THE SYNTHESIS, INTERFACIAL ELECTROCHEMISTRY, ORDERING, AND SINTERING OF MONODISPERSE TiO₂ POWDERS

by

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ABSTRACT 

A ceramics processing study was performed which utilized the principles and experimental techniques of the Colloid Chemical and Ceramic Sciences. Colloid chemistry was combined with the ceramics processing paradigm to advance the basic scientific understanding of the processes which occur during the fabrication of ceramic materials. Monodisperse titanium dioxide powders and aqueous-based powder dispersions were employed as the model systems for this research, which included powder synthesis, physical properties, surface electrochemistry, interparticle forces, and sintering. 

Monodisperse, spherical TiO₂ powders were formed by the controlled hydrolysis of dilute ethanolic solutions of titanium tetraethoxide. The final particle size, which depended on the initial reagent concentrations, ranged from 0.3 μm to 0.7 μm. The typical powder had a mean diameter of 0.4 μm and a standard deviation of 0.15; the most uniform powders had a standard deviation of about 0.09. A simple kinetic analysis of the precipitation reaction, which was assumed to occur by a homogeneous nucleation and growth process, was performed; the probable reaction path and the major hydrolysis species were identified. 

The interfacial electrochemistry of the TiO₂ particles was investigated using potentiometric titration (surface charge density) and microelectrophoresis (ζ-potential). The point of zero charge (PZC) and the isoelectric points (IEP) were dependent on the powder washing procedure and dispersion aging. Fresh powders had a PZC of 4.0 and an IEP of 4.3, whereas powders aged in water for 3 months had a PZC of 5.2 and an IEP of 5.5. To complement the electrochemical studies, dispersion stability against coagulation
was determined using photon correlation spectroscopy. Although the coagulation results were consistent with the electrochemical data, the model for primary-minimum Brownian coagulation was found to be insufficient for quantitative comparison. Contributions from secondary-minimum coagulation were significant and thus must be included in the models.

Sediments of the monodisperse particles (standard deviation = 0.086) appeared iridescent when illuminated by "white" light, which indicated that the particles were packed in a regular array. A light diffraction technique was employed to measure the interparticle spacing in the close-packed structures; the measured center-to-center spacings (for 0.39 μm diameter particles) ranged from 0.717 μm at 5 \times 10^{-5} M KCl electrolyte concentration to 0.625 μm at 1.27 \times 10^{-3} M KCl concentration (pH ~ 9). These results were compared to the existing theoretical models for particle ordering; good agreement was observed at low electrolyte concentration, yet considerable divergence occurred at the high electrolyte concentrations. This behavior was qualitatively accounted for by including the effects of size polydispersity on the ordering process.

Dense, uniformly packed TiO₂ compacts, consisting of uniform-size particles (\bar{d} = 0.3 μm), were sintered at temperatures ranging from 1020° to 1160°C. Compacts with two initial packing densities (pore distributions) were studied, one set with an initial density of 55% of theoretical and the second set with an initial density of ~ 69% of theoretical. Densification rates were measured using isothermal and constant heating rate dilatometry and microstructure evolution was characterized by scanning electron microscopy. These compacts sintered rapidly to near-theoretical density with little grain growth; the pores remained at the grain boundaries and no exaggerated grains were observed. The sintering kinetics and final microstructure were found to be critically dependent on the particle packing density and uniformity.

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CHAPTER 1

Introduction

Improved and reliable ceramic materials, critical elements for the development of many high technology systems, currently cannot be reproducibly manufactured.\(^1\) The potential utility of these materials, desired for their thermal, mechanical, chemical, and electrical properties, is tremendous. However, actual use is often limited by inadvertent microstructural heterogeneities (flaws) introduced during processing. As a class of engineering materials, ceramics often fail to reach their potential because of the lack of scientific understanding of the basic processes which occur during the manufacturing steps.\(^1\) In short, macrostructures and microstructures are not controlled during fabrication.

The sintering of powders is the major processing method for producing crystalline ceramics.\(^2\) The microstructures developed during the sintering process are determined to a large extent by the powder characteristics (e.g., particle size, size distribution, shape, state of agglomeration, and chemical composition) and the particle packing in the green microstructure.\(^1,3\) Recent studies have suggested improved stability of the microstructure against exaggerated grain growth, with a narrow-sized, unagglomerated powder\(^4\) and significant reduction of sintering time and temperature with a narrow particle size distribution and with uniform (but not
necessarily the highest) green density. Thus, an approach to processing and microstructural control involves the control of the powder properties and the interparticle forces which influence particle packing.

For this approach, one can state the properties of an ideally sinterable powder to produce a theoretically dense ceramic: a fine size (between 0.1 and 1.0 µm), a narrow size distribution, an equiaxed shape, and a non-agglomerated state. Not only do these uniform powders possess intrinsic processing advantages, such as enhanced dispersion stability, isotropic interaction forces which lead to uniform green microstructures, and controlled sintering behavior, but they also represent ideal systems for basic research and model studies. Analytical models based on ideal particles and particle-packing geometries can be developed and then quantitatively tested using these ideal experimental systems.

The basic goal of this research was to synthesize a model oxide powder/ dispersion system and to investigate the interparticle forces which control aggregate formation and particle packing during powder processing. The interdependence of powder properties (physical and chemical), interfacial electrochemistry, dispersion stability, particle packing in the green ceramic bodies, and sintering behavior allowed for a total study of processing, which was, because of this interdependence, extremely complex. Each topic was investigated independently and then the relationships between each were established.
The very nature of this study required the application of both concepts and experimental techniques from the ceramic and colloid sciences. Ceramic science provided the directives as to the desires and requirements for controlled processing, whereas colloid science provided the means for accomplishing the identified tasks, which were: 1) synthesize a high-purity, uniform-size powder; 2) investigate the oxide/liquid interfacial electrochemistry; 3) understand (quantify) the influence of electrochemistry on the interparticle forces which govern colloidal stability and particle packing; and 4) study the densification process which results from uniform particle packing in green bodies to determine whether it is more controllable and if the rate is enhanced.

Titanium dioxide powders and aqueous based dispersions were chosen as the model system for this study. This choice was based on titania's low solubility, the extensively investigated TiO₂/aqueous interfacial electrochemistry, and the availability of several possible techniques for synthesizing the desired powders. One technique, based on the hydrolysis of titanium alkoxides, yielded adequate quantities of high-purity, monodispersed TiO₂ powders; these powders formed the basis for the subsequent investigations into electrochemistry and particle interactions.

The research reported in this thesis is presented as a series of self-contained chapters, each written in the form of a manuscript. Chapter 2, published in the Journal of the American Ceramic Society (65, C-199 (1982)), serves as an overview for all of
the topics investigated and demonstrates the critical relationship between the colloid and ceramic sciences for controlling and enhancing ceramics processing. The remaining chapters discuss the investigations into each topic in more detail. To make this document more comprehensible, detailed descriptions of several theoretical models and experimental techniques, and discussion of supplemental data are given as Appendices.
CHAPTER 2

Formation, Packing and Sintering of Monodisperse TiO₂ Powders

2.0 Preamble

This chapter, published in the J. Am Ceram. Soc., 65, C-199 (1982), serves the purpose of an overview for the thesis. Although the details are quoted in later chapters, this chapter demonstrates the significance of controlled powder formation and controlled interparticle forces on particle packing in the green body, and on the subsequent sintering behavior.

2.1 Introduction

The microstructures developed during the sintering of ceramic materials are determined to a large extent by the powder characteristics (e.g., particulate size, size distribution, shape, state of agglomeration, and chemical and phasic composition) and the green microstructure. ¹⁻³ Recent studies have suggested improved stability of the microstructure against exaggerated grain growth with a monodisperse powder,⁴ and a significant reduction of sintering time and temperature with a narrow particle size distribution and with a uniform, but not necessarily high, green density.⁵

The properties of an ideally sinterable powder to produce a theoretically-dense, single-phase ceramic are believed to be a fine
size (between 0.1 and 1.0 μm), a narrow size distribution, an equiaxed shape, and a non-agglomerated state. Techniques for synthesizing such powders (e.g., Cr(OH)₃, AlOOH, TiO₂, and SiO₂) through controlled nucleation and growth of particles in dilute solutions have been established by colloid chemists, in particular the work of Matijevic. However, ceramics are generally not produced from powders synthesized with this level of control. For instance, Mazdiyasni, et al., produced high-purity, submicron-sized oxide powders by vapor-phase thermal decomposition of the metal alkoxides. However, these small, pure powders (average size approximately 100 Å) were often agglomerated; thus, although improvements were made using conventional pressing and sintering processes, large and nonuniform grains often resulted. In addition to powder synthesis techniques, colloid chemistry provides the principles for dispersing ceramic powders, for manipulating the particulates, and for flocculating the dispersions into dense, uniformly-packed bodies - a more ideal microstructure for eventual sintering.

This communication describes the synthesis, dispersion, and packing of high-purity, uniform-size, equiaxed TiO₂ powders, and demonstrates that controlled densification occurs, without the use of sintering aids, when a dense, uniformly packed body is sintered.
2.2 Experimental

The TiO₂ powders were prepared by the controlled hydrolysis of dilute alcoholic solutions of titanium tetraisopropoxide, Ti(\(\text{OC}_3\text{H}_7\))₄, or titanium tetraethoxide, Ti(\(\text{OC}_2\text{H}_5\))₄ (Alfa Products). Since homogeneous nucleation of particulates was desired, all liquids were ultrafiltered through 0.22 μm pore-size Millipore filters to minimize the level of insoluble impurities (photometric grade isopropanol, 200 proof ethanol, alkoxides, and deionized water). For a given synthesis experiment, an alkoxide was dissolved in the appropriate alcohol, Ti(\(\text{OC}_3\text{H}_7\))₄ in isopropanol and Ti(\(\text{OC}_2\text{H}_5\))₄ in ethanol. Water was dissolved in a separated portion of the alcohol. The two solutions were mixed using a magnetic stirrer, giving a solution with concentrations of 0.1 to 0.2 M alkoxide and 0.3 to 1.5 M water. The molar ratio of water to alkoxide was always 3 or greater. Precipitation of amorphous, hydrated TiO₂ occurred in 2 to 90 seconds (at room temperature); the time decreased as the concentration of either reagent was increased. The powder was repeatedly washed with deionized water and ultrasonically dispersed in slightly basic aqueous solutions (pH = 9 to 10). Powder compacts, prepared by gravitational or centrifugal settling of the dispersions, were vacuum dried at 160°C and sintered in air at 800°C for the isopropoxide derived powder, TiO₂ I, and at 1050°C for the ethoxide derived powder, TiO₂ II.

Physical properties were measured for both powders.
Assessments of particle shape and state of agglomeration and
qualitative size distributions were obtained from scanning electron micrographs. Specific surface area was determined by a multipoint BET (Quantachrome Corp.) method and density was measured using a stereopycnometer (Quantachrome Corp.) The powders were also studied by transmission electron microscopy and by X-ray diffraction. Semiquantitative impurity analyses for the ethoxide and the TiO$_2$ II powder were obtained by emission spectroscopy. Carbon content for washed and heat-treated TiO$_2$ II powder was measured using an inert gas fusion technique. Finally, the effects of powder dispersion on particle packing density, and subsequently on the sintered microstructure, were assessed by SEM observations and bulk density measurements.

2.3 Results and Discussion

The data and micrographs reported are representative of the results obtained in the preliminary stages of the investigation. Figure 2.1 shows an equiaxed isopropoxide-derived powder, TiO$_2$ I, and a spheroidal ethoxide-derived powder, TiO$_2$ II. The successful synthesis of the uniform-size TiO$_2$ II powder required the simultaneous satisfaction of several conditions. First, proper reagent concentrations are necessary to promote single-nucleation-regime homogeneous nucleation. Second, insoluble impurities must be removed from reagents to prevent heterogeneous nucleation. Third, reagents must be completely mixed prior to particle nucleation, so that nucleation occurs uniformly throughout the solution. Fourth,
Figure 2.1. Transmission electron micrographs of (A) a titanium isopropoxide derived powder, TiO_2 I ([Ti(\text{OC}_3\text{H}_7)_4] = 0.2 M, [H_2O] = 1 M), and (B) a titanium ethoxide derived powder, TiO_2 II ([Ti(\text{OC}_2\text{H}_5)_4] = 0.15 M, [H_2O] = 0.45 M).
although small particles (diameter below 0.1 μm) are susceptible to flocculation upon collision, colloid stability should be maintained during the growth stage of the reaction by employing repulsive steric or electrostatic forces. However, the required reaction conditions can result in low stability (e.g., TiO$_2$ in a neutral solution); thus, rapid growth rates of particles from the nucleus size to about 0.1 μm diameter are required to minimize the residence time of small particles.

Although no nucleation and growth data exists for the alkoxide hydrolysis reaction, the experimental results support the validity of the above guidelines. Using the procedure described in the previous section, dilute ethoxide and water concentrations, and molar ratios of water to ethoxide greater than 3, the more ideal TiO$_2$ II powders were reproducibly synthesized. Conversely, the fourth condition and possibly the first condition listed in the preceding paragraph were not obeyed in the synthesis of TiO$_2$ I powders; the growth rate was too slow and small particles flocculated during the growth stage to form multi-nuclear particles. Hence particle size and other properties were not predictable based on reagent concentrations.

The physical properties, determined primarily for the TiO$_2$ II powders, are given in Table 2.1. Both powders were amorphous in electron and X-ray diffraction. The average particle size of the TiO$_2$ II powders decreased for increased water concentrations and fixed alkoxide concentration, and increased slightly for increased
Table 2.1

Summary of the Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>TiO\textsubscript{2} I</th>
<th>TiO\textsubscript{2} II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkoxide</td>
<td>Ti((\text{OC}_3\text{H}_7)_4)</td>
<td>Ti((\text{OC}_2\text{H}_5)_4)</td>
</tr>
<tr>
<td>Crystal Form</td>
<td>Amorphous</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Average Particle Size Range</td>
<td>0.07-0.3 µm</td>
<td>0.3-0.7 µm</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
<td>3.0-3.2 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>-</td>
<td>~ 15 m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>Shape</td>
<td>Equiaxed</td>
<td>Spheroidal</td>
</tr>
<tr>
<td>Substructure</td>
<td>Multi-nuclei particles</td>
<td>Mostly singlets</td>
</tr>
</tbody>
</table>

Table 2.2

Chemical Properties of TiO\textsubscript{2} II Powder

Semiquantitative: < 10 ppm Al, Ca, Cu, Mg
Analysis < 100 ppm Si

Carbon Analysis: (Wt. %)
- 0.18 .... as synthesized powder
- 0.04 .... 900°C for 4 minutes
- 0.03 .... 900°C for 120 minutes
alkoxide concentrations and fixed water concentration. The size
distribution was very narrow for these powders. As a rule, the size
ratio of the largest particles to the smallest particles was less
than 3, and the ratio of the largest particles to the mean size was
less than 2. The surface area decreased slightly and the density
increased slightly as water concentration was increased for a given
alkoxide concentration; however, uncertainties in these results
prevented the establishment of definitive trends. Calculated
equivalent spherical diameters \(\frac{6}{(\text{surface area} \times \text{density})}\), 3 to 5
times smaller than microscopically observed sizes, indicate that the
particle surfaces are rough and have some open porosity.

Semiquantitative spectroscopic results (Table 2.2) for the
\(\text{Ti(OC}_2\text{H}_5)_4\) and the \(\text{TiO}_2\) II powder show a low cation impurity level.
Carbon analysis indicates that very little residual alcohol and
alkoxy groups remain in the washed powder, and that most of the
organic material is burned out upon heat treatment. DTA and TGA
analyses for water washed powder show a broad endothermic peak at
130 to 160°C, corresponding to evaporation of the water of hydration
(8 to 12 weight percent), and a sharp, intense exothermic peak,
typical of an ignition process, at 390 to 400°C. These data,
combined with visual observations, indicate that the unreacted
alkoxy groups are oxidized at about 400°C. Thus, removal of gases
well below the onset of densification prevented \(\text{CO}_2\) entrapment and
bloating during sintering.
The state of aggregation of the dispersed powder and subsequent powder packing into green bodies, both of which significantly affect the sinterability of the compact, depend on the stability of the powder dispersion. Stability against coagulation for aqueous dispersions of oxide powders requires a low electrolyte concentration (generally less than 0.01 M) and a solution pH several pH units above or below the isoelectric point (IEP) of the oxide. The IEP, the pH at which no net charge exists in the particle/liquid interface region, is between 4.5 and 6.0 for crystalline TiO$_2$ and was assumed to have a similar value for the amorphous powders. Dispersing the TiO$_2$ I and TiO$_2$ II powders in distilled water at a pH above 9 or below 4 always resulted in stable dispersion - the particles remained non-agglomerated.

The adverse effects of improperly chosen dispersion conditions on agglomeration and powder packing is shown in Figure 2.2. In this case, TiO$_2$ II powder was dispersed in deionized water at a pH of 5.7 (slightly acidic due to the absorption of atmospheric CO$_2$), which is near the IEP for the powder. As a result, the particles flocculated during sedimentation and subsequently formed a powder compact with nonuniform distribution of porosity. However, similar powder, when dispersed at a pH of 9.5 (NH$_4$OH solution), remained non-agglomerated. Upon settling the powder from this dispersion a uniformly packed, dense green body was formed, as shown in Figure 2.3. These compacts, with approximate bulk densities of 65 percent of the powder density, have a uniform distribution of pore
Figure 2.2. Scanning electron micrograph of a fracture surface of a compact formed from flocculated TiO$_2$ II Powder ([Ti(OC$_2$H$_5$)$_4$] = 0.2 M, [H$_2$O] = 0.6 M). The compact has a low green density and non-uniform particle packing.
Figure 2.3. Scanning electron micrographs of dense, uniform compacts formed by sedimentation of monodisperse TiO₂. (A) compact fracture surface, (B) compact top and fracture surfaces \([\text{[Ti(OC₃H₅)₄]} = 0.1 \text{ M}, [\text{H₂O}] = 0.3 \text{ M}],[C\text{r}]\) and (C) top surface showing ordered packing \([\text{[Ti(OC₃H₅)₄]} = 0.15 \text{ M}, [\text{H₂O}] = 0.45 \text{ M}]\).
volume and contain few voids larger than one particle diameter in size. The average number of particle-particle contacts appears to be greater than 11. Figure 2.3B, showing the fracture and top surfaces of a compact, indicates that the uniform packing on the top surface continues into the compact. In fact, the spherical particles were often ordered into face-centered cubic arrays (Fig. 2.3C) which exhibited iridescence when illuminated with white light.

The sintered microstructures, shown in Figures 2.4, 2.5 and 2.6, clearly demonstrate the effects of powder packing uniformity on the final microstructure. Attempts to sinter a porous compact consisting of agglomerated TiO$_2$ II powder (Fig. 2.4A) resulted in the low density structure shown in Fig. 2.4B. Conversely, dense, uniform compacts of TiO$_2$ II powders (Fig. 2.5A), sintered to greater than 99% of theoretical density at 1050°C (Fig. 2.5B), a temperature much lower than the 1300-1400°C reported to sinter conventional TiO$_2$ powders to 97% of theoretical density. The average particle size in the green compact was 0.35 µm and the average sintered grain size was approximately 1.2 µm. The large grains (3-5 times larger than the small grains) observed in the microstructures resulted from simultaneous crystallization and densification processes; no attempts were made to avoid the large grains by optimizing the firing schedule.

Dense compacts of TiO$_2$ I powder (Fig. 2.6A) sintered to similar densities at temperatures as low as 800°C (Fig. 2.6B), a reduction
Figure 2.4. Scanning electron micrographs of (A) a porous compact of agglomerated TiO$_2$ II powder ([Ti(OC$_2$H$_5$)$_4$] = 0.15 M, [H$_2$O] = 1 M), and (B) the final microstructure after sintering 90 minutes at 1000°C.
Figure 2.5. Scanning electron micrographs of (A) the top surface of a dense, uniform green compact of TiO$_2$ II powder ([Ti(OC$_2$H$_5$)$_n$] = 0.15 M, [H$_2$O] = 0.45 M), and (B) the microstructure after sintering to > 99% of theoretical density in 90 minutes at 1050°C.
Figure 2.6. Scanning electron micrograph of (A) the fracture surface of a compact consisting of TiO$_2$ I powder ([Ti(OC$_3$H$_7$)$_4$] = 0.2 M, [H$_2$O] = 1 M), and (B) the microstructure after sintering to > 99% of theoretical density in 90 minutes at 800°C.
of 500-600°C in sintering temperature. For this sample, the average particle size was 800 Å and the final grain size was approximately 0.15 μm. In both cases, uniform, fine-grained microstructures were obtained without using sintering aids; thus demonstrating that a uniform particle size provides a measure of stability against exaggerated grain growth. The observed enhanced sinterability was the result of the small particle sizes and the uniform pore distribution in the powder compacts.

2.4 Conclusions

This research, although preliminary, has demonstrated several features about processing TiO₂ powders.

1. High-purity, uniform-size titania powder was synthesized; the average size varied with reagent concentrations.

2. Proper dispersion of the powders resulted in the formation of uniform, dense packing in the green bodies.

3. Sintering of these bodies resulted in > 99% of theoretical density, without the use of sintering aids, at temperatures much lower than those required for conventional TiO₂; uniform, fine-grained microstructures were obtained.
CHAPTER 3

TiO₂ Synthesis and Physical Properties

3.1 Introduction

Titania powders have been widely used in industrial applications as pigments, opacifiers, photocatalysts, and fillers. These powders have been obtained either directly from titanium bearing minerals¹⁸ or by precipitation from solutions of titanium salts or alkoxides.⁹ The most common procedures have been based on the hydrolysis of acidic solutions of Ti(IV) salts; however, many new processes have been investigated and developed.

Gas phase oxidation reactions have been successfully employed in generating finely-divided, high-purity TiO₂ pigments.¹⁹⁻⁻²¹ Anatase and rutile powders, having a mean particle diameter ranging from 100-2000 Å, have been formed using TiCl₄. Similar quality oxide powders have been synthesized by Mazdiyasni and coworkers¹¹⁻⁻¹³,²² using pyrolysis or solution hydrolysis of the metal alkoxides. These alkoxide processes, although of considerable utility in the fabrication of high-quality ceramic components, do not yield powders with the ideal characteristics (i.e., equiaxed, uniform-sized, and non-agglomerated).

Recently, techniques have been reported for synthesizing powders with ideal characteristics through controlled nucleation and growth processes in dilute Ti(IV) solutions. Matijevic and
coworkers\textsuperscript{9} studied the controlled acid hydrolysis of TiCl\textsubscript{4} and formed hydrosols of spherical anatase and rutile particles. Visca and Matijevic\textsuperscript{23} hydrolyzed liquid aerosols to produce uniform, spherical anatase particles from TiCl\textsubscript{4} and monodispersed, amorphous particles from titanium alkoxides. However, in both cases the oxide yields\textsuperscript{9,23,24} were very low, therefore, these techniques were not considered applicable to investigations in ceramics processing.

The TiO\textsubscript{2} powders used in this study were synthesized through the controlled hydrolysis of titanium tetraethoxide; the synthesis procedure, developed by the author, is described in this chapter. The physical properties of the powders and the effects of reagent concentrations and aging on these properties are discussed. Finally, the hydrolysis and condensation reactions are discussed in relation to particle nucleation and growth.

3.2 Experimental

3.2.1 TiO\textsubscript{2} Synthesis

The uniform-size TiO\textsubscript{2} powders were prepared by the controlled hydrolysis of dilute ethanolic solutions of titanium tetraethoxide (Alfa Chemical, Danvers, MA). Since homogeneous nucleation of particles was desired, all liquid reagents (200 proof anhydrous ethanol, ethoxide, and deionized water) were ultrafiltered through

\textsuperscript{†} No quantitative data was reported; however, synthesis experiments performed using the recipe given in Reference 9 yielded < 0.5 g TiO\textsubscript{2}/liter.
0.22 μm pore-size Millipore filters (Type FG, Millipore Corp., Bedford, MA) to minimize the level of insoluble impurities. To prevent water contamination, and thus premature hydrolysis, all work was conducted in a glove box (Labconco Corp., Kansas City, MO) having a dry atmosphere. For a given synthesis experiment, the ethoxide was dissolved in ethanol and water in a separate portion (~ 1/2 of total) of ethanol. The two solutions were rapidly mixed using a magnetic driven stirrer, giving a solution with concentrations of 0.1 to 0.2 M ethoxide and 0.3 to 0.7 M water; the molar ratio of water to ethoxide was always > 2.5. After mixing (2 to 5 seconds), the stirring rate was reduced to a minimal level to prevent coagulation of titania particles during the growth stage of the reaction (discussed further in results section). Precipitation of amorphous hydrated powders occurred in 2 to 90 seconds (T = 298K); the time for observed turbidity, measured with a stop-watch, was the time between solution mixing and the first visual observation of turbidity. Slow stirring was continued for an additional 5 to 10 minutes to attain reagent/product equilibrium.

* Synthesis experiments were primarily conducted in dry air that was recirculated through drierite columns; although not measured, the water content was ~ 100 ppm (column specification). Powders used in the electrochemical studies were prepared under dry nitrogen (from a liquid N₂ source) for which the H₂O concentration was < 10 ppm.
The TiO$_2$ alcosols were transferred out of the glove box and the powders were washed with deionized water by repeated centrifugation (4000 g force) and ultrasonic (probe) dispersion cycles, replacing the supernatent with deionized water prior to each dispersion step; four cycles were usually performed. The powders were then ultrasonically dispersed in the desired aqueous solutions. To prevent agglomerate formation by dissolution/reprecipitation processes, the washing procedure was initiated within 30 minutes of alcosol removal from the glove box. Although, this technique was effective in removing the alcohol and unreacted alkoxide, it generated an undesired result. The initial contact of water with the residual ethoxide on the particle surface caused the formation of a surface coating of very small (50-100 Å) crystalline precipitates. As will be discussed, this coating dominated the interfacial properties of the powder.

Alternate washing techniques using ethanol and various water/ethanol solutions were attempted to avoid the precipitation problem; however, they were generally not effective. Two ethanol washes, followed by vacuum drying, and then water washing prevented precipitate formation. Unfortunately, the powders could not be completely redispersed (without agglomerates), thus they were useful only in the physical properties characterization studies.
3.2.2 Physical Properties

Physical properties were determined for all powders. Powder density was measured using a stereopycnometer (Quantachrome Corporation, Syosset, NY) and helium gas. Specific surface areas were measured by multipoint BET (Quantachrome Corporation), using N₂ gas as the adsorbate and assuming a cross-sectional area of 16.2 Å² per molecule. Powders were vacuum outgassed for > 14 hours at 30°C; this procedure was found by Yates⁵ to be effective in removing physically adsorbed water, but not chemisorbed water. Complete nitrogen adsorption/desorption isotherms were measured for the powders and were analyzed using the αₛ method of Sing.²⁶,²⁷ The experimental procedures and the results are discussed in detail in Appendix B1.

Assessments of particle shape, state of agglomeration, and qualitative size distributions were obtained from scanning electron micrographs. Quantitative distributions were obtained for > 500 particles from TEM micrographs using a histogram method.¹⁰² Particle substructure was investigated by transmission electron microscopy and X-ray diffraction. Semiquantitative impurity and carbon analyses of water washed powder showed a low cation impurity level and low residual carbon content (~ 0.005 mole fraction ethanol). To confirm the purity, quantitative chemical analysis was performed using inductively coupled plasma emission spectroscopy (performed by W. Zamachek, Union Carbide, Tarrytown, N.Y.).
3.3 Results and Discussion

3.3.1 Synthesis and Physical Properties

Figure 3.1 shows an example of a TiO$_2$ powder synthesized using 0.15 M Ti(OC$_2$H$_5$)$_4$ and 0.5 M H$_2$O; the particles are spherical and have a narrow size distribution. The surface coating of fine (5-10 nm) precipitates was the result of the water washing procedure. Figure 3.2 gives the TEM-histogram analyzed size distribution for the powder; the mean diameter was 0.39 μm and the standard deviation was 0.086. Dilute TiO$_2$ sols were sufficiently uniform to exhibit higher-order Tyndall spectra and dispersions of some powders settled to form iridescent ordered arrays (face-centered cubic particle packing), as was shown in Fig. 1.3. These powders are the most uniform titania powders reported in the literature, and the synthesis technique provides a route to form sufficient quantities of material for further investigations. In addition, these powders have a high purity, as shown in Table 3.1.

Synthesis data are given in Table 3.2 for powders formed for a matrix of initial reagent concentrations and T = 25.5 ± 0.2°C. The approximate yields, determined by dry weight analysis (vacuum dried at 80°C), were based on the total possible TiO$_2$ from the ethoxide, assuming 100% conversion. The particle number densities were calculated from the mean size and yield, assuming that only singlets were present. The data show that the mean size decreased as water concentration was increased (for fixed [Ti(OC$_2$H$_5$)$_4$]) and increased
Figure 3.1. TEM micrograph of a powder synthesized using 0.15 M Tl(OC₂H₅)₄ and 0.5 M H₂O; the particles are spherical and have a narrow size distribution.

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>40 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>80 ppm†</td>
</tr>
</tbody>
</table>

Elements not detected: Al, As, B, Ba, Be, Cd, Ce, Cr, Co, Cu, Fe, Ga, Gd, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sb, Sc, Se, Sn, Sr, V, Zn, Zr.

* UCP by W. Zamachek, Union Carbide Corp., Tarrytown, NY.
† Wavelength dispersion analysis on electron microprobe gave 90 ppm Si content.
Figure 3.2. TEM-histogram size distribution for the TiO$_2$ powder shown in Figure 3.1. The mean diameter is 0.39 µm and the geometric standard deviation is 1.09.
Table 3.2

Powder Properties as a Function of Initial Reagent Concentration
(T = 25.5°C)

<table>
<thead>
<tr>
<th>[Ti(O(C₂H₅)₅] (M)</th>
<th>[H₂O] (M)</th>
<th>Mean Size (μm)</th>
<th>% Yield</th>
<th>Number Density (cm⁻³)</th>
<th>Induction Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>0.50</td>
<td>30</td>
<td>1.2 x 10¹⁰</td>
<td>~ 69</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4</td>
<td>0.44</td>
<td>47</td>
<td>2.6 x 10¹⁰</td>
<td>25</td>
</tr>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>0.38</td>
<td>54</td>
<td>4.8 x 10¹⁰</td>
<td>12.5</td>
</tr>
<tr>
<td>0.1</td>
<td>0.6</td>
<td>0.35</td>
<td>72</td>
<td>8.3 x 10¹⁰</td>
<td>7</td>
</tr>
<tr>
<td>0.1</td>
<td>0.7</td>
<td>0.31</td>
<td>74</td>
<td>1.2 x 10¹¹</td>
<td>4.5</td>
</tr>
<tr>
<td>0.15</td>
<td>0.4</td>
<td>0.47</td>
<td>~70</td>
<td>4.5 x 10¹⁰</td>
<td>15</td>
</tr>
<tr>
<td>0.15</td>
<td>0.5</td>
<td>0.43</td>
<td>~78</td>
<td>6.8 x 10¹⁰</td>
<td>7.8</td>
</tr>
<tr>
<td>0.15</td>
<td>0.6</td>
<td>0.38</td>
<td>~83</td>
<td>1.0 x 10¹¹</td>
<td>4.7</td>
</tr>
<tr>
<td>0.15</td>
<td>0.7</td>
<td>0.34</td>
<td>~84</td>
<td>1.5 x 10¹¹</td>
<td>3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.5</td>
<td>0.49</td>
<td>↑</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>0.2</td>
<td>0.6</td>
<td>0.44</td>
<td>&gt;80</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7</td>
<td>0.37</td>
<td>↓</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>
as the ethoxide concentration was increased (for fixed \([H_2O]\)). The yields increased as either reagent concentration was increased.

Although quantitative size distributions were not obtained for the powders given in Table 3.2, SEM observations showed a slight increase in distribution width as the concentration of either reagent was increased. Reaction kinetics (i.e., multiple nucleation) may have contributed to the increased width; however, the increased number of doublets present indicated enhanced coagulation. Particle coagulation was a significant problem for the TiO\(_2\) synthesis under the nominally neutral conditions (near the IEP), especially in early experiments where rapid stirring rates were employed. The number of doublets and triplets present in the final dispersion was high for rapid stirring rates, but decreased significantly as the rate was reduced. For the reaction series presented in Table 3.2, more rapid stirring rates were required for the higher reagent concentrations (short reaction times) to ensure complete mixing. This probably accounts for the increased distribution width. In addition, the increase in particle number density with increasing reagent concentrations (Table 3.2) contributed to the increased coagulation during the growth phase of the reaction. Attempts to enhance stability by adding acids or bases catalyzed the hydrolysis reaction and resulted in the uncontrolled precipitation of wide size distribution powders and/or the formation of gels.
The average measured density for the TiO$_2$ powders was $3.1 \pm 0.1$ g/cm$^3$; no variation in density with reagent concentration and washing procedure was observed within experimental error. This density was considerably lower than the densities for anatase (3.84 g/cm$^3$) and rutile (4.26 g/cm$^3$).$^{29}$

The specific surface area for ethanol washed powders was 8 to 9 m$^2$/g, which is approximately twice the value expected for a 0.4 $\mu$m particle diameter. The adsorption isotherm did not indicate the presence of any porosity, thus the excess area was due to slight surface roughness. The specific surface areas of water-washed powders (powder < 1 week old) ranged from 250 to 320 m$^2$/g. These high values were the result of the surface coating of fine, spherical precipitates. These precipitates are seen on the particles shown in Figure 3.3. The powder, designated TiO$_2$ B in the remaining text, had a BET area of 304 m$^2$/g; the adsorption isotherm and the $\sigma_5$-plot, given in Figs. B5 and B6 (Appendix B.1), revealed the presence of both micropores and mesopores. The specific surface areas of powder aged for several months in the dispersed state (pH = 6) were reduced to less than 200 m$^2$/g. In addition, the surface precipitates coarsened to form a rough, ill-defined surface, as shown in Fig. 3.4. This powder, herein designated TiO$_2$ A, had a BET area of 186 m$^2$/g; the adsorption/desorption isotherm (Appendix B.1) showed hysteresis characteristic of mesopores with radii between 15 and 180 A. The porosities observed for both TiO$_2$ A
Figure 3.3. TEM micrograph of a water-washed powder (fresh), designated TiO₂ B, with a surface coating of fine, crystalline precipitates.

Figure 3.4. TEM micrograph of powder aged 3 months in water (TiO₂ A). The surface precipitates have coarsened to form a rough, ill-defined surface.
and TiO$_2$ B correspond to the capillaries formed by the surface precipitates.

Within the detection limit for the X-ray diffraction analyses of approximately one weight percent crystallized, the powders appeared to be amorphous; however, TEM observations indicated that the surface precipitates were crystalline. The electron diffraction patterns were difficult to index due to the low number of spots comprising the ring pattern. Surface precipitates on TiO$_2$ B (fresh powder) seemed to consist of a mixture of anatase and rutile, whereas the surface coating on TiO$_2$ A (aged 3 months) consisted only of anatase. These surface precipitates and the slow coarsening process significantly altered the electrochemical properties of the powders, as discussed in Chapter 4.

3.3.2 Particle Formation:

Hydrolysis and Condensation Reactions

Table 3.2 also gives the measured time for observed turbidity, $\tau$, as a function of reagent concentrations. For the slowest reactions (i.e. lowest concentrations), the slow increase in observed turbidity caused an appreciable error ($\sim 30\%$) in the measured time for initial turbidity. However, for the faster reactions ($\tau < 30\text{ sec}$) the turbidity increase was very rapid; the solutions went from clear ($\sim 100\%$ transmission) to turbid ($\sim 0\%$ transmission) almost instantaneously. For the calculated number densities and the reaction vessel used (5 cm path length), this
transition occurred as particles grew from less than 20 nm to greater than 100 nm, thus indicating a rapid growth process. As a result, the time required to observe initial turbidity was assumed to be a good indicator of the induction time for particle nucleation. Using these data and evidence from the literature, a possible reaction mechanism can be identified.

The overall precipitation reaction for the TiO$_2$ particles consists of hydrolysis and condensation steps, schematically given as

\[
\text{Hydrolysis: } \text{Ti(OR)}_4 + 4\text{H}_2\text{O} \leftrightarrow \text{ROH} \rightarrow \text{Ti(OH)}_4 + 4\text{ROH} \tag{3.1}
\]

\[
\text{Condensation: } \text{Ti(OH)}_4 \leftrightarrow \text{TiO}_2(\text{s}) + 2\text{H}_2\text{O} \tag{3.2}
\]

where \( R = C_2H_5 \). The hydrolysis reaction has four possible steps:

1) \( \text{Ti(OR)}_4 + \text{H}_2\text{O} \leftrightarrow \text{Ti(OR)}_3(\text{OH}) + \text{ROH} \);

\[
\beta_1 = \frac{[\text{Ti(OR)}_3(\text{OH})][\text{ROH}]}{[\text{Ti(OR)}_4][\text{H}_2\text{O}]} \tag{3.3}
\]

2) \( \text{Ti(OR)}_3(\text{OH}) + \text{H}_2\text{O} \leftrightarrow \text{Ti(OR)}_2(\text{OH})_2 + \text{ROH} \);

\[
\beta_2 = \frac{[\text{Ti(OR)}_2(\text{OH})_2][\text{ROH}]}{[\text{Ti(OR)}_3(\text{OH})][\text{H}_2\text{O}]} \tag{3.3}
\]

3) \( \text{Ti(OR)}_2(\text{OH})_2 + \text{H}_2\text{O} \leftrightarrow \text{Ti(OR)}(\text{OH})_3 + \text{ROH} \);

\[
\beta_3 = \frac{[\text{Ti(OR)}(\text{OH})_3][\text{ROH}]}{[\text{Ti(OR)}_2(\text{OH})_2][\text{H}_2\text{O}]} \tag{3.3}
\]

4) \( \text{Ti(OR)}(\text{OH})_3 + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_4 + \text{ROH} \);

\[
\beta_4 = \frac{[\text{Ti(OH)}_4][\text{ROH}]}{[\text{Ti(OR)}(\text{OH})_3][\text{H}_2\text{O}]} \tag{3.3}
\]
where the $\beta$'s are the stepwise equilibrium constants. The overall equilibrium constant for the hydrolysis reaction through step $j$, $K_j$, is formed as the product of the stepwise constants ($K_j = \prod_{i=1}^{j} \beta_i$).

The condensation reaction is the mode by which the hydrolysis species polymerize to form higher molecular weight products (nuclei and subsequently, particles). Condensation proceeds either through a water elimination reaction,

$$\text{Ti-OH} + \text{HO-Ti} \rightarrow \text{Ti-O-Ti} + \text{H}_2\text{O} \quad (3.4)$$

or an alcohol elimination reaction,

$$\text{Ti-OR} + \text{HO-Ti} \rightarrow \text{Ti-O-Ti} + \text{ROH} \quad (3.5)$$

Although the reaction rate for reaction 3.4 is expected to be faster than that for reaction 3.5, the dominant mechanism depends on the relative rates of the hydrolysis and condensation reactions and the number of hydroxyl groups on the major hydrolysis species.

Winter$^{44}$ and Boyd$^{45}$ studied the hydrolysis behavior of titanium tetrabutoxide as a function of water to butoxide molar ratio. For ratios $< 2.5$ a variety of mixed (oxide-butoxide) polymers were formed, while TiO$_2$ precipitated for ratios $> 3$. Both investigators concluded that the fourth butoxy group was difficult to remove and that water was adsorbed into the polymer in addition to being consumed during hydrolysis. Ishino and Minami$^{46}$ also studied the hydrolysis of Ti(OBu)$_4$ in butanol and concluded that hydrolysis was fast and condensation was the slower step, thus the
overall reaction apparently had an equilibrium state with respect to temperature and initial water concentration. Again, removal of the fourth butoxy group was found to be difficult.

The kinetic interpretations for the results of the previous studies are questionable because of the simultaneous presence of other processes (e.g., evaporation). However, Bradley, et al., found similar hydrolysis behavior for Ti(O\text{C}_2\text{H}_5)_4 in ethanol. For dilute ethoxide solutions and low molar ratios of water (<1.5), trimeric ethoxide units cross linked to form several mixed polymers, but at higher water concentrations the ethoxide behaved more as dimers. Water concentrations > 1.7 molar ratio yielded colloidal precipitates; these precipitates were TiO_2 for ratios > 2.5.

Unfortunately, the investigations were conducted for low water concentrations and in boiling ethanol (78-80°C); thus, the results cannot be extrapolated to the conditions employed in the present study.

The TiO_2 powders synthesized in this study are assumed to form by a homogeneous nucleation and growth process, which is schematically represented in Fig. 3.5 (after Overbeek\textsuperscript{49}). Nucleation occurs when the concentration of the rate limiting hydrolysis species, C, becomes greater than the critical supersaturation concentration, C\textsuperscript{*}; the nuclei which form grow rapidly toward their final size. Since particle nucleation coincides with the initial phase of the condensation reaction, the induction time must reflect the rate at which critical
Figure 3.5. Schematic representation of the homogeneous nucleation and growth process assumed for the alkoxide hydrolysis (precipitation) reaction.
supersaturation is achieved. Hence, the observed induction times can be directly correlated to the hydrolysis reaction, which appears to be the rate limiting process.

Figure 3.6 shows the plot of log \( \tau \) versus log \([H_2O]_{\text{initial}}\) for the three ethoxide concentrations; the average slope is 2.96 ± 0.1. The equivalent plot for log \([\text{Ti}(\text{OC}_2\text{H}_5)_4]_{\text{initial}}\) yields an average slope of 1.23 ± 0.1 (Fig. 3.7). These slopes lead to the following approximate rate equation for the formation of the rate controlling hydrolysis species \((R = \text{C}_2\text{H}_5)\):

\[
\text{Rate} = k[H_2O]^3[\text{Ti}(\text{OR})_4]^1.
\] (3.6)

Although the formation reaction for the rate controlling species consists of several steps (Eq. 3.3), the kinetic equation, Eq. 3.6, represents the accumulation rate of a species having the formula \(\text{Ti}(\text{OR})(\text{OH})_3\), for which the corresponding net hydrolysis reaction is given by

\[
\text{Ti}(\text{OR})_4 + 3H_2O \leftrightarrow \text{Ti}(\text{OR})(\text{OH})_3 + 3\text{ROH},
\] (3.7)

where the equilibrium constant \((K_3 = \prod \beta_i)\)

\[
K_3 = \frac{[\text{Ti}(\text{OR})(\text{OH})_3][\text{ROH}]^3}{[\text{Ti}(\text{OR})_4][H_2O]^3}.
\] (3.8)

The above equations have been written for reactions involving monomeric species, yet the actual species present may exist as dimers or trimers.\(^{47,48}\) Nevertheless, the stoichiometry expressed in Eq. 3.7 would still apply. In addition, condensation was assumed to
Figure 3.6. Delay time for the initial observation of turbidity as a function of initial water concentration for the initial ethoxide concentrations of 0.1 M, 0.15 M, and 0.20 M. The average slope is 2.96 ± 0.1.
Figure 3.7. Delay time for the initial observation of turbidity as a function of initial ethoxide concentration for the initial water concentrations of 0.5 M, 0.6 M and 0.7 M. The average slope is $1.23 \pm 0.1$. 

\[ \text{[H}_2\text{O}] \]

○ 0.5 M
△ 0.6 M
□ 0.7 M

\[ \text{[Ti(OC}_2\text{H}_5)_4\text{]} \]

DELAY TIME FOR TURBIDITY (sec)
be insignificant during hydrolysis; however, the observed reaction order for the ethoxide of 1.23 indicates that some simultaneous condensation may have occurred. The presence of this condensation and its effects on the above analysis cannot be assessed without more extensive kinetic data.

Equation 3.7 implies that the fourth alkoxy group remains in the hydrolysis species, in agreement with previous observations, yet it can be eliminated during the condensation reaction. The reaction describing the condensation (polymerization) of the hydrolysis species to form the hydrated oxide is

$$Ti(OR)(OH)\rightarrow TiO_2 \cdot xH_2O + (1-x)H_2O + ROH \quad (3.9)$$

In this reaction both water elimination and alcohol elimination reactions, given in Eqs. 3.4 and 3.5, occur. The overall reaction, given by the sum of Eqs. 3.7 and 3.9, becomes

$$Ti(OR)_4 + (2+x)H_2O \leftrightarrow TiO_2 \cdot xH_2O + 4ROH \quad (3.10)$$

The value of x for the water of hydration is probably between 0.5 and 1.0, based on the thermal gravimetric analyses which showed a residual water content of approximately 10 to 20 wt.%. Since the TGA weight loss depended on the drying and outgassing history and the technique could not differentiate between surface and internal water, no exact value of x can be assigned. However, the open structure (and bonding) in the amorphous particles allows coordinative bonding of the eliminated water and ethanol to the Ti atoms. The low carbon content of the TiO$_2$ powder, measured to be
approximately 0.18 wt.% (0.005 mole fraction C₂H₅OH), supports the conclusion that the groups on condensing hydrolysis species (Eq. 3.9) were primarily hydroxyl groups. Thus, some water was trapped inside the particles and a value for \( x \) of about 0.5 seems reasonable.

The narrow particle size distributions observed for the spherical TiO₂ powders is the result of a single nucleation regime precipitation process (Fig. 3.5). Upon nucleation, \( C \) drops below \( C^* \), and as long as the growth (condensation) reaction removes the hydrolysis species faster than they are generated, then \( C \) remains less than \( C^* \). Hence, nuclei grow to their final size and no additional nuclei are formed. In addition, the size distribution for nuclei generated in the finite nucleation regime becomes insignificant as the particle size increases toward the final value \( (\bar{d} \sim 0.4 \, \mu m) \). Although no quantitative nucleation studies were conducted, the data and observations appear to be self-consistent. A more detailed study is required to further illuminate the precipitation process.

3.4 Summary and Conclusions

(1) High-purity, uniform-size, spherical titania powders were synthesized; the average particle size decreased as the initial concentration of either reagent was increased. The synthesis procedure gave the most uniform titania powders reported in the literature. In addition, the
reaction and technique were scalable to sufficiently large quantities to allow further investigation.

(2) The particle surface structure was found to be dependent on the washing procedure and dispersion aging in water. Fresh, water-washed powders had an amorphous interior, but were coated with fine (50-100 Å), crystalline precipitates as a result of water washing. The surface areas of these powders ($S_{\text{BET}} \sim 300 \, \text{m}^2/\text{g}$) decreased upon aging to less than 200 $\text{m}^2/\text{g}$. The surface precipitates had an anatase crystal structure.

(3) Particles were assumed to form by a homogeneous nucleation and growth process. A simple kinetic analysis, based on precipitation data, yielded the approximate rate equation ($R = C_2H_5$),

$$\text{Rate} = k[Ti(OR)_4][H_2O]^3.$$  

This equation was assumed to represent the accumulation rate of the rate controlling hydrolysis species for which supersaturation was required for particle nucleation. The corresponding hydrolysis and condensation reactions for this species were:

$$Ti(OR)_4 + 3H_2O \rightarrow Ti(OR)(OH)_3 + 3ROH$$

and

$$Ti(OR)(OH)_3 \rightarrow TiO_2 \cdot xH_2O + (1-x)H_2O + ROH,$$

where $x$ was given as 0.5.
CHAPTER 4

Interfacial Electrochemistry and Dispersion Stability

4.1 Introduction

The interfacial electrochemistry of TiO₂ powders has been extensively discussed in the literature; however, the precise electrochemical properties for a specific powder are determined by the atomic structure (crystal phase and chemical composition) and by the microstructure of the surface. The surface structure of the ethoxide derived powders seems to differ significantly from that of powders formed by other methods. As a result, electrochemical data could not be extracted from the literature, and thus a complete investigation was necessary.

The electrochemical data were critical elements of the data base required to interpret the ordering studies. In addition, to control dispersion stability, which strongly influences particle packing in green compacts and subsequent sinterability, the effects of electrochemistry on interparticle forces must be understood. This chapter addresses the electrochemistry of the ethoxide-derived powder/water interface, which includes measurement of the surface charge density through potentiometric titration and the zeta-potential through microelectrophoresis, and determination of the electrochemical effects on dispersion stability. Supplementary material on the electrical double layer models and the experimental
technique for stability determination are given in Appendices A (Electrolyte Complexation Double-Layer Model) and C (Colloid Stability Determination for Monodisperse Powders Using Photon Correlation Spectroscopy), respectively. Those unfamiliar with these topics should consult the appendices prior to reading the relevant sections.

4.2 Review of the DLVO Theory of Stability

In dispersions of fine particles in a liquid, frequent encounters between particles occur due to Brownian motion, to gravity, and to convection. Whether such encounters result in permanent contact (coagulation) or whether the particles remain free is determined by the forces between them. The basic theory describing these interactions in liquids containing electrolytes is the DLVO treatment (Derjaguin - Landau - Verwey - Overbeek),\(^5\)\(^0\) excellent reviews exist in the literature.\(^5\)\(^1\),\(^5\)\(^2\)

The general equation describing the two-particle interaction energies consists of attractive, \(V_A\), and repulsive, \(V_R\), terms:

\[
V_T = V_A (\text{van der Waals}) + V_R (\text{electrostatic}) + V_R (\text{others}) \quad (4.1)
\]

The van der Waals attraction between two spherical particles of radius \(a\) and center-to-center distance \(r\) is given by\(^5\)\(^3\)

\[
V_A = -\frac{A}{6} \left[ \frac{2a^2}{r^2} + \frac{2a^2}{r^2} - \ln \frac{r^2 - 4a^2}{r^2} \right] , \quad (4.2)
\]

where \(A\), the Hamaker constant, depends on the properties of the
particles and the dispersion medium.

The electrostatic repulsion arising from the interaction of electrical double layers surrounding the dispersed particles is given for small $\phi_d$ and $\kappa a \gg 1$ by

$$V_R = \frac{\varepsilon a \phi_d^2}{2} \ln \left[ 1 + \exp(-\kappa H) \right],$$  \hspace{1cm} (4.3)

where $\varepsilon$ is the medium dielectric constant, $\phi_d$ is the diffuse layer potential, and $H$ is the surface separation distance. The quantity, $1/\kappa$ is the Debye-Huckel length given by

$$1/\kappa = \left[ \frac{\varepsilon k_B T}{4\pi N_a e^2 \sum \frac{n_i z_i^2}{i}} \right]^{1/2}$$  \hspace{1cm} (4.4)

where $e$ is the electron charge, $k_B$ is the Boltzmann constant, $N_a$ is Avagadro's number, and $n_i$ and $z_i$ are the counterion concentration and valence, respectively.\(^{51}\)

The total two-particle interaction energy curve has the general form as shown in Fig. 4.1. When two particles are in very close proximity, a deep potential energy minimum occurs due to the addition of van der Waals attractive energy and a short-range Born repulsive energy for adsorbed water and counterions. This minimum sets the distance of closest approach, $H_o$, to a few angstroms. At intermediate surface separations, the electrostatic repulsion dominates the interaction (given that appropriate ions have adsorbed to the surface) so that a primary maximum occurs; the height and extent of this repulsion is governed by the potential and the
Figure 4.1. General form of the two-particle interaction energy versus surface separation distance curve (after Ottewill\textsuperscript{52}).
electrolyte concentration, through Eqs. 4.3 and 4.4. At larger separations, the exponential decay of the repulsion causes it to decrease more rapidly than the van der Waals energy and a secondary minimum may result (depends on $\phi_d$ and $\kappa$).52

The rate of coagulation of a dispersion depends on the sign and magnitude of the interaction energies. The frequency of Brownian encounters determines the maximum coagulation rate in the absence of repulsive forces. Smoluchowski54 modeled coagulation as a two-particle reaction obeying the following second order rate law

$$\frac{dN}{dt} = -kN^2,$$

(4.5)

where $N$ is the particle number density and $k$ is the coagulation rate constant. The rate constant for rapid Brownian coagulation was given as

$$k = \frac{8k_B T}{3\eta},$$

(4.6)

where $k_B$ is the Boltzmann constant and $\eta$ is the fluid viscosity.

The retardation of coagulation due to repulsive interactions was evaluated in 1934 by Fuchs55 through the introduction of the stability factor, $W$, given as

$$W = \frac{k_r}{k_s} = 2a \int_{a}^{\infty} \exp\left(\frac{V_t}{k_B T}\right) \frac{dr}{r^2}$$

(4.7)

where $k_s$ is the rate constant for slow coagulation. Although this theory is restricted to the formation of doublets from primary particles, stability factors can be experimentally determined; these
data often supplement electrokinetic results in the interpretation of electrochemical phenomena.

4.3 Experimental

4.3.1 Sol Preparation

The powders used for electrophoretic mobility, surface charge, and stability determinations were prepared using reagent concentrations of 0.15 M Ti(OC_2H_5)_4 and 0.45 M H_2O, and were further purified by ion exchange (after van den Hul and Vanderhoff^56). Dispersions of washed powders (~ 300 ml total) were put into cellulose membrane tubing (Spectrapore Membrane, Spectrum Medical Industries, Los Angeles, CA), which had been purified using a procedure supplied by the manufacturer. These membranes were placed in a clean polypropylene bottle containing 4 liters of deionized water and ~ 20 g of a prepurified mixed-bed ion exchange resin (NM-60, Ionac Chemical Co., Birmingham, NJ). This amount of resin represented a large excess of exchange capacity. Van den Hul and Vanderhoff^52 reported that polyelectrolytes could be leached out of impure exchange resins and that adsorption of these species onto particle surfaces would cause errors in electrochemical investigations, thus prior to adding the membranes to the container, conductance measurements were made. These measurements (conductance = 0.06 μmho) indicated no measurable level of polyelectrolytes (H^+ and OH^- only).
After about 4 days exposure to the resin at $T = 6^\circ C$, the dispersions were removed from the membranes and placed in polypropylene bottles. These dispersions served as stocks for subsequent experiments; experimental samples were prepared by diluting small portions of the stock in the desired KCl solutions.

4.3.2 Chemicals

All water used in this study was deionized ($\rho \approx 16 \times 10^6$ ohm-cm) by a Millipore Continental Water System (Bedford, MA). All chemicals were of analytical reagent grade and were used without further purification. Fresh solutions of HCl and KOH (i.e. CO$_2$-free) were used to set the pH in the experiments. Prepurified N$_2$, saturated with water vapor, was employed to degas solutions and provided an inert atmosphere in the titration vessels. These precautions were required because atmospheric CO$_2$ is readily absorbed into water to form carbonate species which cause a shift in the solution pH and an increase in the electrolyte concentration.

4.3.3. Surface Charge

The surface charge as a function of pH and electrolyte concentration was determined by potentiometric titrations with acid and base in the manner first used by Parks and de Bruyn; an excellent review is given by Yates. Titrations were conducted using a Radiometer Series 80 Automatic Titration System (Copenhagen, Denmark); pH was measured with the Radiometer pHM 84 unit and a
Radiometer K701 calomel (double bridge) reference electrode. This electrode was used to prevent incorrect pH measurements due to the suspension effect. The inner bridge contained saturated KCl and the outer bridge was filled with the same type and concentration of electrolyte as used in the titrated suspension.

Samples were prepared by diluting stock suspension in the desired salt solutions; the samples, 33.3 ml volume, contained approximately 20 m² of TiO₂ surface. Suspensions were aged for 24 hours at a pH ≈ 6 to ensure ion adsorption equilibrium, as suggested by Yates. Equilibration near the IEP was required to prevent the surface changes due to slow acid/base interactions with TiO₂ (also observed by others: Bérubé and de Bruyn, and Yates). Prior to titrations, samples were outgassed with saturated N₂ for at least 1 hour to remove absorbed CO₂ and then transferred to the titration unit and further outgassed until the pH stabilized (≤ 5 min).

Titrations were conducted in an inert atmosphere (saturated N₂) using a titration rate of 6 pH units per hour. This titrant addition rate was rapid enough to avoid the slow adsorption process, but slow enough to ensure adsorption equilibrium for the rapid interactions which lead to surface charge development. Manual titrations, using a 5 unit/hour rate (after Yates), gave identical results for comparison samples; thus, the automatic titration technique and a rate of 6 units/hour was assumed to be acceptable for all titrations. Three samples were titrated at each electrolyte
concentration; the data deviated by less than 5% for all pH values. Blank titrations were also carried out on electrolyte solutions having the appropriate concentrations.

The surface charge as a function of pH was determined from the net adsorption densities, $\Gamma_i$ (moles/cm$^2$), using the equation\(^1\)

$$\sigma = F(\Gamma_{H^+} - \Gamma_{OH^-})$$

$$= F\left[ (n^{b}_{H^+} - n^{b}_{OH^-}) - (n^{b}_{H^+} - n^{b}_{OH^-}) \right]/S$$

(4.8)

where $n^{b}_{H^+}$ and $n^{b}_{OH^-}$ are the total number of moles of $H^+$ and $OH^-$ added to the suspension, $n^{b}_{H^+}$ and $n^{b}_{OH^-}$ are the number of moles added to the blank to give the same pH, and $S$ is the available surface area. The surface charge was calculated from the average of the three sample titration curves and the average of the two blank titrations. Equation 4.8 assumes that the adsorption of $CO_2$ is negligible and that $TiO_2$ is insoluble in the electrolyte solution. In the former, $CO_2$ contamination was avoided by flowing nitrogen over the samples. Insignificant $TiO_2$ solubility to affect titrations was confirmed by Yates,\(^25\) and although solubility may be higher for the fine surface precipitates, it was assumed negligible in this study. An excellent review of the titration technique, slow acid/base adsorption, and surface charge studies on $TiO_2$ prior to 1975 is given by Yates.\(^25\)

4.3.4 Electrophoresis

Electrophoretic mobilities (for review see Hunter\(^59\)) were measured with a Rank Brothers Particle Microelectrophoresis
Apparatus Mark II (Cambridge, England), using a cylindrical cell, at 25.0 ± 0.2°C. Five to ten particles were timed in each direction, and a mean value of the mobility was calculated. The average deviation from the mean value of the mobility was approximately ± 0.1 μm sec⁻¹/V cm⁻¹ for mobilities greater than 1 μm sec⁻¹/V cm⁻¹ and as high as ± 0.15 μm sec⁻¹/V cm⁻¹ for lower mobilities.

Samples for specific experiments were prepared by adding a known amount of stock dispersion to test tubes and diluting with degassed electrolyte solutions; greater than 10 hours was allowed for powder equilibration in the KCl and BaCl₂ solutions. The powder concentration used was 6.1 x 10⁻⁵ g TiO₂ per ml dispersion (6.3 x 10⁸ particles/ml for 0.4 μm diameter particles). In the experiments, the dispersion pH was rapidly adjusted and measured; the sample was quickly transferred to the cell and the mobilities were measured. Although solution contact with atmospheric CO₂ was not avoided, contact was minimized by rapid handling.

Electrophoretic mobilities were converted to ζ-potentials using the tables and figures of Wiersema, Loeb, and Overbeek⁶¹ and O'Brien and White;⁶² no difference was noted in the two methods for these data. For 10⁻³ M KCl solutions and particles with a 0.2 μm radius, the error in the ζ-potential corresponding to an error of ± 0.1 μm sec⁻¹/V cm⁻¹ is ± 2 mV for mobilities > 1 μm sec⁻¹/V cm⁻¹. For lower mobilities, an error of 0.15 μm sec⁻¹/V cm⁻¹ corresponds to a 1.5 mV error. These errors become smaller as the electrolyte concentration is increased.
Particle size errors also affect the determined ζ-potential. An underestimation of particle size by a factor of two (i.e., small agglomerates) results in an approximate overestimation in the ζ-potential of 7% for 10^{-3} M KCl. Size underestimation is most probable for higher electrolyte concentrations and a pH near the IEP where coagulation is significant. Under these conditions, k_a is already large, thus size errors cause minimal errors in ζ-potential. Conversely, an overestimated size by a factor of two results in a similar magnitude underestimated ζ-potential; however, this case is not likely for the uniform-size TiO_2 powders. A final source of possible error is the high surface roughness on the particles due to the precipitate coating, which causes an additional hydrodynamic drag factor not considered in the models.

4.3.5 Coagulation

Coagulation rates were determined by measuring the rate of change of the average particle size in dilute dispersions using photon correlation spectroscopy (PCS). A 120-channel Malvern Ltd. K7025 correlator (Malvern, England) was employed to determine the z-average translational diffusion coefficient by measuring the fluctuations in intensity that occur over very short time periods due to Brownian motion of the colloidal particles. PCS has recently been reviewed by Cummings and Pusey;^{63} the data acquisition and analysis techniques are discussed in detail in Appendix C.
The z-average diffusion coefficient, \( D \), is related to the hydrodynamic radius, \( r_h \), by the Stokes-Einstein equation

\[
D = \frac{k_B T}{6\pi \eta r_h}
\]  

(4.9)

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \eta \) is the viscosity. The initial rate constant for slow coagulation, \( k_s \), is calculated from the time rate of change of the average size by

\[
k_s = \frac{1}{r_{h,1} \left( \sqrt{2} - 1 \right) N_0} \left. \frac{dr_h}{dt} \right|_{t = 0}
\]  

(4.10)

where \( r_{h,1} \) is the singlet radius and \( N_0 \) is the initial particle number density; the doublet radius was assumed to be equal to \( \sqrt{2} \cdot r_{h,1} \). Equation 4.10 is valid only for the initial stage of coagulation, where the fraction of doublets present is small. The stability factor, \( W \), was calculated from \( k_s \) using Eqs. 4.6 and 4.7.

A stock dispersion for the coagulation experiments was prepared by diluting the concentrated, deionized stock sol in a solution of 10^{-6} M KOH (pH = 8). The powder was dispersed by ultrasonic agitation and stored in an inert atmosphere. Although this suspension was stable against coagulation, intermittent agitation was required to prevent sedimentation. Particle concentration, determined by dry weight analysis (for 50 ml of the dispersion), was \( 4.0 \times 10^9 \) particles/cm³.
A sample for a specific coagulation experiment was prepared by
diluting (1:20) the stable stock dispersion in the desired
electrolyte solution for which the pH was adjusted immediately prior
to stock addition; the initial particle concentration in the
scattering cell, \( N_0 \), was \( 2 \times 10^8 \) particles/cm\(^3\). The sample was
mixed by inverting and rapidly placed in the scattering chamber.
Data acquisition began within ten seconds of powder addition to the
cell; particle size measurements were obtained at a rate of one
measurement per minute. The pH for the sample was determined by
measuring the pH after completion of the coagulation experiment and
by making an identical sample and quickly measuring the pH; the data
for the sample was discarded if the two measurements deviated by
greater than \( \pm 0.2 \) pH units. Although sample contamination with CO\(_2\)
was not completely avoided, its effects were minimal. This was
confirmed by the non-variance in pH measurements for pH between 7
and 9, where CO\(_2\) absorption would cause measurable shifts.\(^{64}\)

4.4 Results and Discussion

4.4.1 Interfacial Electrochemistry

The surface charge of TiO\(_2\) A as a function of pH is shown in
Fig. 4.2 for KCl concentrations of \( 10^{-1} \) M, \( 10^{-2} \) M, and \( 10^{-3} \) M; the
complementary \( \zeta \)-potential data are shown in Fig. 4.3. The point of
zero charge (PZC) is \( 5.2 \pm 0.1 \) and the isoelectric point (IEP) is
\( 5.5 \pm 0.1 \). The decrease in \( \zeta \)-potential for \( 10^{-3} \) M KCl and pH \( > 8 \)
was due to absorbed CO\(_2\).
Figure 4.2. Surface charge density of TiO$_2$ A as a function of pH for the KCl electrolyte concentrations of $10^{-1}$ M, $10^{-2}$ M, and $10^{-3}$ M.

Figure 4.3. Zeta-potential of TiO$_2$ A as a function of pH for the KCl electrolyte concentrations of $10^{-1}$ M, $10^{-2}$ M, and $10^{-3}$ M.
The magnitudes of the surface charge for TiO$_2$ A are approximately 60% larger than those reported by Yates$^{25}$ and others$^{15,58,65}$ for rutile (PZC = 5.8-5.9), but are very similar to those reported by Bérubé and de Bruyn$^{58}$ for anatase (PZC ~ 5.8), as shown in Fig. 4.4. Tschapek, et al.$^{66}$ also reported lower surface charge for an anatase powder (Degussa P25) but he reported a PZC of 5.3, which is similar to that obtained for TiO$_2$ A. Conversely, the ζ-potentials for TiO$_2$ A are much lower than those reported by Wiese and Healy$^{60}$ (IEP = 5.9) and Tschapek, et al.$^{66}$ (IEP ~ 6.5), however, an IEP of 5.3 was obtained by Visca and Matijevic$^{23}$ for an amorphous TiO$_2$ formed by the hydrolysis of a Ti(O$_2$C$_2$H$_5$)$_4$ aerosol. Many values for the IEP have been reported in the literature for a variety of TiO$_2$ powders.$^{14,15,23,60,66,67}$ Parfitt$^{68}$ and Furlong and Parfitt$^{14}$ concluded that variations in the IEP were often caused by anionic impurities (especially Cl) and that the "best" value for a clean TiO$_2$ was in the range of 4.8 and 5.6. The significant differences in the surface charge and ζ-potential of TiO$_2$ A, which was shown to have a high purity (Table 3.1), and most of the TiO$_2$ powders reported in the literature warrant further analysis.

The surface charge data was analyzed using the complexation model for the electrical double layer developed by James, et al. $^{41,69,79}$; the model and analysis techniques are discussed in detail by James and Parks$^{41}$ and are reviewed in Appendix A. The assumed surface reactions and the intrinsic ionization constants, $K_a^{\text{int}},$ and ionization complexation constants, $K_x^{\text{int}},$ are
Figure 4.4. Surface charge density as a function of $\Delta \text{pH}_{\text{pzc}}$ ($= \text{pH} - \text{pH}_{\text{pzc}}$) for TiO$_2$ A and an anatase powder reported by Bérubé and de Bruyn$^{58}$ (solid line).
given by:

\[
\begin{align*}
\text{TIOH}_2^+ & \leftrightarrow \text{TIOH} + H^+_s \\
K_{a1}^\text{int} &= \frac{[\text{TIOH}][H^+]_s}{[\text{TIOH}_2^+]} \quad (4.11) \\
\text{TIOH} & \leftrightarrow \text{TIO}^- + H^+_s \\
K_{a2}^\text{int} &= \frac{[\text{TIO}^-][H^+]_s}{[\text{TIOH}]} \quad (4.12) \\
\text{TIOH} + K^+_s & \leftrightarrow \text{TIO}^- - K^+ + H^+_s \\
K_{K^+}^\text{int} &= \frac{[\text{TIO}^- - K^+][H^+]_s}{[\text{TIOH}][K^+]_s} \quad (4.13)
\end{align*}
\]

and

\[
\text{TIOH}_2^+ - \text{Cl}^- \leftrightarrow \text{TIOH} + \text{Cl}^- + H^+_s \\
K_{\text{Cl}^-}^\text{int} &= \frac{[\text{TIOH}][\text{Cl}^-][H^+]_s}{[\text{TIOH}_2^+ - \text{Cl}^-]} \quad (4.14)
\]

where the subscript \( s\) denotes surface species. The concentrations of these surface species at a location \( i\) in the double layer, \([A_i]\), are related to the bulk concentrations, \([A]\), by the Boltzmann distribution,

\[
[A_i] = [A] \exp\left(-ze\psi_i/k_BT\right) \quad (4.15)
\]

where \( z\) is the valence, \( e\) is the electron charge, and \( \psi_i\) is the potential at location \( i\). The protons are located at the solid/liquid interface, and hence \( \psi_i\) becomes \( \psi_s\), the surface potential. For the electrolyte ions located in the Helmholtz plane, \( \psi_i\) becomes \( \psi_B\), the Helmholtz potential. This term must be included to adequately describe the electrochemical potential of surface species.
The values of the intrinsic ionization and complexation constants were determined using the double extrapolation technique introduced by James, et al.\textsuperscript{70} (See Appendix A for details.) The ionization constants were obtained by plotting the negative log of the apparent equilibrium constants, $pQ_a$ (where $pQ_a = -\log Q_a$), vs. $\alpha + \sqrt{C}$ for the three KCl concentrations, C, and extrapolating to the conditions of $\alpha = 0$ (i.e., $\sigma_o = \psi_o = 0$) and $C = 0$, where $\alpha$ is the experimental fraction of ionized sites and is defined below. Under these conditions the apparent equilibrium constants, $Q_a$, approximate the intrinsic constants. The constant $Q_{a_1}$, for example, is given by

$$Q_{a_1} = \frac{[\text{TIOH}][H^+]}{[\text{TIOH}_2^+]} = K_{a_1}^\text{int} \exp(e\phi_o/kT). \quad (4.16)$$

The apparent constants were obtained from the experimentally determined surface charge using

$$pQ_a = pH \pm \log \left( \frac{\alpha}{1 - \alpha} \right) \quad (4.17)$$

where $\alpha$ is the net fraction of ionized sites, and

$$\alpha = \sigma_o/eN_s \quad (4.18)$$

where $N_s$ is the number of ionizable protons per unit surface area.\textsuperscript{41} The two terms in Eq. 4.17 were added to get $pQ_{a_1}$ and subtracted to get $pQ_{a_2}$. Figure 4.5 gives $pQ_{a_1}$ and $pQ_{a_2}$ as a function of $\alpha + \sqrt{C}$ for TiO$_2$ A, using $N_s = 13.0$ sites/nm$^2$. This value of $N_s$ was obtained from the chemisorbed water determinations discussed in detail in Appendix B.2. The extrapolated intrinsic ionization
Figure 4.5. Double extrapolation plot for determination of $pK_{\text{int}}$ and $pK_{a_2}^{\text{int}}$ for TiO$_2$ A in aqueous KCl solutions ($N_s = 13.0$ nm$^{-2}$).
constants are $pK_{a1}^{\text{int}} = 2.0$ and $pK_{a2}^{\text{int}} = 8.5$, which are consistent with the observed PZC, where

$$pH_{\text{pzc}} = \frac{pK_{a1}^{\text{int}} + pK_{a2}^{\text{int}}}{2}. \quad (4.19)$$

The intrinsic complexation constants were obtained by plotting $p^{*}Q_{x}$ vs. $\alpha + \log C_{0}$, and extrapolating to the conditions of $\alpha = 0$ and $C = 1$, as shown in Fig. 4.6, where $p^{*}Q_{x}$ is given by

$$p^{*}Q_{x} = pH \pm \log \frac{\alpha}{(1 - \alpha)C_{KCl}}. \quad (4.20)$$

The two terms were added to get $p^{*}Q_{Cl^-}$ and subtracted to get $p^{*}Q_{K^+}$. The extrapolated ionization complexation constants are $pK_{K^+}^{\text{int}} = 6.5$ and $pK_{Cl^-}^{\text{int}} = 4.1$.

The values for the complexation constants are similar to those reported by James and Parks$^{41}$ for the TiO$_2$ surface charge data of Yates$^{25}$ and Bérubé and de Bruyn.$^{58}$ However, the intrinsic ionization constants are significantly lower than the typical values of $pK_{a1}^{\text{int}} = 2.7$ and $pK_{a2}^{\text{int}} = 9.1$ for rutile and $pK_{a1}^{\text{int}} = 3.2$ and $pK_{a2}^{\text{int}} = 8.7$ for anatase.$^{41}$ This difference is due to the higher PZC reported for the cited studies (PZC $\sim 5.9$); the significance of the lower values (PZC and IEP) for TiO$_2$ A is discussed below.

The set of electrochemical equations describing the oxide/aqueous solution interface were solved for unique values of $\sigma_{0}$ and $\psi_{d}$, the diffuse layer potential, corresponding to selected
Figure 4.6. Double extrapolation plot for determination of $p^*_{K^{int}}$ and $p^*_{K^+}$ for TiO$_2$ A in aqueous KCl solutions ($N_s = 13.0$ nm$^{-2}$).
values of pH and KCl concentration once values were chosen for the fixed parameters $N_s$, $K_{a1}^{\text{int}}$, $K_{a2}^{\text{int}}$, $K_{K^+}^{\text{int}}$, $K_{Cl^-}^{\text{int}}$, $C_1$ and $C_2$. This was accomplished, once $C_1$ and $C_2$ were defined, using a modified version$^{41}$ of the generalized chemical equilibrium computer code MINEQL.$^{71}$

The value for $C_1$ used in the calculation was obtained using the technique discussed by Smit and Holten (see Appendix A).$^{72}$ The values of $p^{*}Q_x$ for the higher electrolyte concentrations were plotted as a function of $\pm \alpha$; the slope, $b$, from the linear fit yielded $C_1$ through the relationship

$$C_1 = \frac{e^2 N_s}{2.3 k_B T_b} \tag{4.21}$$

Figure 4.7 gives the plot of $p^{*}Q_{K^+}$ and $p^{*}Q_{Cl^-}$ for TiO$_2$ A. The slopes for $\alpha < 0$, where Cl$^-$ adsorption dominates, are 26.3 (correlation coefficient = 0.989) for 0.01 M KCl and 24.3 (correlation coefficient = 0.998) for 0.1 M KCl; the average slope yielded $C_1 = 132.7$ μF/cm$^2$. The slopes for $\alpha > 0$, where K$^+$ adsorption dominates, are 21.1 (correlation coefficient = 0.995) for 0.01 M and 18.9 (correlation coefficient = 0.998) for 0.1 M KCl; the average slope gave $C_1 = 167.8$ μF/cm$^2$. The outer capacitance, $C_2$, was assumed to be 20 μF/cm$^2$, a valid assumption based on the recent determination of $C_2 = 22.8$ μF/cm$^2$ for anatase by Foissy, et al.$^{73}$, using a radiotracer adsorption technique.
Figure 4.7. The plot of $p^* Q_{Cl^-}$ and $p^* Q_{K^+}$ as a function of the fraction of sites ionized, $\alpha$, for TiO$_2$ A in aqueous KCl solutions ($N_s = 13.0$ nm$^{-2}$). The slopes are related to the inner integral capacitance, $C_1$.72
The results of MINEQL calculations for TiO₂ A, given in Fig. 4.8, show poor agreement with the experimentally determined surface charge and ζ-potential. Similar disagreement was reported by James and Parks for the anatase data measured by Bérubé and de Bruyn. Not only are the calculated values of σ₀ too low and of φ_d too high, but the asymmetry in the curves suggests slight excess Cl⁻ adsorption. This is contrary to the measured behavior; the asymmetry in both σ₀ and the ζ-potential imply excess K⁺ adsorption. The higher calculated inner capacitance for the negatively charged surface, C₁ = 168 μF/cm², as compared to the capacitance for the positively charged surface, C₁ = 133 μF/cm², confirms excess K⁺ adsorption. Finally, the separation in the PZC (5.2) and IEP (5.5) also indicates excess cation adsorption. Although KCl has usually been considered to be an indifferent electrolyte, asymmetry in surface charge and shifts in the PZC and IEP have been observed for potassium salts. Unfortunately, small shifts can also be caused by trace cation impurities (e.g., ~ 200 ppm Si), thus the results and the conclusions for the reported studies may be powder sensitive.

Attempts were made to improve the MINEQL calculations by changing the fixed parameters. The site density employed for the results in Fig. 4.8, N₈ = 13.0/nm², although on the low end of the

† Calculations performed by Dr. R. O. James, Eastman Kodak Co., Research Laboratories, Rochester, NY.
Figure 4.8. The surface charge density (open points) and $\zeta$-potential (solid points) for TiO$_2$ A in $10^{-1}$, $10^{-2}$, and $10^{-3}$ M KCl solutions. Solid lines represent the same properties calculated by MINEQL for the surface ionization and complexation model using the parameters shown in the figure.
measured range of \( N_s = 13.0 \) to 16.1/nm\(^2\), was the average value obtained by Yates\(^{25}\) for anatase. Increasing \( N_s \) to 16 H\(^+\)/nm\(^2\) caused a slight increase in \( \Delta p_{K_a} \), a larger increase in \( \Delta p_{K_x}^* \) (from 3.0 to 3.5), and smaller capacitances (see Appendix A.6); the net result was further disparity between the calculated and experimental \( \sigma_e \). Alternatively, using \( N_s = 13.0/nm^2 \) and a variable integral capacitance (i.e. \( C_1 = 120 \mu F/cm^2 \) at pH = 4 increasing by 10 \( \mu F/cm^2 \) per pH unit to \( C_1 = 180 \mu F/cm^2 \) at pH = 10) slightly improved the fit to the experimental \( \sigma_e \) and gave lower \( \phi_d \) values as compared to the initial results (\( C_1 = 170 \mu F/cm^2 \)) shown in Fig. 4.8, but the fit was still not acceptable. A further arbitrary increase to \( C_1 \sim 230 \mu F/cm^2 \) would be required to give a more reasonable fit to the surface charge, neglecting the asymmetry mismatch. However, the \( \zeta \)-potentials would still be compressed when compared to the calculated \( \phi_d \). Since this compression may be due to errors in the \( \zeta \)-potentials caused by the surface roughness, an independent check is performed in the next section to identify the actual potentials which govern particle interactions.

The inability of the double layer model and MINEQL to adequately reproduce the surface charge and \( \zeta \)-potential for TiO\(_2\) A was also experienced by James and Parks\(^{41}\) for the anatase data reported by Bérubé and de Bruyn.\(^{58}\) There are several possible sources for the apparent model deficiency. The first source is possible errors in the experimentally determined surface area, and
hence surface charge through Eq. 4.8, as a result of micropores that are too small for \( \text{N}_2 \) detection, yet large enough for counterion and proton penetration.\(^{41}\) Davis and Leckie,\(^{40}\) studying an amorphous iron oxyhydroxide, found that the measured specific surface area depended on the technique employed. The BET method gave a surface area 50% lower than that determined by a negative adsorption technique due probably to surface decomposition upon drying the powder; the surface area obtained by negative adsorption yielded a quantitative fit of their data to the double-layer model.\(^{40}\)

Surface decomposition processes are not expected for \( \text{TiO}_2 \) A; however, the enhanced surface charge may result from ion penetration into the amorphous surface and ionization of the internal coordinated water (near the interface). Although a slow pH drift during potentiometric titrations, characteristic of proton penetration,\(^{75}\) was not observed, this possibility should not be ruled out. Similar microporosity and ion penetration would also explain the high \( \sigma_o \) measured by Bérubé and de Bruyn.\(^{58}\) The anatase used in their study was poorly crystallized, as indicated by extensive X-ray line broadening, and had a BET surface area of 125 \( \text{m}^2/\text{g} \).\(^{58}\) In these cases the complexation double-layer model, derived for atomically flat surfaces, cannot be strictly applied.\(^{41}\)

Errors in measured surface area and ion penetration into the surface may contribute to the large \( \sigma_o \) obtained in the present study; however, they cannot contribute to the observed shift in the PZC and the IEP to the lower values. This behavior is attributed to
the different surface characteristics of anatase, and especially the nonideal surface of TiO₂ powders studied. Specifically, the rough surface of TiO₂ A, consisting of a coarsened crystalline coating on an amorphous substrate, has much different bonding characteristics than a smooth crystalline rutile surface.

Herman and Boehm⁷⁶ and Primet, et al.,⁷⁷ concluded that free hydroxyls on a partially dehydrated anatase surface react as a relatively strong acid, while those on rutile show no acidic tendency. This acidity, was attributed to the different bond environments surrounding the Ti atoms at the surface. For anatase, the oxygen atoms surrounding the Ti atom at the surface are closer to the hydroxyl groups than for rutile. These electronegative oxygen atoms are more likely to increase the electron density of the hydroxylic oxygen by polarizing the O-H bond, and hence the hydrogen atom becomes more protonic.⁷⁷ Since the bonding is not as structured for TiO₂ A, the surface hydroxyls may be more polarized by the closer neighboring oxygen atoms, thus the hydroxyl acidity for the poorly crystallized anatase and amorphous surface of TiO₂ A should be as strong and possibly stronger. In addition, although not studied by the previous authors,⁷⁶,⁷⁷ the higher acidity found for surface hydroxyl groups should also apply for the coordinated water molecules. Hence, the shift in the PZC to 5.2, the lower pKᵦ values, and the high surface charge found for TiO₂ A result from the higher acidity of the hydrated surface. Such a dependence of surface acidity (and PZC) on atomic packing was also observed by
Healy, et al. for δ-MnO (PZC = 1.5) and β-MnO (PZC = 7.3); the PZC increased regularly as the atomic packing in the crystal lattice (and at the surface) increased.

The behavior observed for TiO$_2$ A was exaggerated for TiO$_2$ B (fresh powder). Figure 4.9 gives the surface charge of TiO$_2$ B as a function of pH for KCl concentrations of 10$^{-3}$ M, 10$^{-2}$ M, and 10$^{-1}$ M KCl; the data for pH > 7 on the 10$^{-3}$ M KCl curve was omitted because further titrant additions changed the background electrolyte concentration. The corresponding ζ-potentials are shown in Fig. 4.10. The magnitudes of σ*, much higher than those observed for TiO$_2$ A, are similar to the magnitudes obtained for precipitated SiO$_2$. Both sets of data (σ* and ζ-potential) show a high level of asymmetry, indicating considerable excess cation adsorption. The PZC of 4.0 ± 0.1 and IEP of 4.3 ± 0.1 are shifted significantly toward acidic conditions. This was expected for the more disordered surface consisting of a fine precipitate coating on a fresh amorphous substrate.

The double extrapolation technique, using N$_s$ = 12.2 H$^+$/nm$^2$ from isothermal dehydration (Appendix B.2), gave the following intrinsic ionization (Fig. 4.11) and ionization complexation (Fig. 4.12) constants: pK$_{a1}^{\text{int}}$ ≈ 0.8, pK$_{a2}^{\text{int}}$ = 7.1, pK$_{\text{Cl}^-}^{\text{int}}$~ 2.6, and pK$_{K^+}^{\text{int}}$ = 5.6. An estimate of the inner capacitance was obtained from the slope of the pQ$_{K^+}$ vs α plot, shown in Fig. 4.13; two distinct linear regions were observed. The first section, extending to α < 0.3 (pH ~ 7.5),
Figure 4.9. Surface charge density of TiO$_2$ B as a function of pH and KCl electrolyte concentration.

Figure 4.10. ζ-potential of TiO$_2$ B as a function of pH and KCl electrolyte concentration.
Figure 4.11. Double extrapolation plot for determination of $pK_{a_1}^{\text{int}}$ and $pK_{a_2}^{\text{int}}$ for TiO$_2$ B in aqueous KCl solutions ($N_s = 12.2$ nm$^{-2}$).

TiO$_2$ B

$N_s = 12.2$ nm$^{-2}$

$pK_{a_2}^{\text{int}} = 7.1$

$pK_{a_1}^{\text{int}} \sim 0.8$
Figure 4.12. Double extrapolation plot for determination of $p^*_{K_{Cl}}$ and $p^*_{K^{+}}$ for TiO$_2$ B in aqueous KCl solutions ($N_s = 12.2$ nm$^{-2}$).
Figure 4.13. The plot of $p^* Q_{\ell^-}$ and $p^* Q_{K^+}$ as a function of the fraction of sites ionized for TiO$_2$ B in aqueous KCl solutions ($N_s = 12.2$ nm$^{-2}$). The inner integral capacitance, $C_1'$, is obtained from the slope.
gave an average $C_1$ of 603 $\mu$F/cm$^2$ (corr. coef. = 0.998). The second section yielded an average $C_1$ of 225 $\mu$F/cm$^2$ (corr. coef. = 0.999). These data indicate considerable penetration of electrolyte ions, especially $K^+$, into the acidic porous surface region. No attempt was made to perform MINEQL calculations, as modifications must be made to accommodate porous surfaces and more than two intrinsic ionization reactions in the electrical double layer model.

4.4.2 Dispersion Stability

The rates of coagulation of TiO$_2$ A, expressed in terms of the stability ratio, as a function of pH for KCl concentrations of 0.025 M, 0.015 M, and 0.0075 M are given in Fig. 4.14. The coagulation behavior corresponds well with what would be predicted from the $\zeta$-potential data given in Fig. 4.3. Not only are the stability curves centered at the IEP, but the positions of the critical coagulation conditions and the slopes show the qualitative behavior predicted by the asymmetry in the $\zeta$-potential curves. Specifically, for pH $>$ IEP the suppressed $\zeta$-potentials (Fig. 4.3) cause the slopes, which are proportional to $d\log W/dpH$, to decrease and the shift in critical pH to increase as ionic strength is increased. Conversely, the rapidly changing $\zeta$-potentials for pH $<$ IEP result in high and approximately constant slopes and small changes in critical pH with increasing ionic strength.

Effective Hamaker constants, $A_{121}$, were determined for the critical coagulation conditions using the method derived by Reerink
Figure 4.14. Coagulation rates for TiO$_2$ A, expressed in terms of stability ratios, as a function of pH for KCl electrolyte concentrations of 0.025 M (+), 0.015 M (Δ), and 0.0075 M ( ).
and Overbeek. The average $A_{121}$ for the three conditions above the IEP was $1.36 \times 10^{-20}$ joules (standard deviation = $4.5 \times 10^{-22}$ joules) and the average for the three conditions below the IEP was $2.86 \times 10^{-20}$ joules (standard deviation = $2.7 \times 10^{-21}$ joules); the average effective Hamaker constant using KCl to force coagulation was $2.11 \times 10^{-20}$ joules. This value compares well with the average value of $1.83 \times 10^{-20}$ joules obtained from conventional log $W$ vs. log electrolyte concentration data reported in Appendix C (Fig. C.6). These effective Hamaker constants for the amorphous TiO$_2$ are slightly lower than those reported by Visser for crystalline TiO$_2$, which ranged from 2.5 to $5.9 \times 10^{-20}$ joules.

The consistency of the coagulation data given in Fig. 4.14 and the $\zeta$-potentials were investigated using the DLVO theory of stability. Stability factors were calculated for coagulation into the primary minimum for the required particle size and size distribution width using a numerical procedure which employed the Hogg-Healy-Fuerstenau formalism for the interaction energies of two dissimilar spherical particles. Table 4.1 gives the extrapolated $\zeta$-potentials (from Fig. 4.3) and the calculated stability factors for 0.025 M KCl and standard deviations, $\sigma$, of 0, 0.10, and 0.20. Table 4.2 gives similar data for 0.0075 M KCl electrolyte concentration. The stability factors for both electrolyte concentrations decrease as the magnitude of $\zeta$-potential decreases and as $\sigma$ increases; this behavior is similar to that obtained by Cooper.
### Table 4.1

Extrapolated ζ-Potentials and Calculated Stability Ratios for 0.025 M KCl Concentration and Three Width Parameters (σ = 0, 0.10, and 0.20)

<table>
<thead>
<tr>
<th>pH</th>
<th>ζ-Potential mV</th>
<th>Log W σ = 0</th>
<th>Log W σ = 0.10</th>
<th>Log W σ = 0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>35</td>
<td>17.7</td>
<td>14.4</td>
<td>11.6</td>
</tr>
<tr>
<td>4.0</td>
<td>29.5</td>
<td>5.53</td>
<td>4.1</td>
<td>3.53</td>
</tr>
<tr>
<td>4.5</td>
<td>22.8</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>5.0</td>
<td>14.6</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>5.5</td>
<td>0.0</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>6.0</td>
<td>-8.3</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>6.5</td>
<td>-13.8</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>7.0</td>
<td>-17.5</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>7.5</td>
<td>-20.1</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>8.0</td>
<td>-22.1</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>8.5</td>
<td>-23.5</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
</tbody>
</table>

### Table 4.2

Extrapolated ζ-Potentials and Calculated Stability Ratios for 0.0075 M KCl Concentration and Three Width Parameters (σ = 0, 0.10 and 0.20)

<table>
<thead>
<tr>
<th>pH</th>
<th>ζ-Potential mV</th>
<th>Log W σ = 0</th>
<th>Log W σ = 0.10</th>
<th>Log W σ = 0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>40.5</td>
<td>50.7</td>
<td>37.4</td>
<td>26.9</td>
</tr>
<tr>
<td>4.0</td>
<td>35.2</td>
<td>32.4</td>
<td>25.4</td>
<td>19.3</td>
</tr>
<tr>
<td>4.5</td>
<td>28.0</td>
<td>13.5</td>
<td>11.0</td>
<td>9.11</td>
</tr>
<tr>
<td>5.0</td>
<td>17.5</td>
<td>-0.05</td>
<td>-1.15</td>
<td>-1.16</td>
</tr>
<tr>
<td>5.5</td>
<td>0.0</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>6.0</td>
<td>-13.0</td>
<td>-0.057</td>
<td>-1.16</td>
<td>-1.16</td>
</tr>
<tr>
<td>6.5</td>
<td>-18.2</td>
<td>-0.035</td>
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<td>-1.14</td>
</tr>
<tr>
<td>7.0</td>
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<td>2.84</td>
<td>1.62</td>
<td>1.39</td>
</tr>
<tr>
<td>7.5</td>
<td>-24.5</td>
<td>6.69</td>
<td>5.16</td>
<td>4.45</td>
</tr>
</tbody>
</table>
The size width parameter for the TiO₂ powder studied was between \( \sigma = 0.10 \) and 0.20; a value of 0.20 was used for comparison. Fig. 4.15 shows the inclusion of the \( \sigma = 0.20 \) results in Fig. 4.14. The calculated curves show higher stability for pH \(<\) IEP, whereas a much different relationship is observed for pH \(>\) IEP. These relationships are discussed in the following paragraphs.

Figures 4.16 and 4.17 show the two-particle DLVO interaction energies calculated from Eqs. 4.1-4.4 for 0.025 M and 0.0075 M KCl, respectively, using the extrapolated \( \zeta \)-potentials for pH = 3.5 to 5.0 (from Tables 4.1 and 4.2). The primary maxima in these interaction energy curves correspond well with the measured stability factors. For Fig. 4.16 (C = 0.025 M), the \( \zeta \)-potential at pH = 3.5 is large enough to give a high stability, but as pH increases (\( \zeta \)-potential decreases), the primary maximum height is insufficient to prevent coagulation; rapid Brownian coagulation occurs for pH = 5.0 and 5.5, where no barrier to coagulation exists. Similar qualitative agreement is found for the maxima in Fig. 4.17.

The deviation between the measured and the calculated stability factors for pH < IEP (Fig. 4.15) is due to a secondary minimum coagulation contribution to the overall measured stability factor. Although not included in the calculation model, secondary minimum coagulation lowers the overall dispersion stability and is expected to occur when secondary minima in the interaction energies deeper than \( \sim 1 \) kT are present. This is the case for the interaction energies plotted in Figs. 4.16 and 4.17.
Figure 4.15. Comparison of the experimental stability ratios with those calculated for primary coagulation in a dispersion with a finite size distribution ($d = 0.39 \mu m$, $\sigma = 0.20$) for two KCl concentrations: 0.0075 M (---) and 0.025 M (----).
Figure 4.16. The two-particle DLVO interaction energies for 0.025 M KCl electrolyte concentration using the extrapolated ζ-potentials of (a) 35 mV, (b) 29 mV, (c) 22 mV, and (d) 15 mV for the pH values of 3.0, 3.5, 4.0 and 4.5, respectively.
Figure 4.17. The two-particle DLVO interaction energies for 0.0075 M KCl electrolyte concentration using the extrapolated ζ-potentials of (a) 40 mV, (b) 35 mV, (c) 28 mV, and (d) 17 mV for the pH values of 3.0, 3.5, 4.0 and 4.5, respectively.
A similar relation should exist for the measured and calculated stability factors for pH above the IEP; however, this behavior is not present. This observed discrepancy is probably caused by using extrapolated \( \zeta \)-potentials that are too low in the stability calculations. This possibility, which was not ruled out by the results of the MINEQL calculations (§ 4.4.2), was investigated by comparing stability factors calculated using larger \( \zeta \)-potentials.

Tables 4.3 and 4.4 give the stability factors calculated for increased magnitudes of the \( \zeta \)-potential (for \( \text{pH} > \text{IEP} \)) for 0.025 M and 0.0075 M KCl, respectively; the corresponding stability curves for \( \sigma = 0.20 \) are shown in Fig. 4.18. Apparent from these curves, an increase in \( \zeta \)-potential by about 5 to 7 mV (for \( \sigma = 0.20 \)) results in a more symmetric relationship between the calculated and measured factors above and below the IEP. Since the actual standard deviation, \( \sigma \), was less than 0.20, an increase in \( \zeta \)-potential of 5 mV for pH above the IEP seems appropriate. This correction will be applied in Ch. 5 when interaction energies for the concentrated (ordered) dispersions are calculated.

Figure 4.19 gives the stability ratios as a function \( \text{BaCl}_2 \) concentration for the pH values of 7.5, 8.9, and 9.3. The relative positions of these three curves are reversed from the normal order, where the critical coagulation concentration should increase as the pH, and hence \( \zeta \)-potential, are increased. The observed reversal in the order indicates specific adsorption of \( \text{Ba}^{2+} \), which is confirmed by the electrophoretic mobilities and stability ratios given as a
Table 4.3

Stability Ratios Calculated for 0.025 M KCl Concentration and $\sigma = 0.20$ Using Increased $\zeta$-Potentials

| pH | $|\zeta|$ | $|\zeta| + 5\text{mV}$ | $|\zeta| + 10\text{mV}$ |
|----|---------|-----------------|-----------------|
| 5.5| -1.16   | -1.16           | -1.16           |
| 6.0| -1.16   | -1.16           | -1.16           |
| 6.5| -1.16   | -1.16           | -1.16           |
| 7.0| -1.16   | -1.16           | 0.756           |
| 7.5| -1.16   | -1.13           | 4.39            |
| 8.0| -1.16   | 0.234           | 7.30            |
| 8.5| -1.16   | 2.12            | 9.37            |

Table 4.4

Stability Ratios Calculated for 0.0075 M KCl Concentration and $\sigma = 0.20$ Using Increased $\zeta$-Potentials

| pH  | $|\zeta|$ | $|\zeta| + 5\text{mV}$ | $|\zeta| + 10\text{mV}$ |
|-----|----------|-----------------|-----------------|
| 5.5 | -1.16    | -1.16           | -1.16           |
| 6.0 | -1.16    | -1.15           | 2.58            |
| 6.5 | -1.14    | 2.82            | 9.38            |
| 7.0 | 1.39     | 7.74            | 14.7            |
| 7.5 | 4.45     | 11.2            | 18.3            |
Figure 4.18. Comparison of the experimental stability ratios (solid lines) with those calculated for \( \text{BaCl}_2 \) electrolyte concentrations of 0.025 M (---) and 0.0075 M (--) using the extrapolated \( \zeta \)-potentials plus corrections of (a) 5 mV and (b) 10 mV.
Figure 4.19. Coagulation rates for TiO₂ A, expressed in terms of stability ratios, as a function of BaCl₂ electrolyte concentration for solution pH values of 7.5 (+), 8.9 (Δ) and 9.3 (□).
function of pH at several BaCl₂ concentrations in Figs. 4.20 and 4.21, respectively. The mobilities, corresponding very well to the measured stability ratios, show similar adsorption and charge reversal behavior reported by Fuerstenau, et al., for Ba²⁺ and other alkaline earth ions onto rutile.

4.5 Summary and Conclusions

1. The TiO₂/aqueous interface electrochemistry was investigated using KCl electrolyte solutions; surface charge densities and ζ-potentials were determined for both fresh (TiO₂ B) and aged (TiO₂ A) powders. The electrochemical properties, which were controlled by the surface precipitates (formed during washing), indicated enhanced surface acidity relative to crystalline powders. These results are summarized in Table 4.5.

2. The electrolyte complexation double-layer model developed by James and coworkers was applied to the surface charge data for TiO₂ A and TiO₂ B. Acceptable model fit was not obtained, probably because of the rough, porous surface structure of these powders.

3. A new technique was developed for measuring coagulation kinetics for dispersed particulate systems. The technique
Figure 4.20. Electrophoretic mobility of TiO$_2$ A as a function of pH and BaCl$_2$ electrolyte concentration.
Figure 4.21. Coagulation rates for TiO$_2$ A, given as stability ratios, as a function of pH for the BaCl$_2$ electrolyte concentrations of 10$^{-4}$ M (+), 8 x 10$^{-5}$ M (Δ), and 5 x 10$^{-5}$ M (□).
<table>
<thead>
<tr>
<th>Powder</th>
<th>PZC</th>
<th>IEP</th>
<th>Surface Area m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ A</td>
<td>5.2</td>
<td>5.5</td>
<td>186</td>
</tr>
<tr>
<td>TiO₂ B</td>
<td>4.0</td>
<td>4.3</td>
<td>304</td>
</tr>
<tr>
<td>Typical TiO₂</td>
<td>5.9</td>
<td>5.9</td>
<td>~20</td>
</tr>
</tbody>
</table>
employed photon correlation spectroscopy, which is a
dynamic light scattering method for rapid particle size
determination; the technique is discussed in detail in
Appendix C. Coagulation kinetics were measured for
dispersions of TiO₂ A in KCl and BaCl₂ solutions and the
results were analyzed using the method of Reerink and
Overbeek⁸⁵ to yield an effective Hamaker constant of
2.0 \times 10^{-20} J.

(4) Electrophoretic mobility and coagulation rate measurements
indicated that barium ions specifically adsorbed onto the
TiO₂ surface. This strong adsorption phenomenon was
confirmed by the recent electrophoresis data reported by
Fuerstenau, et al.⁸⁷

(5) Dispersion stability was controlled by particle
interactions, which were governed by the electrostatic
potential (ζ-potential or ψ_d) through the DLVO equations.
Thus the stability measurements served as a complementary
technique for testing the consistency of the measured
ζ-potentials. Comparison of the ζ-potentials and the
stability factors for KCl solutions indicated that the
secondary minimum coagulation process
significantly contributed to the coagulation of the 0.4 µm
diameter TiO₂ powders.
CHAPTER 5

Ordering of Monodisperse TiO₂

5.1 Introduction

Controlled particle packing in the green microstructure, as demonstrated in Chapter 2, requires control over the interparticle forces and dispersion stability, not only in dilute dispersions, but especially in concentrated suspensions. The previous chapter addressed the aqueous electrochemistry of the TiO₂ particles and the effects of the electrochemistry on interparticle forces and stability in dilute suspensions. In this chapter, the long-range ordering phenomenon which occurs in dispersions of monodisperse TiO₂ particles is investigated to extend the understanding of the effects of electrochemistry on particle interactions to concentrated dispersions.

5.2 Background

The long-range ordering phenomena in stable, uniform-size colloidal dispersions has been known to exist for several decades.¹²⁰-¹²³ However, it has recently become possible to produce monodisperse suspensions of spherical latex¹²⁴-¹²⁶, silica¹⁰⁶, and titania particles for which an ordered phase is observed when the volume fraction of solids (ϕ) and the electrolyte concentration (Cₑ) are suitably adjusted. The ordered phase is iridescent, due to Bragg diffraction¹²⁴-¹²⁶, when the interparticle spacing is on the
order of the wavelength of visible light, while the equilibrium disordered phase (if present) appears milky white;\textsuperscript{124} such a system is illustrated in Fig. 5.1. Many experimental studies have been performed on the ordered systems and some interesting observations have been made using an inverted metallurgical microscope.\textsuperscript{127,128}

In particular, Okamoto and Hachisu\textsuperscript{128} studied the ordered phase of a monodisperse gold sol with 0.4 μm diameter particles in which they observed single crystal domains extending over several hundred microns. The particles, undergoing small vibrations and rotations, were bound to their respective lattice sites; exchange of lattice positions was rare, even when the interparticle spacing (\(\sim\) 1.0 μm) was large enough to allow vibrations of large amplitudes. In addition, high-angle grain boundaries, edge dislocations, low-angle boundaries, and diffusing vacancies existed for this solid-like structure.\textsuperscript{128}

The ordering of the monodisperse colloids was initially attributed to the secondary minimum in the pair potential energy curve.\textsuperscript{122,123,129} However, from the DLVO theory a decrease in electrolyte concentration will decrease the depth of the secondary minimum. Consequently, if phase separation is caused by particle aggregation into the secondary minimum, then a decrease in electrolyte concentration should result in the dissolution of the ordered phase. The fact that the opposite effect is observed, that is decreasing ionic strength results in increased ordering, indicates that double-layer repulsive forces are responsible for
Figure 5.1. Pictorial representation of the appearance of a latex dispersion in sedimentation equilibrium. The iridescent region has long-range crystal-like order, while the diffusely colored region has a short-range liquid-like structure (after Takano and Hachisu).
ordering. This is further demonstrated in dilute latex systems of about 0.1 μm particles with very low electrolyte concentrations where the particles are separated by several microns. With these conditions, no secondary minimum exists, thus in such dispersions order is obtained through repulsive forces in which the particles attempt to separate as far as possible, but being constrained in a finite solution, are forced to order themselves into either a one-phase or a two-phase system\textsuperscript{130}, depending on φ, C_e and external forces. To qualify this further, the above statements do not imply that the particles in the ordered phase do not reside in a potential minimum. In fact, each particle sits in the local potential well generated by the summation of the repulsive potentials of the surrounding particles; however, in most cases this minimum has no connection to a secondary minimum in the pair potential.

To explain the ordering process, Hachisu, et al.\textsuperscript{124,131-135} and Wadati and Toda\textsuperscript{136} resorted to theories from liquid and solid state physics and what is known as the Kirkwood-Alder transition. Kirkwood\textsuperscript{137}, in his approximate treatment for liquids composed of spherical, nonpolar molecules, concluded that a limiting density (less than 74%) might exist above which a liquid structure is unstable. Alder, et al.,\textsuperscript{138} refining this theory, predicted for a finite hard-sphere system that a transition from a liquid to a solid starts at a volume fraction of about 0.50, the freezing point, and is complete at a volume fraction of about 0.55, the melting point.
Hachisu, et al., tested the theory using nonaqueous and aqueous dispersions of monodisperse latex spheres. Equilibrium melting and freezing volume fractions measured for nonaqueous dispersions, where essentially no electrostatic forces were present, and for high-electrolyte-concentration, surfactant-stabilized aqueous dispersions qualitatively agreed with the Kirkwood-Alder predictions for hard spheres.

To test the theory for systems characterized by long-range electrostatic interactions, Hachisu, et al., measured the volume fraction of the ordered phase at various electrolyte concentrations and generated the $\phi$ versus $C_e$ phase diagram shown in Fig. 5.2. Dispersions with high $\phi$ and low $C_e$ formed an ordered, single-phase system (upper left on diagram), while those with low $\phi$ and high $C_e$ formed a disordered system (lower right). Intermediate conditions yielded a two-phase region in which the volume fractions in the coexisting phases for a specific $C_e$ were given by the intersection of a verticle line at that concentration with the "solidus" and "liquidus".

The measured volume fractions for the monodisperse latex have been qualitatively tested against theoretical predictions for several simple models for electrostatic interactions, most of which are based on the hard-sphere transition model. Brenner modified the hard-sphere transition model to take into account the double layer interactions. The latex particles were treated as hard spheres with an effective diameter (Fig. 5.3) given
Figure 5.2. Spectroscopically determined phase diagram for latex: 
(●) ordered phase; (○) melting point; (▲) visually determined 
melting and freezing lines (Takano and Hachisu133).
Figure 5.3. Effective particle diameter for the hard-sphere model, given by the sum of the actual diameter ($2a$) and the interparticle spacing ($H$) at which the interaction energy is on the order of thermal energy.
by the sum of the actual diameter and the interparticle spacing, \( H \), at which the interaction energy was on the order of thermal energy (i.e. \( 1-2 \ k_B T \)). The ionic strength dependence of the interaction energy, calculated using the electrostatic equation obtained by Bell, et al.,\(^{145}\) yielded an effective diameter that decreased with increasing salt concentration. However, quantitative comparison between calculations and Hachisu's melting curve was not possible due to uncertainty in the surface potential of the latex particles used to calculate interaction energies.\(^ {140}\)

Barnes, et al.\(^ {143}\) analyzed Hachisu's data\(^ {124}\) and found that the effective diameter was directly related to the double-layer length, \( 1/\kappa \), by

\[
d_{\text{eff}} = 2a + \lambda / \kappa
\]  

(5.1)

where \( \lambda \) was given as 3.8 for the 850 Å radius latex particles. The interaction energies corresponding to Eq. 5.1 (i.e. \( \kappa H = 3.8 \)) are 3-4 \( k_B T \) for high salt concentrations (\( \sim 10^{-3} \) M) and about 10 \( k_B T \) for low concentrations (\( \sim 10^{-5} \) M). They also gave an empirical expression relating \( \lambda \) to particle size:\(^ {143}\)

\[
\lambda = 3.8 + 2 \ln(a/0.085)
\]  

(5.2)

However, this equation can only be used for systems that have the same surface (or diffuse layer) potential.

Similar results were obtained by van Megen and Snook\(^ {141,142}\) using the hard-sphere transition model and the DLVO equations (Eqs. 4.1-4.4) for 0.6 μm radius particles. The range for strict
applicability of the model and a \( k_B T \) interaction energy criterion for the effective size was for conditions where \( \kappa a \gg 1 \).\(^{142}\) For \( \kappa a \ll 1 \) (very low salt concentrations), the repulsion was much softer, i.e. lower \( \partial V_T / \partial H \), and the effective particle size was defined by an interaction energy of approximately \( 11 k_B T \).\(^{141}\) In addition, for the condition of \( \kappa a \gg 1 \) the effective diameter was related to the double layer length (Eq. 5.1) by \( \lambda \sim 7 \);\(^{141}\) the value predicted by Eq. 5.2 for 0.6 \( \mu m \) radius latex particles is \( \lambda = 7.6 \). Hence, van Megen and Snook's calculated transition conditions agree well with the experimental\(^{124}\) melting curve.

Agreement between the hard-sphere model and measured transition conditions was also reported by Furusawa and Yamashita.\(^{139}\) Equilibrium "melting" volume fractions were given for several latex particle systems which varied in particle size and surface charge density (and \( \zeta \)-potential). The effective particle diameters defined by the measured transition conditions corresponded to an interaction energy (using DLVO equations) of \( 1.5 k_B T \), which is in accordance with the value calculated by van Megen and Snook.\(^{142}\)

The hard-sphere model is based on simple pair-interaction energies (DLVO); however, Marcelja, et al.\(^{144}\) argued that for long-range electrostatic forces, especially at low electrolyte concentrations, many-body effects are important. To account for these interactions a Wigner-Seitz cell model\(^{146}\) was employed, where the interactions with the surrounding particles confined each
particle to a cell. The Poisson-Boltzmann equation was solved in the cell for the appropriate boundary conditions to determine the approximate increase in energy for displacements of the particle from its equilibrium position. The melting points for given volume fraction solids were obtained by applying the Lindemann melting rule; \(^{147}\) their results also showed good agreement with the experimental melting conditions. \(^{124}\)

The calculated results of Brenner \(^{140}\) and Marcelja, et al. \(^{144}\) are shown in Fig. 5.4 along with the experimental melting curves for 0.17 \(\mu\)m diameter latex particles reported by Hachisu, et al. \(^{124}\) and Furusawa and Yamashita. \(^{139}\) Although Brenner \(^{140}\) attempted to fit Hachisu's data, the potential(\(\psi\)) used to calculate the two curves for interaction energies of 1 and 100 \(k_B T\) (shown in Fig. 5.4) was close to that given by Furusawa and Yamashita for their latex. As seen in Fig. 5.4, Brenner's 1 \(k_B T\) curve agrees with the experimental melting curve, which, as discussed previously, was described by an interaction energy of 1.5 \(k_B T\). \(^{139}\)

Barnes, et al. \(^{143}\) van Megen and Snook \(^{141}\) (not shown in Fig. 5.4), and Marcelja \(^{144}\) qualitatively reproduced the experimental \(^{124}\) melting curve; no significant differences were noted for these simple models. Therefore the effective hard-sphere model for the Kirkwood-Adler transition, \(^{138}\) which appears to be qualitatively applicable to dispersions of spherical, monodisperse particles, is used in this thesis.

To further quantify the ordering process, a more general
Figure 5.4. Comparison of the calculated results for the ordering models with the experimental melting curves for 0.17 μm diameter latex spheres. The parameter $\gamma$ is the interaction energy (kT units) used to define the effective diameter.
approach was taken by Snook and van Megen\textsuperscript{148-153} in applying statistical mechanical methods to an assemblage of particles characterized by the DLVO pair interaction energy (Eqs. 4.1-4.4). The equilibrium properties of dispersions were calculated using the Monte Carlo method to evaluate configurational averages for the particle ensemble. The equilibrium osmotic pressures and radial distribution functions, calculated as a function of electrolyte concentration for various volume fractions, indicated that a transition from a disordered structure to an ordered structure occurred as the volume fraction solids was increased. In addition, a reduction in the electrolyte concentration lowered the volume fraction at which the transition occurred and increased the equilibrium particle separation.\textsuperscript{148-150} The results were in accord with the experimental observations\textsuperscript{131-135,139} and the predictions of the hard-sphere model.

The Monte Carlo calculations, although in principle as exact as the assumed interparticle potential, requires a very large number of computer calculations to identify the phase transition conditions and the coexistence region. In order to expedite the computations while sacrificing little accuracy, Snook and van Megen\textsuperscript{151,152} applied a cell model first introduced by Lennard-Jones and Devonshire to the ordered phase. Osmotic pressures and free energies calculated as a function of volume fraction for various electrolyte concentrations\textsuperscript{151} and for various particle sizes\textsuperscript{152} were almost identical to those given by the Monte Carlo method. Further,
since at the phase transition the pressure and free energy for the
two phases are equal, these two quantities calculated for the
ordered and disordered regions were compared to precisely locate the
coexistence region. Figure 5.5 gives the calculated osmotic
pressures as a function of volume fraction for several electrolyte
cent rations; the Monte Carlo results are also shown for
comparison.\textsuperscript{151}

The equilibrium volume fractions of the coexisting disordered
($\phi_f$) and ordered ($\phi_m$) phase\textsuperscript{151} appear in Table 5.1. As shown in
Table 5.1, these values compare very well with those predicted by
the Kirkwood-Alder theory when the effective particle size is set by
an interaction energy of $1.3 \, k_B T$, except at the lowest electrolyte
concentrations. Under these conditions, strict application of the
hard-sphere model is questionable.\textsuperscript{142} For this comparison, the
effective volume fraction was calculated from

$$\phi_{\text{eff}} = \phi (d_{\text{eff}} / 2a)^3$$

(5.3)

where $\phi$ is the actual volume fractions solids.

The calculated transition conditions and osmotic pressures have
been qualitatively confirmed by the experimental results for
monodisperse latex reported by several investigators;\textsuperscript{134,135,154-157}
however, for the purpose of this thesis the details of these
investigations are not necessary.

Thus far only monodisperse colloidal systems have been
discussed; however, polydispersity (i.e., a size distribution) has
Figure 5.5. The calculated reduced osmotic pressure as a function of volume fraction for the KCl electrolyte concentrations: (a) $10^{-3}$M; (b) $10^{-4}$; and (c) $10^{-5}$ (after van Megen and Snook$^{151}$).
Table 5.1

Volume Fraction Solids Predicted for the Disordered and Ordered Phases at the Phase Transition

<table>
<thead>
<tr>
<th>$c$ (mole/m³)</th>
<th>$\Delta\phi_{MC}$</th>
<th>$\phi_f$</th>
<th>$\phi_m$</th>
<th>$\phi_{eff}$</th>
<th>$\phi_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>.05-.15</td>
<td>.11</td>
<td>.12</td>
<td>.45</td>
<td>.50</td>
</tr>
<tr>
<td>0.05</td>
<td>.15-.25</td>
<td>.23</td>
<td>.25</td>
<td>.47</td>
<td>.52</td>
</tr>
<tr>
<td>0.1</td>
<td>.25-.35</td>
<td>.29</td>
<td>.32</td>
<td>.49</td>
<td>.54</td>
</tr>
<tr>
<td>0.5</td>
<td>.35-.5</td>
<td>.39</td>
<td>.43</td>
<td>.50</td>
<td>.55</td>
</tr>
<tr>
<td>1.0</td>
<td>.35-.5</td>
<td>.43</td>
<td>.47</td>
<td>.50</td>
<td>.54</td>
</tr>
</tbody>
</table>

(1) $\Delta\phi_{MC}$, the region of the phase transition estimated by the MC method.

(2) The volume fractions for coexisting disordered ($\phi_f$) and ordered ($\phi_m$) phases as calculated by the combination of the perturbation and cell models, and

(3) Volume fractions corrected for the effective particle size for $V(2r_{eff}) = 1.3 \ k_BT$. 
an appreciable effect on the osmotic pressure of concentrated systems. Dickinson\textsuperscript{158} found that under conditions where repulsive forces dominate, the effect of polydispersity is always to increase the pressure and free energy of an ordered phase and to disrupt the long-range order. For disordered dispersions the overall influence is always toward the disruption of short-range order and a reduction of the pressure. For the ordered phase, Fig. 5.6 shows that for a thin double-layer (high electrolyte concentration) the relative change in pressure with respect to a monodisperse sol, $\Delta P/P$, is sensitive to the degree of polydispersity, whereas the converse is true for thick double-layers. This is due to the fact that for $\kappa a > 1$, the repulsion is soft and the double-layers are deformable, thus the structure and the pressure are relatively insensitive to particle size variations.\textsuperscript{158}

To complete this discussion of the models describing the coexistence conditions and the behavior of the disordered and ordered phases, one final point must be considered. The assumption of pairwise additivity of the interaction potential, which considerably simplifies the theory, may be questionable, particularly in moderately concentrated dispersions in which the double-layers overlap. However, many properties, such as the occurrence of a disorder to order transition, are not critically dependent on the inclusion of many-particle potentials nor on the precise details of the pair potential.\textsuperscript{159} This statement is substantiated by the overall agreement between experiments and
Figure 5.6. The effect of size polydispersity on an electrostatically stabilized dispersion. The increase in osmotic pressure relative to a monodispersed system, $\Delta P/P$, is plotted against the degree of polydispersity, $\delta$: (a) $\kappa a = 5$; (b) $\kappa a = 10$; (c) $\kappa a = 25$, and (d) $\kappa a = 50$ (after Dickinson\textsuperscript{158}).
statistical mechanics calculations, based on pair potentials, for 134,135,154,160 both molecular systems and colloidal systems.

Further, since the pressure is very sensitive to the precise form of 159 the interaction potential, "The reasonable agreement between the calculated and measured osmotic pressures in concentrated dispersions illustrates that the effect of three or more particle potentials is not large under the conditions studied so far, and that the pair potentials formulated in the DLVO theory should certainly be adequate for determination of the structure." 153

5.3 Experimental

5.3.1 Technique and Apparatus

The interparticle spacings in the ordered TiO$_2$ dispersions were measured using a light analogue to an X-ray diffractometer. The apparatus, shown in Fig. 5.7, was based on the diffraction system described by Hiltner and Krieger. 126 The dispersion was illuminated with a 5 mW HeNe laser, having a 0.8 mm beam diameter (Coherent 80-2H, Palo Alto, CA), and the reflected intensity was measured by a photoconductor detector (PIN 5D, United Detector Technology, Culver City, CA); these elements were mounted on supports that were connected to a gear system which maintained an identical angle for the source and the detector relative to the cell.

The cell, schematically shown in Fig. 5.8a, was constructed of Delrin. A solid glass half-cylinder (Pyrex) was used as the cell
Figure 5.7. Schematic of the light diffractometer.
Figure 5.8. (a) Schematic of the diffraction cell, and (b) schematic showing the beam path through the window and the dispersion/window interface region.
window to prevent beam refraction prior to striking the
glass/suspension interface. The laser light entered the cell along
radii of the semi-cylindrical window, refracted at the
glass/suspension interface, reflected from the particle array, and
exited the suspension with one final refraction at the interface
(Fig. 5.8b). This configuration, having a minimum number of beam
refractions, considerably simplified the analysis.

The Bragg conditions for an ordered suspension were obtained by
moving the source (and detector) and recording the angles of maximum
reflected intensity. The maxima were converted to interparticle
 spacings, D, using the modified Bragg equation,\textsuperscript{122,126}

\[
D^2 = \frac{3/8 m^2 \lambda_o^2}{n_s^2 - n_g^2 \cos^2 \theta},
\]

(5.4)

where \( m \) is the diffraction order, \( \lambda_o \) is the incident radiation
wavelength (632.8 nm for the HeNe laser), \( n_s \) is the refractive index
of the ordered dispersion, \( n_g \) is the refractive index of the cell
window (1.474 for Pyrex® at 632.8 nm\textsuperscript{161}), and \( \theta \) is the measured
diffraction angle. This equation was derived for a close-packed
lattice, which was the observed structure for all reported
\textsuperscript{106,122,124-128,131-134} cases, except for latex dispersions at a
volume fraction of less than 0.01 for which a bcc structure was
confirmed.\textsuperscript{162}

The accuracy of the calculated interparticle D-spacings is
strongly dependent on the accuracy of the value used for the
dispersion refractive index, \( n_s \). In previous studies, \(^{122, 126, 163} n_s \) was obtained from the dependence of the Bragg diffraction angle on the incident wavelength; a monochromator was used as the light source. However, a more intense, fixed wavelength source was used in this study, thus an alternate technique was employed. This technique utilized the condition for total internal reflection of the incident beam at the glass/dispersion interface, which occurred for suspensions having a refractive index less than that of Pyrex\(^\circledR\).

The critical condition for total internal reflection, written for the geometry shown in Fig. 5.8, was satisfied for

\[
n_s = n_g \sin(90 - \theta_c),
\]

(5.5)

where \( \theta_c \) was the critical angle.\(^{164} \) For incident angles greater than \( \theta_c \) the laser beam penetrated the glass/dispersion interface and diffuse multiple scattering caused the dispersion to glow (bright appearance). Conversely, for angles less than \( \theta_c \) the incident beam was totally reflected at the interface, thus no light penetrated into the cell (dark appearance).

Experimentally, the critical angle was obtained by observing the transition from a bright cell condition (beam penetration) to a dark condition (total reflection) as the incident angle was decreased. The accuracy in the measured critical angles was \( \pm 0.5 \) degrees, hence the accuracy in the D-spacings, through Eqs. 5.4 and 5.5, was \( \pm 60 \) \( \text{Å} \). The validity of this technique was confirmed by measuring the critical angle for the glass/clear-supernatant (H\(_2\)O)
interface; the measured $\theta_c$ was 24.5°, which yields $n_s = 1.34$ using Eq. 5.5. This value compares very well to the actual refractive index of pure water of 1.331 at 25°C.165

5.3.2 Procedure

The TiO$_2$ powder used for the ordering experiments was synthesized using the initial reagent concentrations of 0.15 M Ti(OC$_2$H$_5$)$_4$ and 0.5 M H$_2$O. A TEM micrograph of the particles was shown in Fig. 3.1 and the TEM-histogram analyzed size distribution was given in Fig. 3.2; the distribution is also shown in Fig. 5.9 in the form of a cumulative plot on probability paper. Once formed, the powder was washed with water and further purified using the procedure outlined in § 4.3.1 and stored in a CO$_2$-free environment.

Solutions of KCl, KOH, and HCl were prepared using analytical grade reagents and deionized water. These solutions (except HCl) were outgassed with presaturated N$_2$ to remove absorbed CO$_2$; the solutions were stored in a CO$_2$-free environment (desiccator filled with ascarite-II). Solution pH was measured using a Corning 125 pH meter (Corning, NY) and a Fisher Microprobe combination Electrode (Fisher Scientific, Pittsburg, PA). Sample preparation for the diffraction cell was conducted in a glove bag under an inert atmosphere (N$_2$).

The procedure given in the remaining portion of this section was used to prepare the diffraction samples. The cell volume as a function of position (height) in the cell was calibrated at every
Figure 5.9. Cumulative plot of the TEM-histogram analyzed size distribution.
0.5 ± 0.03 ml using a pipeteman (Rainin Instruments, Woburn, MA); the total cell volume was 7.0 ± 0.1 ml. The cell was filled, using a pipette, with the powder dispersion extracted from the ordered (top) portion of the purified powder sediment. The cell was sealed and the particles were allowed to settle below the 3.5 ml mark (i.e. 1/2 of the cell volume). The clear supernatant at the top was removed until the meniscus was at the 3.5 ml mark, and then 3.5 ml of a 10⁻⁴ M KCl solution was added to the cell. In addition, two drops of 10⁻² M KOH solution (pH = 12) was added to the cell contents to raise the pH above 7.0, which enhanced the repulsive interparticle interactions. The cell was resealed and the particles were allowed to settle to a stable equilibrium condition.

Once sedimentation equilibrium was achieved (took ~ 5 days), as indicated by no change in sediment volume over a 24 hour period, the diffraction measurements were conducted. The first order (θ₁) and second order (θ₂) diffraction peaks and θ_c were recorded for several positions in the sediment. In addition, sediment volume and supernatent pH, measured after the diffraction experiment, were recorded.

The electrolyte concentration and pH were readjusted for the next experiment by carefully extracting 3.5 ml of supernatent from the cell and replacing it with 3.5 ml of 2 x 10⁻⁴ M KCl solution and the required KOH. Careful addition of the salt solution resulted in almost no resuspension of the sediment, thus equilibration time was reduced to two days. Diffraction data, sediment volume, and
supernatent pH were obtained as previously described. The readjustment and measurement procedures were repeated for 10^{-3} M and 2 \times 10^{-3} M KCl solutions. The experimental conditions used in these four sets of measurements are given in Table 5.2; the potentials listed were extrapolated from the measured \( \zeta \) -potentials (Fig. 4.3) and the salt concentrations include the salt already in the cell plus the added salt.

5.4 Experimental Results

An example of a typical intensity scan (detector output voltage versus \( \theta \)) for the ordered TiO_2 is given in Fig. 5.10. Also shown for comparison is a typical scan from an ordered dispersion of monodisperse SiO_2, which was synthesized using the method reported by Stober, et al.\(^{10}\) The peaks for the TiO_2 dispersion are much broader and less intense than those for the SiO_2 dispersion.

The observed peak broadening and intensity reduction are directly related to diffuse scattering and beam attenuation.\(^{126,166}\) Diffraction peaks for SiO_2 and latex systems are intense and sharp because the low relative refractive index \( (n_{\text{particle}}/n_{\text{water}} < 1.2) \) allows light to penetrate deep into the ordered array, which thus results in reinforcement of the diffraction peaks.\(^{166}\) However, the TiO_2 particles have a higher relative index \( (n_p/n_{H_2O} > 1.5) \). This causes enhanced diffuse scattering and beam attenuation so that fewer particle layers contribute to the diffraction peaks, thereby increasing the background scattering, decreasing the peak intensity,
Table 5.2
Electrolyte Conditions for the Ordering Experiments

<table>
<thead>
<tr>
<th>Concentration (KCl)</th>
<th>pH</th>
<th>$\kappa$</th>
<th>$\kappa a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-5}$ M</td>
<td>9.0</td>
<td>23.3</td>
<td>4.6</td>
</tr>
<tr>
<td>$1.25 \times 10^{-4}$</td>
<td>9.0</td>
<td>36.8</td>
<td>7.2</td>
</tr>
<tr>
<td>$5.5 \times 10^{-4}$</td>
<td>8.4</td>
<td>77.2</td>
<td>15.1</td>
</tr>
<tr>
<td>$1.27 \times 10^{-3}$</td>
<td>9.2</td>
<td>116.5</td>
<td>22.7</td>
</tr>
</tbody>
</table>
Figure 5.10. Typical scan of scattered intensity (detector output voltage) versus scattering angle for the ordered TiO$_2$ and an ordered SiO$_2$ showing the first ($\theta_1$) and the second ($\theta_2$) order diffraction peaks and the critical angles for total internal reflection ($\theta_c$).
and increasing the peak width. In addition, packing imperfections, which were significant at high salt concentrations (discussed later), contribute to these processes.\textsuperscript{126}

The iridescence and diffraction peaks observed for the ordered TiO$_2$, as well as for the other systems, can be attributed to the diffraction of light from hexagonally ordered layers of particles that are stacked parallel to the window surface.\textsuperscript{106,122,163} Yet, Tomita, et al,\textsuperscript{167} showed that many diffraction phenomena can be generated by the two-dimensional grating formed by the close-packed layer of particles adjacent to the glass/displacement interface. Although they concluded that a three-dimensional array is not required for most diffraction phenomena, the "darkening effect" (i.e. a decrease in the intensity of diffusely scattered light) results from satisfaction of the Bragg condition for regularly separated parallel planes of particles in a three-dimensional structure.\textsuperscript{167} This darkening effect was observed for the ordered TiO$_2$ when illuminated at the Bragg angle, hence the measured spacings represent the three-dimensional packing of the particles.

Figure 5.11 gives the volume fraction TiO$_2$ as a function of the distance from the top of the ordered sediment, h, for the four experimental conditions listed in Table 5.2; the volume fractions were calculated from the measured Bragg angles using Eq. 5.4 and the following relation:

\[ \phi = 0.74 \left( \frac{2a}{D} \right)^3 , \quad (5.6) \]
Figure 5.11. Volume fraction TiO$_2$, calculated from the measured Bragg diffraction angle, as a function of the distance from the top of the ordered sediment, $h$, for the four experimental conditions given in the figure.
where close-packing and no vacancies were assumed ($\phi_{\text{max}} = 0.74$). The data given in Fig. 5.11 corresponds to the osmotic pressure for the electrostatic interactions as a function of volume fraction in the ordered sediment, where the osmotic pressure at any level in the sediment is equal to the sedimentation pressure exerted by the particles suspended above that level. The behavior of these data is examined later, but first the equilibrium order/disorder transition conditions are discussed.

The particle volume fraction in the ordered phase in equilibrium with the disordered phase, which existed as a thin region (~ 0.2 mm thick) at the top of the ordered sediment, was obtained from Fig. 5.11 by extrapolating to the zero height condition ($h \to 0$). As shown in Table 5.3, the equilibrium volume fractions at the melting point ranged from 0.119 ± 0.005 at $5 \times 10^{-5}$ M KCl to 0.179 at $1.27 \times 10^{-3}$ M KCl, which correspond to surface separations (D-2a) of 0.327 ± 0.006 μm and 0.235 μm, respectively. For these surface separations, van der Waals forces are negligible; therefore, particle packing should be controlled by the repulsive electrostatic interactions. As a result, the hard-sphere transition model discussed in § 5.2 is applicable to the TiO$_2$ system.

Although the accuracy in the measurements was given in the previous paragraph, the consistency of the data and the validity of the technique employed to prepare the diffraction sample should be examined before comparing the results to model predictions. The
Table 5.3

Equilibrium D-Spacings and Volume Fractions for the Ordered Phase at the Transition

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>Potential (mV)</th>
<th>D-Spacing (μm)</th>
<th>( \phi_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x 10^{-5} M</td>
<td>54</td>
<td>0.717</td>
<td>0.119</td>
</tr>
<tr>
<td>1.25 x 10^{-4}</td>
<td>49</td>
<td>0.651</td>
<td>0.160</td>
</tr>
<tr>
<td>5.5 x 10^{-4}</td>
<td>42</td>
<td>0.639</td>
<td>0.168</td>
</tr>
<tr>
<td>1.27 x 10^{-3}</td>
<td>38</td>
<td>0.625</td>
<td>0.179</td>
</tr>
</tbody>
</table>

Table 5.4

Consistency Check of the TiO_2 Ordering Data

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>Average ( \phi )</th>
<th>Sediment Volume, V mL</th>
<th>Powder Volume ( \phi \cdot V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x 10^{-5} M</td>
<td>0.139</td>
<td>2.15</td>
<td>0.2989</td>
</tr>
<tr>
<td>1 x 10^{-4}</td>
<td>0.177</td>
<td>1.75</td>
<td>0.3092</td>
</tr>
<tr>
<td>5 x 10^{-4}</td>
<td>0.191</td>
<td>1.60</td>
<td>0.3064</td>
</tr>
<tr>
<td>1 x 10^{-3}</td>
<td>0.200</td>
<td>1.50</td>
<td>0.3000</td>
</tr>
</tbody>
</table>

Actual powder weight = 0.863 g; density = 3.1 g/cm³
Powder volume = 0.2784 cm³
consistency of the data given in Fig. 5.11 and Table 5.3 was checked using the recorded sediment volumes and the weight of powder in the cell, which was determined at the end of the experiments. Table 5.4 shows the average volume fraction of the ordered sediment ($\bar{\phi}$), the sediment volume ($V$), and the calculated powder volume given by the product $\bar{\phi} \cdot V$. These results indicate that the measured data are self-consistent, whereas the average value for the powder volume ($\bar{\phi} V$) deviated from the actual powder volume by about 8%. This small deviation, which may be caused by errors in the actual powder density (± 5%) and in the weight determination, seems insignificant in view of the data self-consistency.

The validity of the sample preparation technique, discussed in § 5.3.2, was confirmed by conducting an independent experiment using an alternate preparation technique. In the previous method salt solutions were added to the cell without disturbing the sediment; this was done to minimize the required equilibration time. In the alternate technique, 3.5 ml of deionized dispersion, 3.5 ml of $10^{-3}$ M KCl, and 2 drops of $10^{-2}$ M KOH were added to the cell. The powder, which was well dispersed in the electrolyte solution, was allowed to settle to an equilibrium volume (7 days) and then the sediment volume and the diffraction data were measured. This procedure was repeated using the $2 \times 10^{-3}$ KCl solution. The results for these two experiments were within 2% of those given in Table 5.3; thus, the data and the measurement technique are acceptable.
5.5 Discussion

The predicted equilibrium volume fractions for the ordered TiO$_2$ at the transition were calculated using the hard-sphere model developed by van Megen and Snook. This model, discussed previously (§ 5.2) in relation to monodisperse latex, employed the Barker-Henderson criterion for the effective particle diameter and the data given in Table 5.2 to determine the melting volume fractions, $\phi_m$, given in Table 5.5.* Calculations were also performed using twice the electrostatic potential; the effect was to decrease the calculated $\phi_m$ by $\sim 0.03$. Also included in Table 5.5 are the transition points obtained by calculating the effective particle diameters for an interaction energy of $1.0 \, k_B T$ using the DLVO equations (Eqs. 4.1-4.4) and comparing to the Alder transition using Eq. 5.3, where $\phi_{\text{eff}} = 0.55$. This energy criterion for the effective diameter results in agreement with the hard-sphere model and is in accord with those obtained for the latex systems. As an additional note, the relative insensitivity of the transition volume fraction to a large change in potential and the agreement obtained using the extrapolated $\zeta$-potentials with a $1 \, k_B T$ energy criterion for the effective size indicate that the 5 mV correction for the

* The calculations were performed by Dr. Ian Snook, Royal Melbourne Institute of Technology, Melbourne, Australia.
Table 5.5

Hard-Sphere Transition Model Results for the TiO₂ System (d = 0.39 μm and A = 2 x 10⁻²⁰ J)

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>Potential</th>
<th>$\phi_m(\phi)$*</th>
<th>$\phi_m(2\phi)$*</th>
<th>$\phi_m(\psi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-5}$ M</td>
<td>54</td>
<td>0.098</td>
<td>0.076</td>
<td>0.010</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>49</td>
<td>0.153</td>
<td>0.125</td>
<td>0.157</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>42</td>
<td>0.304</td>
<td>0.264</td>
<td>0.310</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>38</td>
<td>0.370</td>
<td>0.335</td>
<td>0.370</td>
</tr>
</tbody>
</table>

* Calculated for data in Table 5.2 by I. Snook, Royal Melbourne Institute of Technology, Melbourne, Australia.

Figure 5.12. The DLVO pair-interaction energy curves for the experimental conditions: (a) $5 \times 10^{-5}$ M KCl; (b) $1.25 \times 10^{-4}$ M KCl; (c) $5.5 \times 10^{-4}$ M KCl; and (d) $1.27 \times 10^{-3}$ M KCl.
ζ-potential discussed in § 4.4.2 is insignificant and need not be considered.

The DLVO pair-interaction curves for the four experimental cases (Table 5.2) are shown in Fig. 5.12. For the lower electrolyte concentrations, where repulsion dominates the particle interactions, the hard-sphere model is valid; however, at the highest electrolyte concentration a 0.7 k_B T secondary minimum exists. This minimum causes a slight error in the calculated transition volume fraction (\(\phi_m\) too high by \(\sim 0.002\)), but this error will not affect the basic conclusions.

The calculated melting curve (Table 5.5) based on the hard-sphere transition model, and the experimental results for the ordered TiO_2 (Table 5.3) are compared in Fig. 5.13. The model and the data are in accord for the two lower salt concentrations, yet considerable deviation occurs at 5.5 x 10^{-4} M and 1.27 x 10^{-3} M KCl. Since the data were shown to be consistent, the deviation must result from a deficiency in the modelling. Specifically, the hard-sphere model employed \(^{141,142}\) is valid only for monodisperse systems and not for systems that have a finite size distribution width, such as the TiO_2 powder (\(\bar{d} = 0.39 \mu m, \sigma = 0.09\)). Thus, one probable source for the deviation is size polydispersity, and although no transition models incorporating polydispersity exist, the model developed by Dickinson\(^{158}\) for polydispersity effects on osmotic pressure is useful for a qualitative description.

The effect of polydispersity is to increase the osmotic
Figure 5.13. The experimentally determined volume fractions at the melting transition (from Table 5.3) and the calculated melting curve based on the hard-sphere transition model (from Table 5.5).
pressure in the ordered phase relative to a monodisperse system (Fig. 5.6). The width parameter, $\delta$, used in the Dickinson model has a value of about 0.13 for the TiO$_2$ powder. Although the model does not extend to this level of polydispersity, extrapolation to $\delta = 0.13$ for the $\kappa a$ values given in Table 5.2 yield relative pressures, $\Delta P/P$, of 12 for $1.27 \times 10^{-3}$ M and 3.5 for $5.5 \times 10^{-4}$ M KCl; the relative pressure is about zero for the lower salt concentrations. The effect of the increased pressure is to cause an "expansion" of the sediment to a larger volume (lower $\phi$) than predicted for the monodisperse system and a disruption of long-range order. Hence, an increasing salt concentration (and relative pressure) should cause further deviation in the behavior of the polydisperse system relative to the monodisperse system. This increasing deviation is seen in Fig. 5.13, yet the actual shift in $\phi_m$ due to polydispersity is not known. In addition, visual observation of the cell contents indicated that the amount of sediment that appeared iridescent decreased considerably for $10^{-3}$ M KCl as compared to the lower KCl concentrations. Thus, the polydispersity model qualitatively explains the experimental observations; however, further modelling is required for quantitative analysis.

* The $\delta$ parameter was defined for a box distribution, where $\delta = |a - \bar{a}|/\bar{a}$. The value was obtained for $|a - \bar{a}| = 0.05 \mu m$ and $\bar{a} = 0.195 \mu m$. 
Returning to Fig. 5.11, the effect of sediment height (pressure) on the measured volume fractions is now discussed. However, since all available models are based on monodisperse particles and/or confine the ordered sediment to a fixed volume (applicable for latex particles), direct model application to this data is not warranted. Nevertheless, the results are compared to the predictions based on statistical mechanics calculations for spherical molecules.

The osmotic pressure developed at a given position in the sediment, \( h \), depends on the amount of powder suspended above that position. Hence, the pressure can be obtained using the following expression:

\[
P(h) = \Delta \rho \cdot g \int_{0}^{h} \phi(h')dh'
\]  

(5.7)

where \( \Delta \rho \) is the relative density for the powder in the solvent \( (\Delta \rho = 3.1 - 1.0 = 2.1 \text{ g/cm}^3) \), and \( g \) is the acceleration due to gravity; the relation \( \phi(h') \) was obtained by fitting a line through the data in Fig. 5.11. The osmotic pressure obtained for the four experimental conditions are shown in Fig. 5.14. As expected, the pressures developed for a given sediment height increases with increasing electrolyte concentration due to the increase in volume fractions, and thus an increase in the amount of powder above that position.

The osmotic pressure and reduced pressure for the ordered phase at the order-disorder transition boundary can be determined from
Figure 5.14. Osmotic (sedimentation) pressure as a function of the distance from the top of the ordered sediment for the four experimental conditions.
Fig. 5.14. The osmotic pressure, $P_m$, was extracted from the curves for the observed thickness of the disordered sediment, which was above the ordered region (thickness $\sim 0.2$ mm). The reduced pressure, $P_m/V/k_B T$, was calculated for $P_m$ using the equation given by Takano and Hachisu:

$$P_m V/nk_B T = P_m \cdot \frac{2a}{(\pi \phi_m k_B T/6)}, \quad (5.8)$$

where $\phi_m$ was taken from Table 5.3. The results of these calculations are summarized in Table 5.6. These reduced pressures are much larger than the value (11.6) predicted by Alder, et al. for the transition of hard spheres; however, the increasing reduced pressure with decreasing electrolyte concentration is in qualitative accordance with the computed results for soft-core systems by Hoover, et al. Since the calculated relative transition pressures are strongly dependent on the actual thickness of the disordered region, which were not accurately measured (need $\pm 0.05$ mm accuracy for the thin regions), no further discussion is warranted.

A second set of representations of the pressure data is obtained by plotting osmotic pressure and reduced relative pressure (using Eq. 5.8) as a function of volume fraction, as shown in Fig. 5.15 and 5.16, respectively. The reduced pressure plot is the presentation form used when the equations of state derived for various models are plotted (eg. see Fig. 5.5). No attempt is made to analyze the data in detail; however, the curves for
Table 5.6
Approximate Reduced Pressures for the Ordered Phase at the Melting Transition

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>$\phi_m$</th>
<th>$P_m^\ast$ (dyne/cm²)</th>
<th>$P_mV/\hbar k_B T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-5}$ M</td>
<td>.12</td>
<td>$\sim 8.6$</td>
<td>90</td>
</tr>
<tr>
<td>$1.25 \times 10^{-4}$</td>
<td>.16</td>
<td>$\sim 8.2$</td>
<td>115</td>
</tr>
<tr>
<td>$5.5 \times 10^{-4}$</td>
<td>.168</td>
<td>$\sim 7.0$</td>
<td>140</td>
</tr>
<tr>
<td>$1.27 \times 10^{-3}$</td>
<td>.179</td>
<td>$\sim 5.8$</td>
<td>197</td>
</tr>
</tbody>
</table>

* Sedimentation pressure at melting point was extracted from Fig. 5.13, pressure vs. sediment height.
Figure 5.15. Osmotic pressure as a function of volume fraction solids for the four experimental conditions.
Figure 5.16. Reduced osmotic pressure, $P_{m}V/Nk_{B}T$, as a function of volume fraction solids for the four experimental conditions.
5 x 10^{-5} \text{ M} \text{ and } 1.25 \times 10^{-4} \text{ M KCl}, \text{ for which polydispersity effects were minimal, show the proper qualitative behavior based on the DLVO curves shown in Fig. 5.12. That is, pressure is proportional to the volume derivative of energy (dV_T/dv), and for a given change in particle separation (or } \phi \text{) the energy changes more rapidly for the } 10^{-4} \text{ M curve. Thus, the pressure increases more rapidly for } 10^{-4} \text{ M KCL than for } 5 \times 10^{-5} \text{ M, in agreement with the behavior in Fig. 5.15. For the higher salt concentrations, polydispersity effects complicate the behavior; quantitative analysis requires an extension of the current models.}

To complete this chapter, one final, and yet interesting observation should be discussed. Upon completion of the initial set of ordering experiments (Table 5.2), about 4 ml of supernatent was extracted from the diffraction cell and about 3 to 4 ml of 1 M (NH_4)_2CO_3 was carefully added; this salt was added to compress the double-layer and collapse the ordered dispersion into a compact (for use in the sintering experiments). The observed effect was that the sediment volume decreased only a small percentage over a 16 hour period, or equivalently the volume fraction solids increased from 0.20 to about 0.25. At this point the sediment appeared rigid. The supernatent was extracted and air drying was initiated. After 2 hours all visible water had evaporated (no additional volume change); a wet cake remained which had sufficient strength that handling was possible. The cake was dried overnight at 60^\circ \text{C}, followed by 3 hours at 100^\circ \text{C under vacuum. Considerable shrinkage
was observed upon water removal, yet the cake retained its shape; the dry compact relative density (i.e. $\phi$) was approximately 0.65 to 0.70. In addition, SEM observations of the dried compact (see Fig. 6.23) showed uniform and dense particle packing.

The phenomenon described above is not explainable based on DLVO theory and any related models. One possible explanation for such a constant volume in the sediment is that the particles coagulated to form a rigid, open (porous) structure. However, a coagulated structure would not collapse to the high level of green density ($\rho_{\text{rel}} > 0.65$) and packing uniformity observed for the TiO$_2$ compact. Alternatively, the stable structure of the sediment may be due to structured water at the particle surfaces. Such an explanation is used to describe the stable separation of clay particles in compressed clay bodies $^{169,170}$, yet the maximum water film thickness determined for a system of kaolin particles was 0.034 $\mu$m. $^{170}$ This spacing is much smaller than the approximate 0.20 $\mu$m spacing of the TiO$_2$ particles in the sediment (and wet cake), thus ordered water is not the source of this structure. An additional possibility is that counterions in the overlapping double-layers become distributed in such a manner that "pockets" of high counter-charge concentration form in interstitial regions between particles, hence creating some type of "ionic" array. Although the origin of this observed phenomenon is not known, it may occur for other oxide powders; therefore, its presence and effects on processing should be investigated.
5.6 Summary and Conclusions

(1) Monodisperse, spherical TiO$_2$ particles (\( \bar{d} = 0.39 \mu m \), \( \sigma = 0.09 \)), when dispersed under controlled electrolyte conditions, settled to form iridescent, ordered arrays. This iridescence, caused by Bragg diffraction of visible light, is the second reported occurrence for metal oxide particles; ordered SiO$_2$ had been reported previously.$^{106}$

(2) Equilibrium particle spacings were measured as a function of salt concentration and sedimentation pressure; the spacings ranged from 0.717 \( \mu m \) at 5 \( \times \) \( 10^{-5} \) M KCl to 0.588 \( \mu m \) at 1.27 \( \times \) \( 10^{-3} \) M KCl. Good agreement between the hard-sphere theory$^{141,142}$ and the measured spacings at low electrolyte concentrations was obtained when the \( \zeta \)-potentials were used to calculate the interaction energies through the DLVO equations. Thus, the DLVO pair-interaction theory$^{50}$ adequately describes the ordered systems under these conditions, in agreement with Snook and van Megen.$^{148-153}$

(3) The equilibrium melting volume fractions for the ordered TiO$_2$ deviated considerably from the predicted values at the higher salt concentrations (5.5 \( \times \) \( 10^{-4} \) M and 1.27 \( \times \) \( 10^{-3} \) M KCl). This behavior was qualitatively
explained by the effects of size polydispersity as modelled by Dickinson.\textsuperscript{158}

(4) The sedimentation pressures calculated from the volume fraction versus sediment height data (Fig. 5.11) showed the proper volume fraction dependence only at the low electrolyte concentrations. In addition, the calculated reduced transition pressures were in accordance with computations for a soft-core system given by Hoover, et al.\textsuperscript{169}

(5) Quantitative modelling of the equations of state in concentrated suspensions requires inclusion of the effects of size (and shape) polydispersity. At present, no such model exists and until the models are developed, predictive control over suspensions of less-than-ideal powders is not possible.
CHAPTER 6

The Sintering of Monodisperse TiO₂

6.1 Introduction

In recent years the sintering of TiO₂ has been investigated using a variety of techniques ranging from sphere-to-sphere (or plate) neck growth ¹⁷¹-¹⁷³ to shrinkage measurements for compacts consisting of spherical particles. ¹⁷⁴,¹⁷⁵ The mechanisms employed to theoretically explain the observed kinetics have been surface diffusion,¹⁷¹ evaporation-condensation,¹⁷² grain boundary diffusion¹⁷⁷ and volume diffusion¹⁷³-¹⁷⁶. Although most of the recent (and accepted) interpretations are based on oxygen lattice diffusivity control of the densification process,¹⁷⁴-¹⁷⁶ these conclusions should not be unequivocally accepted.

Attempts have been made to understand the sintering mechanisms through transformation of the basic flux equations to sintering models. Many models of this sort exist for the different stages of sintering, yet most sintering data cannot be adequately described by any one model.¹⁷⁸ As an example, an attempt made by Pejovník, et al.¹⁸¹ to fit carefully selected UO₂ shrinkage data to the various models yielded no difference in the quality of the fit. This inability of the models to quantitatively describe sintering kinetics is due to the simple assumptions on which the models are based.²⁰⁰
Most existing models are derived for regular arrays of particles (and/or pores) having a uniform size and shape and assume that a single mechanism is rate controlling. However, in experimental systems multiple (coupled) mechanisms may control the densification kinetics; this alone invalidates most simple models.  In addition, particles having appreciable distributions of size and shape are usually nonuniformly packed; this leads to nonuniform local densification and porosity rearrangement during sintering which are not modelled. Therefore, mechanistic interpretations for densification based on a simple data set (e.g., shrinkage data only) must be treated with caution.

Investigations of sintering kinetics and microstructural development which utilize compacts having a uniform, dense packing of monodisperse, spherical particles avoid many of the limitations discussed above. Uniformly packed green compacts should densify with minimal particle rearrangement and grain growth; this has been observed for TiO$_2$ (Chapter 2) and for Y$_2$O$_3$-stabilized ZrO$_2$ by Rhodes. In addition, the reduced sintering temperatures and times predicted by the scaling laws for fine particles have been observed for the uniform compacts. Thus, if a single densification mechanism is justified (by the data) for a given system, then the sintering data may be analyzed using the existing models.

In this chapter, the predicted enhanced densification rates and
microstructural control for uniform, dense compacts are investigated using a monodisperse, ethoxide-derived TiO₂ powder and two initial packing densities (55% and ~ 69% of theoretical density). The effects of particle agglomeration on packing were discussed in Chapter 2, and since the compacts employed in the present study were formed from particle dispersions, the understanding of the effects of solution chemistry on particle interactions (Chapters 4 and 5) was utilized to maximize packing uniformity. Densification kinetics were obtained using isothermal and constant heating rate (CHR) dilatometry and the sintered microstructures were examined in the SEM. It should be stressed that this chapter is not meant as a definitive study of TiO₂ sintering kinetics, rather the purpose is to demonstrate the potential of such model systems in the analysis and the control of densification kinetics.

6.2 Experimental

6.2.1 Powder and Sample Preparation

The TiO₂ powder used in the sintering experiments was synthesized and washed using the procedures outlined in Chapter 3; the initial reagent concentrations were 0.15 M Ti(OC₂H₅)₄ and 0.5 M H₂O. The mean particle diameter, determined from SEM observations, the sedigraph unit (Micromeritics, Norcross, GA) and photon correlation spectroscopy (see Appendix C), was 0.34 μm and the standard deviation was 0.15 μm. The powder was dispersed (~15 wt.% solids) in water at a pH of 9 using an ultrasonic probe.
Under this electrolyte condition the suspension was stable against coagulation.

Disk-shaped compacts were formed using a dispersion sedimentation technique. Polyethylene vials (flat bottom) were filled with the powder dispersion and the particles were allowed to settle to form a sediment. A salt solution (1 M (NH₄)₂CO₃) was added to the vial contents to compress the electrical double-layer, and thus collapse the sediment into a rigid compact; this salt was chosen based on the ease of decomposition and the harmless products formed. The electrolyte solution above the compact was extracted using a pipette; the compacts were slowly air dried for 24 hours, followed by vacuum drying at 100°C for about 18 hours. The dried samples were stored in a desiccator.

The approximate dimensions (~ 1 cm diameter and 2 mm thick) and the weight of several disks were measured; the average green density was about 60% of the powder density, where \( \rho(\text{powder}) = 3.1 \text{ g/cm}^3 \). Because of the limited number of available samples and the desire to perform all of the experiments with essentially identical compacts (i.e. same packing density and pore distribution), each disk was broken into three pieces. This size reduction was also required for sample loading into the dilatometer.

6.2.2 Sintering Experiments

The sintering kinetics were determined by isothermal and constant heating rate dilatometry using a Netzsch 402E Electronic
Dilatometer (Netzsch Inc., Exton, PA). The horizontally oriented dilatometer employed a thermostated inductive displacement transducer to measure differences in dilatation of the test sample and the Al$_2$O$_3$ sample support tube. Contact of the scanning rod with the sample was maintained by a 70 g constant-load spring system; thus the samples were under a 3.2 psi load during dilatometry measurements (for a 0.25 inch diameter rod). The dilatometer was calibrated using a Vacromium standard supplied by the manufacturer; the system was accurate to within ± 0.5 µm.

Isothermal and constant heating rate (CHR) dilatometry was performed on amorphous and crystalline powder compacts. The crystalline compacts were obtained by prefiring the initially amorphous compacts for 3 hours at 785°C; the rutile crystal structure was confirmed by X-ray diffraction. The CHR experiments were conducted using heating rates of 5°, 10°, 21°, and 55°C/min. The maximum temperatures required to achieve near theoretical density (i.e. an essentially flat shrinkage curve) ranged from about 1300°C for a 5°C/min rate to about 1400°C for a 55°C/min rate. The amorphous and crystallized samples were fired to the same final temperature (for a given rate) so that the effects of the initial state on the observed kinetics and the final microstructure could be assessed.

Isothermal dilatometry was conducted at temperatures of 1020°, 1060°, 1100°, and 1160°C. A heating rate of 55°C/min was used to attain the desired firing temperatures. Essentially no
densification (shrinkage) occurred during heat-up for the lower
temperatures; however, some shrinkage occurred prior to reaching
1100°C, whereas about 30% of the total shrinkage occurred prior to
1160°C.

The sample baseline calibrations for the dilatometer were
obtained by measuring the dilatation for a 2 mm thick Al₂O₃ disk
(same approximate thickness as samples); baseline scans were
measured for the constant heating rate of 5°, 10°, 21°, and
55°C/min. Reproducibility was assessed by repeating the
measurements 2 additional times for the 10° and 21°C/min heating
rates; the scans were identical to the initial scans, respectively,
to within ± 1 μm. The effect of sample thickness (i.e. LVDT
linearity) was checked by measuring the dilatation for 1 and 3 mm
thick Al₂O₃ disks. The maximum deviation for sample thickness
variations was about 2 μm. Finally, the isothermal baseline curves
were obtained for the 2 mm Al₂O₃ disk by heating at a rate of
55°C/min to 1060°, 1100°, and 1160°C and then holding at a constant
temperature.

The shrinkage data reproducibility was checked by sintering a
second sample for several of the isothermal and CHR conditions. For
all cases tested, except one, the data agreed to better than 5%. A
10% deviation was observed for the 10°C/min test run, yet a third
sample agreed with the second sample within 3%. It is realized that
more samples should be sintered to obtain a more complete
statistical representation of the TiO₂ sintering kinetics. However,
because of the uniform particle packing and pore distribution in these samples (and sample uniformity), the data is sufficient for simple modelling and assessment of kinetic enhancement.

Microstructure development was investigated for the isothermal conditions of 1060°, 1100°, and 1160°C and firing times ranging from 3 minutes to 8.4 hours using scanning electron microscopy. The samples, wrapped in platinum foil, were fired in air in an Al₂O₃-tube furnace; the samples were rapidly heated to sintering temperature and air-quenched. Polished and fracture surfaces were viewed and the approximate grain size for a specific time and temperature was obtained from the micrographs of the fracture surface.* Thirty to fifty grains were measured for each sample and an approximate size was calculated.

Finally, microstructural development was investigated for the "ordered" compact formed at the end of the ordering experiments (see Section 5.5). The green density of this compact was approximately 0.69% of the powder density. The compact was broken into several pieces and prefired at 780°C for 3 hours to convert the particles to

* Attempts to view the polished surfaces were generally unsuccessful. The pure TiO₂ could not be chemically etched and high temperature thermal etching was not acceptable for microstructure analysis. Limited success was achieved with a 700°C reducing (90% N₂/10% H₂) thermal etch.
rutile. As discussed later, no particle rearrangement or density reduction occurred upon crystallization. Samples were fired in the Al₂O₃-tube furnace at 1060°C for 1, 3, 10, 30 and 60 minutes.

6.3 Results and Discussion

6.3.1 Isothermal Sintering

Figure 6.1 shows the top and fracture surface of an amorphous green compact; the particle packing is uniform and relatively dense. Figure 6.2 shows the top surface of a crystallized compact (rutile), which was prefired at 785°C. Although the particles seemed to be densely packed in the amorphous compact, crystallization, and the associated particle volume change, has caused the pore volume to increase. That is, during prefiring the particles experience two phase transformations, the first being from amorphous (\(\rho = 3.1 \text{ g/cm}^3\)) to anatase (\(\rho = 3.84 \text{ g/cm}^3\)) and then to rutile (\(\rho = 4.26 \text{ g/cm}^3\)). As a result, particles that were not touching in the amorphous compact became further separated when the particle size decreased (diameter decreased from 0.34 \(\mu\)m to 0.30 \(\mu\)m for the 30% volume change). This observed reduction in packing density was confirmed by a measured reduction in relative green density from 0.60 to 0.55. Thus the initial packing density is similar to that obtained in most reported sintering studies, and yet the more uniform particle and pore distributions differentiate these TiO₂ compacts from typical compacts.

The isothermal shrinkage data for the sintering temperatures of
Figure 6.1. The top and fracture surfaces of an amorphous-particle compact; the particle packing is uniform and relatively dense. Bar = 1 μm.
Figure 6.2. Top surface of a crystallized-particle compact (rutile); the pore volume has increased upon particle crystallization because of the associated particle volume change. Bar = 1 μm.
1020°, 1060°, 1100° and 1160°C are presented in Fig. 6.3 as a plot of \( \ln(\Delta l/l_0) \) versus \( \ln t \), where \( l_0 \) is the initial thickness and \( \Delta l \) is the shrinkage. The data show that as temperature is increased from 1020° to 1160°C the densification kinetics increase significantly. Although quantitative curve fitting procedures were not employed, three linear regions are present in Fig. 6.3, which correspond to the initial, intermediate, and final stages of the sintering process. The parallel behavior of the four curves for the intermediate stage and the three curves for the final stage suggests that a single mechanism dominates the densification process, hence further analysis of the data in these regions is warranted. However, the uncertainty in the initial time for isothermal sintering, especially for the data obtained at 1100° and 1160°C, causes quantitative analysis of the data in this form to be questionable.\(^{182}\)

An alternate, and more useful form of representation is the plot of relative density as a function of time, as shown in Fig. 6.4. The relative densities, \( \rho/\rho_{th} \), were calculated from the shrinkage data in Fig. 6.3 using the relation

\[
\rho/\rho_{th} = \rho_0/\rho_{th}[1-\Delta l/l_0]^{-3}
\]

(6.1)

where \( \rho_0/\rho_{th} \) was the initial (green) density. The measured value for green density of 0.55 was also the value calculated, using Eq. 6.1, from the total relative shrinkage, \( \Delta l/l_0 = 0.18 \) (average value for 1060°, 1100°, and 1160°C experiments), assuming that the
Figure 6.3. The relative linear shrinkage ($\Delta l/l_0$) as a function of time for the isothermal sintering temperatures of 1020°, 1060°, 1100°, and 1160°C.
Figure 6.4. The relative density, $\rho/\rho_{th}$, as a function of time for the isothermal sintering conditions.
dilatometry curves flattened out as $\rho/\rho_{th}$ approached 1.0. This assumption was valid based on the observed final microstructures. The densification rates observed in Fig. 6.4 decrease as temperature is decreased, yet densification seems to be significantly slower at 1020°C than at 1060°C. Even after 5 hours at 1020°C the relative density is only 0.83. This value is much lower than the density of 0.98 achieved for the same sintering time at a 40°C higher temperature. This marked decrease in kinetics at 1020°C, which was confirmed by the porous final microstructure (shown below), is not understood.

Microstructural development for the sintering temperatures of 1060°C, 1100°C, and 1160°C and firing times of 3 min, 25 min, 50 min, 2 hours, and 3.5 hours was investigated through scanning electron microscopy. These microstructures are presented in the following pages. The relative density reported on each micrograph was extracted from Fig. 6.4 for the corresponding time and temperature.

Figure 6.5 shows the polished and fracture surfaces for samples sintered at 1060°C for 3, 25, and 50 min. This series of micrographs, which represent the only polished surfaces successfully examined, illustrate the relationship between the polished surfaces and the fracture surfaces. The fracture surfaces for times ranging from 3 minutes to 8.4 hours are presented in Fig. 6.6. The transitions from the initial stage (3 min) of sintering through the intermediate stage (25, 50, and 120 min) and into the final stage
Figure 6.5. The polished and fracture surfaces for samples sintered at 1060°C for 3, 25 and 50 minutes. Bar = 1 μm.
Figure 6.6. Micrographs of the fracture surfaces for firing times ranging from 3 minutes to 8.4 hours showing the microstructural development at 1060°C. Bar = 1 μm.
(3.5 and 8.4 hours) are clearly illustrated in Figs. 6.5 and 6.6.

Similar sets of micrographs for the fracture surfaces are given for 1100°C and 1160°C in Figs. 6.7 and 6.8, respectively. These micrographs, in accordance with the data in Fig. 6.4, illustrate the more rapid densification process which occurs as temperature is increased. A more direct comparison of the microstructures developed at a given time for the three temperatures is shown in Fig. 6.9 (25 min) and in Fig. 6.10 (50 min). In addition, the final micrograph given in each of the three series (Figs. 6.6, 6.7 and 6.8) is for the dilatometer sample; these microstructures agree with the final densities calculated for Fig. 6.4. Finally, the microstructure of the 1020°C dilatometer sample is given in Fig. 6.11; this sample shows little grain growth and some open porosity.

At this point, several important microstructural features should be discussed. First, transgranular fracture is observed in many of these micrographs, especially for the higher relative densities. Although this mode of fracture is unusual for ~ 1 µm grain-size systems, this behavior may be a result of the high purity of the TiO₂. Second, coarsening, as well as exaggerated grain growth, is suppressed in this system; this is discussed in more detail later. Third, the pores remain at the grain boundaries and the triple-grain junctions; no intragranular porosity is observed! These three features, which are well illustrated in Fig. 6.12, enhance the applicability of sintering models for analysis of the densification data.
Figure 6.7. Micrographs of the fracture surfaces for firing times ranging from 3 minutes to 3.5 hours showing the microstructural development at 1100°C. Bar = 1 μm.
Figure 6.8. Micrographs of the fracture surfaces for firing times ranging from 3 minutes to 50 minutes showing the microstructural development at $1160^\circ$C. Bar = 1 $\mu$m.
Figure 6.9. Direct comparison of the microstructures developed after 25 minutes for the three sintering temperatures. Bar = 1 μm.
Figure 6.10. Direct comparison of the microstructures developed after 50 minutes for the three sintering temperatures. Bar = 1 μm.
Figure 6.11. The microstructure of the 1020°C dilatometer sample. Bar = 1 μm.
Figure 6.12. Micrographs showing the basic microstructural features: (1) predominant intragranular fracture (all micrographs taken of areas having maximum intergranular fracture to optimize microstructure observations - many areas showed no intergranular fracture); (2) fine grain size (no exaggerated grain growth); and (3) pores at grain boundaries (no intragranular porosity). Bar = 10μm.
Although Johnson, and others have stressed the necessity of using general, multiple-mechanism models to analyze sintering kinetics (e.g., simultaneous shrinkage and grain growth$^{185}$), the data in Fig. 6.3 suggested a single dominant mechanism, especially during the intermediate stage. This conclusion is supported by the parallel behavior observed in the plot (Fig. 6.13) of densification rate at a specific relative density as a function of inverse temperature. These rates were obtained by fitting the densification data for a given temperature in Fig. 6.4 (actually fitted $\rho/\rho_{th}$ versus log $t$) with a fifth degree polynomial; slopes were then calculated for relative densities of 0.75, 0.80, 0.85, 0.90 and 0.95. An estimate of the activation energy for the sintering process was obtained from the slope of the five curves in Fig. 6.13; the average value was 72 kcal/mol. This value agrees well with activation energies reported in the literature.$^{174,176,178}$

Quantitative analysis of the sintering kinetics requires grain growth data.$^{178,185}$ Fig. 6.14 gives the relative grain size, i.e. grain size divided by the initial particle size ($GS/PS_0$), as a function of relative density, where the grain sizes were obtained from the micrographs. These data indicate that the grain size at a specific relative density is independent of the sintering temperature (for the measured range). This conclusion is in accord with the results reported by Coble and Gupta,$^{187}$ Coble,$^{188}$ and
Figure 6.13. The natural logarithm of the densification rate as a function of $1/T$ for the relative densities of 0.75, 0.80, 0.85, 0.90 and 0.95. The average slope yields an activation energy, $Q$, of 72 kcal/mol.
Figure 6.14. Relative grain size, i.e., grain size divided by the initial particle size, as a function of relative density; the grain size at a specific density is independent of firing temperature.
Clare, where grain size was found to be independent of temperature as long as the initial density was constant. For such cases, grain growth seems to be controlled by the porosity at the grain boundaries.

An important feature observed in the microstructures and in Fig. 6.14 is that little grain growth occurs until the relative density becomes greater than 0.93; above this density grain growth is rapid. Yet, the onset of rapid grain growth is at a much higher density for the monodisperse TiO$_2$ than for the TiO$_2$ powder investigated by Yan and the Al$_2$O$_3$ powder by Wang, as shown in Fig. 6.15. Since the initial grain size was the same for these cases (PS$_0$ = 0.30 µm), the differing grain growth behavior was the result of different initial densities, particle size distributions and packing uniformities, and in the differing relative magnitudes of the diffusivities for the competing mechanisms. However, the gross differences observed for the TiO$_2$ powders must be due to differences in the particle size distributions and packing (porosity) uniformity. Unfortunately, no micrographs of Yan's initial TiO$_2$ compacts were given, thus no further discussion is possible.

Before proceeding with the model application, one final observation with respect to grain size development is presented. Fig. 6.16 gives the grain size as a function of time for the three sintering temperatures. These data show a linear time dependence which is not characteristic of normal grain growth kinetics. Thus
Figure 6.15. Comparison of the relative grain size as a function of relative density for the monodisperse TiO$_2$ particles, a TiO$_2$ powder investigated by Yan$^{190}$, and an Al$_2$O$_3$ powder by Wang.$^{191}$ The change in relative grain size is much smaller for the uniform compacts of monodisperse TiO$_2$. 
Figure 6.16. The plot of relative grain size as a function of time showing the linear time dependence.
grain growth is controlled by another mechanism, one which is
probably linked to the distribution of porosity.

The intermediate stage sintering models were introduced by
Coble\textsuperscript{192} and extended by Coble and Gupta.\textsuperscript{187} The models for various
geometries and controlling mechanisms have the general form\textsuperscript{187}

\[ \frac{dP}{dt} = \frac{K\gamma\Omega D}{(GS)^m k_B T} \]  \hspace{1cm} (6.2)

where $P$ is the porosity ($=1-\rho/\rho_{th}$), $K$ a constant defined by the
geometry, $\gamma$ the solid-vapor surface free energy, $\Omega$ the vacancy
volume, and $D$ the diffusivity (actually $\omega D_b$ for boundary diffusion).
The exponent, $m$, has a value of 3 for lattice diffusion controlled
kinetics and a value of 4 for boundary diffusion control.\textsuperscript{187}

To determine which mechanism controlled intermediate stage
sintering for the TiO\textsubscript{2} powder, the grain size exponent was required.
This value was obtained by extracting the grain size and
densification rate for given values of $\rho/\rho_{th}$ and temperature from
Figs. 6.14 and 6.13, respectively, and plotting the $\ln($rate$)$ versus
$\ln($GS$)$, as shown in Fig. 6.17. The average exponent value given by
the slopes was 2.96 (standard deviation $= 0.18$). This grain size
dependence indicates that volume diffusion controls intermediate
stage sintering.

To obtain the activation energy, $Q$, for the process represented
in Fig. 6.4, the rate equation (Eq. 6.2) was written as
Figure 6.17. Log-Log plot of the densification rate versus grain size for the relative densities of 0.75, 0.80, 0.85, 0.90 and 0.95. The average slope of -2.96 (σ = 0.18) indicates volume diffusion control of intermediate stage sintering.
\[
\frac{d\left(\rho/\rho_{th}\right)}{dt} = K_y \omega D_0^g \exp(-Q/RT),
\]
where \( D_0^g \) was assumed to be constant. The activation energy was determined, using the data in Figs. 6.13 and 6.14, by plotting the natural logarithm of the LHS of Eq. 6.3 as a function of \( 1/T \) (Fig 6.18). Rather than drawing lines through the five sets of points (corresponding to the relative densities, 0.75-0.95), the average of the five points for the three temperatures were fitted using a least squares procedure. The activation energy given by the slope (correlation coefficient = 0.9999) was 74.3 kcal/mol.

The preexponential term was obtained by multiplying Eq. 6.3 by \( T \), and plotting the average value of the LHS as a function of \( T \), as shown in Fig. 6.19. The slope, given as

\[
\text{Slope} = \ln(K_y \omega D_0^g),
\]
was equal to -38.02 (corr. coef. = 0.9999). By using a vacancy volume of \( 1.57 \times 10^{-23} \text{cm}^3 \), (assuming oxygen ion diffusion is rate limiting \(^{174, 176, 178}\)), a value for the surface free energy of 600 erg/cm\(^2\), and a value for \( K \) of 335, the value of \( D_0^g \) was calculated to be 9.75. Therefore, application of the intermediate stage sintering model\(^{187}\) to the densification and grain size data yielded the rate controlling diffusivity,

\[
D = 9.75 \exp(-74300/RT), \text{ (cm}^2/\text{sec})
\]
which is in accord with the measured values for oxygen tracer
Figure 6.18. Arrhenius plot for the volume diffusion controlled intermediate stage sintering model (Eq. 6.3). The slope yielded an activation energy of 74.3 kcal/mol.
Figure 6.19. Determination of the temperature independent preexponential term for the intermediate stage model (Eq. 6.3).
diffusion in TiO$_2^{194,195}$ and those determined from sintering data.$^{174,176,178}$

6.3.2 Constant Heating Rate Sintering

The use of constant heating rate conditions to investigate densification kinetics has recently been emphasized because of the potential for a rapid review of sintering mechanisms and the avoidance of experimental errors associated with isothermal dilatometry (i.e. transient temperature changes and errors in the initial time).$^{196-198}$ However, quantitative analysis and interpretation of experimental results is very difficult. This is due to the microstructural features in green compacts which also limit the applicability of isothermal sintering models and the additional uncertainty of possible overlapping and changing mechanisms.$^{182}$ Nevertheless, constant heating rate sintering was performed to examine the effects of heating rates on the densification kinetics and the final microstructures.

The CHR dilatometry data is given in Fig 6.20 as a plot of \( \ln(\Delta l/l_0) \) versus $1/T$ for the heating rates, $C$, of $5^\circ$, $10^\circ$, $21^\circ$, and $55^\circ$C/min. The shrinkage, and thus density, for a given temperature is higher for the slower heating rates because the transient time for a given temperature range is longer than for the fast heating rates. That is, 20 minutes was required at $5^\circ$/min to traverse the temperature range of $1100^\circ$ to $1200^\circ$C, whereas less than 2 minutes were required at $55^\circ$C/min.
Figure 6.20. Relative shrinkage as a function of inverse temperature for the constant heating rates of 5°, 10°, 21° and 55°C/min.
The activation energy for the CHR process was obtained by extracting the temperature required to achieve a specific relative shrinkage from Fig. 6.20, and plotting these data as a function of heating rates, as shown in Fig. 6.21. The parallel behavior of the three curves for the intermediate stage ($\Delta l / l_0 = 0.07, 0.10$ and $0.15$) suggests that a single mechanism is operative, thus this data may be suitable for application of CHR models (not done in this thesis). The average activation energy obtained from the slopes of these curves was 64.9 kcal/mol ($\sigma = 5$ kcal/mol); this activation energy is slightly lower than that obtained from the isothermal sintering data, but is still in agreement with the reported values for diffusion processes in TiO$_2$.

The microstructures of the CHR dilatometry samples are shown in Figs. 6.22-6.25; the relative densities accompanying the micrographs were obtained from Fig. 6.20, assuming a green density of 0.55. Fig. 6.22 shows the top (as sintered thermal etch) and fracture surfaces for 5°C/min to 1350°C. Although this sample was exposed to higher temperatures than the maximum isothermal condition employed (1160°C) for over 100 minutes, the approximate average grain size is only 3 µm (GS/PS$_o \sim 10$) and all pores have remained at the grain boundaries. A smaller grain size and higher porosity is shown in Fig 6.23 for 10°C/min to 1400°C. Figures 6.24 and 6.25 show the top and fracture surfaces for 21°C/min to 1300°C and 55°C/min to 1400°C, respectively.

Figure 6.24 also shows the top and fracture surfaces for an
Figure 6.21. Heating rate as a function of the temperature required to achieve a specific relative density. An activation energy of 64.9 kcal/mol was obtained for the intermediate stage ($\Delta l/l_0 = 0.07, 0.10$ and $0.15$) of the CHR process.
Figure 6.22. The top (as-sintered thermal etch) and fracture surfaces of a compact heated at a rate of 5°C/min to 1350°C. The average grain size is \(\sim 3 \, \mu m\) and all pores are at the grain boundaries. Bar = 1 \, \mu m \) (top) and 10 \, \mu m."
Figure 6.23. The fracture surface of a compact heated at a rate of 10°C/min to 1400°C. Bar = 10 μm.
Figure 6.24. The top and fracture surfaces for "amorphous" and crystallized compacts heated at a rate of 21°C/min to 1300°C. The "amorphous" sample densified more rapidly than the crystallized sample.
Figure 6.25. The top and fracture surfaces of a compact heated at a rate of 55°C/min to 1400°C. Bar = 10 μm.
"amorphous" compacted sintered at a CHR of 21°C/min to 1300°C. For identical firing schedules, a larger grain size and a higher density is obtained for the amorphous compact. Although the total dilatation measured for the amorphous compact was the same as that calculated for the rutile compact (dilatation plus 30% volume shrinkage), the amount of shrinkage which occurred during the "sintering" portion of the firing cycle (900°C-1300°C) for the amorphous compact was about 60% of that measured for the rutile samples. Thus, some densification occurred at lower temperatures as the particles were dehydrated and crystallized.

The enhanced sintering behavior of the amorphous powders, revealed in the micrographs and through dilatometry, was similar to the enhanced behavior observed by MacKenzie\textsuperscript{199} for a hydrated anatase powder. The greater sinterability of the anatase powder was attributed to the volatiles which were released during firing. For instance, water vapor may have assisted sintering through the formation of transient hydroxy species which increased diffusivities.\textsuperscript{199} A similar explanation could apply to the hydrated, amorphous TiO\textsubscript{2} powder.

6.3.3 "Ordered" Compact Sintering

In a final attempt to demonstrate the role of particle packing in the green compact on sintering and grain growth, the "ordered" compact (from ordering experiments in Chapter 5) was sintered at 1060°C. The microstructure of the crystallized compact (Fig. 6.26)
Figure 6.26. The top and fracture surfaces for the crystallized (3 hours at 780°C) "ordered" compact. A high packing density ($\rho/\rho_{th} = 0.69$) and uniformity was retained upon crystallization. Bar = 1 µm.
shows that a much higher packing density (~ 0.69) and uniformity was retained upon crystallization than for the previously discussed compacts (Figs. 6.1 and 6.2).

The microstructures developed after 1, 3, 10 and 60 minutes at 1060°C are shown in Figs. 6.27-6.30, respectively; outer and fracture surfaces are shown for all cases, except at 60 min (outer only). These micrographs indicate that densification was rapid, with almost no concurrent grain growth. In only 10 minutes (Fig. 6.29) the relative density was about 0.90 and the grain size was approximately 0.4 μm; the time required to achieve the same relative density in the previous experiments (Fig. 6.4) was greater than 100 minutes. As shown in Fig. 6.31, grain growth was insignificant during sintering. Even after 60 minutes (Fig. 6.30) the grain size had increased by only 50% and the sample density was greater than 95% of theoretical density. These results clearly demonstrate that enhanced densification for fine particles is critically dependent on the particle packing density and uniformity.

6.4 Summary and Conclusions

1. Uniform compacts (55% dense) of monodisperse TiO₂ spheres sintered to near-theoretical density at the sintering temperatures of 1060° (8.4 hours), 1100° (3.5 hours), and 1160°C (50 minutes). The final microstructures were uniform and fine grained; the grain size increase during
Figure 6.27. The microstructure of the "ordered" compact after 1 minute at 1060°C: (a) outer surface (b) fracture surface. Bar = 1 μm.
Figure 6.28. The microstructure of the "ordered" compact after 3 minutes at 1060°C: (a) outer surface (b) fracture surface. Bar = 1 μm.
Figure 6.29. The microstructure of the "ordered" compact after 10 minutes at 1060°C: (a) outer surface (b) fracture surface. Bar = 1 μm.
Figure 6.30. The microstructure (outer surface) of the "ordered" compact after 60 minutes at 1060°C. Bar = 1 μm.
Figure 6.31. Approximate grain size as a function of relative density for the "ordered" compact (---). Dense, uniform packing in the green microstructure has led to rapid densification to >95% of theoretical density with only a 50% increase in grain size.
sintering was less than a factor of 5 and no exaggerated grains were observed. All pores remained at the grain boundaries. More enhanced densification rates and a finer grain size resulted for compacts that were more uniformly and densely packed (\( \sim 69\% \) of theoretical density). Therefore, a major conclusion is that the powder characteristics and the green microstructure determine the sintering kinetics and the final microstructure. As a corollary, an ideally packed green microstructure (\( \sim 70-74\% \) dense with a uniform distribution of pore volume) will sinter very rapidly to theoretical density with almost no grain coarsening.

2. The results from isothermal and CHR dilatometry indicated that one mechanism dominated the intermediate and final stage densification for the TiO\(_2\) compacts. The intermediate stage isothermal shrinkage and grain size data were analyzed using models developed by Coble;\(^{187,192}\) volume diffusion control of intermediate stage sintering was established. The data yielded the following diffusion coefficient for the isothermal sintering process:

\[
D = 9.75 \exp(-74300/RT)
\]
CHAPTER 7

General Conclusion and Future Research

7.1 General Conclusion

Spherical, monodispere TiO₂ powders and aqueous based particulate dispersions were used as a model system for a total study of ceramics processing, which included powder synthesis and characterization, surface electrochemistry, interparticle forces, particle packing, and sintering. The interdependence of the sequential steps in the processing of ceramic materials has been clearly demonstrated. The microstructures obtained during sintering were critically dependent on the green microstructure; both density and uniformity of particle packing affected the sintering behavior, as was shown in Chapters 2 and 6. Particle packing was predictably controlled through the physical and surface electrochemical properties of the powder. By manipulating the interfacial electrochemistry, and thus the interparticle forces (Chapters 4 and 5), particle compacts having a porous structure (flocculated particles, Chapter 2) or a dense, uniform structure (Chapter 6) were formed.

The equiaxed, uniform-size particles possessed the intrinsic processing advantages of enhanced dispersion stability, isotropic interaction forces which allowed formation of the uniform green microstructures, and controlled sintering behavior. In addition,
models developed for these uniform-size powders were used as predictive tools for the fabrication of the desired microstructures. Therefore, the desired sintered microstructures for TiO₂, and probably for many other ceramic materials, may be obtained by understanding and controlling the processes which occur during each of the sequential fabrication steps.

7.2 Future Research

The following items are suggested areas for future research:

1. The alkoxide hydrolysis technique for TiO₂ synthesis should, because of its simplicity, be applicable to other oxide systems, both single- and multiple-cation oxides. Reactions involving simple alkoxides and complex, multiple-cation alkoxide precursors should be investigated. Organometallic compounds may also be suitable precursors in some cases. The advent of such spherical, monodisperse oxide powders would surely advance ceramic science and technology (when coupled with colloid chemistry). It should be noted that during the past year the technique has been successfully extended to doped TiO₂ (dopants include Nb, Ta, Ba, Sr, Cu, Bi), ZrO₂, yttria-stabilized-ZrO₂, and doped ZnO.

2. The TiO₂ precipitation reaction was assumed to occur through a homogeneous nucleation and growth process.
Although a quantitative study of the kinetics was not performed, the TiO$_2$ system, as well as those listed above and the SiO$_2$ system, forms an ideal experimental system for such studies. Dynamic light scattering techniques (e.g. photon correlation spectroscopy) could be used for rapid measurements of particle size (down to $\sim 20 \text{ Å}$) as a function of time; these data would be suitable for quantitative modelling of the kinetic processes.

3. Spherical, monodisperse powders are ideal experimental systems for studies of the surface electrochemistry and the electrokinetic phenomena. Thus the TiO$_2$ powders may be used to quantitatively verify and extend the double layer models, such as the ionization and complexation model discussed in Chapter 4 and Appendix A. In addition, the amorphous and crystalline powders (TiO$_2$, ZrO$_2$, ZnO) can be used to study the effects of atomic packing on the surface properties in greater detail.

4. The theoretical models used to describe the interparticle forces and structures for the liquid- and solid-like arrangements of monodisperse particles must be extended to polydisperse particulate systems, since perfectly monodisperse ceramic powders will never exist. These models are required to control the rheological
properties of ceramic powder dispersions and the particulate structures which are formed during processing.

The ideal model powder for the necessary experimental studies would be the monodisperse SiO$_2$, because the mean size ($\bar{d} = 0.2-0.8 \ \mu$m) and the distribution width ($\sigma = 0.03$) can be precisely controlled. Powders of several sizes could be blended to generate specific polydisperse systems and the effects on particle ordering could be assessed. In addition, since the osmotic pressure of an ordered structure is strongly affected by size polydispersity, a pressure cell should be employed to extend the experimental range of osmotic pressure above that of simple sedimentation pressure.

5. The potential for using monodisperse, spherical particles in quantitative studies of sintering kinetics seems to be tremendous. Carefully prepared compacts (ideal particle packing) of TiO$_2$, SiO$_2$, ZrO$_2$, etc., could be used to experimentally verify the sintering models developed over the past 30 years. In addition, compacts formed from powders having different mean diameters would allow a more refined use of scaling law studies and mechanism determination.
6. Finally, the ability to control the sintered microstructure, especially the grain size, allows for quantitative studies of microstructure - property relationships. The effects of grain size and porosity on the mechanical and electrical properties are two areas for promising research.
APPENDIX A

Electrolyte Complexation Double-Layer Model

A.1 Background

When a particle is immersed in a liquid, a charge and an electrical potential may be developed at the surface which is balanced by the accumulation of counter charge in the liquid. The counter charge may consist of a diffuse region of counterions or a compact layer of bound charge and a diffuse region. The surface charge and the compact and diffuse layer charges comprise the electrical double layer.\(^\text{41}\)

Several models have been developed to relate the surface and space charge densities to the field potentials. Guoy and, independently, Chapman\(^\text{79}\) derived equations for the charge densities in terms of the surface potential by describing the diffuse distribution of counterions accumulated near a charged interface as a Boltzmann distribution. Stern\(^\text{80a}\) and Grahame\(^\text{80b}\) refined this model, recognizing that the counterions are unlikely to approach the surface more closely than the distance, \(\beta\), about the dimension of the ionic radii of anions and the hydrated radii of cations. Stern\(^\text{80a}\) also introduced the idea of ion adsorption at the interface to form a compact region, called the Stern layer. Specific layers of charge and linear potential drops are now parts of the model known as the Guoy-Chapman-Stern-Grahame (GCSC)
This model is schematically illustrated in Figure A1; the equations for the GCSG model are

\[ \sigma_0 + \sigma_\beta + \sigma_d = 0 \]  \hspace{1cm} (A1)

\[ \sigma_d = -(8\varepsilon k_BT)^{1/2} \sinh \left( \frac{ze\phi_d}{2k_BT} \right) \]  \hspace{1cm} (A2)

\[ \phi_\sigma - \phi_\beta = \sigma_0/C_1 \]  \hspace{1cm} (A3)

\[ \psi_\beta - \psi_d = \frac{\sigma_0 + \sigma_\beta}{C_2} = -\sigma_d/C_2 \]  \hspace{1cm} (A4)

where,

- \( C \) = electrolyte concentration (assuming a 1:1 electrolyte, i.e. KCl);
- \( \varepsilon \) = medium dielectric constant;
- \( z \) = counterion valence;
- \( \sigma_0, \phi_\sigma \) = surface charge density and potential, respectively;
- \( \sigma_\beta, \phi_\beta \) = charge density and potential at the inner Helmholtz plane (defined by adsorbed ions);
- \( \sigma_d, \phi_d \) = diffuse layer charge density and potential; and
- \( C_1, C_2 \) = inner and outer integral capacitances.

The GCSG model establishes the correct electrostatic equations, but it does not address the mode of surface charge development. Parks and de Bruyn, Overbeek, and others pointed out that charge development on oxide surfaces occurs by direct proton transfer between the solution and the hydroxylated surface.
Figure A1. Schematic representation of (a) the titania/water interface showing possible locations of charged aqueous species at the ionized surface sites, and (b) the electrical potential, $\psi$, in the double-layer. The symbols shown are defined in the accompanying text.
Attempts to apply the GCSG model to experimentally determined interfacial properties were not successful.\textsuperscript{82,83} In addition, despite the high surface charge measured on oxides, studies of electrokinetic potential and stability indicated a small diffuse layer charge (\textasciitilde{} 20\% of $\sigma_o$) and potential. This difference in charge was balanced by the adsorption of electrolyte ions in the compact region.\textsuperscript{69} Yates, et al.\textsuperscript{25}, suggested that ions form weak ion-pair complexes with charged sites on the surface. These complexes not only influence particle electrokinetics, but also provide a mechanism by which electrolyte ions influence the surface charge acquired by ionization processes.\textsuperscript{41}

A.2 Electrolyte Complexation Double Layer Model

The modifications introduced by Yates\textsuperscript{25} have been further refined by Davis, et al.\textsuperscript{69,70}, and James and Parks;\textsuperscript{41} the present model is known as the electrolyte site-binding (complexation) double-layer model for amphoteric surfaces.\textsuperscript{41} This model and the required data analysis techniques are discussed in the remaining portion of this appendix.

The amphoteric ionization reactions of the surface sites and the intrinsic equilibrium constants, written for the TiO$_2$/H$_2$O interface, are\textsuperscript{41}
\[
K_{a1}^{\text{int}} = \frac{[\text{TiOH}][H^+]_s}{[\text{TiOH}_2^+]} \quad \text{(A5)}
\]

and

\[
K_{a2}^{\text{int}} = \frac{[\text{TiO}^-][H^+]_s}{[\text{TiOH}]} \quad \text{(A6)}
\]

where the subscript \(s\) denotes surface species. The concentration of protons at some location, \(i\), in the double layer is related to the bulk solution concentration by the Boltzmann distribution:

\[
[H^+]_i = [H^+] \exp(-e\psi_i/k_B T). \quad \text{(A7)}
\]

Thus,

\[
K_{a1}^{\text{int}} = \frac{[\text{TiOH}][H^+]_s}{[\text{TiOH}_2^+]} \exp(-e\psi_0/k_B T) \quad \text{(A8)}
\]

and

\[
K_{a2}^{\text{int}} = \frac{[\text{TiO}^-][H^+]_s}{[\text{TiOH}]} \exp(-e\psi_0/k_B T). \quad \text{(A9)}
\]

The surface complexation ionization reactions and the associated intrinsic equilibrium constants, using KCl as the electrolyte, are given by

\[
\text{TiOH} + K^+_s \rightleftharpoons \text{TiO}^- + K^+ + H^+_s \quad \text{(A10)}
\]
\[
1/ K_{\text{Cl}^-}^{\text{int}}
\]

\[
\text{TiOH} + \text{H}^+ + \text{Cl}^- \rightarrow \text{TiOH}_2^+ - \text{Cl}^-, \quad (A11)
\]

where ions complexed at the surface are represented by \(\text{TiO}^- - \text{K}^+\) and \(\text{TiOH}_2^+ - \text{Cl}^-\). The surface complexation ionization reactions, Eqs. A10 and A11, are related to the intrinsic complexation reactions through the equilibrium constants, as follows:

\[
K_{\text{K}^+}^{\text{int}} \quad \frac{\text{TiO}^- + \text{K}^+_s}{\text{TiO}^- - \text{K}^+_s} \quad ; \quad K_{\text{K}^+}^{\text{int}} = \frac{[\text{TiO}^- - \text{K}^+]}{[\text{TiO}^-][\text{K}^+_s]} \quad (A12)
\]

\[
K_{\text{Cl}^-}^{\text{int}} \quad \frac{\text{TiOH}_2^+ + \text{Cl}^-_s}{\text{TiOH}_2^+ - \text{Cl}^-} \quad ; \quad K_{\text{Cl}^-}^{\text{int}} = \frac{[\text{TiOH}_2^+ - \text{Cl}^-]}{[\text{TiOH}_2^+][\text{Cl}^-_s]} \quad (A13)
\]

where

\[
k_{\text{K}^+}^{\text{int}} = k_{\text{K}^+}^{\text{int}} k_{\text{K}^+}^{\text{int}} \quad (A14)
\]

and

\[
k_{\text{Cl}^-}^{\text{int}} = k_{\text{Cl}^-}^{\text{int}} k_{\text{Cl}^-}^{\text{int}} \quad (A15)
\]

The mass law quotients in the previous equations are thermodynamic constants only if the equilibria are expressed in terms of species activities at the surface. If evaluated using solution concentrations, the quotients will vary with pH and electrolyte concentration as surface charge and surface potential vary. Quotients calculated at a specific pH from potentiometric
titration using bulk concentrations are "apparent" reaction quotients (e.g. $Q_{a1}$ or $Q_{K^+}$). Intrinsic reaction constants can be determined from the apparent constants using special limiting conditions; this technique is discussed later.

The surface charge is determined by proton balance using potentiometric titration, as described in Chapter 4. The surface charge, $\sigma_s$, represents the net number of protons released or consumed by all surface reactions, and thus surface complexation provides a mechanism for the development of surface charge in addition to the role of protons and hydroxyl ions. The surface and bound (Helmholtz) charges can be written in terms of surface concentrations of each species:

$$\sigma_s = \frac{F}{S} \left( [\text{TIOH}_2^+] + [\text{TIOH}_2^- - \text{Cl}^-] - [\text{TIO}^-] - [\text{TIO}^- - \text{K}^+] \right)$$  \hspace{1cm} (A16)

$$\sigma_\beta = \frac{F}{S} \left( [\text{TIO}^- - \text{K}^+] - [\text{TIOH}_2^- - \text{Cl}^-] \right)$$  \hspace{1cm} (A17)

where $F$ is the Faraday constant and $S$ is the specific surface area. The surface species are distributed among the total number of available sites, $N_s$:

$$N_s = \frac{N_a}{S} \left( [\text{TIOH}_2^+] + [\text{TIOH}_2^- - \text{Cl}^-] + [\text{TIOH}] + [\text{TIO}^-] \right.$$  
$$+ [\text{TIO}^- - \text{K}^+] \right)$$  \hspace{1cm} (A18)

where $N_a$ is Avagadro's number. The surface site density is experimentally obtainable by various methods, such as IR
spectroscopy, tritium exchange, and isothermal dehydration. \(^{25, 41}\)

The concentration of each surface species is calculated from the solution concentration, the intrinsic reaction constants, and the Boltzmann distribution for the electrostatic interaction energy:

\[
[TiOH_2^+] = [TiOH][H^+] \exp(-e\psi_o/k_B T)/K_{a_1}^{\text{int}} \tag{A19}
\]

\[
[TiO^-] = \frac{[TiOH]}{[H^+]} \exp(e\psi_o/k_B T)K_{a_2}^{\text{int}} \tag{A20}
\]

\[
[TiO^-\ K^+] = \frac{[TiOH][K^+]}{[H^+]} \exp[(\psi_o - \psi_B)e/k_B T]^*K_{K^+}^{\text{int}} \tag{A21}
\]

\[
[TiOH_2^-\ Cl^-] = [TiOH][H^+][Cl^-] \exp[(\psi_B - \psi_o)e/k_B T]^*K_{Cl^-}^{\text{int}} \tag{A22}
\]

The set of equations (Eqs. A1-A4, A16-A22) can be solved for unique values of \(\sigma_o\) and \(\psi_o\) corresponding to selected values of pH and electrolyte concentration, once values of fixed parameters \(N_s\), \(K_{a_1}^{\text{int}}, K_{a_2}^{\text{int}}, K_{K^+}^{\text{int}}, K_{Cl^-}^{\text{int}}, C_1\) and \(C_2\) are chosen. This can be done by an approximate method described by James and Parks.\(^{41}\)

Alternatively, the set of equations are solved simultaneously through the use of a generalized chemical equilibrium computer code MINEQL, developed by Westall,\(^{71}\) which was modified by James, et al.,\(^{41, 69, 70}\) to include the charge and mass balances for the surface and the model of the physicochemical structure for the oxide/aqueous electrolyte interface. Quantitative application of the model requires values of the intrinsic ionization and complexation constants.
A.3 Determination of Intrinsic Ionization and Complexation Constants

The intrinsic ionization and complexation constants needed for the models are not amenable to direct experimental measurement because the near-surface activities of ions cannot be measured. The most easily obtained data is surface charge, $\sigma_s$, as a function of pH and salt concentration. Intrinsic equilibrium constants can be derived from such data using reasonable approximations given by James and Parks.\textsuperscript{41}

The technique takes advantage of the fact that the apparent equilibrium constants approximate the intrinsic constants under the proper conditions. For example, $Q_{a_1}$ and $^{*}Q_{K^+}$ are given as

$$Q_{a_1} = \frac{[\text{TiOH}][H^+]}{[\text{TiOH}^+]^2} = k_{a_1}^{\text{int}} \exp(e\psi_0/k_BT) \quad (A23)$$

$$^{*}Q_{K^+} = \frac{[\text{TiO}^- - K^+][H^+]}{[\text{TiOH}][K^+]} = k_{K^+}^{\text{int}} \exp[(\psi_0 - \psi_0^B)e/k_BT] \quad (A24)$$

These potentials $(\psi_0, \psi_0^B)$ cannot be measured, however in dilute solutions (electrolyte concentration $\sim 10^{-3}$ to $10^{-4}$ M) $\psi_0$ approaches zero as $\sigma_s$ approaches zero, while in moderately concentrated solutions (0.1 and 1M), $(\psi_0^B - \psi_0)$ approaches zero as $\sigma_s$ approaches zero. In addition, for solution pH much higher than the pH$_{pzc}$ (i.e., the pH where $\sigma_s = 0$), the surface charge is dominated
by TiO\textsuperscript{-} and TiO\textsuperscript{2-} K\textsuperscript{+} sites and for pH much lower than the pH\textsubscript{pzc}, \(\sigma_o\) is dominated by TiOH\textsuperscript{+} and TiOH\textsuperscript{2+} Cl\textsuperscript{-}. Thus for a pH different from the pH\textsubscript{pzc},

\[
[TiOH] = \frac{SN_s}{Na} - \frac{S|\sigma_o|}{F} = \frac{S}{Na} N_s (1 - \alpha) \tag{A25}
\]

where \(\alpha\) is the fraction of sites ionized, calculated from experimental data by

\[
\alpha = \frac{\sigma_o}{eN_s} . \tag{A26}
\]

Also, \(\sigma_o\) is dominated by uncomplexed sites at very low ionic strength and by complexed sites at high ionic strengths. Thus, manipulation of the two parameters \(\alpha\), through the pH, and ionic strength (electrolyte concentration) allow intrinsic constants to be estimated. The approximations and intrinsic constant estimates are shown in Table Al.

The intrinsic ionization constants are determined by extrapolating to the low ionic strength condition for which surface site complexation can be ignored\textsuperscript{1,70}. The technique involves calculation of \(pQ_{a1}\) and \(pQ_{a2}\) (where \(pQ_a = -\log Q_a\)) from the experimental \(\sigma_o\) data using Eq. A26 and

\[
pQ_a = pH \pm \log \frac{\alpha}{1 - \alpha} \tag{A27}
\]

where the log term is added to pH to yield \(pQ_{a1}\) and subtracted to yield \(pQ_{a2}\). The calculated values are plotted versus \(\alpha + Cl^{1/2}\) (\(C =\) electrolyte concentration) as shown in Fig. A2 for TiO\textsubscript{2} A.
Table Al
Approximations Useful in Estimating Intrinsic Ionization and Complexation Constants for Selected Ranges of pH and Electrolyte Concentration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH &lt; pH_{pzc}</th>
<th>pH &gt; pH_{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$[\text{TiOH}^+] = S\sigma_o/F$</td>
<td>$[\text{TiO}^-] = S\sigma_o/F$</td>
</tr>
<tr>
<td></td>
<td>$[\text{TiOH}] = (zeN_s-\sigma_o)S/F$</td>
<td>$[\text{TiOH}] = (zeN_s-\sigma_o)S/F$</td>
</tr>
<tr>
<td>C = 0</td>
<td>$(Q_{a_1})<em>{\sigma_o=0} = k</em>{a_1}^\text{int}$</td>
<td>$(Q_{a_2})<em>{\sigma_o=0} = k</em>{a_2}^\text{int}$</td>
</tr>
<tr>
<td></td>
<td>$Q_{a_1} = [\text{TiOH}][H^+]/[\text{TiOH}^+]_2$</td>
<td>$Q_{a_2} = [\text{TiO}^-][H^+]/[\text{TiOH}]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C &gt;&gt; 0</td>
<td>$[\text{TiOH}^+\text{Cl}^-] = S\sigma_o/F$</td>
<td>$[\text{TiO}^-\text{K}^+] = S\sigma_o/F$</td>
</tr>
<tr>
<td></td>
<td>$[\text{TiOH}] = (zeN_s-\sigma_o)S/F$</td>
<td>$[\text{TiOH}] = (zeN_s-\sigma_o)S/F$</td>
</tr>
<tr>
<td></td>
<td>$(^*Q_{\text{Cl}^-})<em>{\sigma_o=0} = k</em>{\text{Cl}^-}^\text{int}$</td>
<td>$(^*Q_{\text{K}^+})<em>{\sigma_o=0} = k</em>{\text{K}^+}^\text{int}$</td>
</tr>
<tr>
<td></td>
<td>$^*Q_{\text{Cl}^-} = \frac{[\text{TiOH}][\text{Cl}^-][H^+]}{[\text{TiOH}^+\text{Cl}^-]_2}$</td>
<td>$^*Q_{\text{K}^+} = \frac{[\text{TiO}^-\text{K}^+][H^+]}{[\text{TiOH}][\text{K}^+]}$</td>
</tr>
</tbody>
</table>
Figure A2. Double extrapolation plot for determination of $pK_{aq}^{int}$ and $pK_{a1}^{int}$ showing the variation of surface acidity quotients, $pQ_{a1}$, for dissociation of positive and negative sites on TiO$_2$ A in the aqueous dispersion with fractional surface charge, $\alpha$, and KCl electrolyte concentration.
Two extrapolations are possible:

1. For each ionic strength, a smooth curve is drawn through the points and extrapolated to intersect the verticle line defined by $\alpha + C^{1/2} + C^{1/2}$; at this point, both $\sigma_0$ and $\psi_0$ are zero. A smooth curve is then drawn through the $\alpha = 0$ points and extrapolated to $\alpha + C^{1/2} = 0$. For this point, $C$ must also equal zero, thus the intercept for $pQ_{a_1}^{\text{int}}$ estimates $pK_{a_1}^{\text{int}}$.

2. A second estimate of $pK_{a_1}^{\text{int}}$ is obtained using the same data. Intersection points are obtained along the constant ionic strength curves for arbitrary $\alpha$ and smooth curves drawn for each $\alpha$ are extrapolated to intersect the verticle line defined by $\alpha + C^{1/2} = \alpha$. A smooth curve is then drawn through the $C = 0$ points and again extrapolated to $\alpha + C^{1/2} = 0$, thus giving the estimated $pK_{a_1}^{\text{int}}$.

Complexation constants are obtained by a similar double extrapolation technique; however, for these constants the important conditions used are $\alpha = 0$ and $C = 1$. In this case, the apparent complexation constants, $pQ_\alpha^* = pH \pm \log \frac{\alpha}{(1 - \alpha)C_{KCl}}$, are plotted versus $\alpha \cdot \log C$, as shown in Fig. A3. The two terms on the RHS are subtracted to get $pQ_{K^+}^*$ and added to get $pQ_{Cl^-}^*$. Estimations of intrinsic constants are obtained by drawing $C = 1$ curves for
Figure A3. Variation of surface complexation quotients, $p^*Q_x$, for reaction of positive and negative sites on TiO$_2$ A surface in aqueous suspension with fractional surface charge, $\alpha$, and KCl electrolyte concentration. Extrapolated intercepts give estimates of $p^*K_{\text{Cl}^-}^{\text{int}}$ and $p^*K_{K^+}^{\text{int}}$. 

TiO$_2$ A - KCl

$N_s = 13.0 \text{ nm}^{-2}$

$p^*K_{K^+}^{\text{int}} = 6.5$

$p^*K_{\text{Cl}^-}^{\text{int}} = 4.1$
extrapolated points for given $\alpha$ values, and then extrapolating these curves to $\alpha - \log C = 0$. The $\alpha = 0$ points are obtained as previously described and extrapolated to the $\alpha - \log C = 0$ condition to get the second estimate of the intrinsic constants, $\mathbf{p}_* \mathbf{K}_{K^+}^{\text{int}}$ and $\mathbf{p}_* \mathbf{K}_{\text{Cl}^-}^{\text{int}}$.

A.4 Estimation of Integral Capacitance

The final values which must be defined are the integral capacitances, $C_1$ and $C_2$. A technique for obtaining $C_1$, the inner integral capacitance, has recently been presented by Smit and Holten. This technique utilizes the condition of high electrolyte concentration for which the observed surface charge is dominated by surface complexation reactions. Thus, $\alpha$ is given by

$$\alpha = \frac{N_a}{S \cdot N_s} ([\text{TiO}^\text{-} - K^+] - [\text{TiOH}_2^+ - \text{Cl}^-]) = \frac{\sigma_B}{eN_s}. \quad (A28)$$

From Eqs. A5, A6, A12-A15, and A24, and neglecting the concentrations, $[\text{TiO}^-]$ and $[\text{TiOH}_2^+]$,

$$\mathbf{p}_* Q_{K^+} = \mathbf{p}_* K_{K^+}^{\text{int}} - e(\psi_\alpha - \phi_\beta)/2.3 \ k_B T \quad (A29)$$

and

$$\mathbf{p}_* Q_{\text{Cl}^-} = \mathbf{p}_* K_{\text{Cl}^-}^{\text{int}} - e(\psi_\alpha - \phi_\beta)/2.3 \ k_B T \quad (A30)$$

where

$$\mathbf{p}_* Q_{K^+} = pH - \log \left(\frac{\alpha}{1 - \alpha}\right) + \log \gamma_+ [K^+] \quad (A31)$$
\[ p^{*}Q_{Cl^-} = pH - \log \left( \frac{\alpha}{1 - \alpha} \right) - \log \gamma_{+} [Cl^-] \]  \hspace{1cm} (A32)

and \( \gamma_{+} \) is the mean ion activity coefficient of the electrolyte.

Differentiating Eqs. A31 and A32 with respect to \( \alpha = \sigma_{\beta}/\sigma_{\beta} \) and substituting for \( (\psi_{\beta} - \psi_{\beta}) \) using Eq. A3:

\[ \frac{d(p^{*}Q_{K^+})}{d\alpha} = -\frac{eN_{S}}{2.3} \frac{d\ln(\gamma_{+}/\gamma_{-+})}{d\sigma_{\beta}} - \frac{e^{2}N_{S}}{2.3 k_{B}T C_{1}} \frac{d\sigma_{\beta}}{d\sigma_{\beta}} \]  \hspace{1cm} (A33)

and

\[ \frac{d(p^{*}Q_{Cl^-})}{d\alpha} = -\frac{eN_{S}}{2.3} \frac{d\ln(\gamma_{-+}/\gamma_{\circ})}{d\sigma_{\beta}} - \frac{e^{2}N_{S}}{2.3 k_{B}T C_{1}} \frac{d\sigma_{\beta}}{d\sigma_{\beta}} \]  \hspace{1cm} (A34)

where \( \gamma_{-+} \) refers to a positive ion bound to the negative surface site, \( TiO^{2-}K^+ \), \( \gamma_{+-} \) to a negative ion bound to a positive surface site, \( TiOH^{+}-Cl^- \), and \( \gamma_{\circ} \) to the neutral site, \( TiOH \).\(^{72}\)

Figure A4 shows the plot of \( p^{*}Q_{K^+} \) and \( p^{*}Q_{Cl^-} \) versus \( \alpha \) for \( TiO_2 \) A. Several possible explanations for the linear behavior exist; the one usually assumed is that \( d\sigma_{\beta}/d\sigma_{\beta} = 1 \) and the ratio \( \gamma_{\circ}/\gamma_{+-} \) (or \( \gamma_{+}/\gamma_{\circ} \)) is nearly independent of \( \sigma_{\beta} \), with \( C_{1} \) independent of \( \sigma_{\beta} \). These assumptions are the most reasonable\(^{72}\) and were also the assumptions made by Davis, et al.\(^{69}\) Thus, the slope is given by

\[ \text{slope} = \frac{e^{2}N_{S}}{2.3 k_{B}T C_{1}} = 33.59/C_{1} \text{ at 298 K.} \]  \hspace{1cm} (A35)

The slopes for \( \alpha < 0 \), where \( Cl^- \) adsorption dominates, are 26.3
Figure A4. Determination of the inner integral capacitance, $C_1$, from the plot of $p^*Q_{Cl^-}$ and $p^*Q_{K^+}$ as a function of fractional surface charge, $\alpha$, for TiO$_2$ A in aqueous KCl solutions ($N_s = 13.0$ nm$^{-2}$).
(correlation coefficient \(cc\) = .989) for 0.01 M KCl and 24.3 
\(cc = .998\) for 0.1 M KCl; the average slope yields \(C_1 = 132.7\) 
\(\mu F/cm^2\). The slopes for \(\alpha > 0\), where \(K^+\) adsorption dominates, are 
21.1 \(cc = .995\) for 0.01 M and 18.9 \(cc = .998\) for 0.1 M KCl; the 
average slope yields \(C_1 = 167.8\) \(\mu F/cm^2\). The significance of the 
capacitance values is discussed in Chapter 4.

A.5 MINEQL Results

The calculated results from MINEQL using the estimated 
parameters (given in Fig. A5) are listed in Tables A2, A3 and A4.* 
Figure A5 shows the graphical representation of these results and 
also gives the experimental surface charge and \(\zeta\)-potential. The 
poor agreement shown in Fig. A5 is discussed in Chapter 4, 
§ 4.4.1.

A.6 Supplemental Results

This section contains the figures not given in the text, 
although the results were discussed. Figures A6 through A8 are the 
extrapolation plots for TiO\(_2\) A, where \(N_s = 16.0\) \(H^+/nm^2\). The 
intrinsic ionization constants were determined in Fig. A6, the 
intrinsic complexation constants in Fig. A7, and CI in Fig. A8.

* Calculations performed by R. O. James, Eastman Kodak Co., 
Rochester, NY
Figure A5. The surface charge density (open points) and \( \zeta \)-potential (solid points) for TiO\(_2\) A in 10\(^{-1}\), 10\(^{-2}\), and 10\(^{-3}\) M KCl solutions. Solid lines represent the same properties calculated by MINEQL for the surface ionization and complexation model using the parameters shown in the figure.
Table A2
Calculated Results from MINEQL for $10^{-3}$M KCl
Concentration ($\psi$ in mV and $\sigma$ in $\mu$C/cm$^2$)

<table>
<thead>
<tr>
<th>pH</th>
<th>$\phi_o$</th>
<th>$\phi_\beta$</th>
<th>$\phi_d$</th>
<th>$\sigma_o$</th>
<th>$\sigma_\beta$</th>
<th>$\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>48.6</td>
<td>45.8</td>
<td>33.1</td>
<td>0.471</td>
<td>-0.215</td>
<td>-0.256</td>
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<tr>
<td>4.5</td>
<td>27.6</td>
<td>26.4</td>
<td>19.3</td>
<td>0.213</td>
<td>-0.071</td>
<td>-0.142</td>
</tr>
<tr>
<td>5.0</td>
<td>7.4</td>
<td>7.1</td>
<td>5.2</td>
<td>0.055</td>
<td>-0.017</td>
<td>-0.038</td>
</tr>
<tr>
<td>5.5</td>
<td>-12.6</td>
<td>-12.2</td>
<td>-8.9</td>
<td>-0.077</td>
<td>0.012</td>
<td>0.065</td>
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<td>-31.6</td>
<td>-23.0</td>
<td>-0.231</td>
<td>0.059</td>
<td>0.172</td>
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<td>6.5</td>
<td>-54.0</td>
<td>-51.3</td>
<td>-36.8</td>
<td>-0.473</td>
<td>0.183</td>
<td>0.289</td>
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<td>7.0</td>
<td>-76.1</td>
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<td>-49.8</td>
<td>-0.932</td>
<td>0.513</td>
<td>0.418</td>
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<tr>
<td>7.5</td>
<td>-99.4</td>
<td>-88.7</td>
<td>-61.1</td>
<td>-1.82</td>
<td>1.26</td>
<td>0.553</td>
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<tr>
<td>8.0</td>
<td>-124.</td>
<td>-104.</td>
<td>-70.4</td>
<td>-3.28</td>
<td>2.60</td>
<td>0.683</td>
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<td>8.5</td>
<td>-149.</td>
<td>-118.</td>
<td>-77.9</td>
<td>-5.29</td>
<td>4.49</td>
<td>0.805</td>
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<td>9.0</td>
<td>-175.</td>
<td>-130.</td>
<td>-84.2</td>
<td>-7.65</td>
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<td>0.920</td>
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<td>9.5</td>
<td>-202.</td>
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<td>-89.9</td>
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<td>9.14</td>
<td>1.04</td>
</tr>
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<td>10.0</td>
<td>-228.</td>
<td>-153.</td>
<td>-95.5</td>
<td>-12.7</td>
<td>11.5</td>
<td>1.16</td>
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Table A3
Calculated Results from MINEQL for $10^{-2}$M KCl
Concentration ($\psi$ in mV and $\sigma$ in $\mu$C/cm$^2$)

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<tr>
<th>pH</th>
<th>$\phi_o$</th>
<th>$\phi_\beta$</th>
<th>$\phi_d$</th>
<th>$\sigma_o$</th>
<th>$\sigma_\beta$</th>
<th>$\sigma_d$</th>
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<td>4.5</td>
<td>23.2</td>
<td>18.4</td>
<td>8.6</td>
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<td>-0.612</td>
<td>-0.197</td>
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<td>6.1</td>
<td>4.8</td>
<td>2.3</td>
<td>0.215</td>
<td>-0.163</td>
<td>-0.052</td>
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<tr>
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<td>-8.8</td>
<td>-4.1</td>
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<td>0.117</td>
<td>0.094</td>
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<td>-10.7</td>
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<td>0.245</td>
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<td>1.36</td>
<td>0.400</td>
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<td>2.90</td>
<td>0.541</td>
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<td>-27.5</td>
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<td>0.660</td>
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<td>-68.9</td>
<td>-31.2</td>
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<td>0.757</td>
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<td>-12.2</td>
<td>11.3</td>
<td>0.837</td>
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<td>22.6</td>
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</table>
Table A4

Calculated Results from MINEQL for $10^{-1}$M KCl
Concentration ($\psi$ in mV and $\sigma$ in $\mu$C/cm$^2$)

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<th>pH</th>
<th>$\psi_0$</th>
<th>$\psi_B$</th>
<th>$\psi_d$</th>
<th>$\sigma_0$</th>
<th>$\sigma_B$</th>
<th>$\sigma_d$</th>
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<td>5.98</td>
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<td>-0.230</td>
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<td>4.5</td>
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<td>1.9</td>
<td>3.28</td>
<td>-3.14</td>
<td>-0.136</td>
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<tr>
<td>5.0</td>
<td>8.2</td>
<td>1.8</td>
<td>0.4</td>
<td>1.08</td>
<td>-1.05</td>
<td>-0.029</td>
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<td>-1.2</td>
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<td>0.087</td>
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<td>0.305</td>
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<td>-9.4</td>
<td>-28.2</td>
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<td>0.681</td>
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<td>-9.9</td>
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<td>31.8</td>
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Figure A6. Double extrapolation plot for determination of $pK^{\text{int}}_{a_1}$ and $pK^{\text{int}}_{a_2}$ for TiO$_2$ A in aqueous KCl solutions ($N_s = 16.0$ nm$^{-2}$).
Figure A7. Double extrapolation plot for determination of $p^* K^\text{int}_{K^+}$ and $p^* K^\text{int}_{Cl^-}$ for TiO$_2$ A in aqueous KCl solutions ($N_s = 16.0$ nm$^{-2}$).
Figure A8. Determination of the inner integral capacitance, $C_1$, from the plot of $p^*Q_{Cl^-}$ and $p^*Q_{K^+}$ as a function of fractional surface charge, $\alpha$, for TiO$_2$ A in aqueous KCl solutions ($N_s = 16.0$ nm$^{-2}$).
APPENDIX B

Surface Studies: Gas Adsorption and Dehydration

B.1 Gas Adsorption

The accuracy of the absolute surface charge densities measured for the TiO₂ powders depends heavily on the accuracy of the measured specific surface areas; the interpretation of surface charge behavior requires knowledge of the surface structure (i.e., crystallinity and porosity). Thus, the surface area was measured by the BET method³⁰ and pore structure was investigated by nitrogen adsorption/desorption using the αₛ-method developed by Sing.²⁶,²⁷,³³ The methods and the data for several TiO₂ powders are given below.

B.1.1 Surface Area Determination

Specific surface areas were obtained for alcohol washed, water washed, and heat treated powders using a multipoint BET method.³⁰,³¹ A detailed description of this method is given by Gregg and Sing³². The specific surface area, S, is calculated from the monolayer capacity, Xₘ, and the cross-sectional area of the adsorbate, Aₙ. The value Aₙ = 16.2 Å² per N₂ molecule is usually used, assuming dense random packing in the nitrogen monolayer.
However, localization of molecules in the monolayer and greater than monolayer coverage can cause variations in measured surface areas.\(^\text{34}\)

The monolayer capacity is determined from the BET equation:

\[
\frac{P}{X(P_\infty - P)} = \frac{1}{X_m C} + \frac{C-1}{X_mC} \frac{P}{P_\infty}, \tag{B1}
\]

where \(P\) is the equilibrium pressure of the adsorbate, \(P_\infty\) is the saturated pressure of the adsorbate at the temperature of adsorption, \(C\) is a constant which is a function of the heats of adsorbate adsorption and of condensation, and \(X\) is the amount (weight) of gas adsorbed.\(^\text{31}\)

The value of \(X_m\) and \(C\) are calculated from the slope, \(M\), and the intercept, \(I\), of the straight line obtained by plotting \(P/X(P_\infty - P)\) as a function of relative pressure \(P/P_\infty\). The quantities \(X_m\) and \(C\) are given as

\[
X_m = \frac{1}{M + I}, \tag{B2}
\]

and

\[
C = \frac{M}{I} + 1. \tag{B3}
\]

The assumed range of validity for the BET equation and linearity in the data is for relative pressures in the range \(0.05 < P/P_\infty < 0.35;\)\(^\text{31}\) however, the range of linearity is often much smaller and should be determined experimentally before the slope and intercept are calculated.\(^\text{25}\)
The specific surface area is obtained from

\[
S_{\text{BET}} = \frac{X N_a A_{cs}}{M_a W_a},
\]

(B4)

where \( N_a \) is Avagadros number, \( M_a \) is the molecular weight of nitrogen (\( M_a = 28.0 \)), and \( W \) is the adsorbent mass.

Although Eq. B1 is based on a simplified adsorption model, it fits many experimental adsorption isotherms very well over the valid \( P/P_0 \) range.\(^{25} \) Furthermore, the use of \( A_{cs} = 16.2 \, \text{Å}^2 \) for \( N_2 \) results in BET areas for non-porous solids which are in reasonable agreement with areas calculated from the mean particle size, \( \bar{d} \), and density \( \rho \), where\(^{31} \)

\[
S = \frac{6}{\rho \bar{d}}
\]

(B5)

Experimental

Nitrogen adsorption was measured using a Quantasorb adsorption system (Quantachrome Corp) for ethanol washed, water washed, and heat treated powders. The effect of these treatments on the surface structure was mentioned in Section 3.3.1, and is briefly reviewed. The water washing procedure caused the formation of small, crystalline precipitates on the amorphous particles, as was shown in Fig. 3.3 (\( TiO_2 \) B). Upon aging these powders in deionized water, the precipitates coarsened and became less defined (\( TiO_2 \) A). Conversely, ethanol washing followed by vacuum drying prevented the
formation of the precipitates; hence, clean amorphous surfaces were
generated. Finally heat treatment caused crystallization of these
particles into anatase or rutile, depending on the temperature,
each of which had smooth, non-porous surfaces. The crystalline
powder used in these experiments was formed from TiO$_2$ A by heating
at 620°C for 20 minutes; X-ray diffraction gave sharp anatase
peaks. These powders formed the basis of the surface studies and
subsequent investigations.

Prior to measurements, the powders were dispersed in water to
fully hydrate the surface (especially the ethanol washed and heat
treated powders), dried at room temperature, and outgassed in
vacuum. The proper temperature for outgassing TiO$_2$ has been
reported to be less than 30°C (for about 12-24 hours);$^{25,35,36}$
these conditions were sufficient to remove hydrogen-bonded,
physically adsorbed water molecules, but did not alter chemisorbed
molecular water and hydroxyl groups. Outgassing at higher
temperatures removed molecular water and enhanced N$_2$ adsorption
through specific interactions, thus resulting in excess calculated
surface area.$^{25}$ This result was confirmed by measuring the BET
area of an ethanol washed powder after outgassing at 30, 75, and
160°C, as shown in Fig. B1 and Table B1. Outgassing at 75°C and
160°C resulted in surface areas that were in excess by 22% and 40%,
respectively. Yates$^{25}$ reported a similar increase in the measured
surface areas for rutile with higher outgassing temperatures; the
BET constant also increased, indicating stronger N$_2$ adsorption.
Table B1

The Effect of Outgassing Temperature on BET Area for an Amorphous TiO$_2$ Powder

<table>
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<tr>
<th>Outgas T</th>
<th>$S_{BET}$(m$^2$/g)</th>
<th>BET Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>9.29</td>
<td>83.3</td>
</tr>
<tr>
<td>75°C</td>
<td>11.32</td>
<td>53.2</td>
</tr>
<tr>
<td>160°C</td>
<td>13.0</td>
<td>188.1</td>
</tr>
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</table>

Figure B1. Nitrogen adsorption isotherms for an amorphous TiO$_2$ powder outgassed at 30°C, 75°C, and 160°C for ≥ 12 hours. The adsorbed volume and BET surface area increased as outgassing temperature was increased.
Thus, outgassing conditions of 25°C for > 12 hours were employed for the remaining determinations.

Results and Discussion

Figure B2 shows the volume of N₂ adsorbed as a function of P/P₀ onto the four powders, where a second amorphous powder was used here and in § B.1.2 (different batch than that used to test outgassing conditions). The calculated areas are given in Table B2. The surface area for the anatase sample (5.41 m²/g) gave an equivalent spherical diameter of 0.36 µm. The calculated average diameter was 0.37 µm, which was determined from the measured diameter (SEM) of 0.40 µm for the amorphous powder by correcting for a 20% volume reduction upon crystallization. Thus the anatase particles have a smooth, non-porous surface. Slightly higher surface area was measured for the amorphous powder (d = 0.4 µm), indicating some surface roughness. Conversely, the surface areas of TiO₂ A and TiO₂ B were much higher than for the anatase; these data are the result of the precipitate surface coating. The presence of the surface coating and the high surface areas may cause significant errors in the BET analysis, thus a more general technique must be used which employs complete adsorption isotherms.
Figure B2. Nitrogen adsorption isotherms (BET) for TiO₂ A, TiO₂ B, an amorphous powder, and the anatase reference powder.
Table B2

The BET Surface Areas for the TiO₂ Powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>$S_{\text{BET}}$ (m²/g)</th>
<th>BET Constant</th>
<th>Equivalent Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ A</td>
<td>185.6</td>
<td>53.6</td>
<td>104 Å</td>
</tr>
<tr>
<td>TiO₂ B</td>
<td>304.0</td>
<td>116.5</td>
<td>64 Å</td>
</tr>
<tr>
<td>Amorphous TiO₂*</td>
<td>8.14</td>
<td>40.4</td>
<td>0.24 μm</td>
</tr>
<tr>
<td>Anatase</td>
<td>5.41</td>
<td>98.2</td>
<td>0.36 μm</td>
</tr>
</tbody>
</table>

* Different amorphous powder than used for Fig. B1
B.1.2 Surface Porosity Determination

Pores in adsorbents are divided into three categories on the basis of different adsorption characteristics and average pore diameter, \( d_p \): 25

- macropores - \( d_p > 200 \text{ Å} \)
- mesopores - \( 20 \text{ Å} < d_p < 200 \text{ Å} \)
- micropores - \( d_p < 20 \text{ Å} \).

For macropores, the normal monolayer-multilayer adsorption is accompanied by capillary condensation leading to enhanced adsorption at high \( P/P_o \) and often to adsorption/desorption hysteresis. Mesopores give similar adsorption characteristics to macropores, but capillary condensation and hysteresis occur at lower \( P/P_o \). Micropores cause rapid and enhanced adsorption at very low \( P/P_o \) as gas molecules interact simultaneously with several surface atoms. 25

The determination method for surface porosity used in this study was the \( \alpha_s \) - method developed by Sing; 26,27 this method has been successfully employed to study porosity on many solid surfaces. 32-34,37 Porosity is assessed by plotting the adsorption isotherm in a reduced form; the volume of adsorbed \( \text{N}_2 \) at a \( P/P_o \), \( V_{ads} \), is plotted against \( V_s/V_x (= \alpha_s) \), where \( V_s \) is the volume adsorbed by a non-porous reference at the same \( P/P_o \) and \( V_x \) is the volume adsorbed by the reference at a selected value of \( P/P_o \). Although \( \alpha_s = 1 \) can be put at any relative pressure, it is usually
located at \( P/P_0 = 0.4 \) because both monolayer coverage and micropore filling occur for \( P/P_0 \lesssim 0.4 \), whereas condensation and hysteresis occur for \( P/P_0 \gtrsim 0.4 \). Furthermore, higher precision is achieved by locating \( \alpha_s = 1 \) in the middle of the range.\(^{27}\)

The most important consideration in using the \( \alpha_s \) technique is the choice of the non-porous reference solid. This solid must have a smooth surface because all porosity evaluations are relative to the standard. In addition, the standard should be of the same chemical nature so that adsorption differences are due only to porosity.\(^{25}\)

The interpretation of the \( \alpha_s \) plots, using the appropriate reference, has been discussed by Sing.\(^{26,27,33}\) Four types of adsorption behavior are illustrated by the \( \alpha_s \) plots in Fig. B3. Curve A represents normal monolayer-multilayer adsorption on a non-porous surface or one with large pores (\( d_p > 200 \text{ Å} \)) and is linear because the adsorption isotherm has an identical shape of the reference isotherm. Curve B shows normal adsorption followed by capillary condensation into mesopores.\(^{27}\) Curve C is the form of the \( \alpha_s \) plot given by a Langmuir type isotherm; the first linear region is due to micropore filling and the second linear region corresponds to adsorption onto the external surface.\(^{26}\) Finally, curve D, where the multilayer region extrapolates back to the origin and deviation occurs at low \( P/P_0 \), represents stronger adsorption of the \( \text{N}_2 \) onto the surface than on the reference solid.\(^{25}\) In practice, several features may be exhibited
Figure B3. Interpretation of the $\alpha_s$ plots for four types of adsorption behavior: (A) normal monolayer-multilayer adsorption on a non-porous surface; (B) normal adsorption followed by capillary condensation into mesopores; (C) micropore filling (first linear region) and adsorption onto the external surface (second linear region) and; (D) stronger adsorption of N$_2$ onto the surface relative to the reference surface.
simultaneously, thus the $\alpha_s$ plots could lead to erroneous results. However, analysis of the adsorption/desorption isotherms and hysteresis often clarifies the interpretations of $\alpha_s$ plots.

The slope of the linear part of the $\alpha_s$ plot, taken through the origin, is proportional to the surface area, $S_s$. Empirical relations between the slope and the surface area have been established for SiO$_2$ and Al$_2$O$_3$. For example, the equation for SiO$_2$ is

$$S_s = 2.289 \frac{dV}{d\alpha_s}$$

(B6)

where $V$ is in cm$^3$ (STP). The relation for TiO$_2$ was determined from the adsorption isotherm of the anatase reference powder.

Experimental

Complete nitrogen adsorption and desorption isotherms were measured using the Quantasorb adsorption system; nitrogen concentration in the He-N$_2$ mixture was precisely controlled using the Quantachrome mass flow controller mixing system. High purity helium and nitrogen gases (Matheson) were employed.

The samples were outgassed at 25°C in vacuum for at least 12 hours. Adsorption isotherms were obtained by equilibrating the sample with mixtures having the desired $P/P_0$ at room temperature and then adsorbing N$_2$ from the mixtures at 77K. The volumes of N$_2$ desorbed as the temperature was increased to 298K defined the adsorption isotherm. The desorption isotherm was generated by
first saturating the surface using the pure adsorbate at \( T = 77K \), and then equilibrating the surface with the desired mixtures at 77K. The volumes of \( \text{N}_2 \) desorbed upon returning to 298K defined the desorption isotherm. Adsorption and desorption isotherms were measured for the powders discussed in the previous section (anatase, amorphous \( \text{TiO}_2 \), \( \text{TiO}_2 \) A, and \( \text{TiO}_2 \) B).

Results and Discussion

The adsorption isotherm for the reference anatase powder is given in Fig. B4; the adsorption data and the \( \alpha_s \) values for the reference are given in Table B3. The adsorption isotherm agrees well with the isotherms obtained by Parfitt, et al.\(^{39} \), for several anatase powders (e.g. Degussa P25). In addition, as discussed in the previous section, the BET area and the equivalent surface area calculated from the mean particle size agreed within experimental error (~5%), thus the anatase powder is an acceptable adsorption reference. The empirical relation required to calculate surface area, \( S_s \), from the \( \alpha_s \) plots was determined using \( S_{\text{BET}} = 5.41 \text{ m}^2/\text{g} \) and \( V_x (\alpha_s = 1.0) = 2.278 \):

\[
S_s(\text{TiO}_2) = 2.377 \frac{dV}{d\alpha_s}.
\]

The isotherm for the amorphous surface, also shown in Fig. B4, has a similar shape to the reference isotherm. Conversely, the adsorption/desorption isotherms for \( \text{TiO}_2 \) A and \( \text{TiO}_2 \) B, given in Fig. B5, deviate significantly from the normal monolayer-multilayer isotherms of Fig. B4. The hysteresis in the isotherms indicate
Table B3

Nitrogen Adsorption Isotherm and $\alpha_s$ Values for the Anatase Reference Solid

<table>
<thead>
<tr>
<th>P/Po</th>
<th>V(cm³/g)</th>
<th>$\alpha_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>1.127</td>
<td>0.495</td>
</tr>
<tr>
<td>0.05</td>
<td>1.217</td>
<td>0.534</td>
</tr>
<tr>
<td>0.1</td>
<td>1.401</td>
<td>0.615</td>
</tr>
<tr>
<td>0.15</td>
<td>1.467</td>
<td>0.644</td>
</tr>
<tr>
<td>0.2</td>
<td>1.651</td>
<td>0.725</td>
</tr>
<tr>
<td>0.3</td>
<td>1.908</td>
<td>0.838</td>
</tr>
<tr>
<td>0.4</td>
<td>2.278</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>2.554</td>
<td>1.122</td>
</tr>
<tr>
<td>0.6</td>
<td>2.828</td>
<td>1.242</td>
</tr>
<tr>
<td>0.7</td>
<td>3.351</td>
<td>1.471</td>
</tr>
<tr>
<td>0.8</td>
<td>4.048</td>
<td>1.777</td>
</tr>
<tr>
<td>0.9</td>
<td>5.667</td>
<td>2.488</td>
</tr>
</tbody>
</table>

Figure B4. Adsorption isotherms for the anatase reference powder and an amorphous TiO₂ powder. Open points are for the adsorption isotherm and solid points are for the desorption isotherm.
Figure B5. Adsorption (open points)/desorption (solid points) isotherms for TiO$_2$ A, TiO$_2$ B and the amorphous powder. The hysteresis in the isotherms for TiO$_2$ A and TiO$_2$ B indicate capillary condensation.
capillary condensation into mesopores; the approximate pore radius, \( r_K \), can be calculated using the Kelvin equation,

\[
\ln \frac{P}{P_0} = \frac{-2\gamma V_m}{R T r_K} \cos \Theta,
\]

where \( \gamma \) is the surface tension of nitrogen at 77K (8.85 erg/cm²), \( V_m \) is the molar volume (34.7 cm³/mole), and \( \Theta \) is the wetting angle. Assuming \( \Theta = 0^\circ \), the radius is given by

\[
r_K = \frac{4.146}{\log(P_0/P)}.
\]

Hysteresis for TiO₂ A in the range 0.45 < \( P/P_0 \) < 0.9 corresponds to pore diameters ranging from approximately 15 to 180 Å. The range for TiO₂ B, 0.35 < \( P/P_0 \) < 0.75, corresponds to approximate diameters of 10 to 65 Å. These calculated pore diameters agree very well with the scale of observed surface roughness generated by the surface coating of fine precipitates; as shown in Figs. 3.3 and 3.4. The coarsened features on the TiO₂ A particles and interprecipitate spacing for the TiO₂ B particles evidently function as capillaries for nitrogen condensation.

Fig. B6 shows the \( \alpha_s \) plots for the amorphous powder, TiO₂ A, and TiO₂ B. As expected, the data for the amorphous powder forms a straight line; the surface area calculated from the slope \((dV/d\alpha_s = 3.396)\) is \( S = 8.07 \text{ m}^2/\text{g} \), which is within experimental error of the BET area, \( S_{\text{BET}} = 8.14 \text{ m}^2/\text{g} \). The \( \alpha_s \) plot for TiO₂ A shows the expected deviation from linearity for capillary condensation; the slope of the linear region, extrapolated through
Figure B6. The $a_s$ plots for the amorphous powder, TiO$_2$ A and TiO$_2$ B. The positive deviation from linearity observed for TiO$_2$ A and TiO$_2$ B confirms capillary condensation. The micropore volume, $V_p$, for TiO$_2$ B is given by the intercept $V'$, where $V_p = 0.00156$ $V'$. 
the origin, yields \( S_s = 185.9 \text{ m}^2/\text{g} \) which is the same as the BET area \( S_s = 185.6 \text{ m}^2/\text{g} \).

The \( \alpha_s \) plot for TiO\(_2\) B has two linear regions and deviation from linearity in the central \( \alpha_s \) range defined by the hysteresis \( (1.0 \leq \alpha_s \leq 1.4) \); this plot indicates a more complicated behavior than the previous powders. A similar \( \alpha_s \) plot was reported by Bhambhani, et al.\(^{37}\), for a mixture of SiO\(_2\) powders, one having significant microporosity but no other detectable porosity and the second having only mesoporosity. Therefore, the probable adsorption processes occurring for TiO\(_2\) B in the first linear region \( (\alpha_s < 0.9) \) include micropore filling and normal monolayer adsorption, and that in the second linear region \( (\alpha_s \approx 1.4) \) is normal multilayer adsorption onto the external surface. The slope for the first linear region \( (dV/d\alpha_s = 121.3) \) yields a surface area of \( S_s = 288.3 \text{ m}^2/\text{g} \), which is about 5\% lower than the BET area of 304 \text{ m}^2/\text{g}. Since normal monolayer-multilayer adsorption does not occur for this powder, the calculated surface area has an unclear meaning.\(^{37}\)

The presence of mesopores was expected for the surface coated with fine (50-100 Å) precipitates; however, microporosity in the underlying amorphous surface is not consistent with the results obtained for the ethanol washed, amorphous powder. Although the powder handling and outgassing procedures may have collapsed a porous, hydrated surface during dehydration, as has been observed for several amorphous iron oxides\(^{40}\) and silicas,\(^{25}\) all powders in
this study were outgassed under identical conditions. Thus the observed "microporosity" probably originates at the amorphous surface/precipitate interface and at the contact points between precipitates. The micropore volume calculated from the intercept of the second linear region in Fig. B6, $V'$, using

$$ V_p = 0.00156 \, V' \quad \text{(B10)} $$

was 0.19 cc/g (STP). The significance of surface porosity with respect to interfacial electrochemistry is discussed in the text (Section 4.4.1).

B.2 Isothermal Dehydration for Chemisorbed Water Determination

The surface area and pore structure determinations, discussed in Appendix B.1, are necessary to accurately calculate the absolute surface charge density. However, proper interpretation requires additional data on the surface site density of ionizable protons, $N_s$. Site densities, equal to twice the density of chemisorbed water molecules, have been experimentally determined for many oxide powders using tritium exchange, IR spectroscopy, and isothermal dehydration. \cite{41} Although techniques based on dehydration are usually not as reliable as those based on tritium exchange and IR spectroscopy, they are the easiest to perform. In addition, the ease of removal of physically adsorbed water molecules on TiO$_2$ as compared to chemisorbed molecules and hydroxyl groups\cite{25} enhances the applicability of dehydration techniques. Thus, isothermal
dehydration and weight loss measurements were used in this study for chemisorbed water determination.

Yates\textsuperscript{25} used room temperature outgassing for rutile to remove physically adsorbed water molecules, followed by outgassing at higher temperatures to constant weight. Vacuum outgassing for 12 hours (T = 25°C) was sufficient to remove the physically adsorbed water; prolonged outgassing (i.e. t > 35 hrs) caused the slow removal of chemisorbed water molecules. Outgassing at temperatures of approximately 380°C was necessary to remove all but the most tightly bound hydroxyl groups; these groups comprised a small percentage of the chemisorbed water.\textsuperscript{25} Jones and Hockey\textsuperscript{35} employing dehydration and IR spectroscopy, observed similar conditions for complete removal of chemisorbed water. The resultant densities of chemisorbed water reported by Yates\textsuperscript{25} had a range of 5.3 to 8 H\textsubscript{2}O/nm\textsuperscript{2} (N\textsubscript{s} = 10.6 - 16 nm\textsuperscript{-2}) and an average value of 6.5 H\textsubscript{2}O/nm\textsuperscript{2} (N\textsubscript{s} = 13.0 nm\textsuperscript{-2}). These values compared favorably to his tritium exchange results, which had a range of 5.2 - 8 H\textsubscript{2}O/nm\textsuperscript{2} and an average value of 6.2 H\textsubscript{2}O/nm\textsuperscript{2} (N\textsubscript{s} = 12.4/nm\textsuperscript{2}).\textsuperscript{25,42} Day, et al.\textsuperscript{36}, using a water adsorption technique, measured a chemisorbed water density of 6.7 H\textsubscript{2}O/nm\textsuperscript{2}. These values compare well with the theoretically predicted value for rutile\textsuperscript{35} of 6.1 H\textsubscript{2}O/nm\textsuperscript{2}. Although quantitative predictions have not been made for anatase, the estimated water densities are the same as for rutile.\textsuperscript{25}
Experimental

The isothermal dehydration experiments were performed using a Netzsch Simultaneous Thermal Analysis System (STA 429); the accuracy of the weight measurements was ± 0.03 mg. The powders were obtained by sedimenting portions of the stock dispersions, air drying until no water was visible, and then vacuum drying (T = 30°C) for two hours. The powder was stored in plastic containers at ambient conditions and was allowed to equilibrate with atmospheric moisture.

Dehydration experiments were conducted under flowing dry nitrogen at temperatures ranging from 30° to 114°C. The amount of chemisorbed water present on the powder was determined by locating the transition point between desorption of physical water and chemical water and then measuring the weight loss at ~380°C. Since physically adsorbed water is more easily removed than chemical (coordinated) water,25 the dehydration curves (weight loss versus time) showed a change in slope in the transition region. The transition point was thus located by the intersection of lines drawn through the linear segments of the curve corresponding to desorption of physical water and of chemical water.

Results and Discussion

The dehydration results for TiO₂ A (S_BET = 185.6 m²/g) and TiO₂ B (S_BET = 304 m²/g) at 30°C, given in Fig. B7, show a significant difference in the desorption kinetics of physical
Figure B7. Weight loss as a function of time for the isothermal (T = 30°C) dehydration of TiO$_2$ A and TiO$_2$ B.
water. TiO₂ A continues to slowly lose weight after 40 hours, whereas TiO₂ A has lost most of the physically adsorbed water after 21 hours. Both of these powders lost water much slower than Yates' rutile, for which all physically adsorbed water was removed after 12 hours at 25°C (constant sample weight).²⁵ Although this slow desorption and stronger apparent bonding of physical water is not well understood, it may be the result of the surface structure and capillary condensation. Longer times (t > 40 hours) would be required to approach constant weight for TiO₂ A; however, since coordinated water molecules would also be removed,²⁵ the results would be invalid.

Figure B8 shows the weight loss for TiO₂ A as a function of time at temperatures of 52°C, 84°C and 103°C; Table B4 gives the total weight losses, the extrapolated transition points, and the densities of chemisorbed water. The resultant site densities ranged from 16.2 H⁺/nm² at 52°C to 13.1 H⁺/nm² at 103°C. The decrease in Nₕ with increasing temperature again indicates that the physically adsorbed water is held more tightly on TiO₂ A than on a smooth crystalline surface. Since these variations introduce uncertainty in the actual site density, a value must be assumed for use in the electrochemical models. The value of Nₕ = 13.0 nm⁻² was the closest to the reported values,²⁵,⁴¹ hence it was used for the analysis discussed in Section 4.4.1. In addition, Nₕ = 16.0 nm⁻² was used to test model sensitivity.
Table B4

Isothermal Dehydration Results and Surface Site Densities

<table>
<thead>
<tr>
<th>Powder</th>
<th>Temp</th>
<th>Initial Mass (mg)</th>
<th>Total Wt. Loss (mg)</th>
<th>Transition Point (mg)</th>
<th>Chemisorbed Water (H₂O/nm²)</th>
<th>Nₛ (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ A</td>
<td>52</td>
<td>219.7</td>
<td>20.1</td>
<td>10.3</td>
<td>8.10</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>84</td>
<td>226.7</td>
<td>20.3</td>
<td>11.3</td>
<td>7.15</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>103</td>
<td>189.2</td>
<td>18.2</td>
<td>11.3</td>
<td>6.57</td>
<td>13.1</td>
</tr>
<tr>
<td>TiO₂ B</td>
<td>82</td>
<td>190.8</td>
<td>27.6</td>
<td>17.0</td>
<td>6.11</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>202.3</td>
<td>41.5</td>
<td>30.3</td>
<td>6.10</td>
<td>12.2</td>
</tr>
</tbody>
</table>

* Surface saturated with H₂O prior to dehydration

Figure B8. Isothermal dehydration, expressed as weight loss versus time, for TiO₂ A at the temperatures of 52°C, 84°C, and 103°C.
Weight loss for TiO$_2$ B as a function of time at temperatures of 82° and 114°C is shown in Fig. B9; the corresponding data and site densities are given in Table B4. Although the total weight loss for the two conditions differ significantly, due to equilibration of the 114°C sample with water saturated air prior to dehydration, the density of chemisorbed water is the same. That is, no variation in $N_s$ was found for TiO$_2$ B. This behavior, unlike that for TiO$_2$ A, was not unexpected because of the previously noted near normal desorption rate for physical water at 30°C. Thus the site density obtained for TiO$_2$ B, $N_s = 12.2$ H$^+$/nm$^2$, should be valid. This value, equal to the theoretically predicted value for a crystalline TiO$_2$ surface, was used in the electrochemical model discussed in § 4.4.1.
Figure B9. Isothermal dehydration, expressed as weight loss versus time, for TiO$_2$ B at the temperatures of 82° and 114°C.
Appendix C

Colloid Stability Determination for Monodispersed Powders

Using Photon Correlation Spectroscopy

C.0 Preamble

This Appendix, submitted for publication in J. Colloid Interface Sci., provides a detailed discussion of the experimental technique developed to measure dispersion stability and the analysis procedure employed. Results are given for monodisperse Cr(OH)$_3$, SiO$_2$, and TiO$_2$ and classified montmorillonite clay platelets.

C.1 Introduction

The behavior of aqueous colloidal dispersions of inorganic oxides is an important area in modern experimental and theoretical colloid science. In particular, coagulation rates for colloids have been measured in the past fifty years by a variety of methods, such as direct counting in the ultramicroscope$^{81, 88, 89}$ or in the Coulter counter,$^{90, 91}$ light scattering,$^{92-96}$ and turbidimetry.$^{60, 85, 88}$

During coagulation many different processes occur which can be generalized as the interaction of an $m$-particle aggregate with an $n$-particle aggregate to form an $n + m$ particle aggregate. Most methods of observation are not sufficiently detailed to follow each type of interaction, and thus, complex multirate-constant theories$^{97}$ cannot be verified. However, during the initial stage of
\[ C(\tau) = \langle I^*(K,t) I(K,t + \tau) \rangle \]  \hspace{1cm} (C1)

where \( I \) is the scattered intensity, \( t \) is the time, \( \tau \) is the delay time, and \( K \) is the magnitude of the scattering vector, defined as

\[ K = \left( \frac{4\pi n}{\lambda_0} \right) \sin(\theta/2) \]  \hspace{1cm} (C2)

where \( n \) is the refractive index of the medium, \( \theta \) is the scattering angle, and \( \lambda_0 \) is the incident wavelength of the light measured in vacuum.

In the Gaussian approximation the intensity autocorrelation function is related to the field autocorrelation function, \( g'(\tau) \), by

\[ C(\tau) = 1 + |g'(\tau)|^2 \]  \hspace{1cm} (C3)

where

\[ g'(\tau) = \langle E^*_s(K,t) E_s(K,t + \tau) \rangle \]  \hspace{1cm} (C4)

and \( E_s \) is the scattered electric field. For a suspension of monodisperse, spherical particles \( g'(\tau) \) is given by

\[ g'(\tau) = \exp(-\Gamma \tau) \]  \hspace{1cm} (C5)

where \( \Gamma = D K^2 \). The translational z-averaged diffusion coefficient of the particle, \( D \), is related to the hydrodynamic radius, \( R_h \), by the Stokes-Einstein equation:

\[ D = \frac{k_B T}{6\pi\eta R_h} \]  \hspace{1cm} (C6)

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \eta \) is the medium viscosity.
Polydisperse systems can be analyzed by replacing Eq. C5 with

\[ g'(\tau) = \int_0^\infty G(\tau) \exp(-\tau \tau) \, d\tau \]  \hspace{1cm} (C7)

and

\[ \int_0^\infty G(\tau) \, d\tau = 1 \hspace{1cm} (C8) \]

where \( G(\tau) \) is the normalized distribution function in \( \tau \) space.

Thus, the autocorrelation function theoretically contains complete information about the particle size distribution.

One technique of analyzing PCS data is the method of cummulants, which expands the right hand side of Eq. C7 in a Taylor series about the mean, \( \bar{\tau} \):

\[ \ln|g'(\tau)| = -\bar{\tau} \tau + (1/2!)\mu_2 \tau^2 - (1/3!)\mu_3 \tau^3 + \ldots \]  \hspace{1cm} (C9)

The cummulants (\( \mu_2, \mu_3, \ldots \)) are related to the moments of the particle size distribution; however, in practice only the first and second moments (\( \bar{\tau} \) and \( \mu_2 \)) can be reliably obtained. The ratio \( \mu_2/\bar{\tau}^2 \) is the variance of the distribution function \( G(\tau) \) and is a measure of the polydispersity of the suspension.

In the coagulation experiments, \( \bar{\tau} \) and \( \mu_2/\bar{\tau}^2 \) are obtained as a function of time; the value of \( \bar{\tau} \) is converted to a mean hydrodynamic radius, \( \bar{R}_h \), using Eq. C6. During the early stage of coagulation, the mean hydrodynamic radius is dependent on the fraction of doublets, \( X \), and the fraction of singlets, (1-\( X \)): 
\[ \tilde{R}_h = (1 - X)R_{h,1} + XR_{h,2} \]  \hspace{1cm} (C10)

where \( R_{h,1} \) and \( R_{h,2} \) are the radii of the singlet and the doublet, respectively. The hydrodynamic radius of the doublet can be approximated by the surface diameter of the doublet for low Reynolds numbers, \(^{102}\) thus

\[ R_{h,2} = \sqrt{2} \ R_{h,1} \]  \hspace{1cm} (C11)

Substituting for \( R_{h,2} \) in Eq. C10, the mean size becomes

\[ \tilde{R}_h = R_{h,1} [1 + X(\sqrt{2} - 1)] \]  \hspace{1cm} (C12)

As coagulation proceeds and doublets form, the mean hydrodynamic radius increases; the time rate of increase is given by

\[ \frac{d\tilde{R}_h}{dt} = R_{h,1}(\sqrt{2} - 1) \frac{dx}{dt} \]  \hspace{1cm} (C13)

The coagulation of singlets to form doublets obeys the following second-order rate law:

\[ \frac{dN}{dt} = -kN^2 \]  \hspace{1cm} (C14)

where \( k \) is the rate constant, \( N \) is the concentration of singlets given by

\[ N = N_0 (1 - X) \]  \hspace{1cm} (C15)

and \( N_0 \) is the initial concentration of singlets. Substituting Eq. C15 into Eq. C14,
\[
\frac{dX}{dt} = kN_0(1 - X)^2. \tag{C16}
\]

At the initial stage of coagulation, the fraction of doublets is small, thus giving the approximation

\[
\frac{dX}{dt} \bigg|_{t=0} = kN_0. \tag{C17}
\]

Substituting Eq. C17 into Eq. C13 and solving for the rate constant, we find

\[
k = \left[R_h,1(\sqrt{2} - 1)N_0\right]^{-1} \frac{dR_h}{dt} \bigg|_{t=0}. \tag{C18}
\]

Eq. C18, is only valid for the initial stage of coagulation, when the fraction of doublets is small. This was the case for the PCS coagulation experiments.

C.3 Experimental

C.3.A Chemicals and Labware: All chemicals were analytical reagent grade and were used without further purification. The solutions were made using deionized water \((\rho > 16 \times 10^6 \text{ ohm-cm})\). Solutions were prepared in volumetric flasks and stored in polypropylene bottles that had been thoroughly cleaned by acid \((1M \text{ HNO}_3)\) and base \((1M \text{ KOH})\) washes. Solutions were filtered through 0.22 \(\mu\text{m}\) pore-size Millipore filters prior to the coagulation experiments. All experiments were performed at \(25^\circ \pm 0.1^\circ \text{C}\).
C.3.B Colloidal Dispersions

1. **Cr(OH)₃**: The monodisperse, hydrous chromium (III) oxide sol was prepared using the method of Demchak and Matijevic.⁷ A solution 4 × 10⁻⁴ M Cr(NO₃)₃ and 6 × 10⁻⁴ M K₂SO₄ was filtered through a 0.2 μm Millipore filter and aged in a polypropylene bottle for 72 hours at 75 ± 2°C. The resulting Cr(OH)₃ particles were collected, repeatedly washed with 10⁻³ M HNO₃ solution, and resuspended in 10⁻³ M HNO₃ solution with ultrasonication. Particle size was determined from light scattering using the polarization ratio method; the best fit gave a geometrical mean diameter of 0.30 μm with a geometrical standard deviation of 1.17. The particle concentration of the stock suspension was determined by dry weight analysis using a density of 2.42 ± 0.02 g/cm³.⁴⁰⁵

2. **SiO₂**: Monodisperse, amorphous SiO₂ was produced by the hydrolysis of tetraethylorthosilicate in an ethanol solution containing ammonia and water. The initial concentrations of the reagents were 0.3 M orthosilicate, 4.5 M H₂O, and 1.9 M NH₃. After the reaction was complete (~ one hour), the suspension was filtered and washed with deionized water until no NH₃ was detected in the supernatant. The stock dispersion for the coagulation experiments was prepared by suspending the particles in filtered deionized water; particle concentration was determined by dry weight analysis using a density of 2.1 g/cm³. Particle size was measured by image analysis of TEM micrographs, giving a geometric mean diameter of 0.56 μm and a geometric standard deviation of 1.03.⁴⁰⁶
3. TiO₂: Monodisperse, amorphous TiO₂ was produced in a dry box by mixing equal volumes of two ethanol solutions, one 0.3 M in titanium tetraethoxide and the other 0.9 M in H₂O. After the reaction was complete (~ two minutes), the powder was repeatedly washed with deionized water by centrifugation and resuspension cycles, replacing the supernatant in each cycle. A stock sol was prepared by dispersing the particles in a 10⁻⁶ M KOH solution; under these conditions the stock sol showed high stability. Particle size was measured by image analysis of TEM micrographs, giving a mean diameter of 0.39 μm and geometric standard deviation of 1.09. Particle concentration of the stock dispersion was determined by dry weight analysis using a density of 3.1 g/cm³.

4. Montmorillonite: Wyoming montmorillonite, with a designation SWY-1, was thoroughly washed with deionized water and fractionated using the following sedimentation classification technique. A 1% solids suspension was made and allowed to settle in a 6 liter cylindrical container for 15 hours, so that all particles > 1 μm size had settled below the 10 cm level. The top 10 cm of the suspension was removed using a U-tube pipet and redispersed in a clean container. This fractionation procedure was repeated twice, followed by three successive fractionations to remove all particles > 0.5 μm; the required sedimentation time was 59.3 hours. The clay particles had a geometric mean size of 0.52 μm and standard deviation of 1.33 as measured by PCS. Particle concentration was
determined by dry weight analysis using a density\textsuperscript{107} of 2.74 g/cm\textsuperscript{3} and assuming that the clay platelets are 5 nm thick.\textsuperscript{108}

C.3.C Microelectrophoresis

Electrophoretic mobilities were measured with a Rank Bros. Particle Microelectrophoresis Apparatus Mark II, using a cylindrical cell (T = 25.0 ± 0.2°C). Five to ten particles were timed in each direction, and a mean value of the mobility was calculated. The mobilities were converted to ζ-potentials using the methods from Wiersema, Loeb, and Overbeek\textsuperscript{61} and O'Brien and White;\textsuperscript{62} no difference was noted in the two methods for these data.

C.3.D Coagulation

The Malvern K7025 correlator (Malvern Ltd.) used in this study was similar to those described in the literature.\textsuperscript{63,109,110} The light source was the 632.8 nm line of a Spectra Physics 35 mW He-Ne laser. The scattered intensity was measured at a fixed angle of 90° by an ITT FW 130 photomultiplier tube. The 120-channel correlator was controlled by a Commodore 3032 computer, which also analyzed the correlation functions to yield \( \bar{D} \) and \( \bar{R}_h \).

To establish the optimal operating parameters for the correlator, the complete cumulant analysis method\textsuperscript{63,101} was applied to the stabilized SiO\textsubscript{2} sol. The hydrodynamic radius was measured using different sample times, while keeping the total number of samples taken greater than 10\textsuperscript{6} for statistical accuracy; the results
are shown in Fig. C1. A least squares fit of the data gave 
$r^2 = 0.92$ and an intercept of $\bar{R}_h = 0.29 \mu m$, which compares well with 
the diameter of $0.56 \mu m$ obtained by image analysis. Sample times 
less than $100 \mu sec$ gave results with a high degree of scatter and 
were not used in the analysis, whereas times greater than $300 \mu sec$ 
required long experiment times to collect the $10^6$ samples required 
for accuracy. Selection of the parameters for the coagulation 
experiments required a compromise between accuracy and sampling 
(analysis) speed. Speed was especially critical for unstable 
systems; data for a size measurement had to be obtained rapidly 
enough so that the change in average particle size during a 
measurement was small. These requirements were satisfied using a 
sample time of $200 \mu sec$ and $2 \times 10^5$ samples, which allowed data to 
be taken and analyzed at a rate of one hydrodynamic radius per 
minute. Using these sampling parameters, the measured mean size was 
approximately $25\%$ larger than the actual size (Fig. C1). This $25\%$ 
difference does not change during early coagulation, thus the 
measured time rate of change in mean particle size (PCS) represents 
the actual rate of change.

A specific coagulation experiment was performed by diluting a 
stock suspension into a solution having the desired salt 
concentration and pH which was contained in a $3\text{ ml}$ glass cuvette. 
For samples coagulated under basic conditions, the pH was adjusted 
immediately prior to stock addition. The cuvette was capped and
Figure C1. Hydrodynamic radius measured by photon correlation spectroscopy as a function of sample time for a monodispersed SiO$_2$. The hydrodynamic radius obtained from the intercept of 0.29 $\mu$m compares well with the actual radius of 0.28 $\mu$m obtained by TEM-image analysis.
quickly inverted several times to mix the contents and was then transferred to the correlator for analysis. The time between stock addition and analysis initiation was typically < 10 seconds. Sample pH was assessed by measuring the pH of an identical sample immediately after preparation and the pH of the coagulated sample upon completion of the coagulation experiment; data was discarded for pH deviations > 0.2 units.

Figure C2 shows the mean hydrodynamic radius data for SiO₂ sols coagulated at four different KCl concentrations. In each case the data give a straight line with coefficients of determination ($r^2$) between 0.96 and 0.98. The slopes of the curves were calculated using the data where the fraction of doublets (also shown in Fig. C2) was < 0.5. Two or more samples were coagulated for each solution condition; the average slope was used to calculate the coagulation rate constant, $k$, from Eq. C19. The stability ratio, $W$, was calculated using

$$W = \frac{k_R}{k}$$

(C20)

where $k_R$ is the rapid coagulation rate constant defined by Smoluchowski

$$k_R = \frac{8k_BT}{3\eta}$$

(C21)

C.4 Results and Discussion

C.4.A Microelectrophoresis: Figure C3 shows the $\zeta$-potential for

Cr(OH)₃, SiO₂, and TiO₂ as a function of electrolyte concentration,
Figure C2. Mean hydrodynamic radius for SiO$_2$ sols as a function of coagulation time for four KCl electrolyte concentrations and a solution pH of 7.0.
Figure C3. ζ-potential as a function of electrolyte concentration at fixed pH for the systems: Cr(OH)$_3$ in KCl and K$_2$SO$_4$ solutions; SiO$_2$ in KCl and BaCl$_2$ solutions; and TiO$_2$ in KCl and BaCl$_2$ solutions.

Figure C4. Coagulation rates, expressed as stability ratios, for monodisperse Cr(OH)$_3$ at a pH = 3.5 in KCl (+) and K$_2$SO$_4$ (Δ) electrolyte solutions. The normalized curves reported by Bleier and Matijevic$^9$ (—) are included for comparison.
for specific solution pH values. The Cr(OH)$_3$ $\zeta$-potentials for KCl are similar to those reported by Bleier and Matijevic; no data for SO$_4$$^{2-}$ ions exists in the literature. The data for SiO$_2$ in the presence of KCl and BaCl$_2$ are similar to those reported by Yates.

The $\zeta$-potential for TiO$_2$ in KCl solutions are lower than those reported by Wiese for KNO$_3$. The data for the Ba$^{2+}$ ion indicates specific adsorption onto the TiO$_2$ surface; this phenomenon was also observed by Fuerstenau, et al. Since the actual Ba$^{2+}$ concentration in solution is not known for TiO$_2$, the calculated $\zeta$-potentials are only approximate values.

C.4.B Coagulation

1. Cr(OH)$_3$: The results of the coagulation experiments for Cr(OH)$_3$ in KCl and K$_2$SO$_4$ solutions at a pH = 3.5 are shown in Fig. C4. The data compare well with those obtained by Bleier and Matijevic using low angle light scattering, also shown in Fig. C4. Effective Hamaker constants, $A_{121}$, were calculated from the experimentally determined critical coagulation concentrations (CCC) and the extrapolated $\zeta$-potentials (from Fig. C3) using the simple analysis set forth by Reerink and Overbeek. The Hamaker constant is given by

$$A_{121} = 768 \pi n k_B T \gamma^2 / \kappa^3 . \quad (C22)$$

where $n$ is the salt concentration, and $\gamma$ is defined as
\[ \gamma = \tanh \left( \frac{z e \xi}{4 k_B T} \right) \]  

(C23)

where \( z \) is the counterion valence and \( e \) is the electronic charge.

The inverse of the Debye-Hückel length, \( \kappa \), is given by

\[ \kappa = \left[ \frac{F^2 \sigma^2 n_{\text{ion}} z^2}{i \varepsilon \varepsilon_0 RT} \right]^{1/2} \]  

(C24)

The CCC values for Cr(OH)$_3$ were 0.25 M for KCl and 2.14 \( \times \) 10$^{-3}$ M for BaCl$_2$; the ratio of the CCC's was 0.009, which is about 60% of the value of 0.0156 (1/z$^6$) required by DLVO theory.$^{81}$ The corresponding values for \( A_{121} \) were 3.3 \( \times \) 10$^{-21}$ J for KCl, using \( \zeta = 17 \) mV, and 1.58 \( \times \) 10$^{-20}$ J for K$_2$SO$_4$, using \( \zeta = 13 \) mV. The average value was 9.6 \( \times \) 10$^{-21}$ J, which is larger than the value reported by Bleier and Matijevic$^{95}$ by a factor of 7.

The consistency of the analysis was checked by calculating the \( \zeta \)-potential from the slope in Fig. 4 using$^{85}$

\[ \frac{d \log W}{d \log n} = -2.06 \times 10^7 (a \gamma^2 / \xi^2) \]  

(C25)

The \( \zeta \)-potentials calculated from Eq. C25 are approximate; however, the error should be < 3 mV for slopes analyzed over a small concentration range. The slope for K$_2$SO$_4$ yielded a \( \zeta \)-potential of 10 mV, in good agreement with the measured value. Conversely, the calculated value for KCl was 5 mV, which is much lower than the extrapolated value. The low slope (and low calculated \( \zeta \)-potential) for KCl is not understood, yet this behavior was also observed by Bleier and Matijevic.$^{95}$
2. **SiO$_2$:** The stability ratios for SiO$_2$ in KCl and BaCl$_2$ solutions at pH = 7.0 are given in Fig. C5. The ratio of CCC's for KCl and BaCl$_2$ was 0.047, which is three times larger than that predicted by DLVO theory. The Hamaker constants calculated from the CCC for KCl and BaCl$_2$ were 3.35 x 10$^{-21}$ J, using $\zeta = -16$ mV, and 7.60 x 10$^{-21}$ J, using $\zeta = -13$ mV, respectively. The average value of $A_{121}$ was 5.48 x 10$^{-21}$ J, which lies well within the range of theoretically predicted and measured values of 2.0 to 17.0 x 10$^{-21}$ J for vitreous SiO$_2$ reported by Visser. The $\zeta$-potentials calculated from the slopes using Eq. C25 are 8.0 mV for KCl and 7.0 mV for BaCl$_2$, which are about 50% of the extrapolated values.

3. **TiO$_2$:** Stability ratios obtained for the TiO$_2$ sol at pH = 7.5 using KCl and BaCl$_2$ and pH 8.9 using KCl are shown in Fig. C6. As expected, the CCC for KCl at pH = 8.9 was higher than at pH = 7.5 due to the larger $\zeta$-potential at each electrolyte concentration. Better agreement with the Schulze-Hardy rule is observed, as the CCC ratio at pH = 7.5 is 0.011. The effective Hamaker constant for KCl at pH = 8.9 was 1.60 x 10$^{-20}$ J (using $\zeta = -22$ mV) and at pH = 7.5 was 1.68 x 10$^{-20}$ (using $\zeta = -19.5$ mV). For BaCl$_2$ at pH = 7.5, $A_{121}$ was 2.21 x 10$^{-20}$ J (using $\zeta = -8.5$ mV). The average value for $A_{121}$ was 1.84 x 10$^{-20}$ J for amorphous TiO$_2$, which is slightly smaller than those given by Visser for crystalline TiO$_2$ (i.e., 2.5 to
Figure C5. Stability ratios for monodisperse SiO$_2$ in KCl (+) and BaCl$_2$ (Δ) electrolyte solutions at pH = 7.0.

Figure C6. Stability ratios for monodisperse TiO$_2$ in KCl (+) and BaCl$_2$ (Δ) electrolyte solutions at pH = 7.5 and KCl (□) solutions at pH = 8.9.
The \( \zeta \)-potentials calculated from the slopes, using Eq. C25, were -13.5 mV for KCl (pH = 8.9), -13.4 for KCl (pH = 7.5), and -12.0 for BaCl\(_2\) (pH = 7.5). These values deviate significantly from the extrapolated values; however, they agree well with \( \zeta \)-potentials at the CCC of 14 mV reported by Wiese and Healy.\(^{60}\)

4. Montmorillonite: Figure C7 gives the stability ratios for the fractionated montmorillonite using KCl to induce coagulation at pH = 9.2. An augmented Reerink and Overbeek\(^{85}\) analysis, which employed the parallel plate form of the interaction energies, was used to calculate the effective Hamaker constant.\(^{111}\) The electrostatic repulsion was calculated for a constant surface charge of 11.7 \( \mu \)C/cm\(^2\).\(^{112}\) The resulting effective Hamaker constant for the montmorillonite was \( 4.52 \times 10^{-20} \) J. This value, although lower than the range of \( 10^{-70} \times 10^{-20} \) J reported by Visser,\(^{86}\) compares favorably with \( A_{121} = 6.08 \times 10^{-20} \) J calculated from \( A_{11} = 1 \times 10^{-19} \) J obtained by Tabor and Winterton.\(^{113}\)

C.5 Summary

Photon correlation spectroscopy has been shown to be a viable method for measuring the rate of homocoagulation for monodisperse spheres and platelets. The stability data obtained by this technique are similar to those obtained by other techniques, and the effective Hamaker constants agree well with those found in the literature. The results are summarized:
Figure C7. Stability ratios for the fractionated montmorillonite using KCl to induce coagulation at pH = 9.2.
\[ A_{121} \times 10^{20} \text{ (J)} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(OH)</td>
<td>0.96</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.55</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.83</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>4.52</td>
</tr>
</tbody>
</table>

The stability ratios for rapid coagulation for the spherical systems (\( W_{\text{rapid}} = 7.26 \) for SiO₂, 0.79 for Cr(OH)₃, and 0.5 for TiO₂) show the expected relative behavior based on the magnitudes of \( A_{121} \). The authors recognize that Eqs. C22 and C25 cannot be rigorously applied, and thus the actual values of \( W_{\text{rapid}} \) and \( A_{121} \) can only be accurately assessed by using more sophisticated models which include hydrodynamic corrections, \(^{98,99}\) size distribution effects, \(^{6,114,117-119}\) and secondary minimum coagulation. In a future paper these models will be applied to the total stability curves to rigorously determine the Hamaker constants.
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