$.

Negligible resistance in the carbon dioxide film simplifies equation (6-18):

$$N_A = \frac{k_wk_C}{K_{CW}} (A)_C - K_{CW} [A]_W = \frac{k_w}{K_{CW}} \frac{\gamma}{tanh(\gamma)} \left( [A]_C - \frac{K_{CW} [A]_W}{cosh(\gamma)} \right)$$

(6-20)

This flux can be incorporated directly into a dynamic mass balance for $[A]_C$:

$$\frac{d[A]_C}{dt} = -\frac{a}{V_C} \frac{[A]_C - \frac{K_{CW} [A]_W}{cosh(\gamma)}}{\frac{K_{CW}}{k_w} \frac{tanh(\gamma)}{\gamma}}$$

(6-21)
Unlike the model for mass transport with no chemical reaction, \([A]_C\) cannot be related to \([A]_W\) by a simple mass balance and a separate relationship is required. The balance for \([A]_W\) is given by the flux out of the film, based on equation (6-15), and the reaction which occurs in the bulk water phase:

\[
\text{volumetric rate of change of benzoyl halide in the bulk water phase} = \text{flux out of water film into bulk water phase} - \text{consumption of benzoyl halide in the bulk water phase} \tag{6-22a}
\]

or

\[
\frac{d[A]_W}{dt} = -D_{AW} \frac{a}{V_w} \frac{d[A]}{dy} \bigg|_{y = y_L} - k_{\text{rm}} [A]_W \tag{6-22b}
\]

Equation (6-22) requires differentiation of equation (6-15) followed by evaluation at \(y = y_L\):

\[
-D_{AW} \frac{d[A]}{dy} \bigg|_{y = y_L} = \frac{\gamma}{\tanh(\gamma)} \left(1 - \frac{[A]_{W_{\text{int}}}}{[A]_W} \frac{1}{\cosh(\gamma)}\right) k_w [A]_W \tag{6-23}
\]

It is by now well established that the resistance in the carbon dioxide film is negligible and \([A]_{W_{\text{int}}}\) can be replaced by \([A]_C / K_{CW}\). This simplifying assumption allows the balance on \([A]_W\) to be written:

\[
\frac{d[A]_W}{dt} = -\frac{\gamma}{\tanh(\gamma)} \frac{a}{V_w} k_w \left([A]_W - \frac{[A]_C}{K_{CW} \cosh(\gamma)}\right) - k_{\text{rm}} [A]_W \tag{6-24}
\]

Equations (6-19) and (6-23) represent a system of two equations and two unknowns. The mass balance equations can be re-written in more familiar forms:

\[
\frac{d[A]_C}{dt} = -\frac{a}{V_c} \frac{k_w}{K_{CW} \tanh(\gamma)} [A]_C + \frac{a}{V_c} \frac{\gamma}{\tanh(\gamma) \cosh(\gamma)} [A]_W \tag{6-25a}
\]

and

\[
\frac{d[A]_W}{dt} = \frac{a}{V_w} \frac{k_w}{K_{CW} \tanh(\gamma) \cosh(\gamma)} [A]_C - \left(\frac{a}{V_w} \frac{\gamma}{\tanh(\gamma)} + k_{\text{rm}}\right) [A]_W \tag{6-25b}
\]

which are more simply written as:

\[
\frac{d[A]_C}{dt} = -C_1 [A]_C + C_2 [A]_W \tag{6-26a}
\]
and

$$\frac{d[A]_w}{dt} = C_3 [A]_c - C_4 [A]_w$$

(6-26b)

The general solution to equation (6-26), satisfying the initial condition that $[A]_c (t = 0) = [A]_{c,0}$ and $[A]_w (t = 0) = 0$, is:

$$[A]_w = \frac{-\beta}{1 - \beta} [A]_{c,0} \exp(\lambda_1 t) + \frac{1}{1 - \beta} [A]_{c,0} \exp(\lambda_2 t)$$

(6-27a)

and

$$[A]_w = \frac{-\beta}{1 - \beta} \frac{C_1 + \lambda_1}{C_2} [A]_{c,0} \exp(\lambda_1 t) + \frac{1}{1 - \beta} \frac{C_1 + \lambda_2}{C_2} [A]_{c,0} \exp(\lambda_2 t)$$

(6-27b)

where the various constants introduced into equation (6-27) are defined as:

$$\lambda_1 = \frac{-(C_1 + C_4) + \sqrt{C_1^2 - 2C_1C_4 + C_4^2 + 4C_2C_3}}{2}$$

(6-27c)

$$\lambda_2 = \frac{-(C_1 + C_4) - \sqrt{C_1^2 - 2C_1C_4 + C_4^2 + 4C_2C_3}}{2}$$

(6-27d)

and

$$\beta = \frac{C_1 + \lambda_2}{C_1 + \lambda_1}$$

(6-27e)

At this point, we will focus our attention on equation (6-27a), since it is the concentration of reactant in the carbon dioxide which is of primary concern. All of the parameters in equation (6-27a) are known and listed in Table 6-6, thus permitting evaluation of the time constants ($\lambda_1$ and $\lambda_2$) and $\beta$. Pertinent values of the lumped parameters are presented in Table 6-7, for convenient reference. It turns out that $\lambda_2$ is 1000-fold greater than $\lambda_1$ for

<table>
<thead>
<tr>
<th>Physical description</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>water-film mass transport coefficient</td>
<td>$k_w$</td>
<td>$3 \times 10^{-4}$ cm s$^{-1}$</td>
</tr>
<tr>
<td>diffusivity of organic solute in water</td>
<td>$D_{AW}$</td>
<td>$1 \times 10^{-5}$ cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>interfacial area</td>
<td>$a$</td>
<td>20 cm$^2$</td>
</tr>
<tr>
<td>volume of water</td>
<td>$V_W$</td>
<td>40 cm$^3$</td>
</tr>
<tr>
<td>volume of carbon dioxide</td>
<td>$V_C$</td>
<td>47 cm$^3$</td>
</tr>
<tr>
<td>partition coefficient</td>
<td>$K_{CW}$</td>
<td>150</td>
</tr>
</tbody>
</table>
Table 6-7. Values of lumped parameters which appear in equation (6-27).

<table>
<thead>
<tr>
<th>Lumped Parameter</th>
<th>$1 \times 10^{-5}$</th>
<th>$1 \times 10^{-3}$</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>0.033</td>
<td>0.33</td>
<td>33.33</td>
</tr>
<tr>
<td>$C_1$ (s$^{-1}$)</td>
<td>$8.51 \times 10^{-7}$</td>
<td>$8.82 \times 10^{-7}$</td>
<td>$2.84 \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_2$ (s$^{-1}$)</td>
<td>$1.28 \times 10^{-4}$</td>
<td>$1.25 \times 10^{-4}$</td>
<td>$2.84 \times 10^{-17}$</td>
</tr>
<tr>
<td>$C_3$ (s$^{-1}$)</td>
<td>$1.00 \times 10^{-6}$</td>
<td>$9.82 \times 10^{-6}$</td>
<td>$2.23 \times 10^{-19}$</td>
</tr>
<tr>
<td>$C_4$ (s$^{-1}$)</td>
<td>$1.60 \times 10^{-4}$</td>
<td>$1.16 \times 10^{-3}$</td>
<td>10.01</td>
</tr>
<tr>
<td>$-\lambda_1$ (s$^{-1}$)</td>
<td>$5.38 \times 10^{-8}$</td>
<td>$7.76 \times 10^{-7}$</td>
<td>$2.84 \times 10^{-5}$</td>
</tr>
<tr>
<td>$-\lambda_2$ (s$^{-1}$)</td>
<td>$1.61 \times 10^{-4}$</td>
<td>$1.16 \times 10^{-3}$</td>
<td>10.01</td>
</tr>
<tr>
<td>$C_1 / \lambda_1$</td>
<td>15.82</td>
<td>1.14</td>
<td>1.00</td>
</tr>
<tr>
<td>$-\beta / (1-\beta)$</td>
<td>0.995</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>$1 / (1-\beta)$</td>
<td>$4.96 \times 10^{-3}$</td>
<td>$9.23 \times 10^{-5}$</td>
<td>0.000</td>
</tr>
</tbody>
</table>

all values of $\gamma$ of interest. $C_1$ is small compared to $\lambda_2$ and less than or equal to $\lambda_1$ so that $\beta >> 1$. As a consequence, equation (6-27) reduces to:

$$[A]_c = [A]_{c,0} \exp(\lambda_1 t) + \frac{[A]_{c,0}}{\beta} \exp(\lambda_2 t) \approx [A]_{c,0} \exp(\lambda_1 t)$$  \hspace{0.5cm} (6-28)

Of the four constants which define $\lambda_1$, $C_4$ is the largest by a factor of 10, provided that $\gamma > 0.1$, as it is for the reactions in question. Application of the binomial theorem to equation (6-27c) therefore results in a further simplification:

$$\lambda_1 = \frac{-(C_1 + C_4) + \sqrt{C_1^2 - 2C_1C_4 + C_4^2 + 4C_2C_3}}{2} \approx -C_1 + \frac{1}{C_4} \left( C_4^2 + C_2C_3 \right)$$  \hspace{0.5cm} (6-29)

The value of $\lambda_1$ from equation (6-29) is valid within 2% of that from equation (6-27c), provided that $\gamma > 0.1$. For $\gamma > 1$, $C_4$ is sufficiently large to simplify equation (6-29) further:

$$\lambda_1 = -C_1 + \frac{1}{C_4} \left( \frac{C_1^2}{4} + C_2C_3 \right) \approx -C_1 = -\frac{a}{V_c} \frac{k_w}{K_{cw} \tanh(\gamma)}$$  \hspace{0.5cm} (6-30)

resulting in an error of 1% as compared to equation (6-27c). The time constant from equation (6-30) is identical to that from equation (6-21) with $[A]_w = 0$. Thus, for $\gamma > 1$, the rate of disappearance of reactant in the carbon dioxide phase is simply equal to the reaction-enhanced transport through the water film with $[A]_w = 0$. For $\gamma < 1$, the rate of disappearance is slower by an additive constant as indicated by equation (6-29).
Comparison between experimental data and model predictions. Equation (6-28) indicates a first-order disappearance of reactant from the carbon dioxide phase, consistent with the experimental observations plotted in Figure 6-5. It is therefore reasonable to compare the theoretical predictions to the experimental data set. Furthermore, equation (6-30) suggests a time scale for normalizing \( k^*_{\text{silent}} \), \( (V_c K_{CW \; \text{tanh} \; \gamma})/(ak_w \gamma) \).

Normalization of \( k^*_{\text{silent}} \) by this time scale is convenient since the normalized rate should be equal to unity for \( \gamma > 1 \), and less than unity for \( \gamma < 1 \). Table 6-8 lists the silent data from Table 6-5, demonstrating its normalization based on equation (6-30). Figure 6-7 plots \( k^*_{\text{silent}} \), normalized by a factor of \( \lambda_1 \) from equation (6-30), as a function of \( \gamma \). Only data for which \( k_{\text{rxn}} \) is accurately known are plotted in Figure 6-7; benzoyl bromide and \( o \)-anisoyl chloride are excluded from this figure. Error bars in Figure 6-7 are based solely on the uncertainty of the partition coefficient estimates (i.e., \( \pm 30\% \)).

Table 6-8. Observed hydrolysis rate constants of benzoyl halides under silent conditions \( (k^*_{\text{silent}}) \). Hatta numbers, \( \gamma \), defined as \( (k_{\text{rxn}} D_{AW})^{1/2}/k_w \), \( \lambda_1 \), defined as \( (a k_w \gamma)/(V_c K_{CW \; \text{tanh} \; \gamma}) \), and \( k^*_{\text{silent}} \) normalized by \( \lambda_1 \) are also listed. \( \gamma \) and \( \lambda_1 \) are assumed to be greater than those for \( o \)-anisoyl chloride based on their anticipated values of \( k_{\text{rxn}} \).

<table>
<thead>
<tr>
<th>Halide</th>
<th>( k^*_{\text{silent}} \times 10^6 ; \text{s}^{-1} )</th>
<th>( \gamma )</th>
<th>( \lambda_1 \times 10^6 ; \text{s}^{-1} )</th>
<th>( k^*_{\text{silent}} / \lambda_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoyl fluoride</td>
<td>1.7 ( \pm ) 0.1</td>
<td>0.5</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>( p )-nitrobenzoyl chloride</td>
<td>17 ( \pm ) 1</td>
<td>2.4</td>
<td>2.4</td>
<td>6.4</td>
</tr>
<tr>
<td>( m )-anisoyl chloride</td>
<td>3.3 ( \pm ) 0.3</td>
<td>7.5</td>
<td>4.3</td>
<td>0.8</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>11.0 ( \pm ) 0.4</td>
<td>12.5</td>
<td>11.6</td>
<td>0.9</td>
</tr>
<tr>
<td>( p )-anisoyl chloride</td>
<td>65 ( \pm ) 1</td>
<td>35.0</td>
<td>20.2</td>
<td>3.2</td>
</tr>
<tr>
<td>benzoyl bromide</td>
<td>170 ( \pm ) 10</td>
<td>&gt;35</td>
<td>&gt;20</td>
<td>-</td>
</tr>
<tr>
<td>( o )-anisoyl chloride</td>
<td>1050 ( \pm ) 50</td>
<td>&gt;35</td>
<td>&gt;20</td>
<td>-</td>
</tr>
</tbody>
</table>
The predictions based on equation (6-28), normalized in the same fashion, are also plotted for comparison in Figure 6-7. The normalized model predictions deviate from unity only for $\gamma < 1$, as expected. Overall, the predictions agree with the experimental data to within the estimated uncertainty and the trend with $\gamma$ appears to be captured qualitatively at least for $\gamma < 20$. The most striking outlier in Figure 6-7 is $p$-nitrobenzoyl chloride (which appears at $\gamma = 2.4$) which is underpredicted by a multiple of 6. Some of the error in this data point may be due to uncertainty in the estimated partition coefficient of $p$-nitrobenzoyl chloride. The only nitro-compounds considered in the correlations presented in Chapter 3 were phenols. Since the group contribution method failed for hydrogen-bond donating compounds, it was not possible to evaluate this estimation method for nitro-compounds. Consistent with this hypothesis, the emulsion model underpredicts $k^*_{\text{sonic}}$ for $p$-nitrobenzoyl chloride (see below).

Figure 6-7. Measured rate constants for benzoyl halide hydrolysis under silent conditions ($k^*_{\text{sil}}$) normalized by $\lambda_1 = (a_k / a_{k_w} \gamma) / \left( \nu C K_{\text{cw}} \tanh \gamma \right)$ plotted versus the water film Hatta number, $\gamma = (k_{\text{rxn}} D_{AW})^{1/2} / k_w$. The solid line is a prediction of $k^*_{\text{sil}} / \lambda_1$ based on equation (6-29).
Chapter 6: Hydrolysis of Benzoyl Halides

Extrapolation of the silent model for benzoyl bromide and o-anisoyl chloride predicts that \( k_{xn} \) is equal to 400 and 20,000 s\(^{-1}\), respectively for these two compounds. While this rate for benzoyl bromide hydrolysis is reasonably close to the previous estimate of 1 – 100 s\(^{-1}\) (see Section 6.4), that of o-anisoyl chloride is unrealistically fast. Furthermore, the analysis presented earlier in this section (on page 33) suggests that \( k_C \) becomes important for \( k_{xn} > 1,000 \) s\(^{-1}\). In fact, \( k^\text{silent} = 1 \times 10^3 \) s\(^{-1}\) is actually greater than that predicted for negligible water film resistance and \( k_C = 2 \times 10^3 \) cm s\(^{-1}\) assuming that \( \theta/V_C \approx 20 \text{ cm}^2 / 47 \text{ cm}^3 = 0.43 \text{ cm}^{-1}\). It seems more likely that the silent model fails to account for some relevant physical process and thus underpredicts \( k^\text{silent} \) for \( \gamma > 20 \), a hypothesis which is also consistent with the 3-fold underprediction of \( p \)-anisoyl chloride (which is plotted at \( \gamma = 35 \) in Figure 6-7).

**Effect of hydrolysis in the carbon dioxide phase.** One likely explanation for failure of the silent model is that hydrolysis of benzoyl bromide and o-anisoyl chloride in the bulk carbon dioxide phase is not negligible as was assumed in equation (6-25). It was suggested in Section 6.4 that the second-order rate constant for hydrolysis of benzoyl halides should be roughly 700x slower in carbon dioxide than in water. After accounting for the concentration of water in carbon dioxide (roughly 0.1 mol L\(^{-1}\) at 30 °C and 80 bar\(^{84}\)), the pseudo-first order rate constant in water is roughly \( 1 \times 10^6 \) that in carbon dioxide. The fact that the concentration of water in carbon dioxide is 10-fold greater than the initial concentration of the organic reactant indicates an excess of water in this phase. For benzoyl chloride, \( \gamma \) is less than 20 (and \( k_{xn} < 1 \) s\(^{-1}\)) and the rate of reaction-enhanced mass transport predicted by equation (6-30) is 10-fold greater than the predicted carbon dioxide phase hydrolysis rate, 1.4 s\(^{-1}\) divided by \( 1 \times 10^6 \approx 1.4 \times 10^{-6} \) s\(^{-1}\). This implies that reaction in the carbon dioxide phase should indeed be a negligible pathway for benzoyl chloride, hence the good agreement between the model and this data point. To understand why the carbon dioxide pathway may become important for \( \gamma > 20 \), we need to determine how the second-order hydrolysis constant in carbon dioxide scales with \( k_{xn} \) (or \( \gamma \)).

For a reaction which is affected by solvation, the bimolecular rate constant \( (k_2) \) can be defined in terms of the Arrhenius prefactor \( (A) \), the activation energy observed in a vacuum \( (E_{A,\text{vacuum}}) \) and the activation energy contribution due to solvation \( (E_{A,\text{solvation}})\):
\[ \ln k_2 = \ln A - \frac{E_{A,\text{vacuum}} + E_{A,\text{solvation}}}{RT} \] (6-31)

where \( R \) is the universal gas constant and \( T \) is the absolute temperature. Assuming that \( A \) is not affected by solvation, the ratio of reaction rates in the two solvents (denoted as \( k_{2,W} \) and \( k_{2,C} \)) is:

\[ \ln \left( \frac{k_{2W}}{k_{2C}} \right) = \left( \frac{E_{A,\text{vacuum}} + E_{A,\text{solvation},W}}{RT} \right) - \left( \frac{E_{A,\text{vacuum}} + E_{A,\text{solvation},C}}{RT} \right) \] (6-32a)

so that:

\[ \ln \left( \frac{k_{2W}}{k_{2C}} \right) = \frac{E_{A,\text{solvation},W} - E_{A,\text{solvation},C}}{RT} \] (6-32b)

Evaluation of equation (6-32b) is far from obvious, but it will be assumed that the difference in the solvation contributions does not depend on \( k_{2,W} \) and \( k_{2,C} \). This assumption, which should be valid at least to first order, implies that the ratio between \( k_{2,W} \) and \( k_{2,C} \) is constant and that \( k_{2,C} \) scales linearly with \( k_{2,W}, k_{\text{rxn}}, \) and \( \gamma^2 \).

With this scaling in mind, it is now possible to compare the pseudo-first order hydrolysis rate constant in carbon dioxide (which equals \( k_{2,C}/[W]_c \)) to predictions of the apparent first-order rate constant based on equation (6-30). Equation (6-30) indicates linear scaling between \( k^*_{\text{silent}} \) and \( \gamma \), while it has been established that \( k_{2,C} \) scales with \( \gamma^2 \). Thus, the importance of hydrolysis in the carbon dioxide phase is expected to become increasingly important for large \( \gamma \). This may explain why the silent model is accurate for small \( \gamma \), but fails as \( \gamma \) becomes large.

A set of experiments were conducted to investigate the scaling between \( k_{2,W} \) and \( k_{2,C} \). The disappearance of benzoyl halides was followed using UV absorption spectroscopy (at roughly 280 nm) in tetrahydrofuran with known concentrations of water. Although the results were not quantified, as predicted by equation (6-32b), the order of reactivity was benzoyl chloride < \( p \)-anisoyl chloride < \( o \)-anisoyl chloride < benzoyl bromide. Future work will quantify this behavior, but for the present time it seems quite reasonable to assume that \( k_{2,C} \) scales linearly with \( k_{2,W} \).
6.6.2 Sonicated case

The physical situation during sonication is significantly more complex than that described in the silent case. Pulsed ultrasound transiently disperses carbon dioxide into the water phase and water into the carbon dioxide phase. In this set of experiments, the pulse frequency is 1 s, with a cycle duty of 25%. Several cycles of ultrasound resulted in a steady state in which the rate of drop formation equaled that of droplet removal. Given this complicated situation, shown schematically for an instant in time in Figure 6-8, the proper definition of the control volumes to be modeled is not obvious.

It is most convenient to treat the two phases (i.e., water and carbon dioxide) as two separate control volumes. Thus, the droplets are combined with the continuous phase and modeled as one control volume, characterized by an average bulk concentration, either $[A]_C$ or $[A]_W$. Inherent to this definition of the control volumes is the assumption that the reactant concentration in the droplets is equal to that in its respective continuous phase. In actuality, the carbon dioxide droplets will become depleted of reactant as they persist in the water phase while the water droplets will become saturated as they remain in the carbon dioxide phase. These effects are

Figure 6-8. Schematic of a carbon dioxide/water system during ultrasonic pulsing. Carbon dioxide is shaded, water is clear. The carbon dioxide continuous phase and carbon dioxide droplets are lumped together and characterized by a concentration of $[A]_C$, which is the concentration of reactant in the bulk carbon dioxide phase. The water continuous phase and water droplets are also lumped together and characterized by $[A]_W$, the concentration of reactant in the bulk water phase.
negligible provided that the average lifetime of the droplets is short compared to their
diffusion time scales. The diffusion time scale can be determined readily from estimates
of the droplet radius and the diffusion coefficient. For now, it will be assumed that the
concentration of reactants equals that in the respective bulk phases so that an overall
balance can be formulated. Diffusion time scales and droplet lifetimes are considered in
more detail later in this section.

In the general case, there are four source/sink terms to be accounted for in the
balance equations:

\[
\text{Volumetric rate of disappearance of reactant from the carbon dioxide} = \text{Flux from the carbon dioxide droplets to the bulk water} + \text{Flux from the bulk carbon dioxide phase to the water droplets} + \text{Flux through the phase boundary between the two emulsions}
\]

(6-33a)

and

\[
\text{Volumetric rate of appearance of reactant in the water phase} = \text{Flux from the carbon dioxide droplets to the bulk water phase} + \text{Flux from the bulk carbon dioxide phase to the water droplets} + \text{Flux through the phase boundary between the two emulsions}
\]

\[
\text{Volumetric rate of reaction in the bulk water phase} - \text{Volumetric rate of reaction in the water droplets}
\]

(6-33b)

The first two terms on the right hand side of equation (6-33a) arise from emulsification
and will be dealt with separately later in this section. The final two terms in equation (6-
33b) refers to consumption of reactant in both the bulk water phase and the water
droplets.

The third term on the right-hand side of equation (6-33a) is analogous to the flux
formulated in the silent case described above and can be considered without further
model development. Conceptually, equation (6-20) can be substituted into equation (6-
33), except that the action of ultrasound causes interfacial wave formation and therefore
increases both \( k_W \) and \( a \). Quantifying the increases is difficult; however, it can be shown
that it is unlikely that the flux across the boundary between emulsions is significant compared to the fluxes associated with the droplets. From Section 4.5.5, the surface area associated with the carbon dioxide/water emulsion is 6,000 cm$^2$ (200 cm$^{-1}$ multiplied by the total volume of the carbon dioxide/water emulsion, 30 cm$^3$) when sonication is applied at a power density of 0.60 W cm$^{-3}$. The mass transport coefficient from the carbon dioxide droplets can be estimated as $D_{AW} R^{-1}$, which results in an emulsion-based mass transport coefficient of 80 cm s$^{-1}$ (for $D_{AW} = 1 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $R = 7.5$ μm). By comparison, the area of the carbon dioxide/water boundary is 20 cm$^2$ and the mass transport coefficient is $3 \times 10^4$ cm s$^{-1}$. It is extremely unlikely that ultrasound increases $k_{W\beta}$ by four orders of magnitude, so the final term in equation (6-33a) can be neglected. For sonication at power densities lower than 0.60 W cm$^{-3}$, as plotted in Figure 6-4, this assumption may not be valid since the volume fractions of the dispersed phases formed at low power density is considerably less than that formed by sonication at 0.60 W cm$^{-3}$. Sonic enhancement for power densities between 0 and 0.60 W cm$^{-3}$ will be revisited once the sonicated model has been formulated and validated.

It was desired to convert equation (6-33) into mathematical terms, thus necessitating detailed analysis of the fluxes from the carbon dioxide droplets and to the water droplets. Formulating expressions for these fluxes required analyzing the spatial and temporal variations in the concentration profiles of reactants in the droplets.

The analysis of the steady state concentration profiles in the dispersed droplets was guided by the respective Damköhler numbers. In general, the resistances in the carbon dioxide and water phases should be included in this analysis. To determine if both resistances were significant, their relative magnitudes were determined:

$$\frac{\text{water resistance}}{\text{carbon dioxide resistance}} = \frac{D_{AC} K_{CW}}{D_{AW}} \quad (6-34)$$

Based on the data contained in Tables 6-2 and 6-3, equation (6-34) suggests that the water resistance is 1000-fold that of the carbon dioxide resistance. Thus, the Damköhler analysis focuses on the aqueous phase, with the implicit assumption that the carbon dioxide phase was well-mixed. From this point onward, all mass transport resistance is assumed to be contained in the water phase and mass transport in the carbon dioxide phase will not be considered again.
**Damköhler analysis of water droplets.** For reaction/diffusion in a rigid droplet, the Damköhler number is defined as the ratio of the time scales for diffusion and reaction, which for first order reaction is:

$$ Da = \frac{k_{rxn} R^2}{D_{AW}} $$  \hfill (6-35)

Where $R$ is the droplet radius. The Damköhler number can be used to determine whether there is a reaction-induced concentration gradient in the water droplet at steady state. For $Da \ll 1$, diffusion is much faster than reaction, and the spatial concentration profile in the droplet is constant. From Section 4.5, 4.5 μm is the most conservative, that is the largest, estimate for $R$ of the water droplets in carbon dioxide phase. Based on this radius and $D_{AW} = 1 \times 10^{-5}$ cm$^2$ s$^{-1}$, $Da \approx 1$ for $k_{rxn} \approx 50$ s$^{-1}$. Since this value of $k_{rxn}$ is considerably larger than the largest value of $k_{rxn}$ considered in this study, the concentration of reactant is constant throughout the water droplet and equal to that at the interface when the two phases have had sufficient time to equilibrate. Since the resistance in the carbon dioxide phase is negligible, the concentration at the interface is simply $[A]_c / K_{CW}$. This implies that, provided sufficient time for the water droplet to equilibrate with the bulk carbon dioxide phase, the flux to the water droplets is equal to the rate of reaction in the water droplets:

$$ \text{flux to water droplets} = \frac{k_{int} V_{droplets}}{K_{CW}} [A]_c $$  \hfill (6-36)

where $V_{droplets}$ is equal to the entire volume of water droplets in the carbon dioxide phase, calculated by recalling that water accounts for 10% of the volume of the water/carbon dioxide emulsion (Section 4.5). The issue of equilibration times is considered in more detail later in this section.

**Damköhler analysis of the aqueous region surrounding carbon dioxide droplets.** The Damköhler analysis for the water phase around a carbon dioxide droplet embedded in a water phase can be used to determine the influence of reaction on the flux from the droplet. When $Da < 1$, the flux can be modeled as a purely physical phenomenon, otherwise the reaction enhances the transport rate. Setting $R$ equal to 7.5 μm, as suggested in Section 4.5, $Da \approx 1$ for $k_{rxn} \approx 20$. The critical value of $k_{rxn} \approx 20$ is only slightly larger than that for $p$-anisoyl chloride and is probably smaller than $k_{rxn}$ for $o$-
anisoyl chloride and benzoyl bromide. Furthermore, it was not entirely clear whether the
droplet radius, as opposed to say two or three times the droplet radius, is the appropriate
length scale for diffusion from an embedded droplet. It was therefore necessary to
perform a more rigorous analysis.

Formulating the flux expression for reaction-enhanced transport from a carbon
dioxide droplet is analogous to that for the horizontal film of the previous section, albeit
in spherical rather than Cartesian coordinates. In the absence of reaction, the flux from
the carbon dioxide droplet is simply:

$$N_{\text{CO}_2 \text{Droplet,NO mn}} = \frac{D_{\text{AW}}}{R} \left( \frac{[A]_C}{K_{\text{CW}}} - [A]_W \right)$$ \hspace{1cm} (6-37)

Equation (6-37) will serve as a comparison for the reaction-enhanced flux. In the
absence of convection, the governing equation for the concentration of halide reactant as
a function of radial distance, \( r \), away from the carbon dioxide droplet is:

$$\frac{D_{\text{AW}}}{r^2} \frac{d}{dr} \left( r^2 \frac{d[A]_C}{dr} \right) = k_{\text{rn}} [A]_C$$ \hspace{1cm} (6-38)

at steady state. Setting the interfacial concentration equal to that in equilibrium with the
carbon dioxide concentration, \([A]_C\), provides one of the two required boundary
conditions:

1) \([A]_W (r = R) = [A]_{\text{int}} = [A]_C / K_{\text{CW}}\) \hspace{1cm} (6-39a)

Formulating the second boundary condition is more challenging. In the general case,
\([A]_W (r = \infty) \neq 0\), but equation (6-38) has no simple solution which can satisfy this
boundary condition. Recalling that a flux expression is required for \(\text{Da} > 1\) implies that
the boundary condition:

2) \([A]_W (r = \infty) = 0\) \hspace{1cm} (6-39b)

may be accurate for the range of \(\text{Da}\) of interest as, for fast reactions, \([A]_W\) may in fact fall
to zero. The range of \(\text{Da}\) for which equation (6-39b) is valid will be considered later.

Proceeding with the analysis, the solution of equation (6-38) subject to the
conditions in equation (6-39) is:

$$[A]_W (r) = \frac{[A]_C}{K_{\text{CW}}} \exp \left( - \sqrt{\text{Da}} (r / R - 1) \right) \frac{\sqrt{\text{Da}} (r / R - 1)}{(r / R)}$$ \hspace{1cm} (6-40)
Differentiation of equation (6-40) and evaluation at \( r = R \) leads to the following expression for the flux:

\[
N_{\text{CO}_2 \text{Droplet with } n = n} = \frac{[A]_c}{K_{cw}} \left( \sqrt{k_{\text{rxn}}D_{aw}} + \frac{D_{aw}}{R} \right)
\]

(6-41)

For purely physical mass transport, with \([A]_w (\ r = \infty) = 0\), the flux is:

\[
N_{\text{CO}_2 \text{Droplet, NO } n = n} = \frac{[A]_c \cdot D_{aw}}{K_{cw} \cdot R}
\]

(6-42)

Hence, the reaction-enhanced mass transport rate equals the sum of that for purely physical transport and a factor equal to \((k_{\text{rxn}}D_{aw})^{1/2}\). The relative ratio of these two terms is the square root of \(Da\). Thus, reaction enhancement of mass transport is negligible for \(Da \ll 1\), as asserted previously. The lower bounding value of \(Da\) for \([A]_w (\ r = \infty) \neq 0\) will be determined once the overall dynamic balances have been formulated.

**Effect of convection on transport.** Thus far, it has been assumed that convection in the water phase is negligible so that the water-phase mass transport coefficient around the carbon dioxide droplet is given by:

\[
k_w = \frac{D_{aw}}{R}
\]

(6-43)

Acrivos and Taylor\(^9\) provide a means to explore convective transport from an imbedded droplet:

\[
k_w = \frac{D_{aw}}{R} \left( 1 + \frac{1}{4} Pe_d + \text{higher order terms} \right)
\]

(6-44)

where \(Pe_d\) is the droplet diameter based Peclet number:

\[
Pe_d = \frac{U_{\text{slip}} d_p}{D_{aw}}
\]

(6-45)

where \(U_{\text{slip}}\) is the slip velocity between the droplets and an externally imposed velocity field. Determining the range of validity of equation (6-43) requires an estimate of \(U_{\text{slip}}\). Equations (6-43) and (6-44) agree to within 25% for \(U_{\text{slip}} < 0.01 \text{ cm s}^{-1}\). The most obvious slip velocity for the carbon dioxide droplets is the terminal velocity. The terminal velocity is roughly \(4 \times 10^{-3} \text{ cm s}^{-1}\) for Stokes settling of carbon dioxide droplets in the water-based emulsion (Section 4.6) indicating that equation (6-43) is valid for droplets rising at their terminal velocity. \(U_{\text{slip}}\) might be larger than the terminal velocity
in the presence of an externally applied velocity field such as that imposed by acoustic streaming. For the small number of droplets which are accelerated by acoustic streaming, equation (6-43) is a lower bound on the mass transport coefficient. Since the ultrasound is cycled at a duty of 25% and acoustic streaming is confined to a small region of the reactor (less than 50% by volume), any slip velocity resulting from sonication constitutes a negligible deviation from equation (6-43).

**Effect of droplet-droplet interactions.** The entire analysis has been performed assuming that the droplets are infinitely far from each other. For the water/carbon dioxide emulsion this is probably a valid assumption given that the continuous carbon dioxide phase is well mixed, thus smoothing out any local perturbations. For the carbon dioxide/water emulsion, neglecting droplet-droplet interactions in the kinetic model may introduce an error as the concentration profiles around individual droplets may overlap, thus reducing the overall flux. The interdroplet distance must be calculated to analyze this error. For a volume fraction of the dispersed phase equal to 0.05 (as measured in Section 4.5.4), the interdroplet distance is roughly 2.5 times the droplet radius. Based on this interdroplet distance, the error associated with neglecting carbon dioxide interactions should be small.

**Characteristic Damköhler numbers for experiments.** Table 6-9 lists Damköhler numbers for a water droplet in a water/carbon dioxide emulsion ($\text{Da}_W$) and for the water continuous phase surrounding a carbon dioxide droplet ($\text{Da}_C$) for the 7 halides considered in this study. It is clear from this list that $\text{Da}_W \ll 1$, except possibly for $o$-anisoyl chloride and benzoyl bromide, in accordance with the previous analysis of reaction/diffusion in water droplets. On the other hand, $\text{Da}_C$ is slightly more interesting, taking on values close to unity for a number of compounds.

**Time Scale Analysis.** While the Damköhler analysis can be used to draw conclusions regarding spatial variations in concentration at steady state, a time scale analysis is required to determine the time required to reach steady state. A time scale analysis is particularly important given the transient nature of the emulsions considered here. Of paramount importance are the time scales for accumulation and/or depletion as compared to the estimated droplet lifetimes. Table 6-10 contains a list of the pertinent time scales for convenient reference.
Table 6-9. Observed hydrolysis rate constants of benzoyl halides under sonicated conditions \( (k^*_{\text{sonic}}) \) listed with Damköhler numbers \( (Da = (k_{\text{rxn}} D_{\text{AW}} / R^2) \) in the water droplets (i.e., \( D_{\text{AW}} \)) and in the water phase surrounding carbon dioxide droplets (i.e., \( D_{\text{AC}} \)). The diffusion coefficient in water was assumed equal to \( 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \), the radius of water droplets was 4.5 \( \mu \text{m} \), and the radius of carbon dioxide droplets was 7.5 \( \mu \text{m} \). \( D_{\text{AC}} \) and \( D_{\text{AW}} \) for benzoyl bromide and \( o \)-anisoyl chloride are assumed to be greater than those for \( o \)-anisoxyl chloride based on their anticipated values of \( k_{\text{rxn}} \).

<table>
<thead>
<tr>
<th>Halide</th>
<th>( k^*_{\text{sonic}} \times 10^6 \text{ s}^{-1} )</th>
<th>( D_{\text{AC}} )</th>
<th>( D_{\text{AW}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoyl fluoride</td>
<td>7.7 ± 0.2</td>
<td>1.1 x ( 10^{-4} )</td>
<td>4.0 x ( 10^{-5} )</td>
</tr>
<tr>
<td>( p )-nitrobenzoyl chloride</td>
<td>460 ± 20</td>
<td>2.8 x ( 10^{-3} )</td>
<td>1.0 x ( 10^{-4} )</td>
</tr>
<tr>
<td>( m )-anisoyl chloride</td>
<td>700 ± 40</td>
<td>0.028</td>
<td>0.01</td>
</tr>
<tr>
<td>benzoyl chloride</td>
<td>1,800 ± 200</td>
<td>0.078</td>
<td>0.028</td>
</tr>
<tr>
<td>( p )-anisoyl chloride</td>
<td>3,600 ± 300</td>
<td>0.62</td>
<td>0.22</td>
</tr>
<tr>
<td>benzoyl bromide</td>
<td>3,300 ± 200</td>
<td>&gt;1</td>
<td>&gt;0.22</td>
</tr>
<tr>
<td>( o )-anisoyl chloride</td>
<td>27,000 ± 2,000</td>
<td>&gt;1</td>
<td>&gt;0.22</td>
</tr>
</tbody>
</table>

Table 6-10. Pertinent time scales for reactions and droplet lifetimes in ultrasonically agitated emulsions containing carbon dioxide and water. The radius characteristic of water droplets was taken as 4.5 \( \mu \text{m} \), while that for carbon dioxide droplets was 7.5 \( \mu \text{m} \).

<table>
<thead>
<tr>
<th>Physical Process</th>
<th>Time Scale (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ultrasound:</td>
<td></td>
</tr>
<tr>
<td>time &quot;on&quot; during pulse</td>
<td>0.25</td>
</tr>
<tr>
<td>time &quot;off&quot; during pulse</td>
<td>0.75</td>
</tr>
<tr>
<td>total pulse time</td>
<td>1.0</td>
</tr>
<tr>
<td>depletion time for CO(_2) droplet</td>
<td>3</td>
</tr>
<tr>
<td>equilibration time for H(_2)O droplet</td>
<td>0.1</td>
</tr>
<tr>
<td>Smoluchowski collision time for H(_2)O droplet</td>
<td>1.3 min</td>
</tr>
<tr>
<td>Smoluchowski collision time for CO(_2) droplet</td>
<td>80 min</td>
</tr>
</tbody>
</table>

For water droplets, the time scale for accumulation is simply \( d_0^2 / D_{\text{AW}} \approx 0.1 \text{ s} \). Water droplets can be assumed to have equilibrated with the bulk carbon dioxide phase after 0.1 s. For a given water droplet, after 0.1 s have elapsed since its formation, the Damköhler analysis presented previously is valid and the concentration of reagent
throughout the entire droplet volume truly is equal to that in the bulk carbon dioxide phase divided by the partition coefficient.

For carbon dioxide droplets, the depletion time scale is \((d_p^2 K_{CW}) / (12 D_{AW}) \approx 3\) s. This implies that 3 s after the formation of a given carbon dioxide droplet, the concentration in the droplet (which is assumed to be constant throughout as before) has essentially dropped to zero. At this point, the carbon dioxide droplet no longer contributes to the overall flux of reactant to the water phase.

We now have two diffusion-based time scales for comparison with droplet lifetimes, an equilibration time scale for water droplets and a depletion time scale for carbon dioxide droplets. The Smoluchowski analysis presented in Section 4.5.6 provides an upper bound on droplet lifetimes. From Table 6-10, the Smoluchowski collision time is 1.3 min for water droplets and 80 minutes for carbon dioxide droplets. These estimates of droplet lifetimes suggest that the water droplets are in phase equilibrium with the carbon dioxide phase, while the carbon dioxide droplets are completely depleted of reactant. For the carbon dioxide/water emulsion, droplet settling is the primary demulsification mechanism with a half life of roughly 10 min and probably provides a better estimate of the carbon dioxide droplet lifetime. Nonetheless, the estimates of carbon dioxide droplet settling and collision rates under quiescent conditions are much longer than the diffusion based depletion time. In the presence of the intense agitation associated with sonication, however, the diffusion-limited collision rate envisioned by Smoluchowski's coagulation theory is no longer valid. Not only is the number of droplet collisions increased by the agitation-imposed velocity, but also there is the interception and removal of droplets by the acoustic jet. Although no experiments were conducted to probe droplet formation/removal rates during sonication, it was observed that during application of pulsed ultrasound, the turbidity initially increased for the first several cycles before reaching a maximum, steady value. At the point of maximum turbidity, the rates of droplet formation and removal were presumably equal. Based on observations, it seems reasonable to assume that roughly ten cycles, each 1 s in duration, were required to reach this steady state suggesting 10 s as an estimate of droplet lifetimes in the presence of ultrasonic agitation. Note that this is the same argument that was used in Section 5.6.1 to estimate the energy efficiency of emulsification with ultrasound.
Based on an estimated droplet lifetimes of 10 s, it is valid to assume that the water droplets have sufficient time to equilibrate with the carbon dioxide phase since the equilibration time for water droplets is on the order of 0.1 s. The degree of depletion of the carbon dioxide droplets is less clear since the depletion time (3 s) is of the same order of magnitude as the droplet lifetime (10 s). For the purposes of this analysis, the concentration of reactant in the carbon dioxide droplets will be assumed equal to that in the bulk carbon dioxide phase with the realization that this assumption will lead to potentially large overpredictions of the overall hydrolysis rates. Experimental determination of droplet lifetimes would lead to a significant improvement in the mathematical analysis.

**The emulsion model.** At this point, it is possible to make some simplifications to and refinements of equation (6-33). First, it has been argued that the contributions of the terms in equation (6-33) which refer to transport across the boundaries between the emulsions are negligible and can be removed. Second, the combined time scale and Damköhler number analyses suggest that the water droplets are in equilibrium with the carbon dioxide phase for their entire lifetimes, and that the concentration of reactant throughout the entire volume of each water droplet is equal to that in the carbon dioxide phase divided by the partition coefficient. It is therefore more convenient to treat the water droplets as if they were in complete isolation from the bulk water phase. Thus, the second and fifth terms on the right-hand side of equation (6-33b) sum to zero. This implies that the water droplets are embedded in the carbon dioxide phase where they continuously consume reactant. Furthermore, the rate of mass transport from the carbon dioxide phase to the water droplets must equal the rate of consumption in the water droplets as suggested in equation (6-36). These assumptions allow equation (6-33) to be re-written:
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\[\frac{d[A_c]}{dt} = -\frac{D_{AW}}{R} \frac{a_{CW}}{V_c} (\frac{[A_c]}{K_{CW}} - [A_w]) - \frac{V_{droplets}}{V_c} \frac{k_{rcn}}{K_{CW}} [A_c] \quad (6-47a)\]

\[\frac{d[A_w]}{dt} = \frac{D_{AW}}{R} \frac{a_{CW}}{V_w} ([A_c]/K_{CW} - [A_w]) - k_{int} [A_w] \quad (6-47b)\]

where \(a_{CW}\) is the surface area of the carbon dioxide droplets in the water emulsion. It is important to mention that \(V_w\) is no longer the total water loading; rather it is the total water loading less the volume of water that is present as droplets, \(V_{droplets}\).

Equation (6-47) can be written in the form of equation (6-25):

\[\frac{d[A_c]}{dt} = -\left(\frac{D_{AW}}{R} \frac{a_{CW}}{V_c} \frac{1}{K_{CW}} + \frac{V_{droplets}}{V_c} \frac{k_{rcn}}{K_{CW}}\right) [A_c] + \frac{D_{AW}}{R} \frac{a_{CW}}{V_c} [A_w] \quad (6-48a)\]

\[\frac{d[A_w]}{dt} = \left(\frac{D_{AW}}{R} \frac{a_{CW}}{V_w} \frac{1}{K_{CW}}\right) [A_c] - \left(\frac{D_{AW}}{R} \frac{a_{CW}}{V_w} + k_{rcn}\right) [A_w] \quad (6-48b)\]

or, in more compact notation:

\[\frac{d[A_c]}{dt} = -D_1[A_c] + D_2[A_w] \quad (6-49a)\]

\[\frac{d[A_w]}{dt} = D_3[A_c] - D_4[A_w] \quad (6-49b)\]
This is the same structure as equation (6-26), subject to the same initial conditions, so
that the solution is of the same form:

\[ [A]_c = \frac{-\beta}{1-\beta} [A]_{c,0} \exp(\lambda_1 t) + \frac{1}{1-\beta} [A]_{c,0} \exp(\lambda_2 t) \]  

(6-50a)

\[ [A]_w = \frac{-\beta}{1-\beta} \frac{D_1 + \lambda_1}{D_2} [A]_{c,0} \exp(\lambda_1 t) + \frac{1}{1-\beta} \frac{D_1 + \lambda_2}{D_2} [A]_{c,0} \exp(\lambda_2 t) \]  

(6-50b)

where:

\[ \lambda_1 = \frac{-(D_1 + D_4) + \sqrt{D_1^2 - 2D_1 D_4 + D_4^2 + 4D_2 D_3}}{2} \]  

(6-50c)

\[ \lambda_2 = \frac{-(D_1 + D_4) - \sqrt{D_1^2 - 2D_1 D_4 + D_4^2 + 4D_2 D_3}}{2} \]  

(6-50d)

\[ \beta = \frac{D_1 + \lambda_2}{D_1 + \lambda_1} \]  

(6-50e)

The balance on \([A]_c\) is our primary concern and we will now focus on its simplification.

For all cases of interest, \(\beta \gg 1\) (as a consequence of \(\lambda_2\) being much greater than either \(D_1\) or \(\lambda_1\)) so that equation (6-50a) can be greatly simplified:

\[ [A]_c \approx [A]_{c,0} \exp(\lambda_1 t) \]  

(6-51)

Equation (6-50c) can also be simplified for \(Da_C > 5 \times 10^{-3}\) (for which \(D_2, D_4 > D_1, D_3\)):

\[ \lambda_1 = \frac{-(D_1 + D_4) + \sqrt{D_1^2 - 2D_1 D_4 + D_4^2 + 4D_2 D_3}}{2} \approx -D_1 + \frac{1}{D_4} \left( \frac{D_1^2}{4} + D_2 D_3 \right) \]  

(6-52)

And, provided that \(Da_C > 1.1\) (for which \(D_4 > D_1, D_2, \text{ and } D_3\)), this expression can be simplified still further:

\[ \lambda_1 \approx -D_1 + \frac{1}{D_4} \left( \frac{D_1^2}{4} + D_2 D_3 \right) \approx -D_1 = \left( \frac{D_{AW}}{R} \frac{a_{CW}}{V_c} \frac{1}{{K}_{CW}} + \frac{V_{droplets}}{V_c} \frac{k_{mn}}{{K}_{CW}} \right) \]  

(6-53)

So that, still for \(Da_C > 1.1\):

\[ \ln \left( \frac{[A]_c}{[A]_{c,0}} \right) = - \left( \frac{D_{AW}}{R} \frac{a_{CW}}{V_c} \frac{1}{{K}_{CW}} + \frac{V_{droplets}}{V_c} \frac{k_{mn}}{{K}_{CW}} \right) t \]  

(6-54)

Equation (6-54) could have been derived directly from (6-47) with the requirement that \([A]_w = 0\). Therefore, when the flux from the carbon dioxide droplets is assumed to be
independent of reaction, \([A]_W = 0\) for \(Da_C > 1.1\). Clearly, since reaction enhancement is expected to be important for \(Da_C\) greater than roughly 0.5, equation (6-54) is not valuable in any practical sense. Equation (6-54) is used later for physical insight.

It is now necessary to develop an expression for \(Da_C > 1\) (and \([A]_W = 0\)) which accounts for reaction enhancement of transport from the carbon dioxide droplets. In this case, only \([A]_C\) requires attention, since \([A]_W\) has been assumed equal to zero:

\[
\frac{d[A]_C}{dt} = -\left(\frac{D_{AW}}{R} + \sqrt{k_{rn}D_{AW}}\right) \left(\frac{[A]_C a_{CW}}{V_c K_{CW}}\right) - \frac{V_{droplets}}{V_c} \frac{k_{rn}}{K_{CW}} [A]_C
\]

(6-55)

Which implies that:

\[
\ln\left(\frac{[A]_C}{[A]_{C0}}\right) = -\left(\frac{D_{AW}}{R} + \sqrt{k_{rn}D_{AW}}\right) \frac{a_{CW}}{V_c K_{CW}} + \frac{V_{droplets}}{V_c} \frac{k_{rn}}{K_{CW}} t
\]

(6-56)

Equation (6-54) and equation (6-56) are identical, save that the flux in the latter is assumed to be enhanced by reaction. For \(Da_C < 0.5\), equation (6-56) reduces to equation (6-54) as the correction due to reaction enhancement to the overall mass transport rate is less than 25%. Therefore, for instances in which reaction enhancement of mass transport is important, \([A]_W\) actually is roughly zero and the error in assuming so in the reaction-enhancement analysis is trivial provided that \(Da_C > 1.1\). There is a small window corresponding to \(Da_C\) larger than 0.5 and smaller than 1.1 for which neither equation (6-54) nor (6-56) is quite valid. This issue will be explored further in the next section.

**Comparison of emulsion models.** Four distinct models have been formulated for reactions in emulsified systems. For convenience these models are summarized here:

For \(Da_C < 1.0\)

\[
\ln\left(\frac{[A]_C}{[A]_{C0}}\right) = -\left(\frac{D_1 + D_4}{2}\right) + \frac{\sqrt{D_1^2 - 2D_1D_4 + D_4^2 + 4D_2D_3}}{2} t
\]

(6-57)

where \(D_1, D_2, D_3\) and \(D_4\) are defined in equation (6-50).

For \(5 \times 10^{-3} < Da_C < 1\), this reduces to:

\[
\ln\left(\frac{[A]_C}{[A]_{C0}}\right) = -D_1 + \frac{D_4}{4} \left(\frac{D_4}{4} + D_2D_3\right) t
\]

(6-58)

For \(Da_C > 1.1\), ignoring reaction enhancement of mass transport:
\[
\ln \left( \frac{[A]_C}{[A]_{C0}} \right) = -\left( \frac{D_{AW}}{R} \frac{a_{CW}}{V_C} \frac{1}{K_{CW}} \frac{V_{\text{droplets}}}{V_C} \frac{k_m}{K_{CW}} \right) t
\]  
(6-59)

and for \( Da_C > 1 \), incorporating reaction enhancement to mass transport:

\[
\ln \left( \frac{[A]_C}{[A]_{C0}} \right) = -\left( \frac{D_{AW}}{R} \frac{a_{CW}}{V_C} \frac{1}{K_{CW}} \frac{V_{\text{droplets}}}{V_C} \frac{k_m}{K_{CW}} \right) t
\]  
(6-60)

Thus, equations (6-57) - (6-60) constitute four separate model predictions of \( k_{\text{sonic}}^* \), each with its own range of validity. Clearly, all of these models properly predict first order behavior, differing only in their predictions of \( k_{\text{sonic}}^* \). Figure 6-9 contains plots of rate constants predicted by the four equations listed above, normalized by \( (D_{AW} a_{CW})/(RV_C K_{CW}) \) as suggested by the lead term in equation (6-59), versus \( Da_C \). This normalization factor is equal to the flow from the carbon dioxide droplets assuming that \( [A]_W = 0 \) in the absence of reaction enhancement of mass transport. The values of parameters used in model predictions are listed in Table 6-11. The predictions of equations (6-57) and (6-58) are indiscernibly different provided that \( Da_C > 2 \times 10^{-3} \). For \( Da_C < 0.1 \), equations (6-59) and (6-60) deviate significantly from (6-57), indicating that \( [A]_W \neq 0 \) under these conditions. For \( Da_C > 0.5 \), the four models agree rather well, indicating that \( [A]_W = 0 \) in this regime.

There is some positive deviation between equation (6-59) and (6-60) in the vicinity of \( Da_C \approx 0.1 \), but above this value the three models agree within 25%. This positive deviation is not surprising given that equation (6-60) accounts for reaction enhancement of flux from the carbon dioxide droplets. More surprising is that the positive deviation persists only to \( Da_C \approx 2.0 \). The reason for this behavior is that the relative contribution of the carbon dioxide/water emulsion to the overall dynamics becomes small for \( Da_C > 2.0 \). Therefore, properly accounting for reaction enhancement is irrelevant. For \( Da_C > 2.0 \), the water/carbon dioxide emulsion dominates, as indicated by the fact that overall rate constants from equations (6-57) – (6-60), normalized by the carbon dioxide/water contribution, are much greater than unity.
Figure 6-9. Model predictions of $k^*_{\text{sonic}}$ based on equations (6-57) and (6-58) (plotted together), equation (6-59), and equation (6-60). \((\frac{D_{AW@CW}}{RV_C K_{CW}})\), the rate of mass transport for carbon dioxide droplets assuming that the flux is not enhanced by reaction in the water phase and that the reactant concentration in the bulk water phase is zero is used as a normalization factor. \(Da_C\) is the Damköhler number for carbon dioxide droplets embedded in the water phase, based on the hydrolysis rate in pure water, \(k_{\text{rxn}}\), the average radius of the carbon dioxide droplets, \(R\), and the diffusion coefficient of an organic solute in the water phase, \(D_{AB}\). \(V_C\) is the total volume of carbon dioxide in the reactor and \(a_{CW}\) is the surface area between the carbon dioxide droplets and the continuous water phase. Note the log $10$-$\log_{10}$ scale.

Table 6-11. Values of parameters used for numerical simulations of acoustically generated emulsions consisting of carbon dioxide and water using equations (6-57) - (6-60). A range of values was used for \(k_{\text{rxn}}\).

<table>
<thead>
<tr>
<th>Physical description</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusivity of organic solute in water</td>
<td>(D_{AW})</td>
<td>(1 \times 10^{-5}) cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>first-order rate constant in pure water</td>
<td>(k_{\text{rxn}})</td>
<td>(1 \times 10^{-5} - 10) s$^{-1}$</td>
</tr>
<tr>
<td>interfacial area in CO$_2$/H$_2$O emulsion</td>
<td>(a_{CW})</td>
<td>(6,000) cm$^2$</td>
</tr>
<tr>
<td>volume of water</td>
<td>(V_W)</td>
<td>(40 - 5 = 35) cm$^3$</td>
</tr>
<tr>
<td>volume of carbon dioxide</td>
<td>(V_C)</td>
<td>(47) cm$^3$</td>
</tr>
<tr>
<td>volume of water droplets</td>
<td>(V_{\text{droplets}})</td>
<td>(5) cm$^3$</td>
</tr>
<tr>
<td>radius of a carbon dioxide droplet</td>
<td>(R)</td>
<td>(7.5) \mu m</td>
</tr>
<tr>
<td>partition coefficient</td>
<td>(K_{CW})</td>
<td>(150)</td>
</tr>
</tbody>
</table>

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Figure 6-9 suggests that for $DA_C < 0.5$ the flux from carbon dioxide droplets to the bulk water phase is the most important contribution to the overall reaction/transport dynamics. For $DA_C > 0.5$, the consumption of reactant in the water droplets begins to dominate overall dynamics. These conclusions are based on the fact that the overall rate constant from equation (6-57) - (6-60) are many times greater than the rate predicted from consideration of the flux from the carbon dioxide droplets (the normalization factor in Figure 6-9) alone. It is possible to investigate these conclusions in more detail by considering the various contributions to the rate constants which appear in equations (6-57) - (6-60):

1) transport from the carbon dioxide droplets to the bulk water phase in the absence of reaction enhancement, assuming that $[A]_W = 0$: $(DA_W@CW) / (RV_CK_{CW})$

2) transport from the carbon dioxide droplets to the bulk water phase, accounting for reaction enhancement with $[A]_W$ set equal to zero: $(DA_W@CW + (k_{rxn} DA_W)^{1/2}) / (RV_CK_{CW})$

3) consumption in the water droplets: $(V_{drop}k_{rxn}) / V_C K_{CW}$

4) a term which can be interpreted as (see below) the reduction in flux from the carbon dioxide droplets due to finite concentration of reactant in the bulk water phase: $(D_1^2 / 4 + D_2 D_3) / D_4$ as it appears in equation (6-58).

The fourth time constant listed above merits further consideration since its physical meaning is unclear. The rate constant which appears in equation (6-58) consists of two terms: 1) a term which accounts for both reactant flux from the carbon dioxide droplets assuming that $[A]_W = 0$ and the consumption of reactant in water droplets and 2) a term of opposite sign to the first which is a collection of physical parameters lumped together in a manner with no clear physical basis. While it is tempting to ascribe the effect of the non-zero concentration of reactant in the bulk water phase to this second term, it is not entirely correct to do so. This is because the second term in the rate constant of equation (6-58) contains contributions from the reaction in the water droplets (contained in $D_1$) and the bulk water phase ($D_4$). While a term correcting for finite reactant concentration in the bulk water phase is expected to depend on the reaction rate in the bulk water, the appearance of the reaction rate in the water droplets in such a correction term is not physical. Furthermore, above a certain value of $k_{rxn}$ the correction
term begins to be dominated by the reaction in the water droplets. As a result, the correction term begins to increase with increasing $k_{rxn}$. Intuitively, if the correction term is identically related to the effects of non-zero concentration of reactant in the bulk water phase, it would monotonically decrease with $k_{rxn}$. Since it does not, the correction term cannot be clearly attributed to the non-zero concentration of reactant in the bulk water phase for all values of $k_{rxn}$. Mathematical analysis of the correction term reveals that it passes through a minimum at $Da_C \approx 50$. Below this value of the Damköhler number, the correction term can be associated with a modulation of the flux from carbon dioxide droplets due to finite concentration of reactant in the bulk water phase with minimal error. For $Da_C > 50$, the correction term is both a modulation of the carbon dioxide flux and an additional effect pertaining to reaction in the water droplets. It will turn out that the correction term will be negligible for $Da_C > 0.1$, so that the subtle arguments presented in this paragraph are of no major consequence. Also, we are most interested in $Da_C$ less than or equal to unity. Nonetheless, it is worth noting that the fourth term in the list above does not have a clean physical interpretation for all values of $Da_C$.

With the caveat introduced in the preceding paragraph in mind, it is possible to plot the four contributions to the overall rate constant that were introduced in the preceding paragraph as shown in Figure 6-10. Plotted in this figure are the four contributions listed above, normalized by the rate constant for diffusion from the carbon dioxide droplets (the first entry in the above list). As expected, the diffusion rate from the carbon dioxide droplets is not enhanced by reaction in the bulk water phase, provided that $Da_C < 0.1$. The correction to the flux from carbon dioxide droplets due to finite concentration of reactant in the bulk water phase is negligible for $Da_C > 0.5$.

Furthermore, as suggested by Figure 6-9 for small $Da_C$, the overall dynamics are dominated by the flux from the carbon dioxide droplets indicating that the carbon dioxide/water emulsion is more important than the water/carbon dioxide emulsion. For $Da_C > 0.5$, the contribution from reaction in the water droplets becomes increasingly important. These results are entirely consistent with those presented in Figure 6-9. In conclusion, the carbon dioxide/water emulsion dominates for $0.1 < Da_C$, while the water/carbon dioxide emulsion dominates for $Da_C < 1.0$. For $0.1 < Da_C < 1.0$, the contributions from the two emulsions are roughly equal.
Figure 6-10. Plots of various contributions to the overall rate constants which appear in equations (6-57) – (6-60). The factor, \( \frac{D_{AW} a_{CW}}{(R V_C K_{CW})} \), is used for normalization. \( Da_C \) is the Damköhler number for carbon dioxide droplets embedded in the water phase, based on the hydrolysis rate in pure water, \( k_{rxn} \), the average radius of the carbon dioxide droplets, \( R \), and the diffusion coefficient of an organic solute in the water phase, \( D_{AB} \). \( V_C \) is the total volume of carbon dioxide in the reactor and \( a_{CW} \) is the surface area between the carbon dioxide droplets and the continuous water phase. Note the log_{10}-log_{10} scale.

As discussed previously, the behavior of the flux correction term (the fourth term listed above, indicated in Figure 6-10 as the contribution due to \([A]_W \neq 0\)) is not clear cut. The behavior of the correction term as a function of \( k_{rxn} \), and its physical significance, has been discussed previously. The correction term is 2 orders of magnitude less than the rate of diffusion from the carbon dioxide droplets and nearly 4 orders of magnitude less than the reaction rate in the water droplets when the anomalous behavior observed for \( Da_C > 50 \). Therefore, the contribution of the correction term is negligible by the time its physical basis becomes confused.

Several conclusions can be drawn from Figures 6-9 and 6-10. For \( Da_C < 0.1 \) the overall dynamics are completely dominated by the carbon dioxide/water emulsion. For \( Da_C < 0.05 \), \([A]_W \) approaches \([A]_C/K_{CW} \) as suggested by the large values of the flux correction term. Since the reaction occurs in the water phase and the majority of the water is tied up in the carbon dioxide/water emulsion, the overall dynamics are dominated by this emulsion. For \( Da_C > 1.0 \), the overall dynamics are dominated by the water/carbon
dioxide emulsion. This is because the water droplets remain at the equilibrium concentration of reactant, and are fully utilized, while the bulk water phase becomes depleted, and is utilized less efficiently. In fact, the water droplets are fully utilized provided that $D_{ac} \approx 3$ (or equivalently, $D_{aw} < 1.0$).

The fact that reaction dynamics are dominated by the water/carbon dioxide emulsion for $D_{ac} = 1.0$ minimizes the overall error associated with neglecting reaction enhancement of diffusion from the carbon dioxide droplets since this diffusion rate no longer contributes to the overall dynamics for values of $D_{ac} > 1.0$ when reaction enhancement becomes important. Considering the numerous simplifying assumptions made in its formulation, the small error introduced to equation (6-57) by neglecting reaction enhancement of flux is probably less than that associated with the estimations of diffusivities and partition coefficients. Therefore, equation (6-57) is approximately valid and was used exclusively for interpretation of data.

**Summary of assumptions.** The accuracy of equation (6-57) relies on a number of simplifying assumptions. For convenience, the primary assumptions are briefly listed here:

1. Ultrasound was assumed to exert purely physical effects. This assumption is justified based on the high-pressure results for sonochemical oxidation of KI which were presented in Section 5.3.2.

2. Both the carbon dioxide droplets and the carbon dioxide continuous phase were assumed to be well mixed. This was justified by considering that the water phase resistance is 1,000-fold greater than that in the carbon dioxide phase.

3. Concentrations of reactant in the carbon dioxide droplets and the carbon dioxide continuous phase were assumed to be equal. This assumption was made based on an estimated carbon dioxide droplet lifetime of 10 s compared to a depletion time of 3 s.

4. All water droplets were assumed to be well mixed spatially. This was justified based on the small values of the Damköhler number for the water droplets. Furthermore, the time required for the water droplets to equilibrate with the carbon dioxide phase (0.1 s) was much less than their estimated lifetime of 10 s. This time-scale analysis indicated that the concentration in the droplets was equal.
to that in the bulk carbon dioxide phase implying the water droplets is equal to 
$[A]_c K_{CW}^{-1}$ at all times.

5. The interdroplet distance was assumed to be large enough that droplet-droplet 
interactions could be ignored. This assumption was justified for water/carbon 
dioxide emulsions since the continuous phase was considered to be well mixed. 
In the water phase, the error associated with this assumption was minor since the 
estimated interdroplet distance was 2.5 times the average droplet radius.

6. Reaction enhancement of mass transport from the carbon dioxide droplets to the 
continuous water phase was assumed to be small. This assumption is not correct 
for $Da_C > 1$ but, in this range of $Da_C$, the contribution of the carbon dioxide/water 
emulsion was small compared to that from the water/carbon dioxide emulsion. 
Calculations indicate that properly accounting for reaction enhancement of flux 
from the carbon dioxide droplets is only a 20% correction at most.

7. Convective mass transport to the droplets was assumed to be negligible which is 
valid for droplets rising/falling at their terminal velocities.

8. Throughout the analysis, the two emulsions have been assumed to be spatially 
uniform. The measurements of the dispersed phases in the two emulsions were 
made within 1 cm of the carbon dioxide/water interface, in a location at which the 
emulsions are likely to be the most concentrated. For this reason, it is expected 
that the experimental measurements may tend to overestimate the average 
concentration of dispersed phase actually present. Future work should be directed 
at probing the spatial variations in the volume fractions of dispersed phases so 
that the validity of this assumption can be verified.

Of these assumptions, the third is the most troublesome as all indications are that the 
errors associated with the other 7 assumptions are small. Lacking data for droplet loss 
and formation rates, it is not possible to make a reliable estimate of the error introduced 
by the third assumption, though it is expected that finite droplet lifetimes would result in 
a net overprediction of the overall rate. This is because the maximum concentration of 
reactant in the carbon dioxide droplets is equal to that in the bulk carbon dioxide phase is, 
as was assumed. Any deviation from this assumption reduces the reactant concentration
and therefore its flux from these droplets into the continuous water phase, reducing the overall hydrolysis rate.

**Comparison between experimental data and model predictions.** In the silent case, the model itself suggested a convenient time scale for normalizing observed rate constants, but no convenient time scale is suggested by equation (6-57). Instead, a physical argument is used to determine the appropriate normalization factor for $k^*_{\text{sonic}}$. The fastest possible reaction rate in a biphasic system corresponds to complete mixing of the two phases:

$$\ln \left( \frac{[A]_c}{[A]_{c0}} \right) = -\frac{k_{\text{rxn}} V_w}{K_{CW} V_C} t = -k_{\text{well-mixed}} t$$  \hspace{1cm} (6-61)

Thus, $k_{\text{well-mixed}}$ was used to normalize experimental measurements and model predictions of $k^*_{\text{sonic}}$, with the expectation that $k^*_{\text{sonic}} / k_{\text{well-mixed}} < 1$ for all cases.

Figure 6-11 plots the predictions of equation (6-57) and measurements of $k^*_{\text{sonic}}$ normalized by $k_{\text{well-mixed}}$ versus the square root of $Da_C$. The square root was selected because it expanded the scale for $Da_C < 1$. Furthermore, $(Da_C)^{1/2}$ is proportional to $(k_{\text{rxn}})^{1/2}$ just as is $\gamma$ which was used in the silent analysis.

Figure 6-11 shows that the predictions of $k^*_{\text{sonic}}$ are in reasonable agreement with the data, nearly within the estimated uncertainty of $K_{CW}$. This agreement is exceptional given the number of assumptions incorporated in equation (6-57). There is, however, a systematic model overprediction of the data, which is consistent with the finite lifetimes of the carbon dioxide droplets relative to their depletion time scale. This overprediction notwithstanding, the simple emulsion model combined with the emulsion characterization measurements from Chapter 4 properly predicts the qualitative trend in $k^*_{\text{sonic}}$ with $(Da_C)^{1/2}$ and is within a factor of two of the proper magnitude, without the need for fit parameters.

The only exception to model overprediction is $p$-nitrobenzoyl chloride, plotted at $(Da_C)^{1/2} \approx 0.05$, which appears to be underpredicted by the model by a multiple of roughly 2. It is an outlier from the remaining data set by a multiple of 3. This is consistent with the 6-fold underprediction of $k^*_{\text{silent}}$ for this compound. It seems likely that the partition coefficient for this compound was overestimated by a multiple of roughly 3.
Figure 6-11. Measured hydrolysis rates under sonic conditions, $k^*_\text{sonic}$, normalized by the well-mixed prediction of equation (6-61) plotted versus the Damköhler number of carbon dioxide droplets in water, $(D\alpha C)^{1/2} = [(k_{\text{rxn}}R^2) / D_{\text{AW}}]^{1/2}$. $k_{\text{rxn}}$ is the hydrolysis rate in pure water, $D_{\text{AB}}$ is the diffusion coefficient of an organic solute in water, $R$ is the average radius of a carbon dioxide droplet, $V_W$ is the volume of the entire water phase, $V_C$ is the volume of the entire carbon dioxide phase.

A second noteworthy feature of Figure 6-11 is that the well-mixed prediction is approached for $(D\alpha C)^{1/2} < 0.1$. (i.e., $D\alpha C < 0.03$). For reactions slower than this, sonication essentially removes all transport barriers and the reaction proceeds at a rate close to $k_{\text{well-mixed}}$. In more accessible terms, reactions with half-lives longer 2 s when performed in a single-phase system are expected to proceed at the well-mixed rate in the acoustic reactor. Many synthetic transformations require hours or days to reach completion, making sonication an efficient technique for accelerating a wide range of reactions.

The successes of the emulsion model suggest that the large increase in surface area associated with sonication effectively accelerates these mass transport limited reactions. This is purely a physical effect, modeled accurately by a simple physical model containing no fit parameters.

**Effect of hydrolysis in bulk carbon dioxide phase.** The possibility of hydrolysis in the carbon dioxide phase was introduced to the emulsion model described by equation (6-
57), but the predictions were not altered. This is because the transport of benzoyl halide to the water phase is always much faster than the predicted rate of its hydrolysis in the carbon dioxide phase.

The observation that the carbon dioxide hydrolysis pathway is insignificant under sonicated conditions may carry technological ramifications, as sonication may be a means of reducing or eliminating side reactions in the carbon dioxide phase. This result is actually quite powerful, since it implies that sonication might be used to reduce degradation of a reactant while it remains in the “delivery” phase prior to its transport to the “reaction” phase. In such instances, sonication could increase reaction yield and possibly selectivity in addition to rates. The study of olefin epoxidation by hydrogen peroxide in biphasic water/carbon dioxide systems by Nolen et al. is an excellent example. In this study, the authors found that hydrogen peroxide degraded before it could react with the olefin, thus reducing the yields of epoxide by more than 100%. The authors suggested that the problem of degradation was exacerbated by mass transport limitations since the yield increased from 1% to 2% when the vessel contents were agitated using a conventional impeller. Had mass transport been more rapid, there would have been less time for decomposition of the hydrogen peroxide in the carbon dioxide phase and the authors suggest that the yields would have been greater. The physical models described in this chapter provide a quantitative means for determining if sonication might be useful for improving performance (yields, rates, or selectivities) for reacting systems which include degradative pathways.

Consideration of sonic enhancement at low power density. The models presented in this section and the emulsion characteristics presented in Chapter 4 allow qualitative interpretation of the sigmoidal-shaped curve in Figure 6-4. Three regimes are apparent in Figure 6-4: 1) the silent regime (power density = 0 W cm⁻³), 2) the transition regime (0 W cm⁻³ < power density < 0.5 W cm⁻³) in which \( k'_{\text{sonic}} \) increases monotonically with power density and, 3) the saturation regime (power densities > 0.5 W cm⁻³), in which \( k'_{\text{sonic}} \) is no longer a function of power density. The behavior in regime (1) has been considered previously and is well understood. The physical behavior of regime (2) and the transition to regime (3) are of more immediate concern.
Of particular interest in regime (2) is the 10-fold increase in $k^*_{\text{sonic}}$ observed when the system is sonicated at power densities $< 0.1$ W cm$^{-3}$. It was reported in Chapter 4 that a carbon dioxide emulsion containing 2-3% water is formed during sonication at power densities less than 0.10 W cm$^{-3}$. The droplet sizes (though not measured directly) were estimated to be 40 μm in diameter as described in Section 5.2.1, resulting in $Da_N \sim 0.2$. Assuming that the water droplets are saturated with reactant (which is not entirely justified by the Damköhler number) leads to an overall hydrolysis rate of roughly $1 \times 10^{-4}$ s$^{-1}$. This estimate accounts for the contribution from the water droplets and transport across a stagnant water/carbon dioxide phase boundary as per the silent model. Although this predicts the desired 10-fold increase over $k^*_{\text{silent}}$, the assumption that the water droplets are saturated with reactant is probably not justified. Not only is the estimated Damköhler number nearly unity, but the equilibration time for 40 μm droplet is 2 s, indicating the water droplets require a longer time to equilibrate with the bulk carbon dioxide further reducing the consumption of reactant in these droplets as compared to that for saturated droplets. It is likely that the rate may also be accelerated several fold by the interfacial waves which accompany sonication at power densities of 0.1 W cm$^{-3}$, thus accounting for the full 10-fold acceleration that was observed experimentally.

Transition from regime (2) to (3) is associated with the maximum amount of emulsification possible in the acoustic reactor. For power densities between 0 and 0.5 W cm$^{-3}$, the amount of water which can be emulsified into the carbon dioxide increases monotonically with power. Above a power density of 0.5 W cm$^{-3}$, the effect of ultrasound on water phase dispersion saturates. Thus, saturation of $k^*_{\text{sonic}}$ with power density is directly linked to the saturation of the dispersive effects of power ultrasound. Presumably, the reactor design could be optimized to increase $k^*_{\text{sonic}}$ up to $k_{\text{well-mixed}}$ for reactions as fast as the hydrolysis of benzoyl chloride. In that event, equation (6-57) could be used to determine the benefits of decreasing droplet sizes or increasing volume fractions of dispersed phases, at least within the limits of the assumptions listed previously.

### 6.6.3 Sonic enhancement

The two sets of models presented in this chapter provide a rational basis for selecting reactions which can be expected to benefit from either biphasic conditions or
sonication. Although the analysis is strictly valid only for first order kinetics, many reactions can be modeled, at least qualitatively, as pseudo-first order. Provided partition coefficients (which can be estimated using the methods described in Chapter 3) and chemical rates, the silent model can be used to predict the overall kinetics in non-emulsified carbon dioxide/water systems. Dynamics of reactions involving multiple steps often can be modeled by consideration of rate determining steps. For second-order kinetics, reactions are frequently conducted in the presence of an excess reagent, reducing the mathematical rate law to first order. Predictions based on the model described in Section 6.5.2 will inform decisions regarding the use of the biphasic system and suggest possible ways to accelerate the observed dynamics, such as addition of hydrophilic groups or more efficient mixing. In accordance with this, the models in this chapter, in conjunction with emulsion characterization data, can be used to predict when sonication is beneficial. For reactions which are inherently slow, sonic acceleration is expected to be minor. As an example, the half life for the hydrolysis of benzoyl fluoride in water is roughly 10 min and is accelerated only 4-fold by sonication. For reactions slower than this (i.e., when $\gamma << 1$), mass transport resistance is negligible and sonication is expected to have a small effect on overall dynamics. Likewise, reagent partitioning which strongly favors the carbon dioxide phase is predicted to limit the maximum possible $k^*_{\text{sonic}}$ though, since carbon dioxide partitioning also limits $k^*_{\text{silent}}$, sonic enhancement might still be significant. Improvements in the sonic reactor (for instance to obtain smaller droplet sizes) will not increase sonic enhancement of slow reactions ($\gamma << 1$), though an improved reactor is expected to increase the maximum achievable $k^*_{\text{sonic}}$ for $\gamma >> 1$.

6.7 Conclusions

This chapter presents new experimental results and theoretical interpretations of mass transport and chemical reactions in carbon dioxide/water systems. The pseudo-first order, irreversible hydrolysis of benzoyl halides was used to: 1) demonstrate the accelerative effects of ultrasound on a mass transport limited reaction and 2) to validate physical models for mass transport/reaction. Towards the first objective, it was found that sonication of carbon dioxide/water systems always accelerated the overall reaction/transport dynamics and sonic enhancement was greater than 100-fold in some
instances. In general, the accelerative effect was most significant for more reactive halides \( k_{\text{rxn}} > 0.1 \text{ s}^{-1}, \gamma > 1.0 \).

Two transport/reaction models were developed to interpret the experimental results. A simple reaction-enhanced mass transport model was formulated for silent conditions which accurately predicted observed dynamics for \( \gamma < 20 \). This model underpredicted the experimentally measured hydrolysis rates for highly reactive compounds \( (\gamma > 20) \) under silent conditions. The underprediction was attributed to hydrolysis of the reactant in the carbon dioxide phase. It was argued that the importance of this pathway would increase with \( \gamma \). \( p \)-nitrobenzoyl chloride was identified as an outlier.

A second model was proposed to interpret rate constants measured under sonicated conditions. Mass transport from carbon dioxide droplets into the continuous water phase was modeled as a physical process, independent of reaction. A combined time scale and Damköhler analysis suggested that the concentration of reactant in the water droplets embedded in the carbon dioxide phase could be assumed to equal \([A]_c \ K_{\text{CW}}^{-1}\). The simple model agreed with the experimental data within the limits of experimental uncertainty for all compounds considered in this study except \( p \)-nitrobenzoyl chloride. A completely well-mixed model, in which the water phase concentration was equal to that predicted by the equilibrium partition coefficient, agreed with the data for compounds with characteristic, pure water, hydrolysis half-lives greater than 2 s (i.e., \( k_{\text{rxn}} < 0.5 \text{ s}^{-1} \)) and corresponding carbon dioxide droplet Damköhler numbers, \( (k_{\text{rxn}} \ R^2)/D_{\text{AW}} \), less than 0.03. For compounds less reactive than this, sonication completely removes all mass transport barriers, a result which could find application in acceleration of many reactions with synthetic importance. Ultrasound is not expected to accelerate reactions with one-phase half-lives greater than 30 hrs since mass transport resistance is already negligible for such slow reactions. Hydrolysis in carbon dioxide was a negligible pathway under sonicated conditions.

The emulsion model indicated that the overall dynamics are dominated by the carbon dioxide/water emulsion, provided that the carbon dioxide droplet Damköhler number is less than unity. In this regime, the bulk water phase is efficiently utilized and, since the majority of water exists as the continuous phase in the carbon dioxide/water
emulsion, it is this emulsion which determines the overall dynamics. For carbon dioxide
droplet Damköhler numbers greater than unity, the continuous water phase is not fully
utilized and the water/carbon dioxide emulsion dominates the overall dynamics.

The models presented in this chapter provide guidelines for the selection of
reactions to be conducted in two-phase systems consisting of carbon dioxide and water.
Although the models have been developed for first order kinetics, the qualitative trends
should provide insight into reaction/transport interactions for more complicated schemes
involving multiple steps and higher order kinetics. Provided rate and partitioning data,
these models can be used to determine the practicality of conducting the reaction in a
two-phase environment and the benefit which can be expected from sonication.

Author's Note. The study of the effects of ultrasonic power density on benzoyl chloride
hydrolysis was combined with turbidity data from Chapter 4 and published in:
Steinfeld, J.I. Ultrasonic Emulsification of Liquid, Near-Critical Carbon Dioxide-Water
107, 5503.

A detailed treatment of benzoyl halide hydrolysis describing kinetic data will be
published in a second paper.

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CHAPTER 7

WATER AS A CATALYST: RATE ACCELERATION AND SELECTIVITY IMPROVEMENT OF A BIMOLECULAR REACTION IN EMULSIONS OF DENSE CARBON DIOXIDE AND WATER

7.1 Introduction and Motivation

Background. In Chapter 1, water was introduced as a solvent for organic transformations. Water fulfills the dual roles of increased process efficiency and environmental compatibility for many industrially relevant synthetic reactions. While the environmental compatibility of water is clear, the discovery of its technological advantages has been more recent. Prior to the seminal works of Grieco\textsuperscript{1,2} and Breslow\textsuperscript{3,4} in the early 1980’s, water was not considered to be a practical solvent for the large majority of synthetic chemical conversions due to the limited solubility of most organic compounds. Working independently, Grieco\textsuperscript{1} and Breslow\textsuperscript{3} found that certain Diels-Alder reactions proceed at rates nearly 1000-fold faster in aqueous media than in hydrocarbon solvents. These findings changed the common perception of water and fueled two decades of intense investigation of the reactivity of organic compounds in water.

It is now realized that, in addition to many Diels-Alder reactions,\textsuperscript{1-8} dipolar cycloadditions,\textsuperscript{9} Claisen rearrangements,\textsuperscript{10,11} Michael additions,\textsuperscript{12} and Barbier additions\textsuperscript{13} can be accelerated when conducted in water rather than conventional hydrocarbon solvents. A recent review by Lubineau and Auge\textsuperscript{14} describes many chemical reactions which exhibit the advantages of using water as a solvent for chemical reactions. Although the role of water in these reactions is complex, experimental\textsuperscript{5-8,15} and theoretical\textsuperscript{16,17} studies have shown that the hydrophobic effect and enhanced hydrogen bonding of water to highly polarized transition states dominate the accelerative effects of water on reaction rates. The relative contributions of these two mechanisms is the subject of current inquiry.\textsuperscript{18}
Despite academic interest, water has not been adopted as a reaction solvent on a commercial scale. The greatest obstacle barring more general use of water as a solvent for chemical reactions is the limit on production rates associated with the low water solubility of most organic reagents. There are two potential engineering solutions to increase production rates, both of which suffer from severe disadvantages:

1) Use of reactors with volumes sufficiently large to maintain required production rates, while ensuring one-phase conditions. There are two drawbacks to this approach: 1) recovery of low concentrations of organic compounds from aqueous streams is energy intensive and costly and 2) the low solubilities of the organic reactants offsets the increases in production rates anticipated by water-accelerated chemical kinetics.

2) Deploying a second organic phase in addition to the water phase. Use of an organic solvent clearly compromises the environmental advantages of aqueous based chemistry and is not a satisfactory option. Alternatively, one of the reactants could be deployed as a second phase. The primary drawback to this approach is that the favorable selectivities anticipated with aqueous based chemistry will most likely be drastically limited by side reactions in the organic phase. The exothermic polymerization of cyclopentadiene, which proceeds so rapidly that it is an explosion hazard, is a dramatic example of an undesired side reaction which can occur if one of the reagents is present as a separate phase.

Although neither of these simple engineering approaches is acceptable, a wide array of chemistry-based solutions have been proposed. Chemists recognized the limitations of aqueous solubility at an early stage; several years after his initial investigations into aqueous acceleration of Diels-Alder reactions, Grieco demonstrated that addition of carboxylate groups to common dienes increased their water solubility while retaining the other beneficial aspects (e.g., increased rates) of aqueous reactivity. The primary criticism of this work is that it restricts the selection of reactants, thus limiting the spectrum of products that can be obtained. Since Grieco’s studies, a range of techniques have been investigated, including the use of:
• polar cosolvents to increase solubility of organic molecules\textsuperscript{6}
• glucose-grafted dienes for increased water solubility of particular reagents\textsuperscript{20}
• salts\textsuperscript{21} and Lewis acids\textsuperscript{22,23} to further increase Diels-Alder reactivity
• surfactants to solubilize organic reagents\textsuperscript{24}
• combined Lewis acid-surfactants\textsuperscript{25-27}

Although some of these studies have been quite successful, all of them suffer from inherent drawbacks, either the need for additives (Lewis acids, salts, surfactants), limitations in the range of reagents that can be used, or an increase in the number of chemical steps required to form the desired product. An example from the research of Engberts and his coworkers is illustrative. Studying the Diels-Alder reaction between custom-designed bidentate dienophiles and cyclopentadiene, these researchers found that addition of the combined Lewis-acid surfactant, Cu(II) (dodecyl sulfate)\textsubscript{2}, to water resulted in a $1 \times 10^6$-fold acceleration of the reaction rate relative to pure acetonitrile. Although acceleration of a chemical reaction by 6 orders of magnitude is spectacular, this finding has yet to be extended to standard dienophiles, and its general applicability to commercial processes remains uncertain.

This chapter presents an alternative approach to overcome the solubility of water. This approach builds on the findings in Chapter 6 that chemical reactions of hydrophobic compounds can be conducted in biphasic systems consisting of water and dense carbon dioxide. Using carbon dioxide as the second phase in conjunction with water maintains the environmental benefits of aqueous reaction media, while addressing solubility limitations of organic reagents. Power ultrasound can efficiently accelerate chemical reactions which exhibit mass transfer limitations in the biphasic environment. A further advantage of the carbon dioxide/water system is that, potentially, it offers flexibility as the process can be modified simply by varying the ratio of the two solvents.

**Objective.** The objective of this study was to demonstrate that a model synthetic reaction could be conducted in a carbon dioxide/water mixture, obtaining selectivity close to that observed in the pure aqueous solvent without sacrificing production rates. The advantages of using ultrasound to improve rates and selectivities was also investigated.
7.2 The Diels-Alder Reaction as a Model for Reactivity in Carbon Dioxide/Water Systems

The Diels-Alder reaction is the most powerful tool available to chemists for formation of 6-membered rings. Many important pharmaceuticals and natural products contain 6-membered rings, and chemical routes to these products are quite important commercially. In recognition of its importance, Otto Diels and Kurt Alder were awarded the Nobel Prize in Chemistry in 1950 for their discovery of this chemical reaction in 1928.\(^{28}\)

Diels-Alder cycloadditions simultaneously break 2 pi bonds and form 2 sigma bonds. The simplest example is the reaction between ethylene and butadiene to form cyclohexene:

\[
\text{\(\text{C}_2\text{H}_4\)} + \text{\(\text{C}_4\text{H}_6\)} \rightarrow \text{\(\text{C}_6\text{H}_{12}\)} \quad (7-1)
\]

All Diels-Alder reactions take place between a diene (in this case butadiene) and a dienophile (in this case ethylene). For a given diene/dienophile pair, the reaction rate is governed by the electron densities of the two reagents. As a general rule, addition of electron donating groups to the diene and electron withdrawing groups to the dienophile accelerates the rates of Diels-Alder cycloaddition.\(^{29}\)

In addition to its industrial relevance, the Diels-Alder cycloaddition is a convenient choice as a model reaction in supercritical fluids because it:

1) proceeds in controlled fashion to the expected products (without formation of byproducts) at low temperatures (less than 100 °C) without the use of a catalyst.
2) follows classical, bimolecular second-order kinetics – first order with respect to each of the two reagents.
3) yields a mixture of isomers (either regio- or stereo-) depending on the choice of reactants, thus affording an opportunity to study selectivity.
4) reagents can be selected to ensure that the reaction is fast enough to obtain meaningful kinetic data in reasonable times (less than 50 hours), but slow
enough to study in standard batch reactors which are limited to reactions with characteristic half lives greater than several minutes.

Given these advantages, it is not surprising that there have been many investigations of Diels-Alder reactions in supercritical fluids, including those carried out in supercritical carbon dioxide\textsuperscript{30-43} and propane.\textsuperscript{44} Published findings suggests that Diels-Alder reactions proceed at rates that are somewhat slower than in hydrocarbon solvents. For instance, Weinstein\textsuperscript{45} reported that the reaction rate of the Diels-Alder cycloaddition of ethyl acrylate to cyclopentadiene was roughly 50\% that observed in liquid methylene chloride at the same temperature but at atmospheric pressure. Selectivities observed in supercritical carbon dioxide is comparable to those obtained in hydrocarbon solvents. In his study of the regioselectivity of a series of Diels-Alder reactions between substituted butadienes and methyl acrylate, Renslo, Weinstein, and their co-workers\textsuperscript{35} reported nearly identical selectivity in supercritical carbon dioxide and toluene.

It was desired to select one of the many possible diene/dienophile pairs of reagents for an in-depth study in the carbon dioxide/water system. Following the work of Breslow,\textsuperscript{3,4} the cycloaddition of cyclopentadiene to methyl vinyl ketone:

\[
\begin{align*}
\text{Endo} & \\
\text{Exo} & 
\end{align*}
\]

was selected as the model reaction. This reaction was suitable for four primary reasons: 1) the reported reaction rate in water is remarkably faster than in octane and other hydrocarbon solvents; 2) the selectivity enhancement (endo:exo) for this reaction in water is the most dramatic ever reported; 3) the solubility of cyclopentadiene in water is low (\textasciitilde 0.01 mol L\textsuperscript{-1} at 25 °C\textsuperscript{4}); however, it is nearly miscible with carbon dioxide at the conditions of interest; 4) the partitioning of the cycloadducts is expected to favor carbon dioxide, thus facilitating post-reaction separation of the products. Measured rates/selectivities for reaction (7-2) are presented in Table 7.1, illustrating the 1000-fold aqueous rate acceleration and the significant (20:1 as opposed to 4:1 in hydrocarbon solvents) improvements in selectivity. Furthermore, although ultrasound influences the rates and selectivities of some Diels-Alder reactions,\textsuperscript{46} previous investigations have not
revealed any sonochemical acceleration of the reaction between methyl vinyl ketone and cyclopentadiene. Thus, sonochemical effects were not expected to confound interpretation of experimental results.

An additional benefit of this reaction is the expected phase behavior of the dienophile. Methyl vinyl ketone is readily soluble in both water (at room temperature and pressure) and carbon dioxide (in the vicinity of its critical point). Based on its binary phase behavior, the partition coefficient of methyl vinyl ketone was expected to be relatively close to unity, thereby increasing access to water rates and selectivity. Many common dienophiles are less water soluble than methyl vinyl ketone and are expected to partition more favorably into the carbon dioxide phase than the water phase. Qualitatively, reagent partitioning to the water phase favors the water-like selectivities which were targeted by this study. The quantitative relationship between reagent partition coefficients and selectivity is discussed in the next section.

Table 7-1. Literature values for the bimolecular rate constant, \( k_2 \), and endo:exo selectivity of reaction (7-2) when conducted in different solvents. Rate experiments were conducted at 20 °C unless noted otherwise, while selectivity measurements were made in the vicinity of 25 °C. All experiments were performed at 1 bar.

<table>
<thead>
<tr>
<th>solvent</th>
<th>( k_2 \times 10^5 ) (L mol(^{-1}) s(^{-1}))</th>
<th>( S ) (endo:exo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopentadiene</td>
<td>not reported</td>
<td>3.85</td>
</tr>
<tr>
<td>isooctane</td>
<td>5.94 ± 0.3</td>
<td>not reported</td>
</tr>
<tr>
<td>isopropanol</td>
<td>9.12(^*)</td>
<td>not reported</td>
</tr>
<tr>
<td>ethanol</td>
<td>not reported</td>
<td>8.5</td>
</tr>
<tr>
<td>methanol</td>
<td>75.5</td>
<td>not reported</td>
</tr>
<tr>
<td>water</td>
<td>4400 ± 70</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>5190(^*)</td>
<td>not reported</td>
</tr>
</tbody>
</table>

\(^*\) measured at 25 °C by Blokzilj, Blandamer, and Engberts.

7.3 The Well-Mixed Theory for Bimolecular Reactions in Biphasic Systems

Most bimolecular chemical systems generally consist of multiple steps, obey global second-order kinetics, and can be challenging to model in one-phase systems. Although physical models were developed for an idealized chemical system in Chapter 6, more complicated systems do not differ substantially in terms of the underlying physics. Regardless of the complexity of the system, it is the interplay of mass transport, reagent partitioning, and chemical reactivity which governs overall reaction dynamics. For this
reason, development of physical models was not the primary objective in this chapter. Nonetheless, a simplified model, assuming well-mixed phases, was developed as a tool to interpret data obtained from the Diels-Alder system. The primary objectives of this model were to provide a basis of comparison for experimental measurements of conversion and selectivity and to demonstrate the use of carbon dioxide to improve throughput (that is, production rate per unit volume of the chemical reactor).

Figure 7-1 is a schematic of the physical situation to be modeled. Mass transport is assumed to be infinitely fast so that the carbon dioxide and water phases are always in thermodynamic equilibrium at a given time. As a result, the concentrations of solutes in the two phases are related by their respective partition coefficients. Clearly, this is a major simplification compared to the models described in Chapter 6. Nonetheless, for reactions with pseudo-first order rate constants less than roughly 0.5 s\(^{-1}\) (and corresponding water-based Damköhler numbers less than 0.03) observed hydrolysis rates of benzoyl halides are within approximately 50% of a well-mixed prediction, which is nearly within the experimental uncertainty of the data. Typical second-order rate

![Diagram of well-mixed model](image-url)

**Figure 7-1.** Schematic of the well-mixed model depicting concentration profiles of reagent \(A\) in the carbon dioxide and water phases during the course of reaction (from \(t_1\) to \(t_3\)). The concentration profiles are flat in both phases and the concentrations in the two phases are related by the partition coefficient at all times and there is no interfacial resistance to mass transport.
constants for Diels-Alder reactions are on the order of 0.01 L mol$^{-1}$ s$^{-1}$, so that Damköhler numbers for such transformations are anticipated to be considerably less than 0.03, provided that the concentrations of reagents are not much greater than 1 mol L$^{-1}$. Thus, well-mixed predictions of rates and selectivities provide reasonable targets for many reactions of commercial interest in carbon dioxide/water systems under sonicated conditions. Differences between experimental measurements and such predictions can be used as a diagnostic tool to improve understanding. Under silent conditions, the requirement for well-mixed conditions is a water-phase Hatta number, that is $(k_{rnxn} D_{AW})^{1/2} / k_w$, less than roughly 0.1. Based on the mass transport coefficients measured in Section 6.3, carbon dioxide/water mixtures can be assumed to be well-mixed for $k_{rnxn} < 1 \times 10^{-4}$ s$^{-1}$, a much more severe restriction than for sonicated conditions.

To develop expressions for conversion and selectivity, it is necessary to incorporate reaction rates into the well-mixed model described in Figure 7-1. Considering the Diels-Alder reaction between generic reagents $A$ and $B$ to the endo ($N$) and exo ($X$) products, the system of chemical reactions can be written as:

$$A + B \rightarrow N \rightarrow X$$

Cyclopentadiene is arbitrarily designated as $A$, and methyl vinyl ketone as $B$. The rate is first order with respect to both reactants, and the rate law is given by equation (7-5):

$$r_A = -k_2[A][B]$$

In the general case, the two reactions (denoted by their products, $N$ and $X$) occur in both phases ($C$ and $W$ for carbon dioxide and water, respectively) and their characteristic rates will be denoted as $k_C^N, k_C^X, k_W^N$, and $k_W^X$. For a well-mixed system, the concentrations of reactants in the two phases are related to their overall concentrations by the following equation:

$$V_{Tot}[A] = V_C[A]_C + V_W[A]_W$$

where $V_{Tot}$ is the total volume of the reactor, and $V_C$ and $V_W$ are the volumes of the carbon dioxide and water phases, respectively. The quantities $[A]_C$ and $[A]_W$ refer to the
concentrations of \( A \) in the respective phases. It is convenient to define the overall volume fraction (\( \phi_c \) and \( \phi_w \)) of a given phase:

\[
\frac{V_c}{V_{\text{tot}}} = \phi_c \tag{7-6a}
\]
\[
\frac{V_w}{V_{\text{tot}}} = \phi_w \tag{7-6b}
\]

Equation (7-6) implicitly assumes the presence of only two phases, an assumption which will be investigated further in Section 7.6 for a specific Diels-Alder system.

Continuing with the analysis, the partition coefficient of species \( i \) is defined as:

\[
K_{C/W}^i = \frac{[i]_C}{[i]_W} \tag{7-7}
\]

for a well-mixed system. As in Chapter 6, the partition coefficient will always be quoted in terms of molar concentration, since this choice of units is more convenient for partitioning in the presence of chemical reactions.

Equations (7-6) and (7-7) can be combined to provide mass balances of the four species. The mass balance for reactant, \( A \), is:

\[
[A]_{\text{tot}} = \phi_c [A]_C + \phi_w [A]_W = \phi_c [A]_C + \phi_w \left( \frac{K_{C/W}^A}{\phi_c + \frac{\phi_w}{K_{C/W}^A}} \right) [A]_C \tag{7-8}
\]

From the bimolecular rate laws, a dynamic mass balance can be written for \([A]_{\text{tot}}\):

\[
\frac{d[A]_{\text{tot}}}{dt} = -\frac{\phi_c (k_N^C + k_X^C)}{(\phi_c + \frac{\phi_w}{K_{C/W}^A})(\phi_c + \frac{\phi_w}{K_{C/W}^B})} [A]_{\text{tot}} [B]_{\text{tot}} - \frac{\phi_w (k_N^W + k_X^W)}{(\phi_c + \frac{\phi_w}{K_{C/W}^A})(\phi_c + \frac{\phi_w}{K_{C/W}^B})} \frac{1}{K_{C/W}^A K_{C/W}^B} [A]_{\text{tot}} [B]_{\text{tot}} \tag{7-9}
\]

It is convenient to define the ratio of the two reactant concentrations, \( R \), as:

\[
R \equiv \frac{[B]_{\text{tot}}(t = 0)}{[A]_{\text{tot}}(t = 0)} \tag{7-10}
\]

and the conversion, \( X \):

\[
X \equiv \frac{[A]_{\text{tot}}(t = 0) - [A]_{\text{tot}}}{[A]_{\text{tot}}(t = 0)} \tag{7-11}
\]
Chapter 7: Water as a Catalyst

It follows from the definition of \( R \), that:

\[
[B]_{\text{tot}} = [B]_{\text{tot}}(t = 0) - [A]_{\text{tot}}(t = 0)X = [A]_{\text{tot}}(t = 0)(R - X)
\]

(7-12)

In terms of \( X \) and \( R \), equation (7-9) becomes

\[
\frac{dX}{dt} = \left\{ \frac{\phi_c \left( k_c^N + k_c^X \right)}{(\phi_c + \frac{\phi_w}{K_{c/w}^A})(\phi_c + \frac{\phi_w}{K_{c/w}^B})} [A]_{\text{tot}}(t = 0) + \right. \\
\left. \frac{\phi_w \left( k_w^N + k_w^X \right)}{(\phi_c + \frac{\phi_w}{K_{c/w}^A})(\phi_c + \frac{\phi_w}{K_{c/w}^B})} \frac{1}{K_{c/w}^A K_{c/w}^B} [A]_{\text{tot}}(t = 0) \right\} (1 - X)(R - X)
\]

(7-13)

where \( \alpha_c \) and \( \alpha_w \) are defined as:

\[
\alpha_c = \frac{\phi_c \left( k_c^N + k_c^X \right)}{(\phi_c + \frac{\phi_w}{K_{c/w}^A})(\phi_c + \frac{\phi_w}{K_{c/w}^B})} [A]_{\text{tot}}(t = 0)
\]

(7-13a)

and

\[
\alpha_w = \frac{\phi_w \left( k_w^N + k_w^X \right)}{(\phi_c + \frac{\phi_w}{K_{c/w}^A})(\phi_c + \frac{\phi_w}{K_{c/w}^B})} \frac{1}{K_{c/w}^A K_{c/w}^B} [A]_{\text{tot}}(t = 0)
\]

(7-13b)

Equation (7-13) can be integrated directly, with the initial condition that \( X(t = 0) = 0 \) and the specification that \( R > 1 \) (which will be valid in this study). The conversion is then defined in terms of rate constants and partition coefficients:

\[
X = \frac{R - \exp \left\{ (R - 1)(\alpha_c + \alpha_w) t + \ln(R) \right\}}{1 - \exp \left\{ (R - 1)(\alpha_c + \alpha_w) t + \ln(R) \right\}}
\]

(7-14)

It is easily verified that equation (7-14) predicts that \( X(t = \infty) = 1 \), as it should.

An expression for the selectivity, that is the ratio of \([N]\) to \([X]\), can be formulated by writing transient mass balances around the two products. The final result is:
\[
S = \frac{[N]}{[X]} = \frac{k_c^N \phi_c + \frac{k_w^N \phi_w}{K_{C/W}^X K_{C/W}^B}}{k_c^X \phi_c + \frac{k_w^X \phi_w}{K_{C/W}^A K_{C/W}^B}}
\] (7-15)

As expected, for infinitesimally slow reaction in the carbon dioxide phase (or in the absence of a carbon dioxide phase altogether), the selectivity observed in pure water is recovered. Furthermore, low values of the partition coefficients (more water-soluble reactants) favor higher selectivity. Of course, there is a balance between selectivity and production rate enhancement; while the selectivity enhancement (relative to that observed in carbon dioxide) is greatest for reagents which partition most favorably into water, there is little benefit in using carbon dioxide if the reagents are already highly water soluble.

Equations (7-14) and (7-15) can be combined to form an expression for throughput to the endo product in a carbon dioxide/water emulsion relative to that in pure water, \(T_N\), provided a value for \([A](t = 0)\):

\[
T_N = \frac{[A]_{emulsion} S_{emulsion} X_{emulsion}}{[A]_{W,sat} S_{water} X_{water}}
\] (7-16)

where \([A]_{W,sat}\) is the saturation concentration of diene in water and the subscripts are self-explanatory. \([A]_{emulsion}\) can be determined from its saturation concentration in water and its concentration in carbon dioxide (\([A]_C\)):

\[
[A]_{emulsion} = \phi_w [A]_{W,sat} + \phi_c [A]_C(t = 0)
\] (7-17)

Since cyclopentadiene is essentially miscible with dense carbon dioxide, the saturation concentration of the diene in this phase is not a limitation. In practical applications, \([A]_C(t = 0)\) will be on the order of 1 mol L\(^{-1}\), which is much less than its saturation solubility. Combining equation (7-16) with (7-17) yields an expression for throughput:

\[
T_N = \left(\phi_w [A]_{W,sat} + \phi_c [A]_{C,sat}\right) SX
\] (7-18)

The behavior of \(T_N\) depends upon the exact values of the 6 parameters that appear in equations (7-14) and (7-15) (i.e., \(k_c^N, k_c^X, k_w^N, k_w^X, K_{C/W}^A, K_{C/W}^B\)). Equations (7-14), (7-15), and (7-18) will be referred to as the well-mixed model. The next section describes experiments and estimations of the 6 parameters in the well-mixed model and then uses these values to make predictions.
7.4 Estimation of Thermodynamic/Kinetic Parameters

Estimation of partition coefficients. In Chapter 3, the partition coefficient for methyl vinyl ketone was reported as $2.44 \pm 0.04$ (in molar units) at 30 °C and 80 bar and low solute concentrations ($[MVK]_{overall} = 0.05$ mol L$^{-1}$). This confirmed the hypothesis forwarded in Section 7.2 that methyl vinyl ketone partitions roughly equally between the two phases.

It was desired to determine the effect of methyl vinyl ketone concentration on its partition coefficient. Using the experimental procedure described in Chapter 3, $K_{cw}$ was measured as a function of methyl vinyl ketone concentration range from 0.05 – 1.0 mol L$^{-1}$ (in terms of $[MVK]_{overall}$) at 30 °C and 80 bar. The results of these measurements are plotted in Figure 7-2. For $[MVK]_{overall} > 0.66$ mol L$^{-1}$, the partition coefficient assumes a constant value of $\sim 4.6 \pm 0.5$ (in molar units). Below this concentration, the partition coefficient decreases to the value of $2.5 \pm 0.04$ reported in Chapter 3. Given this concentration dependence, it was possible to vary the apparent reaction rate in water by varying $[MVK]_{overall}$.

Also appearing in the design equations is the partition coefficient of cyclopentadiene. Measuring this parameter is confounded by the rapid dimerization of cyclopentadiene in water, the rate of which is rather uncertain. In fact, the two reported

![Graph](image)

**Figure 7-2.** Experimental measurements of the carbon dioxide/water partition coefficient of methyl vinyl ketone as a function of solute concentration. Conditions: 30 °C, 80 bar.
values for the dimerization rate differ by a multiple of 50.\textsuperscript{48,49} To avoid the uncertainties associated with cyclopentadiene dimerization in the two-phase environment, the correlations presented in Section 3.5 were used to estimate $K_{\text{CW}}$. At fixed density, the most accurate estimation method was the following Linear Solvation Energy Relationship (LSER):

$$\log_{10} K_{\text{CW}} = 1.610 - 0.973\pi^H_2 - 3.077\alpha^H_2 - 3.319\beta^H_2 + 2.780V_2$$  \hspace{1cm} (7-19)

where $\pi^H_2$ is the solute polarity/polarizability, $\alpha^H_2$ is the solute hydrogen bond acidity, $\beta^H_2$ is the solute hydrogen bond basicity, and $V_2$ is the molar volume of the solute. These four parameters are referred to as "solute descriptors" and are determined by independent measurements. The values of the coefficients were determined in Chapter 3 by regression analysis. Although LSER solute descriptors were not available for cyclopentadiene, values for a number of related hydrocarbons were. Table 7-2 is a list of published LSER parameters and $K_{\text{CW}}$ estimates for a variety of C5 and 6 hydrocarbons. Although the partition coefficients in Table 7-2 span roughly an order of magnitude, some trends are apparent. In general, both cyclization and introduction of unsaturation increase water solubility and decrease $K_{\text{cw}}$. Introduction of a single degree of unsaturation decreases $\log_{10} K_{\text{CW}}$ by roughly 0.50, while the second double bond decreases $\log_{10} K_{\text{CW}}$ by 0.30 units additional units, at least for the linear hydrocarbons for

### Table 7-2. Solute descriptors from reference (50) and $K_{\text{CW}}$ estimates for C5,6 hydrocarbons. Equation (7-19) was used for estimating $K_{\text{CW}}$ at 30 °C and 80 bar. $\pi^H_2$ is solute polarizability, $\alpha^H_2$ is the solute hydrogen-bond acidity, $\beta^H_2$ is the solute hydrogen bond basicity, and $V_2$ is the solute molar volume.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\pi_2$</th>
<th>$\alpha_2$</th>
<th>$\beta_2$</th>
<th>$V_2$</th>
<th>$\log_{10} K_{\text{CW}}$</th>
<th>$K_{\text{CW}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentane</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.8131</td>
<td>3.31</td>
<td>2100</td>
</tr>
<tr>
<td>1-pentene</td>
<td>0.08</td>
<td>0.0</td>
<td>0.07</td>
<td>0.7701</td>
<td>2.88</td>
<td>760</td>
</tr>
<tr>
<td>penta-1,4-diene</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.7271</td>
<td>2.55</td>
<td>350</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.7045</td>
<td>2.91</td>
<td>820</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.6615</td>
<td>2.36</td>
<td>230</td>
</tr>
<tr>
<td>hexane</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.954</td>
<td>3.70</td>
<td>5100</td>
</tr>
<tr>
<td>1-hexene</td>
<td>0.08</td>
<td>0.0</td>
<td>0.07</td>
<td>0.911</td>
<td>3.27</td>
<td>1900</td>
</tr>
<tr>
<td>hexa-1,5-diene</td>
<td>0.20</td>
<td>0.0</td>
<td>0.1</td>
<td>0.868</td>
<td>2.94</td>
<td>870</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.8454</td>
<td>3.30</td>
<td>2000</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.8024</td>
<td>2.76</td>
<td>570</td>
</tr>
</tbody>
</table>
which data are available. Cyclization decreases $\log_{10} K_{CW}$ by roughly 0.4 units, for both saturated and unsaturated hydrocarbons. Thus, based on $\log_{10} K_{CW} \sim 2.36$ for cyclopentene, it seems that $2.36 - 0.3$ (for the second degree of unsaturation) $\sim 2.1$ is a reasonable estimate for $\log_{10} K_{CW}$ of cyclopentadiene.

It is somewhat difficult to assign an uncertainty to this value, given the guess work involved in the estimation process. Provided accurate values of the solute descriptors, the inherent uncertainty of the LSER correlation is roughly $0.13 \log_{10}$ units. Since the solute descriptors were not known accurately, the uncertainty in the estimated partition coefficient was greater than that inherent to the LSER method. LSER-estimated partition coefficients were extrapolated by $0.3 \log_{10}$ units, and this extrapolation represents the most conservative estimate of the uncertainty. This implies that $\log_{10} K_{CW}$ is equal to $2.1 \pm 0.3$ which corresponds to a value of $K_{cw}$ equal to $130 \pm 90$ for cyclopentadiene at $30 \, ^\circ C$ and 80 bar.

In Chapter 3, it was suggested that the LSER method should be used in conjunction with the octanol/water group contribution approach and a correlation to water solubility to build confidence in partition coefficient estimates. The Leo and Hansch\textsuperscript{51} octanol/water approach for cyclopentadiene (which consists of 5 carbon atoms, 6 hydrogen atoms and two double bonds) yields a value of $K_{CW}$ equal to $70 \pm 50$, which is somewhat lower than, but within the uncertainty of the LSER estimate. The solubility of cyclopentadiene in water ($0.01 \, \text{mol} \, \text{L}^{-1}$) corresponds to $K_{cw}$ equal to $200 \pm 100$; slightly higher than, but still in agreement with the LSER estimate. The rough agreement of these three estimation methods adds credibility to the LSER value, and suggests that the true value of the partition coefficient of cyclopentadiene lies in the range between 50-200. For comparison, the partition coefficient of cyclopentene was reported as roughly $400 \pm 40$ in Section 3.4.

**Measurement of rate parameters in water.** The rate,\textsuperscript{3,5} endo to exo selectivity,\textsuperscript{4} and Arrhenius activation parameters\textsuperscript{5} ($E_A$ and $\ln A$) of reaction (7-2) have been reported in the literature. Unfortunately, it was unclear whether the available selectivity data had been measured in a single phase system given that the reported formal concentration of cyclopentadiene ($0.015 \, \text{mol} \, \text{L}^{-1}$) in these experiments was greater than its saturation concentration ($0.01 \, \text{mol} \, \text{L}^{-1}$). To verify the published rates and Arrhenius parameters and
to clarify reaction selectivity, \( k^N_W \) and \( k^X_W \) for reaction (7-2) were measured at atmospheric pressure over a range of temperatures (10-40 °C). Also, some Diels-Alder reactions are sensitive to the solution pH.\(^{24} \) Since a water phase in contact with pressurized carbon dioxide is acidic (pH \( \approx 3 \))\(^{52} \) and all kinetic data were available at neutral conditions, the pH dependence of reaction (7-2) was evaluated.

In a typical kinetic experiment, 40 \( \mu \)L of methyl vinyl ketone (Sigma Aldrich, 98% purity) and 5 \( \mu \)L of cyclopentadiene (freshly obtained with an estimated purity of 98% from cracking the dimer) were mixed in 100 cm\(^3\) of deionized water (at least 18.0 MΩ cm resistivity). The concentrations of cyclopentadiene and methyl vinyl ketone in the reaction mixture were 0.0025 mol L\(^{-1}\) and 0.12 mol L\(^{-1}\), respectively, thus ensuring pseudo-first order kinetics (with respect to the diene) and single phase conditions. The reaction vessel was placed in a heated (VWR 1110 heater/circulator)/cooled (VWR 1109) bath. Temperature was measured to within ±1.0 °C with a K-type thermocouple and maintained at its set point using a PID controller (Omega, 9122A). The reaction vessel was sealed tightly to minimize evaporative losses. Ten samples were taken over a period of 3.5 hours and analyzed for methyl vinyl ketone, cyclopentadiene, dicyclopentadiene (a possible side product due to dimerization of cyclopentadiene), and the endo and exo cycloadducts using gas chromatography (GC, Agilent, 6890) equipped with a DB-Wax column (J&W Scientific) equipped with a flame-ionization detector (FID). The elution times were: cyclopentadiene (3.0 min), methyl vinyl ketone (6.5 min), dicyclopentadiene (10.2 min), endo cycloadduct (12.0 min), and exo cycloadduct (12.4 min). Three separate runs were performed at each temperature (10, 20, 30, and 40 °C). In two separate trials, conducted at 30 °C, the solution pH was lowered to ~2 by addition of 0.001 mol HCl.

Figure 7-3 contains Arrhenius plots of \( k^N_W \) and \( k^X_W \) including both the current data set (at pH = 7 and 2) and data from the literature. The available literature data agree with the measured rate constants to within ±10%. For example, the second order rate constant measured at 30 °C was 0.0636 ± 0.003 L mol\(^{-1}\) s\(^{-1}\), while the literature value was 0.067 L mol\(^{-1}\) s\(^{-1}\). The effect of acid on the rate constants was negligible; a 5 order of magnitude change in [H\(_3\)O\(^+\)] resulted in a 1% change in the measurements of rate constants, which is not resolvable given the accepted limits of experimental error.
Figure 7-3. Arrhenius plots for the Diels-Alder reaction of cyclopentadiene and methyl vinyl ketone in water at neutral and acidic pH from this thesis was compared to data from Rideout and Breslow and Blokzijl et al. Conditions: 30 °C, 1 bar, 50-fold excess dienophile. Two data points were measured at acidic pH, but the two values agreed so closely with one another that they are indistinguishable in this figure (0.0663 and 0.0661 L mol⁻¹ s⁻¹).

Selectivity for this reaction was a weak function of temperature; at 10 °C endo:exo was roughly 22 ± 3 and by 40 °C it had fallen to 19.2 ± 0.5, roughly comparable within the accepted limits of uncertainty. The measured range of endo:exo selectivities is in good agreement with the reported value of 21.4. Apparently, the small amount of the second phase present in Breslow’s experiments did not appreciably affect the measured selectivity. The selectivity was not affected by acid content. At neutral pH and 30 °C, the selectivity was 20.9 ± 0.3, while under acidic conditions it was 21 ± 0.4.

Table 7-3 lists rate constants (at 30 °C) and Arrhenius parameters measured in this study and from the literature. The measured Arrhenius parameters for the overall reaction agree with the literature value to within roughly 15%. This is reasonably good
Table 7-3. The true second order rate constant ($k_2$) and Arrhenius parameters (i.e., $E_A$ and ln $A$) for reaction (7-2), measured in this study and found in the literature. No values for the individual endo/exo pathways were available in the literature. The reported errors are based on the errors in the best-fit slope and intercept based on the plots in Figure 7-3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_2$ (L mol$^{-1}$ s$^{-1}$)</th>
<th>$E_A$ (kJ mol$^{-1}$)</th>
<th>ln $A$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>overall ($k_w^N + k_w^S$)</td>
<td>0.067*</td>
<td>39.4 ± 0.7</td>
<td>12.7 ± 0.3</td>
<td>Blokzijl 1991 (5)</td>
</tr>
<tr>
<td>overall ($k_w^N + k_w^S$)</td>
<td>0.064 ± 0.003</td>
<td>44.4 ± 2.0</td>
<td>15.0 ± 0.8</td>
<td>this study</td>
</tr>
<tr>
<td>$k_w^N$</td>
<td>0.061 ± 0.003</td>
<td>44.3 ± 2.0</td>
<td>13.2 ± 1.0</td>
<td>this study</td>
</tr>
<tr>
<td>$k_w^S$</td>
<td>0.0029 ± 0.0002</td>
<td>47.7 ± 2.6</td>
<td>14.9 ± 0.8</td>
<td>this study</td>
</tr>
</tbody>
</table>

*extrapolation based on the reported values of $E_A$ and $k_2$ at 25 °C.

agreement considering that correlation between the activation energy and pre-exponential factor often limits reproducible measurement of Arrhenius parameters.

**Measurement of rate parameters in dense carbon dioxide.** The rate and selectivity of reaction (7-2) were measured in pure supercritical carbon dioxide. Weinstein$^{45}$ investigated this reaction in supercritical carbon dioxide, reporting a yield of 29% and an endo:exo selectivity of 4.6:1 after 4 hrs at 50 °C and 103 bar. To supplement this data point, the rate of reaction (7-2) was measured at 30 °C and 80 bar (fluid density of 0.75 g cm$^{-3}$) as part of this study.

The rate measurements were performed in the view cell pressure vessel designed and described in detail by Weinstein$^{35,45}$ thus only its most salient features are repeated here. The reactor was fabricated from a 6.4 cm x 6.4 cm x 12.7 cm block of 316 stainless steel. A cylindrical chamber, with a length of 8.0 cm and a diameter of 1.9 cm was bored into this block. The total working volume of the reactor was roughly 25 cm$^3$ and the maximum operating pressure was estimated as approximately 500 bar (at 25 °C). Six ports were machined into the pressure vessel and were used for the inlet and outlet valves (Whitey, ss-3NBM4), a sampling valve (Valco Instrument Company, Inc., uw-type), pressure measurement, and a thermocouple, respectively. The primary opening to the cylindrical chamber was sealed using a $\alpha$-Al$_2$O$_3$ sapphire window and a stainless steel hex nut, similar to that used for the acoustic reactor described in Chapter 4. The pressure seal was made using a combination of Teflon and buna-N rubber (90 durometer on the Shore A scale) gaskets. Figure 7-4 is a digital photograph of the reactor, stainless steel hex nut, and $\alpha$-Al$_2$O$_3$ sapphire window.
Figure 7-4. High-pressure view-cell reactor designed by Weinstein\textsuperscript{35,45} and used for kinetic measurements in pure carbon dioxide in this work.

The reactor contents could be mixed using a Teflon-coated stir bar coupled to a standard magnetic stir plate. Pressure measurements were made with a Bourdon tube pressure gauge (McDaniels Controls Inc.) with a readability of ±2 bar. As before, temperature was measured to within ±1 °C using a T-type thermocouple (Omega Engineering). The temperature was maintained at its set point using a PID controller (Omega Engineering, 9001CN) and thermal tape (Barnstead).

In a typical experiment, either 500 or 1000 μL of methyl vinyl ketone were loaded into the reactor at atmospheric pressure using a standard pipette. The reactor was then sealed, heated to 30 °C, and pressurized to the vapor pressure of carbon dioxide at room temperature (roughly 60 bar). The reactor and its contents came to thermal equilibrium after 30 min, at which point 15 μL of cyclopentadiene were injected into the reactor through a standard 6-way valve (VICI, uw-type) using pressurized carbon dioxide. The reactor was then fully pressurized to 80 bar and allowed to re-equilibrate for roughly 1 hour. After this equilibration time, 500 μL samples were drawn from the reactor at
known time intervals using a second 6-way valve. The reactor samples were
depressurized through 10 cm$^3$ of cold (≈0 °C) acetone and then analyzed for reactants,
products, and byproducts with the GC method used for aqueous rate measurements.

Three trials were conducted, each lasting roughly 48 hours and yielding 3 time
points. The initial concentration of cyclopentadiene was 6 × 10$^{-3}$ mol L$^{-1}$ and that of
methyl vinyl ketone was 0.2 or 0.4 mol L$^{-1}$ so that the dienophile was in 30-fold excess,
ensuring pseudo-first order kinetics. The reactions were always performed in a one-
phase region which was confirmed visually.

Figure 7-5 is a plot of cyclopentadiene conversion as a function of time. The
slope of this plot (when divided by the known, excess concentration of methyl vinyl
ketone) was taken to be the overall second order rate constant (for both the endo and exo
pathways) and is equal to 3.22 ± 1.47 × 10$^{-5}$ L mol$^{-1}$ s$^{-1}$. The measured endo:exo
selectivity was 4.43 ± 0.08, where the uncertainty is based completely on the standard
devation estimated from the available data set. The measured selectivity is within 5%

![Figure 7-5. Plots of the disappearance of cyclopentadiene (reagent A) in its Diels-Alder reaction with methyl vinyl ketone. Experiments were conducted in liquid near critical carbon dioxide (30 °C, 80 bar, $\rho = 0.7$ g cm$^{-3}$) in the presence of 30-fold excess dienophile.](image)
of that reported by Weinstein\textsuperscript{45} at 50 °C; Weinstein did not report an uncertainty in his value. The individual rate constants for the two pathways were calculated from the measured selectivity and the overall second order rate constant as $2.63 \pm 0.12 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ (for the endo pathway) and $5.94 \pm 0.29 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ (for the exo pathway), respectively. As expected, the rate in dense carbon dioxide is 50% slower than in hydrocarbon solvents and 2000-fold slower than in water.

### 7.5 Model Predictions

Predictions of conversion, selectivity, and throughput based on the well-mixed model are plotted as functions of the volume fraction of water in a biphasic water/carbon dioxide environment in Figure 7-6. Parameter values are listed in Table 7-4. Throughput and conversion are plotted for $[A]_{C,0}$ equal to 0.5, 1.0, and 1.5 mol L\(^{-1}\) and $R = 2$. As the volume fraction of water decreases, the selectivity and conversion decrease monotonically. Physically, this behavior is anticipated by the fact that reaction (7-2) is both faster and more selective toward the endo product in water than in dense carbon dioxide. In contrast, throughput (that is the production rate per unit volume of reactor) is maximized at a water content of roughly 65%, depending on $[A]_{C,0}$. The maxima in throughput are the result of the balance between aqueous reaction rates/selectivities and the increased overall concentration of cyclopentadiene possible using a supercritical carbon dioxide phase.

**Table 7-4.** Measured/estimated values of the kinetic/thermodynamic parameters which appear in equation (7-14), (7-15), and (7-18) at 30 °C and 80 bar.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_C^H$</td>
<td>$2.63 \pm 0.12 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_C^X$</td>
<td>$5.94 \pm 0.29 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_W^H$</td>
<td>$0.061 \pm 0.003 \text{ L mol}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_W^X$</td>
<td>$0.0029 \pm 0.0002 \text{ L mol}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$K_{CW}^A$ (cyclopentadiene)</td>
<td>150 (prediction, molar units)</td>
</tr>
<tr>
<td>$K_{CW}^B$ (methyl vinyl ketone)</td>
<td>$4.66 \pm 0.4$ (molar units)\textsuperscript{a}</td>
</tr>
<tr>
<td>$[A]_{W,sat}$</td>
<td>$0.01 \text{ mol L}^{-1}$\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} for $[MVK]_0 > 0.66 \text{ mol L}^{-1}$.

\textsuperscript{b} from Breslow et al. 1983 (4).
Figure 7-6a,b. Well-mixed selectivity predictions for the Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water mixtures with varying water content. Conversion predictions are presented for varying cyclopentadiene content, $[A]_0$. Conditions: 30 °C, 80 bar. Kinetic and thermodynamic parameters are listed in Table 7-4. For these parameter values, selectivity is nearly a linear function of $\phi_W$. 
Figure 7-6c. Well-mixed throughput predictions for the Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water mixtures with varying water content. Predictions are presented for varying cyclopentadiene content, \([A]_0\), otherwise the conditions are identical to those in Figure 7-6a. Kinetic and thermodynamic parameters are listed in Table 7-4.

As expected, the maximum percentage increase in throughput relative to that in pure water is strongly affected by the concentration of diene. For an initial diene concentration equal to 1.5 mol L\(^{-1}\), there is a 30-fold increase in throughput at the optimal value of water fraction. Figure 7-6 indicates a selectivity of 14:1 at the throughput-optimized volume fraction of water, a significant improvement over that observed in dense carbon dioxide (4:1). In industrial practice it may not be possible to adjust operating conditions to obtain maximum throughput, since a variety of additional economic factors, such as the cost of recovering the desired product, contribute to such decisions. An advantage of the water/carbon dioxide system is its flexibility as it affords optimization based on a combination of throughput, selectivity, and conversion, simply by varying the relative amounts of the two phases.
7.6 Conversion and Selectivity of the Diels-Alder Reaction between Cyclopentadiene and Methyl vinyl ketone in Carbon Dioxide/Water Systems

The predictions presented in Section 7.5 need to be evaluated experimentally. This section describes an experimental investigation of the model Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene conducted in carbon dioxide/water mixtures. The experimental measurements are compared to predictions based on perfect mixing, providing insight into reactor geometry and phase behavior.

7.6.1 Experimental methods

Materials. Methyl vinyl ketone (purity > 99%) and HPLC-grade acetone (purity > 99.55) were obtained from Sigma Aldrich and used as received. Dicyclopentadiene was purchased from Sigma Aldrich and cracked at 180 °C to obtain the monomer with a purity of roughly 98% (as determined by gas chromatography). The freshly prepared monomer was used immediately or stored at −10 °C for up to 12 hours before use. Water was deionized to a minimum resistivity of 18.1 MΩ (Barnstead Nanopure) and used immediately. Grade 5.5 carbon dioxide (purity > 99.9995%) was obtained from BOC Gases and used without further treatment.

Experimental conditions. All experiments were conducted in the acoustic reactor described in Section 4.5.1 and only modifications to the standard setup are noted here. Reactions were run at 30 °C and 80 bar, conditions which were selected for two reasons: 1) the effects of ultrasound were well established under these conditions; 2) the liquid-like density (0.70 g cm⁻³) of carbon dioxide at this temperature and pressure was expected to favor high solubility of the reagents and promote two-phase conditions.

Ultrasound was introduced directly into the reactor using the Branson sonication unit described in Chapter 4. The operating frequency of this instrument is 20 kHz, and the ultrasound was pulsed at a duty of 25% (based on a 1 s cycle) for reactions studied at a power density of 0.55 W cm⁻³. This power density was selected based on earlier the observation that the accelerative effects of ultrasound saturate at roughly 0.5 W cm⁻³.

Two orientations of the sonic horn were investigated. The horn was either inserted in the carbon dioxide phase, and pointed down toward the carbon dioxide/water interface, or in the water phase, and pointed up toward the interface. These two
orientations will be referred to as the "CO₂" and "H₂O" configurations, denoting the fluid phase in which the horn is inserted.

In addition to ultrasound, the contents of the reactor were agitated by the recirculation loop discussed previously in Chapters 4 and 6. In contrast to Chapter 6, the water phase was recirculated as large droplets (several mm diameter) through the carbon dioxide phase. This recirculation method was selected because the primary motivation for this study was not a detailed engineering analysis, but rather a demonstration of the technological advantages of power ultrasound in the carbon dioxide/water environment. Recirculation of the water through the carbon dioxide phase provided better mixing than internal recirculation of water described in Chapter 6 and thus was a more realistic comparison for the acoustic agitation technique.

In Chapter 6, the effect of intrinsic reactivity was explored by varying the reactants. This was not so easily accomplished in the bimolecular Diels-Alder system since more kinetic and thermodynamic parameters (4 rate constants and 2 partition coefficients, compared to 1 rate constant and 1 partition coefficient) are required to interpret experimental results. Instead, the reactions were performed with an excess reagent. Conducting the reaction with one reagent in excess simultaneously simplified the rate law (from second order kinetics to pseudo-first order kinetics) and provided the opportunity to artificially vary the apparent reaction rate constant by varying the concentration of the excess reagent. Since methyl vinyl ketone is quite soluble in both water and dense carbon dioxide, it was the natural choice as the excess reagent. In the presence of an excess reagent, the effective reaction rate in the water phase is

\( (k_w^N + k_w^X)[MVK]_w \). For a well-mixed system, the apparent water phase reaction rate can be written in terms of the initial concentration of methyl vinyl ketone:

\( (k_w^N + k_w^X)[MVK]_0/(\phi_W + \phi_C K_{CW}) \). The equivalent expression in carbon dioxide is:

\( (k_C^N + k_C^X)K_{CW}[MVK]_0/(\phi_W + \phi_C K_{CW}) \). The concentration-dependent partition coefficient data presented earlier were used in conjunction with this approach to determine pseudo-first order rate constants. For example, at a methyl vinyl ketone loading of 1.0 mol L⁻¹, the pseudo-first order rate constant can be estimated as 0.04 in water and 2 x 10⁻⁵ s⁻¹ in
carbon dioxide. For a methyl vinyl ketone loading of 0.1 mol L$^{-1}$, in contrast, the water phase reaction rate is 3 x 10$^{-3}$ s$^{-1}$, while that in carbon dioxide is 1 x 10$^{-6}$ s$^{-1}$.

To formulate an experimental plan with a reasonable number of experiments, it was necessary to select the initial concentration, or range of concentrations, of methyl vinyl ketone. This decision was guided primarily by considerations of the pseudo-first order reaction rate. The bimolecular rate constant for the reaction of methyl vinyl ketone and cyclopentadiene was measured as roughly 0.065 L mol$^{-1}$ s$^{-1}$ at 30 °C (see Table 7-3). Since the study of benzoyl halide hydrolysis in Chapter 6 had shown that, for true first-order reactions, the acoustic acceleration was minimal for first-order reactions with rate constants less than 0.005 s$^{-1}$ (water-phase Hatta numbers less than 0.75), it was decided to conduct the majority of the experiments with as large a dienophile concentration as possible. $[\text{MVK}]_0 = 1.0$ mol L$^{-1}$ was selected because preliminary experiments indicated clear three-phase behavior for larger concentrations of the dienophile in the water/carbon dioxide system at 30 °C and 80 bar. As it turned out, a concentration of methyl vinyl ketone equal to 1.0 mol L$^{-1}$ may have resulted in the formation of a dienophile rich phase. Phase behavior aside for now, using the formula above, a methyl vinyl ketone concentration of 1.0 mol L$^{-1}$ results in a water-based pseudo-first order rate constant of roughly 0.04 s$^{-1}$ and a water-phase Hatta number of approximately 2.

Although it would be interesting to explore the effects of faster reaction rates, larger concentrations of dienophile were not accessible and there have been no reports of faster bimolecular Diels-Alder reactions than that between methyl vinyl ketone and cyclopentadiene. A number of experiments were conducted at concentrations of methyl vinyl ketone lower than 1 mol L$^{-1}$ to explore the “tunability” of the pseudo-first order rate constant and to determine if selectivity could be maximized for slower apparent reaction rates. These results are presented in Section 7.6.2.

**Experimental Protocol.** Selectivity and conversion (after 1 hour) were measured for the Diels-Alder reaction of methyl vinyl ketone and cyclopentadiene in carbon dioxide/water mixtures both in the presence and absence of emulsifying ultrasound. The primary independent variable was the volume fraction of water, which was varied from 0.15 to 0.85 (the carbon dioxide accounted for the remainder). In a typical run, a solution of
methyl vinyl ketone and water was prepared. After this solution was added to the reactor, it was sealed and pressurized to 70 bar with carbon dioxide. The reactor contents were agitated using the recirculating pump (LDC Analytical) operating at a flow rate of 15 cm$^3$ min$^{-1}$ for roughly 30 minutes as thermal equilibrium was achieved. In experiments where it was used, sonication was commenced during this time.

Once thermal equilibrium had been reached, the pressure was increased to 80 bar. The reaction was initiated by injecting 100 µL of cyclopentadiene into the reactor through a calibrated loop via a standard 6-way valve (Valco Instruments Company, Inc., uw-type) using the recirculating water phase. Upon cyclopentadiene injection, the carbon dioxide phase became turbid for several seconds. The carbon dioxide phase cleared within 1-2 min and remained so for the remainder of the experiment. The reaction was concluded after 1 hour by venting the entire reactor contents into cold acetone. A high-pressure metering valve (Autoclave Engineers, 10VRMM2812) heated with thermal tape (Barnstead) operated at 40 V (as set by a standard variable transformer) was used to maintain an even flow of depressurizing carbon dioxide and prevent formation of ice in the vent line. A glass vessel equipped with a frit (10 µm pore diameter) was used to improve recovery of volatile components. Experiments conducted without methyl vinyl ketone present indicated that >95% of the cyclopentadiene (the more volatile reagent with a normal boiling point of roughly 35 °C) could be recovered using this method. The cold acetone into which the reactor contents had been vented was diluted to a standard volume by more acetone and analyzed by GC (Agilent, 6890) using the method described for the measurement of rate data in pure water. The reactor was rinsed with acetone and this wash was also analyzed by GC. Uncertainties in calculated selectivity and conversion were based on the error in the GC calibration which was ± 3%.

7.6.2 Results

Effect of water content. Twenty-five experiments were conducted with $[\text{MVK}]_0 = 1.0$ mol L$^{-1}$ over a range of volume fractions of water. Fourteen of these experiments were conducted with the horn in the CO$_2$ orientation, the remainder in the H$_2$O orientation. Experimental measurements of conversion and selectivity were quite reproducible; 5 replicates, conducted silently at $\phi_W = 0.85$, resulted in a range of conversions from 0.62 to 0.74 and a range of selectivities from 5.82 to 6.25.
Figure 7-7 contains plots of measured selectivities and conversions obtained for reaction (7-2) in the carbon dioxide/water system under both silent and sonicated conditions. Under silent conditions, conversion and selectivity increase with increasing water content. Sonication generally improves both conversion and selectivity, though the effect of ultrasound is small in some instances. Under the best conditions depicted in Figure 7-7 (i.e., 75% water content, sonication in the CO₂ geometry) the selectivity was nearly 13:1, a dramatic improvement over that observed in pure carbon dioxide (4.4:1).

Previous reports of tuning reaction selectivity in supercritical fluids provide a context for the current measurements. Clifford et al.\textsuperscript{36,37} studied the endo:exo selectivity of the Diels-Alder reaction between cyclopentadiene and methyl acrylate:

\[
\begin{align*}
\text{Cyclopentadiene} & + \text{Methyl Acrylate} \\
\quad & \rightarrow \text{Cyclopentadiene} + \text{Methyl Acrylate} \quad (7-20)
\end{align*}
\]

as a function of pressure at 45 °C in pure supercritical carbon dioxide. These authors reported that endo:exo selectivity improved from 3:1 to 3.8:1 as the pressure was increased from 90 bar to 100 bar. At higher pressures, the selectivity returned to 3:1. Kim and Johnston\textsuperscript{41} studied the same reaction also in pure supercritical carbon dioxide and reported that selectivity did not vary appreciably with pressure. Operating at 35 °C, these authors observed that endo:exo selectivity improved from 2.83:1 at 100 bar to 2.90:1 at 300 bar.

The results presented here also compare favorably to those of Oakes et al.\textsuperscript{54} who used the Lewis acid, scandium tris(trifluoromethanesulfonate), to catalyze the Diels-Alder reaction between cyclopentadiene and butyl acrylate in pure supercritical carbon dioxide. At 50 °C and a catalyst loading of 6.5 mol\%, Oakes et al.\textsuperscript{54} report the endo:exo selectivity of this reaction as 10:1 in pure toluene, 4:1 in supercritical carbon dioxide at a fluid density of 0.63 g cm\(^{-3}\), and 24:1 in supercritical carbon dioxide at a fluid density of 1.05 g cm\(^{-3}\). Surprisingly, the endo:exo selectivity of the catalyzed reaction decreased to roughly 3:1 in pure carbon dioxide at a density of 1.2 g cm\(^{-3}\). Although these are dramatic results, there are several mitigating factors. First, a large amount of expensive metallic catalyst is
Figure 7-7a,b. Experimental measurements of (a) conversion, $X$, after one hour and (b) endo:exo selectivity, $S$, for the Diels-Alder cycloaddition of methyl vinyl ketone to cyclopentadiene in carbon dioxide/water systems. Both sonicated and silent results are shown for the "H$_2$O" horn configuration. Conditions: 30 °C, 80 bar, 1 mol L$^{-1}$ [MVK]$_0$. Ultrasound: 20 kHz frequency, 25% duty (on a 1 s cycle), 0.55 W cm$^{-3}$. 
Figure 7-7c,d. (c) experimental measurements of conversion, $X$, after one hour and (d) endo:exo selectivity, $S$, for the Diels-Alder cycloaddition of methyl vinyl ketone to cyclopentadiene in carbon dioxide/water systems. Both sonicated and silent results are shown for the “CO$_2$” horn configuration. Conditions: 30 °C, 80 bar, 1 mol L$^{-1}$ [MVK]$_0$. Ultrasound: 20 kHz frequency, 25% duty (on a 1 s cycle), 0.55 W cm$^{-3}$. 
required. An industrial process would require efficient separation of the catalyst, both for product purity and recycling purposes. Second, the physical mechanism underlying the sharp rise in selectivity at a fluid density of 1.05 g cm\(^{-3}\) is unclear. Without better characterization and improved understanding, it is somewhat difficult to evaluate the results of Oakes et al.\(^{54}\) To this point, there are no confirmations of the effect of Lewis acids on Diels-Alder reactions in supercritical carbon dioxide. Finally, there is some uncertainty regarding the reported density ranges. At 50 °C, a fluid density of 1.2 g cm\(^{-3}\) corresponds to a pressure in excess of 2,000 bar.\(^{53}\) The maximum operating pressure of most typical laboratory vessels is less than 500 bar, making the extreme operating pressures reported for these experiments unbelievable. Accepting the densities as reported by Oakes et al.\(^{54}\), an operating pressure of 2,000 bar is prohibitive for most industrial processes. From a technological standpoint, the results presented in this thesis are at least comparable to those of Oakes et al.\(^{54}\) without the use of expensive, environmentally incompatible catalysts or prohibitively high pressure. Furthermore, it will be shown that our results can be interpreted using the simple theory presented in Section 7.3. The physical interpretation of the effects of the Lewis acid catalyst is not at all obvious, perhaps limiting its scope.

Figure 7-7 indicates optimum values of \(\phi_W\) with regards to the measured selectivity and conversion under sonicated conditions. These maxima occur for different water fractions in the two different horn geometries. It was determined that the maxima in Figure 7-7 correspond to the distance between the tip of the sonic horn and the carbon dioxide/water interface. Because the volume of the reactor and the position of the sonic horn were fixed in these experiments, the standoff distance and volume fraction of water could not be varied independently. Figure 7-8 contains plots of sonic enhancement (that is, the ratio of either conversion or selectivity obtained acoustically to that obtained silently) as functions of the distance between the tip of the sonic horn and the interface. Both selectivity and conversion exhibit maxima with respect to horn:interface distance. Plotting selectivity data from both the H\(_2\)O and CO\(_2\) horn configurations, it is clear that the maximum sonic effect is obtained for a horn:interface distance of roughly 2 cm. Negative values of horn:interface distance in Figure 7-8 correspond to conditions in which either the interface is below the tip of the horn (in the H\(_2\)O configuration) or the
interface is above the tip of the horn (in the CO₂ configuration). Figure 7-8 clearly shows that horn:interface distance, rather than horn configuration, is the key variable to maximize sonic enhancement.

It is necessary to consider the physical basis for the optimal horn:interface distance. Figure 7-9 shows three physical situations corresponding to: a) horn:interface distance less than the optimum, b) optimal horn:interface distance; c) horn:interface distance greater than the optimum. The inefficiency of case (a) is clear since only a small amount (if any) of the phase to be dispersed is actually sonicated. Instead, the acoustic power is dissipated completely in one of the two phases and no emulsification is possible. The analysis of case (c) relies on the finding that cavitation is an important emulsification mechanism as presented in Chapter 5. Intuitively, it seems reasonable to assume that the ultrasonic energy must be dissipated in the vicinity of the interface for emulsification to occur. Literature reports of sonication were explored to verify this hypothesis.

There are many reports describing the depth of cavitation penetration into a sonicated fluid. Dähnke and Keil⁵⁵-⁵⁸ used a theoretical model, based on wave propagation through an absorbing medium containing cavitation bubbles, to predict that the pressure amplitude of an ultrasonic wave of 20 kHz frequency is reduced by roughly 90% in the first several centimeters traveled from the source. Thus a pressure wave with an initial amplitude of 10 bar is reduced to 1 bar within 2 or 3 centimeters of the source. Absorption of the sound wave may reduces its intensity below the cavitation threshold. Although cavitation occurs in the vicinity of the horn, the cavitation zone is sufficiently removed from the interface that emulsification does not occur.

Laborde et al.⁵⁹ provide experimental support for the theoretical calculations of Dähnke and Keil.⁵⁵-⁵⁸ Laborde et al.⁵⁹ used pitting of aluminum foil and sonoluminescence of luminol to show that the cavitation zone extends roughly 2-3 centimeters away from a sonic horn operating at 28 kHz. McMurray and Wilson⁶⁰ also studied the sonoluminescence of luminol and found that the cavitation zone extends a distance of only 1 cm from the tip of the sonic horn for sonication at 20 kHz. These results strongly suggest that, in the presence of cavitation, ultrasound penetrates a maximum of 2-3 cm into the fluid. The optimal horn:interface distance was observed to be roughly 2 cm which is consistent with the literature reports.
Figure 7-8. Ratio of experimentally measured (a) selectivity and (b) conversion under sonicated conditions to that measured under silent conditions for the Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water systems. Data from Figure 7-7 are plotted as a selectivity enhancements as a function of the distance between the tip of the sonic horn and the carbon dioxide/water interface. Negative distances correspond to the situation depicted in Figure 7-9a. Conditions: 30 °C, 80 bar. Ultrasound: 20 kHz ultrasound, 25% duty (on a 1 s cycle), 0.55 W cm⁻³.
Figure 7-9. Pictorial representation of the physical situation for the three cases of horn:interface separation. The horn is depicted as immersed in the water phase (i.e., the “H2O” geometry). (a) the interface is below the carbon dioxide/water interface and the separation is negative. The horn:interface separation is negative and no emulsification occurs in this case.; (b) optimal or near optimal horn:interface distance. Emulsification occurs in this case. (c) horn:interface separation greater than the optimum and no emulsification occurs in this case. The wave amplitude is intended to reflect the degree of agitation at the carbon dioxide/water interface. The length of the horn is roughly 4 cm, measured from the flange.

Measurements of sonic acceleration of metal corrosion rates are consistent with the hypothesis that horn to interface distances larger than 2 cm prevent acoustic emulsification. Ultrasonically-induced corrosion is the result of the combined action of acoustic streaming and cavitation, and, similar to acoustic emulsification, ultrasonic corrosion is believed to be primarily a physical phenomenon. Whillock and Harvey found that the corrosion rate of 304L-stainless steel was accelerated 10-fold when the sonic horn was positioned 1 mm from the metal specimen. Increasing the horn:specimen
distance dramatically diminished the sonic enhancement. For horn: specimen distances greater than 3 cm, sonication had no measurable effect on corrosion rates. This finding is also consistent with the observations reported here.

**Effect of methyl vinyl ketone concentration.** Twelve experiments were conducted in which $[MVK]_0$ was varied from 0.05 to 1.0 mol L$^{-1}$. A 316-stainless steel insert occupied a portion of the reactor volume and allowed experiments to be conducted with a water fraction of 0.85 while maintaining the 2 cm horn to interface distance. Table 7-5 lists estimated mass transport coefficients, rate constants, and Hatta numbers, defined as $(k_{\text{rxn}} D_A)^{1/2} / k_W$, in both phases for the extremes in $[MVK]_0$. The mass transport coefficients listed in Table 7-5 are based on the transport measurements of benzaldehyde described in Chapter 6 and therefore do not take into account transport to water droplets as they recirculate through the carbon dioxide phase. Thus the mass transport coefficients in Table 7-5 underestimate the total mass transport rates between the two phases. The Hatta numbers indicate: 1) mass transport in the water film is slightly enhanced by reaction for $[MVK]_0 = 1.0$ mol L$^{-1}$ as the water-based Hatta number equals 2 in this case; 2) the carbon dioxide phase is well mixed, as the Hatta number is always much less than unity in this phase. Water-based Dämköhler numbers are less than unity (<$1 \times 10^{-2}$).

**Table 7-5.** Characteristic values for rate related processes for dynamics of the reaction between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water systems.

<table>
<thead>
<tr>
<th>Rate process</th>
<th>$[MVK]_0 = 1.0$ mol L$^{-1}$</th>
<th>$[MVK]_0 = 0.05$ mol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2O$</td>
<td>$CO_2$</td>
</tr>
<tr>
<td>pseudo-first order reaction rate$^a$ (s$^{-1}$)</td>
<td>0.04</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>mass transport coefficient (cm s$^{-1}$)</td>
<td>$3 \times 10^{-4}$ (H$_2$O film)</td>
<td>$3 \times 10^{-3}$ (CO$_2$ film)</td>
</tr>
<tr>
<td>Hatta number$^b$</td>
<td>2</td>
<td>0.015</td>
</tr>
<tr>
<td>reaction enhanced transport coefficient (cm s$^{-1}$)</td>
<td>$7 \times 10^{-4}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>overall mass transport coefficient (cm s$^{-1}$), $k_{int} = k_W / K_{OW}$</td>
<td>$6 \times 10^{-6}$</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>with $K_{OW}$ (cyclopentadiene) ≈100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass transport coefficient x specific surface area$^c$ (s$^{-1}$)</td>
<td>$1 \times 10^{-5}$</td>
<td>$6 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$^a$ for the overall rate of disappearance of cyclopentadiene i.e., $k_W^N + k_W^X$, or $k_C^U + k_C^X$

$^b$ Hatta number, $\gamma_W = (k_{\text{rxn}} D_{AN})^{1/2} / k_W$ or $\gamma_C = k_{\text{rxn}} D_{AC})^{1/2} / k_C$

$^c$ assuming that the specific interfacial area = 20 cm$^2$ / 100 cm$^3$ = 0.2 cm$^{-1}$. 
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The results from the variable $[MVK]_0$ experiments are presented in Figure 7-10. Under silent conditions, decreasing the initial concentration of methyl vinyl ketone from 1.0 mol L$^{-1}$ to 0.05 mol L$^{-1}$ increases the selectivity from roughly 6:1 (slightly higher than that observed in pure carbon dioxide) to nearly 16:1 (much closer to the 20:1 observed in pure water). The selectivity behavior can be interpreted in terms of the relative rates of the processes described in Table 7-5. For $[MVK]_0 = 1.0$ mol L$^{-1}$, the pseudo-first order reaction rate constant in carbon dioxide is $2 \times 10^{-5}$ s$^{-1}$ and the overall transport rate (multiplied by specific surface area) is $1 \times 10^{-6}$ s$^{-1}$. The 20-fold difference between these rates implies that the reaction occurs primarily in the carbon dioxide phase before the cyclopentadiene can be transported to the water phase. For $[MVK]_0 = 0.05$ mol L$^{-1}$, the reaction rate in carbon dioxide is $1 \times 10^{-6}$ s$^{-1}$ while the transport rate to the water phase is $6 \times 10^{-7}$ s$^{-1}$, less than a two-fold difference. Based on this analysis, when $[MVK]_0 = 0.05$ mol L$^{-1}$ transport of cyclopentadiene is sufficiently fast compared to reaction in the bulk carbon dioxide that a substantial fraction of the water phase is utilized, leading to a selectivity that approaches that in pure water.

Under sonicated conditions, Figure 7-10 shows that selectivity and conversion are much less sensitive to $[MVK]_0$. Ultrasonic acceleration of mass transport rates allows water-like selectivity and conversion to be accessed even for $[MVK]_0 = 1.0$ mol L$^{-1}$. This is consistent with the findings of Chapter 6 for large water-based Hatta numbers. As $[MVK]_0$ decreases to 0.05 mol L$^{-1}$, a greater fraction of the reaction occurs in the water phase and selectivity increases slightly. At $[MVK]_0 = 0.05$ mol L$^{-1}$, sonication does not improve reaction rates or selectivity, consistent with the findings in Chapter 6 for small water-based Hatta numbers. In Chapter 6, only a 4-fold sonic enhancement was observed for Hatta $< 0.5$, while 100-fold enhancements were observed for Hatta $> 1$. The enhancement observed in this chapter is essentially negligible for Hatta $\sim 0.5$, which is consistent with the results from Section 6.5 and 6.6 considering the improved mixing (and subsequent underestimation of the mass transport coefficient) employed in the Diels-Alder experiments relative to the hydrolysis experiments. For the Diels-Alder experiments described in this chapter, it was decided to recirculate the water phase through the carbon dioxide phase, greatly increasing the interfacial contact area. The
Figure 7-10. Experimental measurements of (a) conversion, $X$, and (b) the selectivity, $S$, of the Diels-Alder cycloaddition of methyl vinyl ketone to cyclopentadiene in carbon dioxide/water systems plotted versus the concentration of dienophile. Both sonicated and silent results are shown for the “H$_2$O” horn configuration with horn:interface distance of 2 cm. Conditions: 30 °C, 80 bar, 85% water by volume, 1 hr reaction time. Ultrasound: 20 kHz ultrasound, 25% duty (on a 1 s cycle), 0.55 W cm$^{-3}$. 

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experiments described in Section 6.4 were conducted with recirculation from the bottom of the water phase to the top, resulting in essentially no increase in contact area and presumably much smaller mass transport rates. Thus, a much smaller acoustic effect was anticipated for the Diels-Alder conversion results, as was observed.

7.6.3 Comparison to Predictions

Figure 7-11 contains plots of experimentally measured conversion/selectivity (under sonicated conditions) and versus predictions of conversion/selectivity based on well-mixed phases. Data points from both Figure 7-7 and 7-10 are plotted in Figure 7-11, though only for horn to interface distances between 1 and 3 cm. Error bars for the predictions were based on variations of the partition coefficient of cyclopentadiene from 50-200 to reflect the uncertainty of this parameter. Although reaction selectivity is consistently overpredicted, the conversion is predicted to within the limits of experimental uncertainty. The most obvious reason for the failure of the well-mixed model is that mass transport is not infinitely fast. However, even finite mass transport rates do not fully describe the discrepancy between the model and the data. Finite mass transport rates are consistent with the overpredictions of selectivity since higher selectivity (and a greater percentage of reaction in the water) is expected for fast mass transport. On the other hand, the good agreement between predictions and measurements of conversion is not consistent with finite mass transport rates, since slow mass transport implies that the reaction occurs in the carbon dioxide phase. The end result would be conversions much lower than observed.

Figure 7-12 plots measurements divided by predictions for conversion and selectivity as functions of methyl vinyl ketone concentration. Figure 7-12 shows that conversion becomes increasingly underpredicted for low methyl vinyl ketone loadings, while selectivity is consistently overpredicted. This behavior is consistent with a 10% underprediction of the Diels-Alder reaction rate in pure carbon dioxide. This offset may be experimental uncertainty, or it may be due in part to the effect of dissolved water on the reaction rate in carbon dioxide phase. It is possible that dissolved water in the near-critical carbon dioxide could accelerate the Diels-Alder reaction rate by a combination of increasing solvent polarity and hydrogen-bond donating ability.
Figure 7-11. Experimental measurements of (a) conversion, $X$, and (b) selectivity, $S$, versus predictions based on a well-mixed assumption for the Diels-Alder cycloaddition between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water systems. Sonicated results are shown for both horn configurations, though data measured at horn to interface separations greater than 1 cm from the optimum value of 2 cm are omitted. Conditions: 30 °C, 80 bar, 1 hr reaction time. Ultrasound: 20 kHz frequency, 25% duty (on a 1 s cycle), 0.55 W cm$^{-3}$. 
Figure 7-12. Experimentally measured conversion, $X$, and selectivity, $S$, divided by predictions based on a well-mixed assumption as a function of methyl vinyl ketone concentration. Sonicated results are shown for both horn configurations, though data measured at horn to interface separations greater than 1 cm from the optimum value of 2 cm are omitted. Conditions: 30 °C, 80 bar, 1 hr reaction time. Ultrasound: 20 kHz frequency, 25% duty (on a 1 s cycle), 0.55 W cm$^{-3}$.

It was desired to pursue this issue further using results from silent experiments. Figure 7-13 compares silent experimental measurements to two types of predictions: 1) well-mixed phases in thermodynamic equilibrium; 2) conversion if the reaction were confined to the carbon dioxide phase. Figure 7-13 clearly demonstrates that the observed conversion is much greater than would be expected if the reaction were confined to the carbon dioxide phase. In contrast, the selectivity data, at least for $[\text{MVK}]_0 > 0.5$ mol L$^{-1}$, indicate that the reaction does not occur in the water phase as is shown in Figure 7-10b. This cannot be explained by mass transport rates, and an alternative mechanism is implied.
Figure 7-13. Experimental measurements of conversion, $X$, of the Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene in carbon dioxide/water systems without sonication. Predictions based on perfect mixing and no mixing (i.e., reaction confined to the carbon dioxide phase) are shown for comparison.

In addition to uncertain measurements of rate constants, it was possible that a small amount of a third, methyl vinyl ketone-rich phase was present during the experiments, which would explain the observed conversion/selectivity behavior. Although it appeared that the reactions were performed under two-phase conditions, a small amount of a third phase can be quite difficult to detect in carbon dioxide/water systems. Since the density of a methyl vinyl ketone rich phase would be intermediate to that of water and carbon dioxide, the hypothetical third phase would collect at the carbon dioxide and water interphase, as depicted in Figure 7-14. Visual detection of a thin layer of a third phase would be difficult to detect at the carbon dioxide/water interface. Qualitatively, it seems reasonable that a methyl vinyl ketone rich phase would decrease selectivity, without reducing conversion, consistent with observations. For this reason, phase behavior and its implications on reaction dynamics were investigated in detail.
**Figure 7-14.** Schematic of the water/carbon dioxide interface with a thin film of methyl vinyl ketone preventing direct mass transport.

**Investigations of phase behavior.** There is some evidence of unusual phase behavior in the water/carbon dioxide/methyl vinyl ketone system. At room temperature and pressure, methyl vinyl ketone is nearly miscible (up to 80% by volume) with water. As the mixture is pressurized under a carbon dioxide atmosphere, the methyl vinyl ketone demixes and forms a second liquid phase. This is observed experimentally at a system pressure of roughly 40 bar, at which point the system is at liquid/liquid/vapor equilibrium. As the system pressure is further increased, the volume of this third phase increases. Above 70 bar, however, the third phase appears to become incorporated into a carbon dioxide fluid phase and only a clear fluid phase and clear liquid phase are visible in the vessel. Since the experiments were conducted at 80 bar, it was thought that only two phases (i.e., carbon dioxide and water) were present and that the methyl vinyl ketone was distributed completely between them. Nonetheless, this acoustic reactor design is not the ideal choice for monitoring phase behavior due to the large percentage of the volume which cannot be observed.

A series of experiments were conducted in the sight gauge pressure cell described in Section 3.3 to investigate the phase behavior of the water/carbon dioxide/methyl vinyl ketone system at 30 °C, 30 bar. The sight gauge pressure vessel is ideal for monitoring phase behavior since the entire volume is open to visual access. Also, its small cross sectional area (roughly 4 cm² versus 20 cm² for the acoustic reactor) ensures that a small
volume of a methyl vinyl ketone-rich layer would be approximately 5 times thicker in the sight gauge than in the acoustic reactor, making it easier to detect.

The ternary phase behavior experiments were guided by studies of water/carbon dioxide/polar solvent reported by G. Maurer’s research group\textsuperscript{62,63} at the University of Kaiserslautern in Germany. Particularly interesting were investigations of the water/carbon dioxide/acetone system. Given the molecular similarity between methyl vinyl ketone and acetone (the molecular formulae are CH\textsubscript{2}=CHC(O)CH\textsubscript{3} and CH\textsubscript{3}C(O)CH\textsubscript{3}), the two solutes were expected to behave similarly in their respective carbon dioxide/water systems. The qualitative behavior of the water/carbon dioxide/acetone system is similar to that observed for the water/carbon dioxide/methyl vinyl ketone system, with both upper and lower demixing pressures leading to liquid/vapor, liquid/liquid/vapor, and liquid/liquid equilibria. Importantly, Maurer’s research has shown that the demixing pressures are critical points and are therefore independent of the composition of the phases.\textsuperscript{63} This greatly simplifies the experiments since the loading of methyl vinyl ketone in the reactor can be tailored to improve phase behavior visualization.

The ternary phase behavior of both water/carbon dioxide/acetone and water/carbon dioxide/methyl vinyl ketone systems was investigated experimentally. In an experiment, roughly 25\% of the volume of the sight gauge was filled with a 50:50 mixture of water and the polar solvent. The air was flushed from the reactor using carbon dioxide at atmospheric pressure. Mixing was supplied to the pressure vessel contents by two high pressure pumps, one for the water (Eldex, BBB-4, rated for 100 cm\textsuperscript{3} min\textsuperscript{-1}) and one for the carbon dioxide (Eldex, B-100-S, rated at 5 cm\textsuperscript{3} min\textsuperscript{-1}). Initially, the system pressure was 1 bar and the vessel contained a single liquid phase and a vapor carbon dioxide phase (L/V equilibrium). The system pressure was increased by introducing carbon dioxide and the pressure at which the polar solvent demixed from the water and formed a third phase was recorded. At this point, the reactor contained liquid water, a liquid polar solvent, and carbon dioxide vapor (L\textsubscript{1}/L\textsubscript{2}/V equilibrium). The pressure was further increased until the polar solvent was completely dissolved into the carbon dioxide phase and the vessel contained a liquid water phase and a fluid phase (L/F equilibrium).
Figure 7-15 is a plot of the lower and upper demixing pressures reported for these two systems, including literature data\(^{63}\) and data measured in this study. Below the lower curve and data points, the system is in L/V equilibrium. As system pressure is increased isothermally, the polar solute demixes. The region between the two curves denotes a state of L\(_1\)/L\(_2\)/V equilibrium. At the upper demixing pressure, the polar solute dissolves in the supercritical fluid phase and the system is at L/F equilibrium. For acetone, the upper transition pressures were quite sharp and the agreement between the observed demixing pressures and the literature values was within 2 bar. For methyl vinyl ketone, however, the transition between liquid/liquid/vapor and liquid/fluid equilibrium was not well defined. Although the interfacial methyl vinyl ketone film disappears at a distinct pressure, the water phase remains slightly turbid at this point. In contrast, the water phase in the water/carbon dioxide/acetone system is completely clear at the upper transition.

**Figure 7-15.** Upper and lower demixing pressures for water/carbon dioxide/polar solvent systems. Literature data\(^{63}\) and experimental data are shown for the water/carbon dioxide/acetone system. Experimental data is shown for the water/carbon dioxide/methyl vinyl ketone system. The upper demixing pressure listed for the methyl vinyl ketone system is that at which the thin film is no longer visible.
demixing pressure. It is likely that the remaining turbidity in the methyl vinyl ketone system is due to a small amount of emulsified organic solute contained in the water phase. When agitation was terminated, the emulsion appeared to slowly break (half life greater than several hours) and the turbidity decreased, supporting the emulsion hypothesis. With agitation, the water phase remains turbid until the system pressure exceeds roughly 90 bar, at which point both the liquid and fluid phases become clear. Based on these results, it seems possible that the Diels-Alder experiments described in Section 7.6.2 were conducted in a three-phase region.

**Reinterpretation of results.** To evaluate the probable effect of a methyl vinyl ketone-rich phase in the Diels-Alder experiments, the reaction rate constants and reagent partition coefficients for such a phase need to be estimated. In terms of partition coefficients, the diene is expected to partition roughly equally between the methyl vinyl ketone and carbon dioxide phases. As a first guess, the second order rate constant in a methyl vinyl ketone-rich phase would be close to that in iso-octane. Although the reaction was too rapid to measure in pure methyl vinyl ketone, the end-point selectivity was measured as roughly 6:1 at 25 °C and 1 bar. The concentration of excess dienophile in the methyl vinyl ketone rich phase is expected to be roughly 10 mol L\(^{-1}\) since the concentration of pure methyl vinyl ketone at 25 °C, 1 bar is 12 mol L\(^{-1}\). Thus, based on the known rate of reaction in iso-octane (6 x 10\(^{-5}\) L mol\(^{-1}\) s\(^{-1}\)) and the estimated concentration of excess dienophile, the pseudo-first order rate in the methyl vinyl ketone phase is estimated to be roughly 6 x 10\(^{4}\) s\(^{-1}\). The pseudo-first order rate constant in carbon dioxide is 2 x 10\(^{-5}\) s\(^{-1}\) which implies the contribution of the methyl vinyl ketone phase to the observed conversion would be roughly equal to that of the carbon dioxide phase, allowing for a 10-fold difference in the volumes of the two phases. Under sonicated conditions, all three phases are emulsified and the effect of the methyl vinyl ketone phase would be to decrease selectivity towards that observed in methyl vinyl ketone (i.e., 6:1) while maintaining high conversion. The effect of the third phase on selectivity would be directly proportional to its volume fraction (on the order of 0.05 or less).

A methyl vinyl ketone rich phase would have a more dramatic effect on silent experiments. As argued previously, a methyl vinyl ketone phase would exist at the
carbon dioxide/water interface, thus separating the two phases under silent conditions. In order to reach the water phase, the cyclopentadiene would first need to diffuse through the methyl vinyl ketone layer. Given the high concentration of dienophile in this phase, a significant fraction of the cyclopentadiene could easily be consumed in the film prior to reaching the water phase. As usual, the diffusion length can be estimated as \((D_{AM}k_{xn})^{1/2}\). For the estimated rate constant of \(6 \times 10^{-4} \text{ s}^{-1}\) and for a diffusion coefficient of \(1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\), the diffusion length is slightly less than 1.3 mm. A significant fraction of the diene would be consumed in a film of this thickness, preventing it from reaching the aqueous phase. The effect of the methyl vinyl ketone film would be much more significant than its volume fraction would suggest. Moreover, a 1.5 mm thick film would be quite difficult to detect visually. The fact that the selectivity under silent conditions is roughly 6:1 (as observed in methyl vinyl ketone) rather than 4.5:1 (as observed in carbon dioxide) strongly suggests reaction in the methyl vinyl ketone, supporting the film hypothesis. As the concentration of methyl vinyl ketone was reduced from 1.0 mol L\(^{-1}\) to 0.05 mol L\(^{-1}\), the thickness of this film would decrease, presumably 20-fold. Thus, the effect of the film would be much less significant.

Failure of the well-mixed model to predict selectivities accurately is most likely the result of slight under estimation of the reaction rate in the carbon dioxide phase (perhaps due to the effect of dissolved water) and the presence of a third, reactant-rich phase. Nonetheless, the well-mixed model works remarkably well given its simplicity and the Diels-Alder reaction presented in here is a nice demonstration of the utility of the theoretical foundation laid in Chapter 6.

7.6.4 Practical limitations and alternate reactor designs

This study suggests two practical limitations to the use of ultrasound to improve rates and selectivities of synthetic reactions in carbon dioxide/water systems: 1) small, polar molecules, which are miscible with water at atmospheric pressure, demix under moderate pressures (20 to 80 bar) in a carbon dioxide atmosphere; 2) emulsification is only effective when the horn:interface distance is roughly 2 cm. The first limitation could be common to many Diels-Alder reactions conducted in carbon dioxide/water reactions since most common dienophiles are small, polar molecules. Operating at a
pressure above 100 bar should ensure two-phase conditions, though the phase behavior should be investigated prior to conducting reactions.

The requirement of a 2 cm distance between the horn and carbon dioxide/water interface is more problematic than managing phase behavior as it may be an issue in process scale up. There are, however, several possible alternative reactor designs which might alleviate the problem. The most obvious approach would be to convert the reactor to a flow-through system. Figure 7-16 contains a schematic of a simple flow-through acoustic reactor. The advantage of this system is that sonication is confined to a small volume. Thus, depending on the flow rates of the two phases, a large emulsion volume could be prepared, while maintaining an optimal standoff distance at all times. Additional mixing could be obtained using turbulent mixing tees or nozzles. A major drawback to the flow-through system is that the residence time downstream of the sonicator must be less than the characteristic time for de-emulsification (roughly 20

![Diagram](image)

Figure 7-16. Simple schematic for a flow-through acoustic reactor for emulsification of dense carbon dioxide and water.
Figure 7-17. Simple schematic for a modified jet-loop reactor with a large “silent zone” and a smaller “sonicated zone”. Some design calculations are presented in the text.

minutes), which might limit its application to rapid reactions. Of course, the reaction mixture could be re-emulsified using a second sonicator, but multiple sonication units would greatly increase both the capital and maintenance costs of the reactor design.

Scale-up of flow-through acoustic reactors should prove easier than that of batch systems. For continuous ultrasonic emulsification of oil and water, Behrend and Schubert have noted that the proper scaling variable is the power density divided by the volumetric flow rate, a parameter which they term “energy density” since it has units of energy per volume. It is likely that energy density is also the critical scaling parameter for ultrasonic emulsification of near-critical carbon dioxide and water.

A second approach, which uses the concept of the flow-through emulsifier, is a modification to the jet-loop reactor. A schematic of the proposed design is presented in Figure 7-17. The modified jet loop reactor could be operated either batch-wise (as shown) or continuously with some minor modifications. Since this design confines sonication to a small volume, the horn would be placed in close proximity to the
water/carbon dioxide interface, even though the volume of the reactor could be much larger. This design has the benefits of a flow-through system but periodically re-emulsifies the system with the use of only one sonication zone. For the contents of the reactor to remain emulsified, the ratio of the overall volume to the recirculation rate (which is a sort of residence time) would need to be smaller than the demulsification time (roughly 20 minutes). Thus, for a 1000 cm$^3$ reactor the recirculation rate would need to be roughly 100 cm$^3$ min$^{-1}$, which is well within the capabilities of conventional high-pressure pumps. If necessary, multiple recirculation loops could be used to reduce the load on each pump, though this design would require multiple sonication zones. Figure 7-16 also depicts a conventional impeller which would be used to pre-emulsify the reaction mixture.

The design of the sonication zone itself deserves some attention. In a flow-through system, the residence time in the sonic zone needs to be sufficient for emulsification. Although the time required for acoustic emulsification was not studied thoroughly, it is estimated to be less than 5 s in the current acoustic reactor. This implies that, for a recirculation rate of 100 cm$^3$ min$^{-1}$, the sonication chamber volume would need to be less than 10 cm$^3$. Sonication of such a small volume should not be a challenge, since 100 cm$^3$ volume was effectively sonicated in the current study. Recent developments in sonochemical engineering, such as cylindrically symmetric sonication$^{65}$ and the multiple sonicator designs reported by Destaillats et al.$^{66}$ might be used for acoustic emulsification of larger flow rates or volumes. Destaillats et al.$^{66}$ report degradation rates of model organic reagents in a sonochemical reactor with a volume of 6 L comparable to those characteristic of small bench-top units. Additional designs are discussed in the recent review on sonochemical engineering by Keil and Swamy.$^{67}$

7.7 Conclusions

Biphasic, acoustically activated carbon dioxide/water systems were demonstrated to provide access beneficial effects of water on chemical rates and selectivities without incurring the drawbacks associated with the addition of expensive or environmentally incompatible additives. The Diels-Alder cycloaddition of methyl vinyl ketone to cyclopentadiene was selected as the model system for a detailed study based on the dramatic effects that water has on reaction selectivity and rate. Experiments were
conducted at 30 °C and 80 bar, over a range of water loadings with a methyl vinyl ketone concentration of 1 mol L\(^{-1}\). In non-emulsified, silent systems, it was found that the selectivity and conversion (after 1 hour) were much less than that expected in well-mixed carbon dioxide/water systems, though both reaction metrics improved as the volume fraction of water approached 1.0. With sonication, both the conversion and selectivity increased dramatically. For example, sonication at a water fraction of 0.60, increased conversion from 30% to 60% and selectivity from 6.5:1 to greater than 10:1. Our results suggested that 2 cm was the optimal distance between the tip of the sonic horn and the carbon dioxide/water interface. Sonic enhancement was much less dramatic for horn:interface distances which differed from this optimal value, consistent with a number of published reports of sonication of fluids.

A set of experiments were conducted at a water volume fraction of 0.85, while maintaining the optimal horn:interface distance and varying the concentration of methyl vinyl ketone from 0.05 to 1.0 mol L\(^{-1}\). When the methyl vinyl ketone concentration was 1 mol L\(^{-1}\), the endo:exo selectivity was nearly 13:1 and the conversion after one hour was greater than 90% under sonicated conditions. This compares favorably to that obtained silently (6:1 selectivity, 70% conversion) or expected in pure carbon dioxide (4.5:1 selectivity, 30% conversion). As the concentration of methyl vinyl ketone was decreased from 1.0 to 0.05 mol L\(^{-1}\), the selectivities and conversions obtained under sonicated conditions approached those from silent experiments (16:1 selectivity, 50% conversion).

Although the experimental and predicted conversions for a well-mixed system agreed within anticipated uncertainties, reaction selectivity was systematically over predicted. To explain this apparent contradiction, it was hypothesized that the reactions were conducted in the presence of a small amount (several cm\(^3\) out of a total volume of 90 cm\(^3\)) of an interfacial methyl vinyl ketone rich phase. Under silent conditions, the methyl vinyl ketone rich phase would exist as a thin layer between the water and carbon dioxide, effectively isolating the water phase from the cyclopentadiene reservoir. By isolating the two phases, the effect of the methyl vinyl ketone phase is much greater than its volume fraction would suggest. Sonication disrupts the film and emulsifies all three phases. Thus, the effect of the reagent phase is proportional to its volume fraction, which
is rather small. An additional source of error in the model predictions is the accelerative
effect of dissolved water on reaction rates in otherwise pure carbon dioxide.

It was concluded that sonication simultaneously reduces the effect of the methyl
vinyl ketone phase and increases mass transport, thus improving the selectivity to that
expected in well-mixed systems (i.e., roughly 15:1) while maintaining conversion above
90%.

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CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The overall goal of this research was to develop power ultrasound as a surfactant-free method for emulsifying carbon dioxide and water, for the specific application of facilitating organic transformations. This research successfully demonstrated that selected chemical reactions can benefit from surfactant-free emulsification of biphasic mixtures. Specifically, ultrasound was used to accelerate the mass transport limited hydrolysis of benzoyl halides by more than 100-fold, relative to that in the silent, non-emulsified case. The sonic enhancement of both the selectivity and conversion of a prototypical Diels-Alder cycloaddition demonstrated that ultrasound can be used to exploit the unique ability of water to influence chemical reactivity. These results both motivate and inform future research into the use of carbon dioxide/water emulsions for synthetic chemistry.

This thesis demonstrates the use of ultrasound for formation of surfactant free carbon dioxide/water emulsions and its potential for accelerating chemical reactions. Ultrasonic emulsification should prove to be a general tool for development of chemical processes which are inherently environmentally benign. More importantly, a solid fundamental understanding has been developed, with particular emphasis placed on the role of mass transport on apparent reaction rates. Several important avenues for future research are suggested by this work. More detailed characterization of the emulsions, perhaps through the use of automated diagnostics, and investigation of the nature of cavitation at elevated hydrostatic pressure should be especially fruitful.

Additionally, a number of new experimental tools were developed, expanding the capabilities of the laboratory. A new acoustic reactor, with an estimated maximum operating pressure of 250 bar at 25 °C, was designed and constructed for conducting acoustically activated reactions under conditions near or above the critical point of carbon
dioxide. The use of microchannel reactors capable of withstanding pressures up to 130 bar was demonstrated as a means of visualizing two-phase conditions near the critical point of carbon dioxide. New methods for sampling high-pressure emulsions and measuring chemical kinetics in biphasic systems were developed. Novel tools for the characterization of high-pressure emulsions were introduced.

The following is a list of the sub-objectives of this thesis, and the specific conclusions and recommendations reached from each study:

**Partitioning of Organic Solutes between Near-Critical Carbon Dioxide and Water**

To make informed choices regarding chemical reactions suitable for a carbon dioxide/water environment, the partitioning behavior of organic solutes must either be known or predicted. Carbon dioxide/water partition coefficient data were sparse, consisting of roughly 20 compounds and focusing nearly exclusively on substituted phenols and halogenated hydrocarbons. This thesis enlarged the data base with measurements of an additional 18 compounds (30 °C and 80 bar). Further, based on this expanded data set, the predictive capabilities of three empirical correlation methods (comparison to water solubility, correlation with an existing group contribution method for predicting octanol/water partition coefficients, and linear solvation energy relationships) were explored. Comparison to water solubility and correlation with the octanol/water group contribution method failed entirely for partitioning of solutes capable of hydrogen bond donation, but were accurate to within ±0.4 log\textsubscript{10} units for non-acidic solutes. Linear solvation energy relationships captured the partitioning behavior of all organic solutes investigated, including those capable of hydrogen bond donation. The accuracy of the linear solvation energy relationship was approximately ± 0.2 log\textsubscript{10} units, comparable to the accuracy of the available data set.

Several practical applications of the correlation methods were demonstrated. The linear solvation energy relationship method was used in conjunction with the group contribution method to predict carbon dioxide/water partition coefficients for highly reactive benzoyl halides. The three methods were used to provide independent predictions of the partition coefficient cyclopentadiene, a compound capable of spontaneous dimerization.
Future work in this area should focus on further expansion of the available database, with specific attention to the behavior of hydrogen bond donating solutes. More robust correlation methods should be developed, possibly incorporating quantum calculations as a theoretical basis.

**Formation and Stability of Carbon Dioxide/Water Emulsions Using Power Ultrasound**

Using power ultrasound, carbon dioxide/water and water/carbon dioxide emulsions were formed simultaneously, a direct consequence of the absence of emulsifying agents which would dictate the identity of the continuous phase. Turbidity measurements indicated that these emulsions broke completely within 30 minutes under all circumstances investigated (30 °C, 65 or 80 bar, 20 kHz, 0 – 1.0 W cm⁻³). Pulsed ultrasound (25% duty cycle) was able to maintain turbid emulsions for several hours, at which point sonication was terminated and the emulsion was allowed to break. For carbon dioxide/water emulsions, demulsification proceeded via droplet settling while water/carbon dioxide emulsions broke as a result of the combined action of Smoluchowski coagulation and hindered settling. The fact that the emulsions broke spontaneously within tens of minutes after termination of ultrasound is considered to be a distinct advantage for synthetic chemistry applications in which recovery of products and/or catalysts is an important consideration and phase entrainment would be considered a source of contamination.

A novel tracer technique was used to measure volumetric concentrations of the dispersed phases in emulsions formed at 30 °C and 80 bar. At an applied power density of 0.6 W cm⁻³, the volume percentage of water in the water/carbon dioxide emulsion was roughly 10%, while that of carbon dioxide in the carbon dioxide/water emulsion was roughly 5%. Formation of the carbon dioxide/water emulsion did not occur below a threshold power density of 0.1 W cm⁻³. Formation of the water/carbon dioxide emulsion did not appear to have a threshold power density. For both types of emulsions, increasing the power density beyond roughly 0.5 W cm⁻³ did not increase the measured volume fractions of dispersed phases.

A high pressure microchannel device was used to measure droplet diameters in emulsions formed at an acoustic power density of 0.6 W cm⁻³ at 30 °C and 80 bar. The Sauter diameter of carbon dioxide droplets was 15.1 μm. No correction was necessary
for the carbon dioxide droplets. Without any correction, the Sauter diameter of the water droplets was 9.1 \( \mu \text{m} \). Water droplets were imaged on a silicon surface, and an attempt was made to correct for their subsequent spreading. Profile images of the droplet attached to the silicon walls suggested a diameter of 2.1 \( \mu \text{m} \); however, the coagulation times predicted for this droplet size were much shorter than the time scale of the experiment leading to an apparent inconsistency. Furthermore, differences in the surface roughnesses of the walls and the floor of the silicon microchannel cast suspicion on the use of wall-adhered droplet profiles to correct for droplet spreading on the floor. Based on considerations of the coagulation time, the Sauter diameter was estimated to be roughly 6 \( \mu \text{m} \). In all instances, the size distributions were roughly log-normal.

The measured droplet diameters were comparable to, but slightly larger than those reported for oil/water emulsions formed by ultrasound in the presence of surfactants or water/carbon dioxide emulsions formed by high-pressure homogenization with the aid of surfactants. The energy efficiency was estimated to be roughly 0.09 \%, in close agreement with that reported for emulsification at ambient pressure.

Formation and stability of emulsions containing near- or supercritical carbon dioxide and water is a new field which should be explored further given its potential technological importance. Published results in this field focus on the design of novel carbon dioxide-pholic surfactants, and have not investigated the importance of the method of emulsification. A comparative study of emulsification using a variety of techniques including power ultrasound would be an important contribution to the field.

Future work should also be directed towards emulsion characterization. The microscopy technique used here is quite labor intensive thus limiting the number of samples which could be analyzed. Development of a more automated diagnostic tool, such as light scattering or ultrasonic spectroscopy, would be an important breakthrough as it would allow emulsion characterization over a much wider range of conditions. An on-line approach would also eliminate the error introduced by droplet spreading and coagulation. Measurement of droplet sizes and emulsion concentrations during the process of demulsification would be particularly useful as the basis for validating physical models of emulsion breaking.
The use of microchannel reactors at pressures exceeding 100 bar offers unique opportunities for chemical reactions. In particular, it might be possible to use microchannel reactors to increase heat transport from highly exothermic reactions or to increase mass transport rates to and from heterogeneous catalysts. Due to their small scale and ease of manufacture, microchannel reactors provide an opportunity for parallel synthesis. It should also be possible to use the narrow channels that can be manufactured using microfabrication techniques to introduce high shear rates, allowing the microdevices to be used as novel emulsification devices.

**Mechanisms of Carbon Dioxide/Water Emulsification and the Role of Cavitation**

At applied power densities of roughly 0.05 W cm\(^{-3}\) and a frequency of 20 kHz it was determined that the formation of unstable waves at the carbon dioxide/water interface was the primary means of emulsification, resulting in the dispersion of water droplets into the carbon dioxide phase. Theory predicted that the average droplet diameters resulting from these waves should be roughly 40 \(\mu\)m, consistent with the observation that these emulsions broke in minutes. The interfacial wave mechanism is also consistent with the absence of a threshold power density for the formation of dilute water/carbon dioxide emulsions, but does not explain the formation of micron-sized droplets at power densities greater than 0.05 W cm\(^{-3}\).

An alternative to the interfacial wave mechanism was required to account for the dispersion of micron-sized droplets into the two phases. At power densities greater than 0.10 W cm\(^{-3}\), acoustic streaming and cavitation were initially proposed as plausible emulsification mechanisms. It was easily shown that the kinetic energy dissipated by acoustic streaming was insufficient to account for the formation of micron-sized droplets. This implied that cavitation, and the resulting formation of microjets which are known to form submicron droplets in oil/water systems, played a primary role in emulsification. First-order theories of cavitation predict that it is suppressed when the applied acoustic pressure is not sufficient to lower the hydrostatic pressure of a fluid below its vapor pressure. It was therefore surprising that cavitation was apparently possible at a hydrostatic pressure of 80 bar and an acoustic pressure of 5 bar, since the Blake threshold pressures of water and carbon dioxide at the experimental conditions are roughly 80 and
15 bar, respectively. Based on this unusual behavior, a set of experiments was conducted to investigate cavitation further.

At 25 °C, visualization indicated that water, maintained at a hydrostatic pressure of 80 bar using carbon dioxide, cavitated with a threshold power density of roughly 1.0 W cm\(^{-3}\) (which corresponds to an acoustic pressure of nearly 20 bar). In these experiments, the carbon dioxide/water interface was removed from both the viewing area and the sonication zone so that cavitation would not be obscured by acoustic streaming. The nature of cavitation at 80 bar was much different than at ambient pressure, as much larger cavitation bubbles were formed and the cavitation cloud penetrated deeper into the liquid at the higher pressure. Apparent cavitation of liquid water at 80 bar may have been the result of cavitation of carbon dioxide (which has a much lower Blake threshold pressure than does water). Consistent with this, liquid carbon dioxide held at a hydrostatic pressure of 80 bar was observed to cavitate with a threshold of 20 bar. Finally, the discrepancy between the observed cavitation threshold pressure (20 bar) and the emulsification threshold pressure (5 bar) was possibly related to self-concentration of the acoustic waves during formation of the sonic jet.

In one of the most surprising results of this thesis, water was observed to cavitate at a threshold acoustic power density of roughly 1.0 W cm\(^{-3}\) (acoustic pressure of 20 bar) at a hydrostatic pressure of 120 bar. At this elevated hydrostatic pressure, it was expected that neither water nor carbon dioxide should cavitate unless the acoustic pressure was at least 60 bar.

A model sonochemical reaction, oxidation of potassium iodide to iodine, was studied to gain qualitative insight regarding cavitation in a high pressure carbon dioxide environment. Although the reaction occurred as expected at ambient pressures in nitrogen and carbon dioxide atmospheres, the oxidation was completely suppressed by a carbon dioxide head pressure of 80 bar. This result suggested that the collapsing bubbles formed during cavitation at 80 bar did not reach the temperatures required for formation of radical species.

After extended operation at 80 bar, pitting was observed on the sonic horn, indicating formation of cavitation microjets. This result suggests that cavitation of water in a high-pressure carbon dioxide environment releases sufficient energy for
emulsification, despite the finding that a sonochemical oxidation reaction is suppressed by pressurized carbon dioxide.

A systematic study of cavitation of water in high-pressure carbon dioxide environments would be useful. Not only are there a number of outstanding scientific questions, but better characterization of the cavitation process could lead to strategies for improving ultrasonic emulsification of water and carbon dioxide. It is known that, during cavitation and subsequent collapse, bubbles emit pressure waves at frequencies which can be related to the nature of cavitation. As one example, the frequencies emitted during “stable cavitation” (that is, repeated formation of a cavity followed by its collapse over many ultrasonic cycles) are different from those emitted during transient cavitation (formation of a cavity followed by collapse which is not repeated). Thus, an internally mounted hydrophone would detect not only the driving frequency of the applied acoustic wave (20 kHz in these experiments), but also background frequencies which carry information regarding cavitation. The temperature within the collapsing bubbles could be investigated using spectroscopic techniques, since there are well known means of relating the rotational spectra of probe molecules to the temperature of their environment. Finally, a chemical reactions which is known to be sonochemically active should be investigated to complement the data generated from the study of potassium iodide oxidation.

**Effect of Power Density on Chemical Reaction Rates**

Hydrolysis of benzoyl chloride was used as a model mass transport limited reaction to investigate the effects of ultrasonic power density on chemical dynamics. It was found that power ultrasound accelerated the apparent hydrolysis rate constant up to 100-fold relative to the rate constant under silent conditions. At power densities below 0.1 W cm\(^{-3}\), the acceleration was roughly 10-fold, corresponding to the action of interfacial waves which: 1) enhanced mass transport at the carbon dioxide/water interface and 2) dispersed large droplets of water (40 \(\mu\)m) into the carbon dioxide phase. The observed rate increased with power density until a maximum was reached at roughly 0.5 W cm\(^{-3}\). The saturation behavior of acoustic rate acceleration was linked to the saturation of the emulsifying abilities of power ultrasound at high power densities. Under all conditions, the disappearance rate of reactant obeyed apparent first-order kinetics.
A comparative study of a range of mass transport operations is a potential follow-through on the results described here. In addition to ultrasound, there are many means of increasing the contact area between immiscible liquids including conventional spray nozzles, electrospay nozzles, static mixers, and impellers. Benzoyl halide hydrolysis could be used as a model reaction to determine the energy efficiency of various mass transport operations.

*Phase-Transfer Reactions in Emulsions Containing Carbon Dioxide and Water*

The results from the benzoyl chloride study were primarily phenomenological and provided the basis for a more detailed kinetic study of the hydrolysis rates of a series of benzoyl halides. The reactants were selected to represent a wide range of intrinsic reactivities, but a small range of partition coefficients and diffusion coefficients. Partition coefficients were estimated with the correlation techniques mentioned previously and diffusivities were estimated from literature values of compounds with physicochemical properties similar to those of benzoyl halides. The intrinsic pseudo-first order reaction rates for benzoyl halide hydrolysis, that is the rate measured when the reaction is performed in pure water, ranged from $2 \times 10^{-3}$ s$^{-1}$ to greater than 10 s$^{-1}$ (25 °C, 1 bar). Sonication at 0.6 W cm$^{-3}$ and 20 kHz always accelerated the observed reaction rate though, for the least reactive cases (e.g., when the intrinsic pseudo-first order rate constant was equal to $2 \times 10^{-3}$ s$^{-1}$), only a modest 4-fold acceleration was observed. In the best case (observed for the hydrolysis of m-anisoyl chloride which has an intrinsic pseudo-first order rate constant of 0.5 s$^{-1}$), sonic enhancement was greater than 200-fold. The disappearance rate obeyed global first-order kinetics for all compounds that were studied under both sonicated and silent kinetics. Two physical models were proposed to interpret the experimental results.

First, a model was proposed to describe hydrolysis kinetics under silent, biphasic conditions. The basis of this model was an expression for reaction-enhanced mass transport from the carbon dioxide phase to the water phase. The critical parameter in this model was the ratio of reaction rate to mass transport rate, as described by the water-phase Hatta number. For Hatta numbers greater than $1 \times 10^5$, the silent model predicted global first order kinetics with respect to the halide reactant, as was observed experimentally. For Hatta numbers less than unity, a significant fraction of the reaction
occurs in the bulk water phase, otherwise the reaction is confined to a water film near the carbon dioxide/water interface. Benzoyl fluoride, the most stable reagent as indicated by its hydrolysis rate constant of $2 \times 10^{-3} \text{s}^{-1}$ (equivalent to a Hatta number of 0.5) in pure water, was the only reagent for which the bulk water phase was accessed under silent conditions. The reaction-enhanced mass transport model agreed with the observed data set to within the limits of experimental error with two exceptions: 1) the hydrolysis of p-nitrobenzoyl chloride was underpredicted by a factor of 6; 2) the hydrolysis rates of reactive halides (for which the pseudo-first order reaction rates were greater than 1 s$^{-1}$) were underpredicted. The partition coefficient of p-nitrobenzoyl chloride was possibly overpredicted, thus resulting in model underprediction of the hydrolysis rate. The model underprediction for reactive halides was possibly due to their rapid hydrolysis in the carbon dioxide phase, bypassing diffusion to the water phase as the rate determining step.

A second model was developed for sonicated conditions. This model was composed of three terms: 1) mass transport of reactant from the bulk carbon dioxide phase to the water droplets, 2) mass transport of reactant from the carbon dioxide droplets to the bulk water phase, and 3) consumption of reactant in both the bulk water phase and the water droplets. For transport of hydrophobic species the mass transport resistance in the water phase is always much greater than in the carbon dioxide phase, simplifying the analysis. Next, the concentration of reactants in the droplets was considered. Based on an estimated mass transport equilibration time of 0.1 s and an estimated droplet lifetime of 10 s, the water droplets were assumed to be in thermodynamic equilibrium with the bulk carbon dioxide phase at all times. Thus, the concentration of reactant in the water droplets was equal to its concentration in the carbon dioxide phase divided by its partition coefficient. Moreover, the flux of reactant from the bulk carbon dioxide phase to the water droplets was equal to the rate of consumption in the water droplets.

The time-scale analysis for the carbon dioxide droplets was not as conclusive. For carbon dioxide droplets, the time scale for reactant depletion was estimated to be 3 s, while their lifetime was estimated as 10 s, indicating that a substantial fraction of the reactant present in the carbon dioxide droplets would be depleted in their lifetime. Faced with a lack of hard data on droplet lifetimes, the assumption was made that the reactant concentrations in the carbon dioxide droplets equaled that in the bulk carbon dioxide
phase. In reality, the concentration of reactant in the carbon dioxide droplets is expected to decrease during their lifetime, leading to model overprediction of the observed reaction rate.

Thus constructed, the emulsion model agreed qualitatively with the experimental data, without the use of any fit parameters. The emulsion model correctly predicted global first order kinetics for all cases of interest. The model did slightly overpredict the observed reaction rates, consistent with the assumptions regarding the concentration of reactant in the carbon dioxide droplets. Overall, the agreement was within a factor of 2 or 3 which is nearly quantitative considering the limits of experimental uncertainty. As under silent conditions, the reaction rate of $p$-nitrobenzoyl chloride was underpredicted though now by a factor of 2. The consistent underprediction of the hydrolysis rate of $p$-nitrobenzoyl chloride supports the hypothesis that its partition coefficient was overpredicted by as much as a factor of 6. Including a term for reaction in the bulk carbon dioxide phase did not affect model predictions, indicating that this process no longer contributed to the overall dynamics. The success of the emulsion model indicates that ultrasonic acceleration is due to dramatically increased rates of mass transport.

The balance between the contributions of the two emulsions was described with the following expression:

$$\frac{\text{carbon dioxide/water emulsion}}{\text{water/carbon dioxide emulsion}} = \frac{D_{AW} a_{CW}}{RV_{\text{drop}} k_{rn}}$$

where $D_{AW}$ is the diffusion coefficient of the organic solute in water (assumed equal to 1 x $10^{-5}$ cm$^2$ s$^{-1}$ at 30 °C), $a_{CW}$ is the interfacial area of the carbon dioxide/water emulsion, $R$ is the diameter of a carbon dioxide droplet, $V_{\text{drop}}$ is the total volume of dispersed water droplets, and $k_{rn}$ is the intrinsic (first-order) rate constant. This expression is valid provided that the Damköhler number (that is the ratio of reaction rate to diffusional transport) of the water droplets is less than unity, as was the case in this study. It is also constrained by the droplet lifetimes and equilibration time scales described previously. Beyond these two restrictions, the above expression is completely general and predicts which sort of emulsion (carbon dioxide/water or water/carbon dioxide) is preferred for a given set of conditions. The balance expression requires modification (as described in Section 6.5) when the water-based Damköhler number surrounding the carbon dioxide
droplets approaches unity to account for reaction enhancement of the transport rate. For the specific conditions considered in this study, carbon dioxide/water emulsion dominated provided that the water-based Damköhler number surrounding the carbon dioxide droplets was less than 0.1 and the water/carbon dioxide emulsion dominated when this parameter was greater than unity.

The results from this study greatly inform the selection of reactions for optimal benefit when conducted in emulsions containing a dense carbon dioxide phase. The silent model, in conjunction with the methods developed in this thesis for predicting partition coefficients, can be used to determine whether chemical reactions will proceed at an acceptably fast rate in the biphasic environment, as defined by process economics or the experimenter. The emulsion model can be used to predict the accelerative effects of ultrasound for a given reaction. As a heuristic, valid for the current reactor geometry, reactions with intrinsic half lives greater than roughly 3 hours will not benefit from ultrasound, as mass transport is not a rate determining step. The benefit of ultrasound is expected to be increasingly important as the reaction rate is increased. Provided that reaction in the bulk carbon dioxide phase is either zero or negligible compared to the rate of mass transport to the water phase under silent conditions, the two mathematical models described above can be used to predict the sonic enhancement expected for a given reaction. As a second rule of thumb, also applicable to the current reactor geometry, reactions with characteristic half lives greater than several seconds will proceed as if the reactor contents were well mixed, which is the maximum rate possible. For reactions faster than this, it might be advantageous to re-design the acoustic reactor to achieve either smaller droplet sizes or larger concentrations of dispersed phases so that the well-mixed limit might be achieved. Finally, it is realized that chemical transformations are typically far more complex than the hydrolysis of benzoyl halides; nonetheless, the simple example described in this thesis contains all of the underlying physical principles required for analysis of more complicated systems.

There are two directions which are recommended for further investigation. The first is the study of reactions which proceed at rates faster than $10 \text{ s}^{-1}$. Though the rates representative of synthetic reactions commonly have half lives on the order of 1-10 hours, this study went beyond that range to half-lives less than 1 s. For some practical
applications, it might be necessary to investigate even faster reaction rates. If this line of research is pursued, the chemical oxidation of sulfite to sulfate (both highly water soluble compounds) is recommended as a model reaction, based on its extremely fast rate and the high solubility of molecular oxygen in supercritical carbon dioxide.

A second possible avenue of future inquiry is directed towards further understanding of reaction/transport dynamics during sonication of carbon dioxide/water mixtures. The greatest uncertainty in the current emulsion model is droplet lifetimes, and a detailed study of droplet break up and re-coalescence rates during sonication would be a valuable contribution. Perhaps most importantly, this information could lead to improvements to the assumption that the reactant concentration in the carbon dioxide droplets equals that in the bulk carbon dioxide phase.

**Water as a Catalyst for Synthetic Transformations**

Acoustically formed emulsions of carbon dioxide and water were used to access the unique ability of water to influence chemical reactivity without sacrificing overall throughput. The Diels-Alder cycloaddition of the dienophile methyl vinyl ketone to the diene cyclopentadiene was selected as a model reaction based on its fast rate and high endo selectivity when conducted in water. Carbon dioxide is a much better solvent for cyclopentadiene than is water, making liquid near-critical carbon dioxide an ideal delivery solvent to obtain high selectivity and conversion, while maintaining high product throughput.

A set of experiments was conducted with a constant excess concentration of methyl vinyl ketone equal to 1.0 mol L$^{-1}$ (based on the overall reactor volume) with variable volume loadings of water. The temperature and pressure were held constant at 30 °C and 80 bar. In silent, biphasic conditions, conversions (60-90%, after one hour) and selectivities (from 6:1 to 12:1) were greater than expected in pure carbon dioxide (25% and 4.5:1, respectively), but much less than observed in pure water (90% and 21:1, respectively). In general, sonication markedly increased both conversion and selectivity as compared to that obtained under silent conditions. At the best conditions (60% water loading), a two-fold increase in selectivity was observed (i.e., from 6:1 to 12:1). With further reactor modifications (described below), the standoff distance was optimized for a
water loading of 85% leading to a selectivity of nearly 14:1 even with the excess concentration of methyl vinyl ketone equal to 1.0 mol L⁻¹.

In general, selectivity and conversion increased with water loading. Water loadings for optimal acoustic enhancement were observed which corresponded to a spacing between the sonic horn and the carbon dioxide/water interface of roughly 2 cm. This optimal standoff distance is an important design consideration for reactor scale up and is a primary conclusion of this study. Physically, the optimal standoff distance is indicative of a balance between the maximum amount of interfacial volume which can be irradiated and the attenuation of the acoustic power as it penetrates the reaction mixture. Thus, for a standoff distance less than 2 cm, only a small volume of the carbon dioxide/water interfacial region is sonicated, while for standoff distances greater than 2 cm the intensity of the acoustic waves at the interface is not sufficient for cavitation and emulsification.

The effect of intrinsic reaction rate on sonic enhancement of conversion and selectivity was quantified. Instead of varying reaction partners (as was done for the benzoyl halide experiments) the excess concentration of methyl vinyl ketone was systematically varied which allowed manipulation of the apparent pseudo-first order rate constant. Experiments were conducted with a constant standoff distance of 2 cm, a constant water fraction loading of 85%, and variable methyl vinyl ketone excess concentration between 0.05 and 1.0 mol L⁻¹. Custom-designed reactor inserts were used to optimize the standoff distance while operating at 85% water loading. As before, the temperature and pressure were held constant at 30 °C and 80 bar and the total reaction time was 1 hr. Measured conversions and selectivities (after one hour) did not vary strongly with methyl vinyl ketone concentration under sonicated conditions, remaining constant at roughly 90% and 14:1. Selectivity under silent conditions improved significantly from 6:1 at a methyl vinyl ketone concentration of 1.0 mol L⁻¹ to nearly 15:1 at a dienophile concentration of 0.05 mol L⁻¹, while conversion varied from 60 to 40% over the same range of dienophile concentrations. Sonication could therefore be used to operate under conditions of high methyl vinyl ketone concentrations, where conversions were greater than 90% and the selectivity was near 14:1. This is a dramatic improvement over that observed in pure carbon dioxide (conversion less than 25%, selectivity equal to
roughly 4.5:1). Our results compare favorably with a literature report on the effect of scandium as a Lewis acid catalyst on reaction selectivity for a Diels-Alder reaction in otherwise pure supercritical carbon dioxide. In comparison, our approach, which does not rely on expensive additives, offers potential advantages in terms of post-reaction separations.

Based on the reaction rate in pure water and the droplet diameters measured previously, the water-based Damköhler number for the Diels-Alder reaction between cyclopentadiene and methyl vinyl ketone was estimated as 0.01 (when the methyl vinyl ketone concentration was 1.0 mol L\(^{-1}\)). Based on the results from the study of benzoyl halide hydrolysis, this value of the Damköhler number suggested well-mixed conditions existed during emulsification. A well-mixed model, consisting of 4 rate constants and 2 partition coefficients, was proposed to interpret the results of Diels-Alder experiments. The physical parameters in this model were measured independently (the partition coefficient of cyclopentadiene being estimated by the previously mentioned empirical correlations) so that it could be used in a predictive fashion. Model predictions of selectivity were always roughly 25% greater than that observed, while predicted conversions agreed with the experimental values to within the limits of experimental uncertainty. The model was also used to predict up to a 30-fold increase in product throughput for a carbon dioxide/water emulsion relative to that in pure water.

Two hypotheses were proposed to account for model underprediction of selectivity: 1) model uncertainty due to errors in the estimates of the six physical parameters and 2) the presence of a small amount of a methyl vinyl ketone-rich phase in the reactor. In particular, the reaction rates in the carbon dioxide phase may have been underestimated as they were measured in pure carbon dioxide, with no dissolved water. Studies were performed which confirmed the probable presence of the postulated third phase, thus highlighting the importance of understanding phase behavior in these complicated systems.

The study of this Diels-Alder reaction in carbon dioxide/water emulsions demonstrates the use of the acoustic technique for improving conversion and selectivity relative to carbon dioxide and throughput relative to water. The Diels-Alder cycloaddition was selected because it represents a wide range of synthetic conversions
which are accelerated in aqueous environments, but with limited commercial utility due to low reagent solubility in water. Future work in this area should be directed at expanding the synthetic scope of carbon dioxide/water emulsions to include additional reactions of commercial interest.

Since the biphasic environment is an ideal means of deploying homogeneous catalysts, we recommend this field for future research. While there has been tremendous progress in the past decade towards developing water-stable Lewis acid catalysts, many of the most effective ones are based on costly lanthanide metals. Recovery of these catalysts is critical for economic viability, and the biphasic environment is a natural means of separating and recovering water-soluble catalysts from carbon dioxide soluble reagents. Future work should investigate homogeneous catalysis in carbon dioxide/water emulsions, with particular attention toward catalyst recycling. Given its industrial importance, hydroformylation of linear olefins is a good candidate as a model reaction for such studies.

**Acoustic Reactor Designs**

The observation of an optimal stand-off distance between the tip of the acoustic horn and the carbon dioxide/water interface presents a major challenge to reactor scale up. To overcome this challenge, future acoustic reactor designs should concentrate on the use of flow-through emulsification, which allows a large amount of fluid to be processed while confining sonication to a small volume. This thesis suggests two important time scales for development of flow-through acoustic reactors. First, the time scale for emulsification was estimated as roughly 10 s (at a power density of 0.5 W cm\(^{-3}\)) as sonication for longer times did not increase either initial turbidity or stability. Thus, 10 s is suggested as a lower limit for the residence time in flow-through emulsifiers.

Second, emulsions broke within tens of minutes after termination of ultrasonic irradiation suggesting a residence time of roughly 10 min down stream of the sonication zone. For promotion of reactions which go to completion within roughly 10 minutes, a simple one-step sonication zone is suggested. In such instances, demulsification in the post-sonication zone is expected to facilitate post-reaction separations. For slower reactions, we recommend a conventional stirred-tank reactor equipped with a recirculation loop including a small volume sonication zone. This design eliminates the need for multiple
sonication zones. In either design, the sonication zone might be based on the design described in this thesis or it might consist of a tube surrounded by externally mounted piezoelectric elements. The second option might be used to provide a more uniform acoustic field than is possible with a horn.

One of the primary recommendations of this thesis is the extension of the acoustic technique to a wider range of chemical reactions. Although the physical models derived from studies of hydrolysis of benzoyl halides are expected to guide selection of model reactions, actually implementing these predictions will require screening experiments. The large volume of the acoustic reactor (nearly 100 cm$^3$) limits its usefulness for studies which require expensive or custom-synthesized reagents. For this reason, it might be desirable to scale-down the acoustic reactor. A reactor design similar to that used in this thesis might be used, while the overall volume could be minimized by use of a miniaturized acoustic horn. For scaling down to even smaller volumes, microfabrication methods might be used to construct reactors with volumes on the order of 100 µL. Sonication of such microreactors would be best effected using externally mounted piezoelectric elements, since minimal acoustic power attenuation is expected in the thin walls of the microreactors.

**Improved Understanding of Chemical Reactivity in Supercritical Fluids**

Rational selection of chemical reactions for the biphasic environment would greatly benefit from an improved understanding of intrinsic chemical reaction rates in supercritical fluids. Future work should be dedicated toward developing analogies between chemical reactivity in conventional solvents and supercritical carbon dioxide. Specifically, fluorocarbon solvents have much in common with supercritical carbon dioxide, and it might be possible to develop an analogy between the two. Currently, researchers compare the solvent effects of supercritical carbon dioxide to those in a wide range of hydrocarbon solvents, including toluene, acetone, and dichloromethane. Demonstration of an analogy between fluorocarbon solvents and supercritical carbon dioxide would greatly improve our understanding of chemical reactivity in carbon dioxide and allow the results of kinetic studies conducted at ambient pressures to be translated into predictions of rates of reactions conducted in supercritical carbon dioxide.
Chapter 8: Conclusions and Recommendations

The effects of cosolvents on chemical reactivity in supercritical carbon dioxide should be investigated further, with special emphasis placed on cosolvents which are capable of specific interactions such as hydrogen bonding. These studies are particularly relevant to this work given the fact that the water dissolved in carbon dioxide is expected to play a significant role in the rates of chemical reactions conducted in carbon dioxide/water systems. The hydrolysis of benzoyl halides in the carbon dioxide phase in contact with a bulk water phase is a case in point. More subtle effects are expected in instances in which water is not a reactant, but may influence rates via hydrogen bond donation or other local solvation effects.
CHAPTER 9

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CHAPTER 10

APPENDICES

10.1 Experimental Data: Partition Coefficients
Data reported in Table 3-1

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</tr>
<tr>
<td></td>
<td>4</td>
<td>45.3 ± 2.2</td>
<td></td>
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<tr>
<td></td>
<td>5</td>
<td>50.9 ± 6.5</td>
<td></td>
</tr>
</tbody>
</table>

data file: acetophenone.xls

<table>
<thead>
<tr>
<th>Benzaldehyde</th>
<th>Run #</th>
<th>$K_{C/W}^*$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>43.7 ± 4.5</td>
<td>39.3 ± 3.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36.6 ± 2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>37.6 ± 2.1</td>
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</table>

data file: benzaldehyde.xls

<table>
<thead>
<tr>
<th>Bromobenzene</th>
<th>Run #</th>
<th>$K_{C/W}^*$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1,074.8 ± 86.7</td>
<td>1088.7 ± 32.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1,126.3 ± 98.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1,065.0 ± 67.5</td>
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data file: bromobenzene.xls

<table>
<thead>
<tr>
<th>Chlorobenzene</th>
<th>Run #</th>
<th>$K_{C/W}^*$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1,191.4 ± 270.3</td>
<td>1141.4 ± 70.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1,091.5 ± 106.9</td>
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data file: chlorobenzene.xls

<table>
<thead>
<tr>
<th>Cyclohexane</th>
<th>Run #</th>
<th>$K_{C/W}^*$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>4,739.8 ± 1,438.2</td>
<td>4,947.7 ± 294.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5,155.5 ± 771.4</td>
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</tbody>
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data file: cyclohexane.xls
<table>
<thead>
<tr>
<th>Compound</th>
<th>Run #</th>
<th>$K'_{c/w}$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>1</td>
<td>1,880.9 ± 259.8</td>
<td>1,880.9 ± 259.8</td>
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<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
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<td></td>
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<tr>
<td>data file: cyclohexane.xls</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>1</td>
<td>1,614.0 ± 204.7</td>
<td>1405.7 ± 188.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1,248.2 ± 195.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1,354.9 ± 253.7</td>
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</tr>
<tr>
<td>data file: cyclopentene.xls</td>
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<td></td>
</tr>
<tr>
<td>Ethyl Benzoate</td>
<td>1</td>
<td>553.7 ± 26.8</td>
<td>574.4 ± 106.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>689.8 ±  57.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>479.7 ±  68.8</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>1</td>
<td>891.9 ± 118.2</td>
<td>785.9 ± 149.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>679.9 ±  82.3</td>
<td></td>
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<tr>
<td>data file: fluorobenzene.xls</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>1</td>
<td>10,187 ± 3,323.1</td>
<td>8870.4 ± 1,146.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8,322.1 ± 4,766.0</td>
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</tr>
<tr>
<td></td>
<td>3</td>
<td>8,101.4 ± 1,939.6</td>
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<td>data file: hexane.xls</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2-Methoxy-acetophenone</td>
<td>1</td>
<td>46.5 ± 2.9</td>
<td>47.3 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>48.1 ± 1.7</td>
<td></td>
</tr>
<tr>
<td>data file: 3-methoxy acetophenone.xls</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3-Methoxy-acetophenone</td>
<td>1</td>
<td>83.8 ± 0.77</td>
<td>84.4 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>85.0 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>data file: 3-methoxy acetophenone.xls</td>
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<td></td>
</tr>
</tbody>
</table>
### Methyl Benzoate

<table>
<thead>
<tr>
<th>Run #</th>
<th>( K_{c/w}^* )</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>182.7 ± 10.2</td>
<td>207.5 ± 21.7</td>
</tr>
<tr>
<td>2</td>
<td>235.5 ± 7.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>207.4 ± 11.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>204.5 ± 7.7</td>
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</tr>
</tbody>
</table>

data file: methyl benzoate.xls

### Methyl vinyl ketone

<table>
<thead>
<tr>
<th>Run #</th>
<th>Concentration (M)</th>
<th>( K_{c/w}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>8.0 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>8.0 ± 0.6</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>7.7 ± 0.3</td>
</tr>
<tr>
<td>4</td>
<td>0.66</td>
<td>17.4 ± 3.2</td>
</tr>
<tr>
<td>5</td>
<td>0.66</td>
<td>15.8 ± 2.6</td>
</tr>
<tr>
<td>6</td>
<td>0.66</td>
<td>13.8 ± 1.0</td>
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<tr>
<td>7</td>
<td>0.99</td>
<td>13.8 ± 0.6</td>
</tr>
<tr>
<td>8</td>
<td>1.33</td>
<td>14.8 ± 1.0</td>
</tr>
</tbody>
</table>

data file: methyl vinyl ketone partitioning.xls

### Propiophenone

<table>
<thead>
<tr>
<th>Run #</th>
<th>( K_{c/w}^* )</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>123.6 ± 8.6</td>
<td>121.6 ± 13.2</td>
</tr>
<tr>
<td>2</td>
<td>105.3 ± 11.1</td>
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</tr>
<tr>
<td>3</td>
<td>120.2 ± 13.1</td>
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</tr>
<tr>
<td>4</td>
<td>137.5 ± 6.5</td>
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</tr>
</tbody>
</table>

data file: propiophenone.xls

### Propyl Benzoate

<table>
<thead>
<tr>
<th>Run #</th>
<th>( K_{c/w}^* )</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,237.3 ± 155.1</td>
<td>1078.2 ± 225.0</td>
</tr>
<tr>
<td>2</td>
<td>919.1 ± 120.9</td>
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</tr>
</tbody>
</table>

data file: propyl benzoate.xls

### Tetrahydrofuran

<table>
<thead>
<tr>
<th>Run #</th>
<th>( K_{c/w}^* )</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8 ± 0.2</td>
<td>8.5 ± 1.0</td>
</tr>
<tr>
<td>2</td>
<td>9.2 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

data file: tetrahydrofuran.xls

### Toluene

<table>
<thead>
<tr>
<th>Run #</th>
<th>( K_{c/w}^* )</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,211.5 ± 205.0</td>
<td>1206.2 ± 281.9</td>
</tr>
<tr>
<td>2</td>
<td>921.6 ± 279.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1,485.4 ± 287.3</td>
<td></td>
</tr>
</tbody>
</table>

data file: toluene.xls
### 10.2 Water Solubility Data and $K_{O/W}^*$

Data plotted in Figure 3-3

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\log_{10} K_{C/W}^*$</th>
<th>$\log_{10} C_{sat}^{(W)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentachlorophenol</td>
<td>2.00</td>
<td>-4.279</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>-0.68</td>
<td>-1.82</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.11</td>
<td>-1.55</td>
</tr>
<tr>
<td>Caffeine</td>
<td>-0.82</td>
<td>-0.97</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td>-0.74</td>
<td>-0.74</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.59</td>
<td>-1.51</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>1.69</td>
<td>-1.28</td>
</tr>
<tr>
<td>Ethyl Benzoate</td>
<td>2.74</td>
<td>-2.32</td>
</tr>
<tr>
<td>Methyl Benzoate</td>
<td>2.31</td>
<td>-1.85</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.32</td>
<td>-0.41</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>1.11</td>
<td>-1.06</td>
</tr>
<tr>
<td>2,4-Dimethyl-phenol</td>
<td>1.00</td>
<td>-1.17</td>
</tr>
<tr>
<td>2-Nitrophenol</td>
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<td>-1.74</td>
</tr>
<tr>
<td>Hexanone</td>
<td>2.07</td>
<td>-0.8</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>1.61</td>
<td>-0.6</td>
</tr>
<tr>
<td>Propiophenone</td>
<td>2.08</td>
<td>-1.83</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.31</td>
<td>-2.22</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>0.27</td>
<td>-0.48</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>3.15</td>
<td>-2.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>3.95</td>
<td>-3.84</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3.69</td>
<td>-3.1</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>3.28</td>
<td>-2.59</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>2.89</td>
<td>-1.8</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>3.08</td>
<td>-2.38</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>3.04</td>
<td>-2.55</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>2.19</td>
<td>-1.06</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>1.90</td>
<td>-1.74</td>
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<tr>
<td>1,1,2-Trichloroethane</td>
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</tr>
<tr>
<td>2-Methyl phenol</td>
<td>0.60</td>
<td>-0.62</td>
</tr>
</tbody>
</table>
10.3 Group Contribution Estimates of $K_{O/W}^*$

Data plotted in Figure 3-4

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\log_{10} K_{C/W}^*$</th>
<th>$\log_{10} K_{O/W}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>1.69</td>
<td>2.4</td>
</tr>
<tr>
<td>Acetyl acetone</td>
<td>0.48</td>
<td>0.3</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.32</td>
<td>1.7</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.59</td>
<td>2.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.54</td>
<td>2.9</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.11</td>
<td>2.7</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>0.28</td>
<td>1.9</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>3.04</td>
<td>3.8</td>
</tr>
<tr>
<td>Caffeine</td>
<td>-0.82</td>
<td>0.7</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>3.06</td>
<td>3.6</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>1.15</td>
<td>2.9</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>0.48</td>
<td>3.3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3.69</td>
<td>4.1</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>1.61</td>
<td>1.6</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>3.28</td>
<td>3.6</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>3.15</td>
<td>3.1</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
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<td>2.2</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>1.85</td>
<td>3.7</td>
</tr>
<tr>
<td>(Karásek et al., 2002)</td>
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</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>1.48</td>
<td>3.7</td>
</tr>
<tr>
<td>(Akgerman and Carter, 1994)</td>
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</tr>
<tr>
<td>2,4-Dichlorophenoxy acetic acid</td>
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<td>3.5</td>
</tr>
<tr>
<td>2,4-Dimethylphenol</td>
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<tr>
<td>Ethyl benzoate</td>
<td>2.74</td>
<td>3.4</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>2.89</td>
<td>3.1</td>
</tr>
<tr>
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<td>1.4</td>
</tr>
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<td>4.6</td>
</tr>
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</tr>
<tr>
<td>Methyl benzoate</td>
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<td>2.9</td>
</tr>
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<td>3.8</td>
</tr>
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<td>3.0</td>
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<td>2.7</td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>0.89</td>
<td>0.8</td>
</tr>
<tr>
<td>Solute</td>
<td>$\log_{10} K'_{C/w}$</td>
<td>$\log_{10} K'_{O/w}$</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Naphthalene</td>
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</tr>
<tr>
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<td>2.6</td>
</tr>
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<td>4-Nitrophenol</td>
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</tr>
<tr>
<td>Parathion</td>
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<td>5.5</td>
</tr>
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<td>Phenol (Roop et al., 1989)</td>
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<td>Phenol (Karásek et al., 2002)</td>
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<tr>
<td>Phenol (Ghonasgi et al., 1991)</td>
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<td>2.2</td>
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<tr>
<td>Propiophenone</td>
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<td>2.9</td>
</tr>
<tr>
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<td>4.3</td>
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<td>5.0</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
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<td>1.3</td>
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<tr>
<td>Toluene</td>
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<td>3.4</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>1.45</td>
<td>2.8</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>2.18</td>
<td>4.2</td>
</tr>
</tbody>
</table>
10.4 Droplet Analysis Image Archive

The following is a complete list of the images taken to determine droplet sizes as presented in Section 4.5.5.

First Round - Performed on Lyca Stereoscope with (Higher Magnification = 10x)
- DSCN3733
- DSCN3735
- DSCN3736
- DSCN3737
- DSCN3738
- DSCN3739
- DSNC3740

Second Round – Performed on Zeiss 200 Axiover (Highest Magnification = 20x)
- timko 80 bar 30C t=0 W in C
- timko 80 bar 30C t=0 W in C 10x
- timko 80 bar 30C t=0 W in C 10x bottom
- timko 80 bar 30C t=0 W in C 20x
- timko 80 bar 30C t=0 W in C 20x bottom
- timko 80 bar 30C t=0 W in C 20x bottom2
- timko 80 bar 30C t=0 W in C 20x bottom3

Third Round – Performed on Zeiss 200 Axiover (Highest Magnification = 20x)
- timko 80 bar 30C t=0 W in C 20x bottom run2-1
- timko 80 bar 30C t=0 W in C 20x bottom run2-1 adjusted
- timko 80 bar 30C t=0 W in C 20x bottom run2-2
- timko 80 bar 30C t=0 W in C 20x bottom run2-3
- timko 80 bar 30C t=0 W in C 20x bottom run2-4
- timko 80 bar 30C t=0 W in C 20x bottom run2-5
- timko 80 bar 30C t=0 W in C 20x bottom run2-6
- timko 80 bar 30C t=0 W in C 20x bottom run2-empty

Fourth Round – Performed on Zeiss 200 Axiover (Highest Magnification = 20x)
- timko 80 bar 30C t=0 W in C 20x bottom run3-1
- timko 80 bar 30C t=0 W in C 20x bottom run3-2
- timko 80 bar 30C t=0 W in C 20x bottom run3-3
- timko 80 bar 30C t=0 W in C 20x bottom run3-4
- timko 80 bar 30C t=0 W in C 20x bottom run3-5
Chapter 10: Appendices

Fifth Round – Perfomed on Zeiss 200 Axiovert (Highest Magnification = 20x)

- timko 80 bar 30C t=0 W in C 20x bottom run4-1
- timko 80 bar 30C t=0 W in C 20x bottom run4-2
- timko 80 bar 30C t=0 W in C 20x bottom run4-3
- timko 80 bar 30C t=0 W in C 20x bottom run4-4
- timko 80 bar 30C t=0 W in C 20x bottom run4-5
- timko 80 bar 30C t=0 W in C 20x bottom run4-6
- timko 80 bar 30C t=0 W in C 20x bottom run4-7
- timko 80 bar 30C t=0 W in C 20x bottom run4-8
- timko 80 bar 30C t=0 W in C 20x side drop run4-1
- timko 80 bar 30C t=0 W in C 20x side drop run4-2
- timko 80 bar 30C t=0 W in C 20x side drop run4-3
- timko 80 bar 30C t=0 W in C 20x side drop run4-4
- timko 80 bar 30C t=0 W in C 20x side drop run4-5
- timko 80 bar 30C t=0 W in C 20x side drop run4-5

Sixth Round – Perfomed on Zeiss 200 Axiovert (Highest Magnification = 20x)

- timko 80 bar t=0 C in W 20x bottom run6-1
- timko 80 bar t=0 C in W 20x bottom run6-2
- timko 80 bar t=0 C in W 20x bottom run6-3
- timko 80 bar t=0 C in W 20x bottom run6-4
- timko 80 bar t=0 C in W 20x bottom run6-5
- timko 80 bar t=0 C in W 20x bottom run6-6
- timko 80 bar t=0 C in W 10x top run6-1
- timko 80 bar t=0 C in W 20x top run6-1
- timko 80 bar t=0 C in W 20x top run6-2
- timko 80 bar t=0 C in W 20x top run6-3
- timko 80 bar t=0 C in W 20x top run6-4
- timko 80 bar t=0 C in W 20x top run6-5
- timko 80 bar t=0 C in W 20x top run6-6

Calibration with PSL Standards – Perfomed on Zeiss 200 Axiovert (Highest Magnification = 20x)

- 4microns_20 X2
- 4microns_20 X3
- 8.8.03 4 um – 1
- 8.8.03 4 um – 2
- 8.8.03 4 um – 3
- 8.8.03 4 um nobin – 1
- 8.8.03 4 um nobin – 2
- 8.8.03 4 um nobin – 3
- 8.8.03 4 um nobine – 4
- 20microns_20 X
- 20microns_20 X2
- 20microns_20 X3
### 10.5 Experimental Data: Sonochemical Oxidation of KI

**Run #2**: carbon dioxide atmosphere, 1 bar, 30 °C, 50 W

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>I$_2$ (μmol L$^{-1}$)</th>
<th>I$_2$ Production Rate (μmol W$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.2 x 10$^{-2}$</td>
</tr>
<tr>
<td>40</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>1.13</td>
<td></td>
</tr>
</tbody>
</table>

**Run #3**: carbon dioxide atmosphere, 1 bar, 30 °C, 100 W

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>I$_2$ (μmol L$^{-1}$)</th>
<th>I$_2$ Production Rate (μmol W$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.7 x 10$^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2.78</td>
<td></td>
</tr>
</tbody>
</table>

**Run #4**: carbon dioxide atmosphere, 1 bar, 30 °C, 100 W

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>I$_2$ (μmol L$^{-1}$)</th>
<th>I$_2$ Production Rate (μmol W$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.7 x 10$^{-2}$</td>
</tr>
<tr>
<td>6</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.35</td>
<td></td>
</tr>
</tbody>
</table>

**Run #5**: nitrogen atmosphere, 1 bar, 30 °C, 100 W

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>I$_2$ (μmol L$^{-1}$)</th>
<th>I$_2$ Production Rate (μmol W$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>9.9 x 10$^{-2}$</td>
</tr>
<tr>
<td>2</td>
<td>5.69</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.13</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.89</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>10.95</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>11.97</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>11.70</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>7.96</td>
<td></td>
</tr>
</tbody>
</table>
**Run #6**: carbon dioxide, 80 bar, 30 °C, 100 W

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$I_2$ (µmol L$^{-1}$)</th>
<th>$I_2$ Production Rate (µmol W$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
10.6 Numerical Simulation Code: Rayleigh-Plesset Equation

This code was used for numerical simulation of bubble dynamics as presented in Section 5.3.3. The program runs in a Matlab environment and is saved as bubbledynamics.m.

function bubbledynamics

tspan = [0; 1e-4];
R0 = [4e-6; 0];

[t,R] = ode15s(@f,tspan,R0);

Rprime = R(:,1)*1e6;

plot(t,R(:,1)/R0(1), 'k');
%xlabel('time (s)')
%ylabel ('R/Ro')
Rmin = min(R(:,1));
kappa = 1;
P0 = 1e5;
R0(1);
Pmax = (P0)*R0(1)^3/Rmin^3

tprint = transpose(t);
%pause
radiusprint = transpose(R);
size(tprint)
size(t);
size(R);
size(R(:,1))
size(radiusprint)
%fid = fopen('out3.txt','w');
%writefile1 = [t, R(:,1)];

%fprintf(fid,'%6.2f %12.8f
',writefile1);
%fclose(fid)

% -----------------------------------------------

function dydt = f(t,R)
%Pgasm = 1e5;
P0 = 1e5;
cL = 1500;
omega = 20*1000*2*3.14;
Pamp = 2e5;
eta = 9e-4;
rhoL = 1000;
R0 = 4e-6;
%sigma = (19.7+59.3*exp(-0.027*P0))/1000;
sigma = 0.072;
h = R0/10;
kappa = 1;
alpha = (P0+2*sigma/R0)*(R0^3-h^3);
dydt = [ (R(2))
          (1/rhoL/R(1)*(alpha/(R(1)^3-h^3)*kappa-Pamp*cos(omega*t)-P0+R(1)/cL*alpha*(-kappa-1)*(R(1)^3-h^3)*3*R(1)^2*R(2)-4*eta*R(2)/R(1)-2*sigma/R(1)-3/2*rhoL*R(2)^2))];
10.7 Experimental Data: Benzoyl Halide Hydrolysis

Data reported in Section 6.4 and 6.5.

**Benzoyl Bromide**

Acoustic, 0.60 W cm\(^{-3}\), 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ( \ln (C/C_0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>120</td>
<td>0.33</td>
<td>0.40</td>
</tr>
<tr>
<td>180</td>
<td>0.47</td>
<td>0.63</td>
</tr>
<tr>
<td>240</td>
<td>0.66</td>
<td>1.08</td>
</tr>
<tr>
<td>300</td>
<td>0.63</td>
<td>1.00</td>
</tr>
<tr>
<td>360</td>
<td>0.73</td>
<td>1.31</td>
</tr>
<tr>
<td>420</td>
<td>0.71</td>
<td>1.23</td>
</tr>
<tr>
<td>480</td>
<td>0.80</td>
<td>1.61</td>
</tr>
<tr>
<td>540</td>
<td>0.80</td>
<td>1.63</td>
</tr>
<tr>
<td>600</td>
<td>0.89</td>
<td>2.23</td>
</tr>
<tr>
<td>600</td>
<td>0.87</td>
<td>2.01</td>
</tr>
<tr>
<td>900</td>
<td>0.91</td>
<td>2.46</td>
</tr>
<tr>
<td>1200</td>
<td>0.99</td>
<td>4.66</td>
</tr>
<tr>
<td>1500</td>
<td>0.98</td>
<td>3.97</td>
</tr>
<tr>
<td>1800</td>
<td>0.94</td>
<td>2.86</td>
</tr>
<tr>
<td>1800</td>
<td>0.97</td>
<td>3.36</td>
</tr>
<tr>
<td>1920</td>
<td>0.87</td>
<td>2.07</td>
</tr>
<tr>
<td>2400</td>
<td>0.93</td>
<td>2.61</td>
</tr>
<tr>
<td>3120</td>
<td>0.82</td>
<td>1.69</td>
</tr>
<tr>
<td>3720</td>
<td>0.79</td>
<td>1.55</td>
</tr>
<tr>
<td>5580</td>
<td>0.74</td>
<td>1.36</td>
</tr>
<tr>
<td>7200</td>
<td>0.74</td>
<td>1.34</td>
</tr>
<tr>
<td>9300</td>
<td>0.81</td>
<td>1.66</td>
</tr>
<tr>
<td>10860</td>
<td>0.73</td>
<td>1.30</td>
</tr>
</tbody>
</table>
Benzoyl Bromide

Silent, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>2700</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>3600</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>3600</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>4500</td>
<td>0.43</td>
<td>0.56</td>
</tr>
<tr>
<td>5400</td>
<td>0.63</td>
<td>0.98</td>
</tr>
<tr>
<td>6300</td>
<td>0.56</td>
<td>0.82</td>
</tr>
<tr>
<td>7200</td>
<td>0.64</td>
<td>1.03</td>
</tr>
<tr>
<td>7200</td>
<td>0.71</td>
<td>1.25</td>
</tr>
<tr>
<td>8100</td>
<td>0.72</td>
<td>1.28</td>
</tr>
<tr>
<td>9000</td>
<td>0.76</td>
<td>1.42</td>
</tr>
<tr>
<td>9900</td>
<td>0.73</td>
<td>1.31</td>
</tr>
<tr>
<td>1800</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>4500</td>
<td>0.46</td>
<td>0.62</td>
</tr>
<tr>
<td>8400</td>
<td>0.76</td>
<td>1.43</td>
</tr>
<tr>
<td>12300</td>
<td>0.87</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Benzoyl Chloride

Acoustic, 0.60 W cm⁻³, 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>120</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>180</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>240</td>
<td>0.37</td>
<td>0.46</td>
</tr>
<tr>
<td>300</td>
<td>0.47</td>
<td>0.64</td>
</tr>
<tr>
<td>360</td>
<td>0.49</td>
<td>0.67</td>
</tr>
<tr>
<td>420</td>
<td>0.58</td>
<td>0.86</td>
</tr>
<tr>
<td>480</td>
<td>0.57</td>
<td>0.85</td>
</tr>
<tr>
<td>540</td>
<td>0.61</td>
<td>0.94</td>
</tr>
<tr>
<td>540</td>
<td>0.76</td>
<td>1.42</td>
</tr>
<tr>
<td>540</td>
<td>0.71</td>
<td>1.22</td>
</tr>
<tr>
<td>600</td>
<td>0.63</td>
<td>1.00</td>
</tr>
<tr>
<td>720</td>
<td>0.79</td>
<td>1.54</td>
</tr>
<tr>
<td>900</td>
<td>0.89</td>
<td>2.22</td>
</tr>
<tr>
<td>900</td>
<td>0.81</td>
<td>1.66</td>
</tr>
<tr>
<td>1200</td>
<td>0.87</td>
<td>2.01</td>
</tr>
<tr>
<td>1500</td>
<td>0.94</td>
<td>2.77</td>
</tr>
<tr>
<td>1500</td>
<td>0.92</td>
<td>2.48</td>
</tr>
</tbody>
</table>
Benzoyl Chloride

Silent, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>$-\ln \left( \frac{C}{C_0} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>5700</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>6000</td>
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<td>0.11</td>
</tr>
<tr>
<td>9600</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>14400</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>21600</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>25200</td>
<td>0.27</td>
<td>0.31</td>
</tr>
<tr>
<td>33600</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>63000</td>
<td>0.51</td>
<td>0.71</td>
</tr>
<tr>
<td>81600</td>
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<td>1.00</td>
</tr>
<tr>
<td>85200</td>
<td>0.65</td>
<td>1.05</td>
</tr>
<tr>
<td>7800</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>10800</td>
<td>0.19</td>
<td>0.21</td>
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<tr>
<td>14700</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>18360</td>
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<td>0.32</td>
</tr>
<tr>
<td>21600</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>25200</td>
<td>0.35</td>
<td>0.43</td>
</tr>
<tr>
<td>41400</td>
<td>0.42</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Benzoyl Fluoride

Acoustic, 0.60 W cm$^{-3}$, 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>$-\ln \left( \frac{C}{C_0} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>2700</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>4500</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>6300</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>7800</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>10200</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>12600</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>18000</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>25200</td>
<td>0.24</td>
<td>0.27</td>
</tr>
</tbody>
</table>
**Benzoyl Fluoride**

*Silent, 80 bar, 30 °C*

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>(-\ln (C/C_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12600</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>27600</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>55020</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>62160</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>97260</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>111600</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>152100</td>
<td>0.29</td>
<td>0.34</td>
</tr>
</tbody>
</table>

**o-Anisoyl Chloride**

*Acoustic, 0.60 W cm\(^{-3}\), 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C*

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>(-\ln (C/C_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>40</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>60</td>
<td>0.63</td>
<td>0.99</td>
</tr>
<tr>
<td>60</td>
<td>0.55</td>
<td>0.80</td>
</tr>
<tr>
<td>60</td>
<td>0.66</td>
<td>1.08</td>
</tr>
<tr>
<td>80</td>
<td>0.81</td>
<td>1.68</td>
</tr>
<tr>
<td>90</td>
<td>0.82</td>
<td>1.73</td>
</tr>
<tr>
<td>105</td>
<td>0.84</td>
<td>1.83</td>
</tr>
<tr>
<td>120</td>
<td>0.94</td>
<td>2.76</td>
</tr>
<tr>
<td>120</td>
<td>0.93</td>
<td>2.60</td>
</tr>
</tbody>
</table>
### o-Anisoyl Chloride

**Silent**, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>450</td>
<td>0.40</td>
<td>0.51</td>
</tr>
<tr>
<td>600</td>
<td>0.42</td>
<td>0.55</td>
</tr>
<tr>
<td>600</td>
<td>0.63</td>
<td>1.00</td>
</tr>
<tr>
<td>750</td>
<td>0.54</td>
<td>0.77</td>
</tr>
<tr>
<td>900</td>
<td>0.58</td>
<td>0.88</td>
</tr>
<tr>
<td>1050</td>
<td>0.76</td>
<td>1.44</td>
</tr>
<tr>
<td>1060</td>
<td>0.64</td>
<td>1.03</td>
</tr>
<tr>
<td>1200</td>
<td>0.68</td>
<td>1.14</td>
</tr>
<tr>
<td>1350</td>
<td>0.73</td>
<td>1.30</td>
</tr>
<tr>
<td>1500</td>
<td>0.85</td>
<td>1.88</td>
</tr>
<tr>
<td>1800</td>
<td>0.75</td>
<td>1.39</td>
</tr>
<tr>
<td>1950</td>
<td>0.89</td>
<td>2.25</td>
</tr>
<tr>
<td>2100</td>
<td>0.88</td>
<td>2.14</td>
</tr>
<tr>
<td>2430</td>
<td>0.95</td>
<td>3.03</td>
</tr>
<tr>
<td>3900</td>
<td>0.99</td>
<td>4.29</td>
</tr>
<tr>
<td>4500</td>
<td>0.99</td>
<td>4.51</td>
</tr>
</tbody>
</table>

### p-Anisoyl Chloride

**Acoustic**, 0.60 W cm⁻³, 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.38</td>
<td>0.32</td>
</tr>
<tr>
<td>60</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>120</td>
<td>0.51</td>
<td>0.56</td>
</tr>
<tr>
<td>120</td>
<td>0.31</td>
<td>0.37</td>
</tr>
<tr>
<td>180</td>
<td>0.62</td>
<td>0.82</td>
</tr>
<tr>
<td>180</td>
<td>0.44</td>
<td>0.59</td>
</tr>
<tr>
<td>240</td>
<td>0.70</td>
<td>1.04</td>
</tr>
<tr>
<td>240</td>
<td>0.55</td>
<td>0.79</td>
</tr>
<tr>
<td>300</td>
<td>0.74</td>
<td>1.18</td>
</tr>
<tr>
<td>300</td>
<td>0.63</td>
<td>1.00</td>
</tr>
<tr>
<td>360</td>
<td>0.79</td>
<td>1.40</td>
</tr>
<tr>
<td>360</td>
<td>0.71</td>
<td>1.23</td>
</tr>
</tbody>
</table>
### p-Anisoyl Chloride

**Silent, 80 bar, 30 °C**

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>(-\ln (C/C_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>1200</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>1200</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>1800</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>1800</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>2520</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>2700</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>3120</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>3600</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>3600</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>3900</td>
<td>0.23</td>
<td>0.26</td>
</tr>
</tbody>
</table>

### m-Anisoyl Chloride

**Acoustic, 0.60 W cm\(^{-3}\), 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C**

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>(-\ln (C/C_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>600</td>
<td>0.34</td>
<td>0.41</td>
</tr>
<tr>
<td>600</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>600</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>900</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>1200</td>
<td>0.57</td>
<td>0.84</td>
</tr>
<tr>
<td>1200</td>
<td>0.47</td>
<td>0.64</td>
</tr>
<tr>
<td>1500</td>
<td>0.56</td>
<td>0.82</td>
</tr>
<tr>
<td>1800</td>
<td>0.66</td>
<td>1.08</td>
</tr>
<tr>
<td>1860</td>
<td>0.61</td>
<td>0.95</td>
</tr>
<tr>
<td>1980</td>
<td>0.74</td>
<td>1.33</td>
</tr>
<tr>
<td>2100</td>
<td>0.73</td>
<td>1.29</td>
</tr>
<tr>
<td>2400</td>
<td>0.80</td>
<td>1.62</td>
</tr>
<tr>
<td>2400</td>
<td>0.79</td>
<td>1.56</td>
</tr>
<tr>
<td>2700</td>
<td>0.86</td>
<td>1.95</td>
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<tr>
<td>3000</td>
<td>0.85</td>
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<td>3000</td>
<td>0.91</td>
<td>2.38</td>
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</table>
**m-Anisoyl Chloride**

**Silent**, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9900</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>14400</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>28860</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>44400</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>69600</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>74170</td>
<td>0.31</td>
<td>0.36</td>
</tr>
<tr>
<td>87000</td>
<td>0.35</td>
<td>0.43</td>
</tr>
<tr>
<td>100800</td>
<td>0.43</td>
<td>0.56</td>
</tr>
<tr>
<td>142800</td>
<td>0.50</td>
<td>0.69</td>
</tr>
<tr>
<td>166200</td>
<td>0.42</td>
<td>0.55</td>
</tr>
<tr>
<td>185400</td>
<td>0.49</td>
<td>0.68</td>
</tr>
<tr>
<td>252000</td>
<td>0.59</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**p-Nitrobenzoyl Chloride**

**Acoustic**, 0.60 W cm⁻³, 20 kHz, 0.25 s duty cycle, 80 bar, 30 °C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>300</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>600</td>
<td>0.34</td>
<td>0.41</td>
</tr>
<tr>
<td>600</td>
<td>0.35</td>
<td>0.43</td>
</tr>
<tr>
<td>900</td>
<td>0.44</td>
<td>0.58</td>
</tr>
<tr>
<td>900</td>
<td>0.45</td>
<td>0.59</td>
</tr>
<tr>
<td>1200</td>
<td>0.50</td>
<td>0.69</td>
</tr>
<tr>
<td>1200</td>
<td>0.54</td>
<td>0.77</td>
</tr>
<tr>
<td>1500</td>
<td>0.54</td>
<td>0.77</td>
</tr>
<tr>
<td>1500</td>
<td>0.56</td>
<td>0.81</td>
</tr>
<tr>
<td>1800</td>
<td>0.65</td>
<td>1.05</td>
</tr>
<tr>
<td>1800</td>
<td>0.61</td>
<td>0.95</td>
</tr>
</tbody>
</table>
**p-Nitrobenzoyl Chloride**

_**Silent,** 80 bar, 30 °C_

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield</th>
<th>- ln (C/C₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7200</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>18000</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>57900</td>
<td>0.61</td>
<td>0.95</td>
</tr>
<tr>
<td>76800</td>
<td>0.69</td>
<td>1.18</td>
</tr>
<tr>
<td>79200</td>
<td>0.75</td>
<td>1.39</td>
</tr>
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<td>88200</td>
<td>0.74</td>
<td>1.35</td>
</tr>
<tr>
<td>97200</td>
<td>0.84</td>
<td>1.81</td>
</tr>
</tbody>
</table>

**Benzoyl Chloride**

_Acoustic Effect of Power Density,* 20 kHz, 0.25 s duty cycle, 60 bar, 30 °C_

<table>
<thead>
<tr>
<th>Run #</th>
<th>Power Density (W cm⁻³)</th>
<th># Points</th>
<th>k* (x₁₀⁵ s⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>5</td>
<td>0.0105</td>
<td>0.994</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>4</td>
<td>0.273</td>
<td>0.964</td>
</tr>
<tr>
<td>3</td>
<td>0.32</td>
<td>4</td>
<td>1.73</td>
<td>0.949</td>
</tr>
<tr>
<td>4</td>
<td>0.63</td>
<td>6</td>
<td>1.81</td>
<td>0.976</td>
</tr>
<tr>
<td>5</td>
<td>0.23</td>
<td>3</td>
<td>0.345</td>
<td>0.987</td>
</tr>
<tr>
<td>6</td>
<td>0.44</td>
<td>5</td>
<td>1.63</td>
<td>0.952</td>
</tr>
<tr>
<td>7</td>
<td>0.30</td>
<td>5</td>
<td>0.77</td>
<td>0.972</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>6</td>
<td>0.365</td>
<td>0.949</td>
</tr>
</tbody>
</table>
10.8 Numerical Simulation Code: Benzoyl Halide Hydrolysis Kinetics

These codes were used for numerical simulation of benzoyl halide hydrolysis as presented in Section 6.5. These programs run in a Matlab environment and are saved as silentmodel.m and emulsionmodel.m. Although both programs were superceded by analytical solutions, they serve to confirm the analytical results.

```matlab
function silentreaction

% This function solves the full water film silent problem for the hydrolysis of benzoyl halides in C/W systems
% Kcw is the partition coefficient, defined by the ratio of molar concentration in the CO2 phase to the water phase
% a is the surface area in cm2
% Vw is the volume of the water phase in cm3
% Vc is the volume of the CO2 phase in cm3
% Vtot is the total volume (Vw+Vc=Vtot)
% phiC, phiW are the volume fractions of the CO2 and water phases (phiC + phiW = 1, by definition)
% krxnW is the intrinsic rate constant in the water phase in 1/s
% kl is the mass transport coefficient in the water film in cm/s
% D is the diffusion coefficient in cm2/s
% gamma is the Hatta number (= (krxnW*D)^(0.5)/kl)
% time is defined as seconds
% y is the matrix of concentrations, the first entry is the concentration of reactant in the CO2 phase, the second is the concentration of
% reactant in the water phase (bulk concentration) in mol/cm3

clear;
tspan = [0; 1e4];
y0 = [1; 0];

options = odeset('AbsTol',[1e-6 1e-20], 'InitialStep', [1e-5]);
[t,y] = ode45(@(f,tspan,y0, options);

% Ato = 0.7*y(1) + 0.3*y(2);

ACO2 = y(:,1);
AH2O = y(:,2);

% y(:,1)
% figure
% r = 0:.1:1;
% z = [r; exp(r)];
% size(z)
```
%fid = fopen('exp.txt','w');
%fprintf(fid,%6.2f %12.8f
',z);
%fclose(fid)

%fid = fopen('out3.txt','w');
%fprintf(fid,%6.2f %12.8f
',AH2O);
%fclose(fid)
%sizet = size(t)
%sizetACO2 = size(ACO2)
%sizetAH2O = size(AH2O)
tprint = transpose(t);
ACO2print = transpose(ACO2);
AH2Oprint = transpose(AH2O);
%sizetprint = size(tprint)
%sizetACO2print = size(ACO2print)
writefile1 = [tprint; ACO2print];
%sizetwritefile1 = size(writefile1)
writefile2 = [tprint; AH2Oprint];
%sizetwritefile2 = size(writefile2)
%write = [t; ACO2];
%write2 = transpose(write);
fid = fopen('out1.txt','w');
%fprintf(fid,%6.2f %12.8f
',writefile1);
%fclose(fid)

fid = fopen('out2.txt','w');
%fprintf(fid,%6.2f %12.8f
',writefile2);
%fclose(fid)

%plot(t,y(:,1))

%fid = fopen('timko.txt', 'w');
%fprintf(fid)
%fclose(fid);

%function dydt = f(t,y)
Kcw = 150;
D = 1e-5;
k1 = 3e-4;
 a = 20;
Vc = 70;
Vw = 30;
krxnW = 1e-3;
krxnC = 0;
gamma = (kRXnW*D)^.5/kl;
tanh(gamma);
yL = D/kl;
%dydt = 1-exp(-D);
dydt = [(-a/Vc*(y(1)-Kcw*y(2)/cosh(gamma))/(Kcw/kl*tanh(gamma)/gamma)-
   kRXnW*y(2)-a/Vw/gamma/sinh(gamma)*(y(2)*yL*cosh(gamma)+y(1)/Kcw*yL*cosh(-gamma)-
   y(2)*yL-y(1)*yL/Kcw))];

******************************************************************************

function emulsionreaction

% This function solves the problem of hydrolysis reactions in carbon
%dioxide/water emulsions
% It stitches together three terms : 1) diffusion out of carbon dioxide droplets
% into a reactive water phase; 2) diffusion out of a bulk carbon dioxide
% phase into water droplets; 3) the planar film problem that was solved
% previously
% Kcw is the partition coefficient, defined by the ratio of molar concentration in the CO2
% phase to the water phase
% a is the surface area in cm2
% Vw is the volume of the water phase in cm3
% Vc is the volume of the CO2 phase in cm3
% Vtot is the total volume (Vw+Vc=Vtot)
% phiC, phiW are the volume fractions of the CO2 and water phases (phiC + phiW = 1,
% by definition)
% R1 = droplet radius (Sauter average or otherwise)
% R2 = the spherical film, based on diffusion only, Sh = 2 implying that
% R2=2*R1
% kl is the mass transport coefficient in the water film in cm/s
% D is the diffusion coefficient in cm2/s
% gamma is the inverse of the reaction length scale (=kRXnW/D)^.5)
% time is defined as seconds
% y is the matrix of concentrations, the first entry is the concentration of reactant in the
% CO2 phase, the second is the concentration of
% reactant in the water phase (bulk concentration) in mol/cm3

clear;

y0 = [.1; 0];
kset = [
0.001
0.01
0.05
0.1
0.5
1
10
20
100
200
];

iter = 10;

kc = linspace(0,0,iter);

for i = 1:iter
    halflife=1/kc(i)*100;
    tspan = [0; halflife];
    %options = odeset('AbsTol',[1e-9 1e-12], 'InitialStep', [1e-8]);
    [t,y] = ode15s(@(f,tspan,y0, [], k(i));

    Ato = 0.7*y(1) + 0.3*y(2);
    %y(:,1)
    %y(:,2)

    ACO2 = y(:,1);
    lnA = -log(ACO2/0.1);

    %manual least squares regression
    sumt = 0;
    sumlnA = 0;
    sumxy = 0;
    sumsqt = 0;
    sumsqlnA = 0;
    sumsqxy = 0;

    spacer = size(t);
    steps = spacer(1);
    xy = linspace(0:0,steps);
    for j = 1:steps
        xy(j) = lnA(j)*t(j);
    end

    for j = 1:steps
sumt = sumt + t(j);
sumlnA = sumlnA + lnA(j);
sumxy = sumxy + xy(j);
end

sqsumt = (sumt)^2/steps;
%sqsumlnA = (sumlnA)^2/steps;
sqsumxy = (sumt)*(sumlnA)/steps;

for j=1:steps
    sumsqt = sumsqt + (t(j))^2;
    %sumsqlnA = sumsqlnA + (lnA(j))^2;
    sumsqxy = sumsqxy + t(j)*lnA(j);
end

Sxx = sumsqt-sqsumt;
%Syy = sumsqlnA-sqsumlnA;
Sxy = sumsqxy-sqsumxy;
kcalc(i) = Sxy/Sxx;
i
kset(i)
kcalc(i)

end

%plot(t,y(:,1))
%plot(t,lnA)
kcalc;
%---------------------------------------------------------------

function dydt = f(t,y, kset)
%Here I set all of the parameters to their respective values
Kcw = 150;
D = 1e-5;
%Assumptions:
%1) the film model derived for the silent case still applies
%2) the water droplets are always saturated with reactant at its bulk
% concentration
%3) there is no enhancement of transport from carbon dioxide droplets due to reaction
kl = 3e-4;
aC = 70*100;
aW = 30*30;
asil = 20;
Vc = 47;

phiW = 0.1;
Vdrop = 0.1*Vc;
\[ V_w = 40 - V_{\text{drop}}; \]
\[ k_{\text{rxnW}} = k_{\text{set}}; \]
\[ \rho = 3.9; \]
\[ k_{\text{rxnC}} = 10^{(\log 10(k_{\text{rxnW}}) - \rho)}; \]
\[ \%k_{\text{rxnC}} = 0; \]
\[ \%\gamma \text{ does not retain its Hatta number meaning from the silent/planar case, instead it is the inverse of the reaction/diffusion length scale} \]
\[ \gamma = (k_{\text{rxnW}} D)^{.5}/k_l; \]
\[ R_C = 5e-4; \]
\[ R_W = 3e-4; \]
\[ y_L = D/k_l; \]
\[ C_w = 1/18.01; \]
\[ dydt = [(-D/R_C aW/Vc*(y(1)/Kcw-y(2)) - \text{asil}/Vc*(y(1)-Kcw*y(2)/\cosh(\gamma)))/(Kcw/k_l*\tanh(\gamma)/\gamma) - V_{\text{drop}}/Vc*k_{\text{rxnW}}*(y(1)/Kcw-k_{\text{rxnC}}*C_w*y(1)) - (D/R_C aW/V_w*(y(1)/Kcw-y(2)) - \text{asil}/V_w D/y_L/\sinh(\gamma)*y(2)*\cosh(\gamma) - y(1)/Kcw - k_{\text{rxnW}}y(2))]; \]
10.9 Experimental Data: Diels-Alder Conversion and Selectivity

Data reported in Section 7.6.

*Effect of Water Loading:*  
\([MVK]_0 = 1.0 \text{ mol L}^{-1}; 30 \, ^\circ\text{C}; 80 \text{ bar}; 0.6 \text{ W cm}^{-3}; 20 \text{ kHz}; 25\% \text{ duty cycle}; 1 \text{ hr}*

<table>
<thead>
<tr>
<th>Silent Conditions</th>
<th>(\Phi_W)</th>
<th>(\Phi_C)</th>
<th>(X)</th>
<th>(S = N/X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>0.14</td>
<td>0.90</td>
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<td>9.6</td>
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<tr>
<td>0.69</td>
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<td>0.48</td>
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<td>0.11</td>
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<table>
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<tr>
<th>Sonicated Conditions</th>
<th>(\Phi_W)</th>
<th>(\Phi_C)</th>
<th>(X)</th>
<th>(S = N/X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP Geometry (horn inserted in water, pointing up)</td>
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<table>
<thead>
<tr>
<th>Sonicated Conditions</th>
<th>(\Phi_W)</th>
<th>(\Phi_C)</th>
<th>(X)</th>
<th>(S = N/X)</th>
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<tr>
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<td>0.66</td>
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<tr>
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Effect of Initial Concentration of Methyl vinyl ketone:
Φₜₚ = 0.85; 30 °C; 80 bar; 0.6 W cm⁻³; 20 kHz; 25% duty cycle; 1 hr

<table>
<thead>
<tr>
<th>Silent Conditions</th>
<th>[MVK]₀ (mol L⁻¹)</th>
<th>X</th>
<th>S = N/X</th>
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<table>
<thead>
<tr>
<th>Acoustic Conditions</th>
<th>[MVK]₀ (mol L⁻¹)</th>
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<th>S = N/X</th>
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