Dynamics in a Photoresponsive Surfactant System

by

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B.S. Chemical Engineering, University of Florida, Gainesville, FL (2001)

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Abstract

The study of surface tension and other surface properties is motivated by the large number of industrially relevant processes involving interfaces, such as coating, detergency, printing, foams, and so forth. These surface properties become increasingly important as the length scale of the system is reduced (as in microfluidic devices). Recently, much research has been focused on developing surfactants which respond to a particular stimulus (such as temperature, pH, light, etc.), so that properties such as surface tension and viscosity can be controlled using a convenient external trigger. Using light for this purpose has some advantages over other methods, as light can easily be focused and patterned (using optical lenses, filters, and masks) to give excellent precision for changing solution properties in a targeted area.

A nonionic photoresponsive surfactant has been developed which incorporates the light-sensitive azobenzene group into its hydrophobic tail. Cis-trans photo-isomerization of this group causes a change in the structure of the surfactant molecule which alters its aggregation state in bulk solution and its adsorption capacity at an air-water interface. NMR studies indicate that a solution removed from light for an extended period of time is comprised almost entirely of the trans isomer, while samples exposed to light of fixed wavelength eventually reach a photostationary state containing significant amounts of both isomers, with UV illumination producing a mixture dominated by the cis isomer.

Surface pressure measurements of adsorbed monolayers of the surfactant under various illumination conditions were made using a Langmuir film balance. The results indicate that adsorbed cis surfactant exerts a greater surface pressure than the adsorbed trans isomer, and that any cis present in a saturated layer tends to dominate the surface pressure behavior of the film. Fluorescence experiments were used to study the aggregation behavior of the surfactant in aqueous solution. The results suggest that the trans and cis isomers segregate into separate, co-existing aggregate phases and that the critical concentration associated with the onset of aggregation is very different for the two isomers.

In measurements performed well above the CMC, the dynamic surface tension of surfactant solutions following the creation of a fresh interface was found to depend strongly on the illumination state of the sample, though the same equilibrium tension was reached in all cases. The observed dynamic behavior is consistent with a mechanism in which the cis and trans isomers present in the mixtures compete for adsorption at the air/water interface.
Diffusion models were developed to estimate the time scales expected for surfactant adsorption and surface tension relaxation in these systems. These models account for the role of aggregates in the adsorption process, and consider limiting behavior for three aggregate properties: mobility, dissolution rate, and ability to incorporate into the interface. Good agreement is found between the model predictions and the experimentally observed relaxation time scales. The results suggest that trans-rich aggregates are important to the adsorption of trans surfactant, but that aggregates play little or no role in the adsorption of the cis isomer. In other experiments, high-intensity illumination focused on a surface saturated with surfactant was used to drive photoisomerization of adsorbed surfactant, resulting in rapid, substantial changes in surface tension. These changes are consistent with proposed conformations of the adsorbed surfactant, and with earlier monolayer studies.

Thesis Supervisor: T. Alan Hatton
Title: Ralph Landau Professor of Chemical Engineering Practice

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Title: Gilliland Professor of Chemical Engineering
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Chapter 1

Introduction

1.1 Motivation

Surface active agents, or surfactants, have been defined as substances that, when present at low concentration in a system, adsorb onto the interfaces of the system and markedly alter the free energies of those interfaces [1]. They appear in a diverse range of products, including motor oils, pharmaceuticals, detergents, and foods. Study of surface tension and other surface properties is motivated by the large number of industrially relevant processes involving interfaces, such as coating, detergency, printing, foams, etc. [2] These surface properties become increasingly important as the length scale of the system is reduced (as in microfluidic devices). Often, only the equilibrium properties of the interface are important. However, many practical applications involve surfactant solutions and the creation of new interfaces on time scales smaller than those needed for the interfacial properties to reach equilibrium values. In these cases, the dynamic interfacial properties have the most relevance, and such circumstances have motivated the focus on system dynamics found in the research reported here. Additionally, there is great incentive for being able to control the properties of a system using a particular stimulus, and this is why a responsive surfactant system is chosen for this study.

1.2 Background: Surfactant Behavior

1.2.1 Structure

Most surfactant properties are consequences of their characteristic molecular structure. They typically contain a structural group that has very little attraction for the solvent, known as a
lyophobic group, together with a group that has a strong attraction for the solvent, called the
lyophilic group [1]. This is known as an *amphipathic* structure. Temperature and other factors
(e.g., electrolyte concentration) affect the amphipathicity of a surfactant molecule in a particular
solvent under a given set of operating conditions. In a polar solvent such as water, the lyophobic
group may be a hydrocarbon, fluorocarbon, or siloxane chain of proper length, while an ionic or
highly polar group may act as the lyophilic group [1]. Surfactants are often classified based on
the ionic character of their lyophilic group: anionic surfactants bear a negative charge, cationic
surfactants bear a positive charge, zwitterionic surfactants have both positive and negative
charges present, and nonionic surfactants bear no ionic charge.

1.2.2 Properties

1.2.2.1 Interfacial Adsorption

When a surface-active agent is dissolved in a solvent, the presence of the lyophobic group in the
interior of the solvent causes a distortion of the solvent liquid structure, increasing the free
energy of the system [1]. When the solvent is water, this disruption of the structure of the water
molecules and its associated phenomena are referred to as the "hydrophobic effect" [3, 4]. It is
therefore more energetically favorable for the surfactant molecule to reside at an interface than in
bulk solution. The presence of the lyophilic group prevents the surfactant from being expelled
completely from the solvent as a separate phase [1, 3], but surfactant molecules nonetheless
accumulate at an interface. This concentration of surfactant at an interface lowers the interfacial
free energy or interfacial tension. The surfactant molecule is positioned at the interface such that
the lyophilic group remains in the solvent while the lyophobic group oriented away from it. This
is illustrated in Figure 1-1 for generic surfactant molecules at an air/water interface.
1.2.2.2 Self-Assembly

In addition to adsorbing at an interface, surfactant molecules in solution may also decrease the distortion of the solvent structure (and reduce the free energy of the system) by aggregating into clusters (micelles) with their lyophobic groups directed toward the interior of the cluster and their lyophilic groups directed toward the solvent [1]. This is illustrated in Figure 1-2 for generic surfactant molecules in an aqueous solution. Micellization is then another mechanism for removing lyophobic groups from contact with the solvent and minimizing the free energy of the system. This comes at the cost of the reduction of freedom for a surfactant molecule now confined to the micelle, and in the case of ionic surfactants, experiencing electrostatic repulsion from other similarly charged surfactant molecules in the micelle [1]. These forces increase the free energy of the system and therefore oppose micellization. Thus, micellization depends on the balance between factors promoting it and those opposing it.
Figure 1-2. Cartoon illustration of micelles formed in a surfactant solution at high concentration. This figure depicts a two-dimensional slice through the micelles, revealing the hydrophobic interior. Micelles are three-dimensional structures in which the hydrophilic groups shield this hydrophobic core from the solvent (water).

The onset of micelle formation is found to take place at a critical concentration referred to as the critical micelle concentration (CMC). Below the CMC, the surfactant exists primarily as unassociated molecules, and above the CMC, additional surfactant added to the solution is incorporated into the surfactant aggregates. The formation of micelles in solution is accompanied by a considerable change in many physical properties of the solution: surface tension, electrical conductivity, osmotic pressure, light scattering, dye solubility, etc. [1] As a result, measurements of these properties are used to determine the CMC of a given surfactant system. For systems not too far above the CMC, the shape of the micelles formed is generally considered to be roughly spherical. Changes in temperature, surfactant concentration, additives in the liquid phase, and structural groups in the surfactant all may cause changes in the size, shape, and aggregation number (number of surfactant molecules contained in the micelle) of the micelle, with structure varying from spherical to rod- or disk-like to lamellar in shape [5]. In concentrated solutions (ten times the CMC or more), micelles are generally nonspherical.
Worm-like micelles, vesicles, lamellar sheets, and other extended structures (e.g. bicontinuous phases) are all possible shapes for surfactant aggregates [6-10]. Surfactant aggregates are not static structures. Rather, they are in dynamic equilibrium with individual surfactant molecules which are constantly being exchanged between bulk solution and the aggregates. Additionally, aggregates themselves are continuously disintegrating and reforming [11].

1.2.2.3 Dynamic Surface Tension

As described earlier, surfactant molecules in solution tend to accumulate at an interface and lower its interfacial tension. The creation of fresh interfaces is common in many industrial processes, including those involving coatings, sprays, foams, and emulsions. Just after a new surface is formed in a surfactant solution, the surface is initially free of surfactant, and the interfacial tension of the surface is the same as that of the pure solvent [12]. As this surface ages, surfactant molecules are delivered to the interface and begin to adsorb, lowering the interfacial tension. This continues until the surface becomes saturated with surfactant and the surface tension* reaches an equilibrium value. The value of surface tension during the course of this adsorption process, which can be measured via tensiometry, bubble pressure, optical techniques, and various other methods [13], is referred to as the dynamic surface tension. A typical plot of surface tension versus the age of a surface in a surfactant system shows a dynamic surface tension profile which decreases monotonically from the pure solvent tension value until it reaches the equilibrium tension value, as illustrated in Figure 1-3.

* The term “surface tension” is used as a special case of the more general term “interfacial tension” in which one of the phases separated by the interface is gaseous, usually air.
The dynamic surface tension behavior of a surfactant system is influenced by the rate of delivery of surfactant to the interface as well as the thermodynamics that govern how effectively a given surfactant reduces the tension of a surface once adsorbed [14]. Adsorption of surfactant at the interface can be limited by transport of surfactant to the interface or by additional barriers to adsorption once the surfactant reaches the interface. The most extensively studied case is that of diffusion-limited surfactant adsorption. Ward and Tordai [15] pioneered the modeling of diffusion-controlled adsorption of monomeric surfactant at a planar interface in 1946, and since then researchers have built upon their work and extended their results to different geometries and more complex systems [16, 17]. Some studies have reported a shift in the controlling mechanism for adsorption from being diffusion-limited at early times (and low coverage of surfactant at the interface) to being limited by kinetic adsorption barriers or a mixed mechanism at long times (and high surface coverages) [18, 19]. For surfactant systems above the CMC, the presence of micelles or other aggregates in solution adds additional factors to the dynamic adsorption process. When surfactant monomer reaches the interface and adsorbs, the local
monomer supply is depleted and the equilibrium between monomers and aggregates is disturbed. To re-establish this equilibrium, aggregates dissolve to replenish the monomer population. The rate at which aggregates can dissolve then plays a role in the adsorption process [20, 21], as aggregates which dissolve quickly replenish the monomer supply faster and augment delivery of surfactant to the interface compared to aggregates which dissolve slowly. Additionally, the aggregates themselves can diffuse towards the interface, enhancing adsorption rates by providing a source of surfactant closer to the interface or, as suggested in recent studies, by adsorbing directly to the interface [22, 23].

1.2.2.4 Mixtures

Almost all practical applications involving surfactants employ surfactant mixtures [24-26]. Often, this is due to the difficulty or prohibitive cost of isolating a chemically pure surfactant [24, 26]. Other times, surfactants are deliberately mixed to take advantage of synergism between the individual surfactant species [24, 26]. In some cases, environmental or health concerns require that a mixture of known and approved surfactants be used for a particular application instead of developing a new surfactant [26]. The widespread use of mixed surfactant systems has led to considerable theoretical and experimental work to understand their properties.

The presence of multiple surface-active species in solution affects the aggregation and adsorption behavior of a system. Mixed micellization occurs when surfactants of different types combine to form aggregates. Binary surfactant mixtures have been the focus of many studies aimed at mixed CMC determination. The variation of CMC with composition in such a system gives an indication of the ideality of mixing in the aggregates [27]. Generally, ideal mixing models have
been successful in describing the CMC behavior of binary ionic [28, 29] and binary nonionic [30] surfactant mixtures, especially for surfactants with the same hydrophilic group. Nonideal mixing effects in the aggregates can result in substantially lower CMCs and interfacial tensions than would be expected based on the properties of the individual components [27]. This type of nonideal mixing is often observed in ionic/nonionic mixtures and anionic/cationic mixtures, and regular solution theory does a good job of modeling many of these systems [31]. Differences between hydrophobic chains in the interior of the aggregates can also be a source of nonideal interactions, so that the ionic character of the headgroup is not the only factor impacting the ideality of mixing. In mixtures of surfactants with unusual hydrophobic groups, such as fluorocarbon or siloxane chains, or of surfactants with unusual structures, sometimes micelle “demixing”, or the formation of more than one stable population of aggregates, is observed [27]. Since mixing in aggregates should be favored by entropy, the potential for demixing seems to require a significant physical basis such as immiscibility of hydrophobic groups in the core of the aggregates, or steric effects which restrict mixing based on the molecular geometries of the surfactants [27]. The poor-miscibility criterion is seen most strongly in mixtures of fluorocarbon and hydrocarbon surfactants, and the steric effects are most pronounced in mixtures of conventional surfactants with bolaform surfactants (which have two hydrophilic headgroups, one on each end of a hydrophobic chain). The mixing behavior in these types of systems is dependent upon the specific makeup of the surfactants involved (length of hydrophobic chain, size and ionic character of headgroup, etc.), but in many cases, mixing in the aggregates is prevented and segregation occurs [32-34].
Each component in a surfactant mixture will tend to preferentially adsorb to an interface, so these systems exhibit mixed surfactant monolayers at interfaces. Measurements of the surface pressure (the difference between the pure solution surface tension and the tension in the presence of surfactant) and molar areas of mixed surfactant monolayers performed at various compositions can give information regarding the impact of each species and of any potential interactions between the adsorbed surfactants [27]. In solutions containing surfactant mixtures in which several species are diffusing and adsorbing to an air/water interface, it has sometimes been observed that one species is significantly more surface active than the others, so that at equilibrium, the interface will be dominated by this most surface-active species [25, 26]. This competitive adsorption between the different species can lead to interesting dynamic surface tension behavior. If less surface-active species are able to diffuse and adsorb to the interface more quickly than the most surface-active species (by either being present in higher concentrations or having larger effective diffusion coefficients), then these less surface-active species will initially adsorb to the interface and dominate the interfacial properties before eventually being displaced by the most surface-active species. This can lead to unusual inflections in a plot of surface tension versus time following creation of a fresh interface [25, 26].

1.3 Background: Responsive Systems

1.3.1 Types of Responsive Systems

Recently, considerable work has been reported on surfactant systems which are responsive to a particular stimulus, such as temperature [35], pH [36], light [37, 38] or reduction/oxidation (redox) reactions [39, 40]. Many of these responsive surfactant systems allow for in situ and reversible control of surfactant-based properties [41], giving rise to a variety of potential

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applications, including controlled spreading and coating of surfaces [42], controlled droplet release [37], triggered release of substrates from micelles [35], control of protein folding [43], and surface tension-driven (Marangoni) flows [40]. The ability to alter the surface activity and/or aggregation state of a surfactant system in a reversible fashion with spatial and temporal control has enormous potential. Light has an advantage over other external stimuli in that it is non-invasive and readily manipulated. For example, the electrochemical approaches require that electrodes be inserted into the system and thus restrict the possible range of application [37]. By contrast, focusing and patterning of light is easily achieved using optical lenses, filters, and masks.

1.3.2 Photoresponsive Surfactants

Incorporation of a suitable chromophore into a surfactant allows UV and visible light to serve as external triggers for a change in solution properties, eliminating the need for composition or temperature changes [38]. Common photosurfactants contain a photocleavable headgroup [44, 45] or incorporate an isomerizable group, such as azobenzene or stilbene, into the hydrophobic chain [37, 38]. The surfactant system studied here, first reported by Shang et al. [46], is nonionic and features the azobenzene group in its hydrophobic tail. As reported elsewhere [47, 48], azobenzene undergoes a reversible photoisomerization upon changes in illumination conditions. The more thermodynamically stable state is the trans form, which has a flat planar structure, as shown in Figure 1-4a. Illumination with ultraviolet light converts the azobenzene into a bent cis state, which reverts back to the trans form under illumination by visible light or by removal from light for an extended period of time. With this azobenzene group present in the tail of the surfactant, as illustrated in Figure 1-4b, cis-trans photo-isomerization of the group alters the
ability of the surfactant to pack into adsorbed monolayers at an air-water interface or into aggregates in solution, thereby causing a significant variation in surface and bulk properties upon changes in the illumination conditions.

![Diagram of photoisomerization of azobenzene](image)

**Figure 1-4.** (a) Photoisomerization of azobenzene. (b) Molecular structure of the photoresponsive surfactant $\text{C}_4\text{AzoOC}_6\text{E}_2$. $\text{C}_4$ = butyl tail group; Azo = azobenzene group; O = ether oxygen middle polar group; $\text{C}_6$ = alkyl spacer with 6 methylene groups; $\text{E}_2$ = surfactant head group consisting of two ethylene oxide moieties. Figure from Shang et al. [46].

Aqueous solutions of azobenzene-containing surfactants strongly absorb light of wavelengths near 320-360 nm when in the *trans* state, with the *cis* state absorbing strongly near 440-460 nm [37, 46, 49]. The precise absorption peak values depend on the substituents which comprise the
rest of the surfactant molecule. Because the absorption bands of the two isomers overlap, illumination cannot be used to drive complete conversion to either the cis or trans isomer [37]. Samples which are illuminated eventually reach a photostationary state containing a mixture of the two isomers. The isomeric composition of the photostationary state depends upon the wavelength of light used for the illumination [50, 51]. Thermal reversion of cis to trans in the absence of light leads to a sample comprised almost entirely of the trans isomer [50].

1.4 Research Overview

The bulk of this research has been performed to accomplish three main goals: i) study and characterize the equilibrium bulk and surface properties of a photoisomeric surfactant mixture, ii) experimentally determine and theoretically model the dynamic surface tension behavior of such a mixture, and iii) determine the response of the system to illumination. Chapter 2 describes the surfactant used in these studies and the results of UV-Vis absorption and NMR characterization of the surfactant. Chapter 3 discusses Langmuir film balance experiments used to determine the behavior of surfactant monolayers adsorbed at an air-water interface as well as fluorescence experiments used to determine the aggregation behavior of the surfactant in aqueous solution. The evolution of surface tension after the formation of a fresh interface is presented in Chapter 4, including both experimental results for this surfactant system and the development of simple mathematical models aimed at describing the data. Chapter 5 focuses on the effect of illumination on adsorbed surfactant and offers an interpretation of the results based on earlier monolayer studies. The impact of temperature on the aggregation and dynamic surface tension behavior of the surfactant is described in Chapter 6.
1.5 References


Chapter 2
Surfactant Synthesis and Characterization

2.1 Introduction

Azobenzene is a convenient chromophore for use in photoresponsive surfactants because its light-induced isomerization between cis and trans conformations allows for reversible changes in surfactant structure. The impact that these changes have on solution properties depends upon the specific architecture of the surfactant molecule. Careful design of the molecule can lead to maximal changes in the adsorption and aggregation behavior of the surfactant upon illumination. For example, Shin et al. [1] report on the properties of an azobenzene-containing cationic bolaform surfactant. The two-headed nature of this surfactant causes more constrained conformations within aggregates or when adsorbed at interfaces, potentially allowing the effects of photoisomerization to be amplified. However, the ionic character of the head groups required that a second, anionic surfactant be added to the solution in order to reduce the average area occupied by these head groups (as electrostatic repulsion would cause a larger effective area for a system containing only cationic head groups), so that the effect of the conformation changes could truly be maximized [1]. With a mixture of this photosurfactant and SDS, the researchers reported substantial changes in the extent of aggregation and the dynamic surface tension of the system upon illumination.

Shang et al. [2] have developed a nonionic surfactant which incorporates the azobenzene group into its hydrophobic tail. The lack of ionic charge on the head group allows for close packing of these head groups without addition of a second surfactant species into solution. This permits changes in tail conformation caused by illumination to have a strong impact on the adsorption
capacity of the surfactant and the structure of aggregates formed in solution. This is the surfactant studied and reported here, and a description of its synthesis and characterization follows in this chapter.

2.2 Experimental

The photoresponsive surfactant synthesized for these studies is shown in Figure 2-1. The azobenzene group is located within the tail and separated from the ethylene oxide head group by an alkyl spacer of six methylenes. This surfactant is termed C₄AzoOC₆E₂, or simply C₆.

![Figure 2-1. Molecular structure of the photoresponsive surfactant C₄AzoOC₆E₂. C₄ = butyl tail group; Azo = azobenzene group; O = ether oxygen middle polar group; C₆ = alkyl spacer with 6 methylene groups; E₂ = surfactant head group consisting of two ethylene oxide moieties. Figure from Shang et al. [2].]

2.2.1 Materials

4-butylaniline (97%), sodium carbonate (99.95%), phenol (99+ %), di(ethylene glycol) (99%), 1,6-dibromohexane (96%), bis(trimethylsilyl)trifluoroacetamide (99+%), and sodium hydride (95%) were purchased from Aldrich (Milwaukee, WI). Sodium nitrite (AR grade), potassium hydroxide (AR grade), hydrochloric acid (37%), and sodium hydroxide (AR grade) were obtained from Mallinckrodt Baker (Paris, Kentucky), and tetrahydrofuran and hexane from EM Science (Gibbstown, NJ). All chemicals were used as received without further purification.
2.2.2 Surfactant Synthesis and Structure

The procedure for synthesis of this surfactant has been laid out in detail by Shang [3], and a schematic of the synthesis pathway is shown in Figure 2-2. A brief outline is as follows:

**4-butyl-4’-hydroxyl azobenzene (II)** was prepared by dissolving 14.9 g of 4-butylaniline in 64 ml of 5M hydrochloric acid and reacting it with 15 ml of aqueous sodium nitrite (6.7 M) at 0 °C for one hour. The resulting diazonium solution was then coupled with phenol in a slurry (9.4 g phenol + 26.5 g sodium carbonate + 50 ml MilliQ water) at 0 °C for one hour. The product was collected by filtration, dried in a vacuum oven over night, and purified by recrystallization in hexane.

**4-butyl-4’-(6-brom)hexoxy azobenzene (III)** was prepared by first dissolving 10 g (II) in 40 ml THF, and adding this solution dropwise to a mixture of 24.4 g 1,6-dibromohexane, 4.5 g potassium hydroxide and 200 ml THF. The mixture was allowed to reflux for 19 hours, and was then extracted with dichloromethane. After the solvent was removed by rotary evaporation, the product was further purified by recrystallization from a hexane/THF mixture (80/20 volume ratio).

**Diethylene glycol mono(4’,4-hexyloxy, butyl-azobenzene) (C₄AzoOC₆E₂)** To prepare C₄AzoOC₆E₂, 2 g of sodium hydride was first reacted with 22 g of di(ethylene glycol) in 80 ml THF under N₂ protection for 2 hours. A solution of 4.1 g (III) with 40 ml THF was added dropwise into this reaction mixture, and the resulting solution was refluxed for 64 hours under N₂. The solvent was removed from the reaction mixture by rotary evaporation, and vacuum distillation was used to remove residual di(ethylene glycol). The product was separated by
chromatography (60 Å silica; ethyl ether/ methanol as eluent), and further purified by recrystallization from hexane.

1H-NMR, mass spectrometry, and gas chromatography were all used to analyze and verify the molecular structure of the surfactant.

![Chemical structures and pathways](image)

**Figure 2-2.** Schematic of the synthesis pathway for the surfactant C₄AzoOC₆E₂.

**2.2.3 Illumination**

The light source used for illumination of surfactant solutions was ordinarily a 200 W mercury lamp (Oriel 6283) mounted in an arc lamp housing (Oriel 66902) and powered by an arc lamp
power supply (Oriel 68910). A heat absorbing filter (Oriel 59042) was placed in the path of the light to reduce heating of samples during illumination. Visible light passed through a 400 nm longpass filter (Oriel 59472), while a 320 nm bandpass filter (Oriel 59800) was used for UV light. Characteristics of these optical filters are given in Figure 2-3.

![Characteristics of optical filters](image)

**Figure 2-3.** Characteristics of the optical filters used to illuminate samples to photostationary states before making physical measurements.

### 2.2.4 Characterization Methods

Equilibrium properties for the system were required to enable proper interpretation of the dynamic results and were established by using UV-Vis, NMR, Langmuir film balance, and fluorescence measurements. The UV-Vis and NMR results are reported here, while discussion of the Langmuir film balance and fluorescence measurements follows in the next chapter.

#### 2.2.4.1 UV-Vis Absorption

UV-Vis absorption spectra were obtained with a Hewlett-Packard HP 8453 spectrophotometer. Surfactant solutions were contained in a quartz cuvette with a 1 cm path length. Measurements
were taken under three different illumination conditions: first, samples were removed from all light and kept in the dark for several days. Next, samples were exposed to visible light using the optical filter described above. Measurements were taken until the absorbance spectrum of the sample ceased to change appreciably upon further illumination. This indicated attainment of a photostationary state [4]. Finally, samples were exposed to UV light (using the appropriate optical filter) until a different photostationary state was reached. These absorbance measurements were repeated at various surfactant concentrations to determine the molar absorptivity of the solutions.

2.2.4.2 NMR

$^1$H NMR scans were obtained at 500 MHz with a Varian Inova-500 NMR Spectrometer. In these studies, solid samples of surfactant were dissolved in deuterated chloroform (CDCl$_3$), scanned and analyzed, and the protons associated with each photoisomer were identified. Integration of these peaks provided estimates of the cis/trans composition of each sample. Ideally, deuterium oxide (D$_2$O) would have been used as the solvent in these experiments due to its similarity to water. but the extremely low critical micelle concentrations (CMCs) of these surfactants in water (in the micromolar range, as first determined by Shang et al.[2], and re-established by fluorescence measurements discussed later) caused overlap of the signal and prevented trans and cis peaks from being fully resolved.
2.3 Characterization Results

2.3.1 UV-Vis Absorption

The absorbance of aqueous C₆ solutions was measured with a UV-Vis spectrophotometer, with measurements taken for samples under each of three different illumination conditions: the dark-adapted or “dark” state, corresponding to the equilibrium attained after prolonged absence of light, and the “visible” and “UV” photostationary states. Measurements were repeated at various dilute concentrations of surfactant and the molar absorptivity spectrum for each illumination state was determined from the absorbance vs. concentration data according to the Beer-Lambert law [5], which is applicable for dilute solutions where scattering of light is insignificant and was found to hold for the C₆ system over the range of concentrations studied (up to about 0.05 mM):

\[ A(\lambda) = C\ell\varepsilon(\lambda) \]  

(2-1)

where \( A \) is the absorbance value at a given wavelength, \( C \) is the concentration of the absorbing species (in this case the surfactant), \( \ell \) is the distance that the light travels through the material (the path length), and \( \varepsilon \) is absorption coefficient or molar absorptivity of the absorbing species at this wavelength. The results are shown in Figure 2-4a. As reported earlier by Shang et al. [2], these surfactants show a strong absorbance band near 325 nm due to a \( \pi-\pi^* \) transition [4], with the visible and UV samples also showing an absorbance band near 440 nm due to an \( n-\pi^* \) transition. The absorbance peaks of a 0.03 mM solution were tracked over time after increments of illumination, starting with a dark sample, with the results shown in Figure 3b. Five minutes of illumination by the Oriel lamp was found to be sufficient for the sample to reach the visible photostationary state, while 1.5 minutes of illumination was enough to reach the UV photostationary state. Figure 3b also illustrates the reversibility of the photoisomerization. as
alternately illuminating the aqueous solutions with visible and UV light led to transitions back and forth between the two photostationary states.

![Figure 2-4](image)

**Figure 2-4.** (a) Molar absorptivity spectra for aqueous solutions of C₆ photosurfactant. (b) Transient behavior of UV-Vis absorbance peaks for 0.03 mM C₆ solution originally in a dark-adapted state, then alternately illuminated with visible and UV light.

### 2.3.2 NMR

The isomeric composition of each of the illumination states was estimated from ¹H NMR measurements [4]. The results indicate that samples in the dark state are almost exclusively
 (>99%) in the trans form, while the two photostationary states contain mixtures of the two isomers (visible: 85-88% trans, UV: 10% trans). This is consistent with literature reporting on other azobenzene-containing compounds where it has been noted that when the absorption peaks of the two isomers overlap, complete conversion to one isomer or the other cannot generally be achieved by illumination, and that the isomeric composition of a photostationary equilibrium state depends upon the wavelength of light used for the illumination [1, 6, 7].

2.3.3 Isomeric Molar Absorptivity Determination

The absorbance of the surfactant at a particular wavelength can be expressed as a linear combination of contributions from the trans isomer and the cis isomer. Thus Eqn. 2-1 can be expanded as

\[
\frac{A(\lambda)}{\ell} = C_{total} \epsilon_{mix}(\lambda) = C_{\text{trans}} \epsilon_{\text{trans}}(\lambda) + C_{\text{cis}} \epsilon_{\text{cis}}(\lambda)
\]

\[
= C_{\text{total}} \left[ x_{\text{trans}} \epsilon_{\text{trans}}(\lambda) + (1 - x_{\text{trans}}) \epsilon_{\text{cis}}(\lambda) \right]
\]

where \(x_{\text{trans}}\) is the mole fraction of trans isomer present in the sample. The molar absorptivity data from Figure 2-4a, when combined with the results of the NMR analysis, provide three composition values by which to estimate the coefficients for the trans and cis isomers. Figure 2-5a shows the fitting of Eqn. 2-2 to absorptivity data at a wavelength of 325 nm. The data are described well by this linear model, and the individual contributions of the trans and cis isomers are found by extrapolating the best-fit line to trans fractions of one and zero, respectively. The results of this fitting are shown in Figure 2-5b. The isosbestic points (points at which the trans and cis isomers exhibit equal absorptivity) which are noticeable in Figure 2-4a at about 300 nm and 385 nm are seen even more clearly in Figure 2-5b. The presence of such points is common among photoisomerizable species [8, 9]. Also worth noting is that, in Figure 2-5a, the
absorbance data, which were taken from aqueous solutions, demonstrate linearity when plotted against isomeric composition estimates taken from NMR measurements which were performed in CDCl₃. This consistency (along with similar chloroform/water consistency seen between Langmuir film studies and dynamic surface tension studies to be discussed later) offers some confidence for the application of the NMR results to aqueous systems.

![Figure 2-5](image)

**Figure 2-5.** (a) Molar absorptivity data at 325 nm for aqueous solutions of C₆ photosurfactant. Solid line represents best-fit line of the form given by Eqn. 2-2. (b) Molar absorptivity of the individual *trans* and *cis* isomers in aqueous solutions as estimated from application of Eqn. 2-2 to the absorptivity data shown in Figure 2-4a.
2.4 Summary

A new class of photoresponsive surfactants has been developed by Shang et al., and has been designed to exhibit large changes in surface and bulk properties upon changes in illumination conditions. These surfactants feature the light-sensitive azobenzene group in their hydrophobic tails, so that cis-trans photoisomerization of this group causes changes in the structural conformation of the surfactant. The surfactants are nonionic, and the absence of strong electrostatic repulsions between the head groups allows them to form a dense adsorbed layer at an air/water interface. It was expected that the effect of photoisomerization on surface tension and other interfacial properties would be more pronounced in a dense adsorbed layer than in a loosely packed layer.

The UV-Vis absorbance spectra of aqueous samples of the surfactant were measured, and three distinct states were characterized: the dark-adapted state (achieved after prolonged removal from light) and the visible and UV photostationary states (attained after exposure to light passed through appropriate optical filters). The results indicate that all of the samples strongly absorb light of wavelengths near 325 nm, and that samples in the UV photostationary state also exhibit significant absorbance near 440 nm. Alternating illumination with UV light and visible light was used to show that conversion between the two photostationary states is reversible. NMR was used to estimate the isomeric composition of samples in each of the three states. The results indicate that dark-adapted samples contain trans isomer almost exclusively, while the two photostationary states contain significant amounts of both isomers. Taken together, the results of the absorption and NMR studies indicate that the trans isomer accounts for most of the
absorption of light near 325 nm while the cis isomer is primarily responsible for the absorption near 440 nm.

2.5 References

3. Shang, T.G., A New Class of Photoresponsive Surfactants. Ph.D. Thesis. in Department of Chemical Engineering. 2005, Massachusetts Institute of Technology: Cambridge, MA 02139
Chapter 3  
Equilibrium Bulk and Surface Properties

3.1 Introduction
The physical conformation of the photosurfactant molecule affects the behavior of monolayers of the surfactant adsorbed at an interface as well as the aggregation behavior of the surfactant in bulk solution at high concentrations. As discussed in the previous chapter, illumination of samples of this surfactant results in solutions containing a mixture of the cis and trans isomers. This property was utilized to prepare solutions of varying isomeric compositions, either by illuminating samples to photostationarity using various optical filters or by mixing solutions of known compositions. These solutions were then used in monolayer and aggregation studies to determine the effect of isomeric composition on these properties.

3.2 Experimental

3.2.1 Monolayer Studies using a Langmuir Film Balance
Surface pressure-area isotherms were obtained with a Model 102M Langmuir film balance from Nima Technology. In these experiments, surfactant was first dissolved in chloroform and illuminated to the desired photostationary state. This chloroform solution was then spread on top of the water subphase and the chloroform was allowed to evaporate. Two coupled, movable Teflon barriers then compressed the surface symmetrically while a small Wilhelmy plate at the center of the trough measured the surface pressure. Due to the solubility of the photosurfactant in the subphase (water), compressions were performed rapidly (100 cm²/min) in order to limit desorption of the surfactant from the interface [1].
3.2.2 Aggregation Studies using Fluorescence Measurements

Steady-state fluorescence spectra (3 s integration time) were obtained with a TimeMaster Fluorescence Lifetime Spectrometer (Photon Technology International). FeliX software (PTI, Version 1.42a) was used for data acquisition and analysis. In these studies, a series of aqueous samples was prepared with varying surfactant concentration and a fixed amount (1.8 μM) of the fluorescent probe Nile Red. Nile Red was chosen as the probe because its excitation peak occurs at a long wavelength (~575 nm) where absorption by the surfactant is minimal (even in the case of the UV-illuminated sample, which exhibits the strongest absorbance of any of the samples at this wavelength, the isomer composition was found to change by less than 2% over the course of a measurement) and because its emission is very environment-sensitive [2, 3]. Nile Red is poorly soluble in water, and in aqueous environments its fluorescence is strongly quenched and red-shifted [2]. In hydrophobic environments, Nile Red fluorescence intensity is much greater and its emission peak shifts to a shorter wavelength. Thus, it is an appropriate probe for detecting the onset of micelles or other aggregates in aqueous solution. Following excitation at 575 nm, the fluorescent emission spectrum was measured for each sample in each of the three illumination states discussed previously. Two more states, corresponding to photostationarity for illumination through additional UV optical filters (a 326 nm narrowband and a 360 bandpass) were also examined. These have trans contents of 40% and 85%, respectively (as estimated from separate UV-Vis absorption experiments). The peak intensities of the resulting spectra and the wavelengths at which these maxima occur were monitored as functions of surfactant concentration.
3.3 Results

3.3.1 Monolayer Studies

The surface pressure-area isotherms of monolayers of adsorbed surfactant obtained with a Langmuir film balance are shown in Figure 3-1. Illumination of the surfactant solutions prior to spreading allowed examination of the film properties at the various isomeric compositions corresponding to photostationary states. In addition to the dark, visible, and UV states, a sample with an estimated trans content of 50% (hereinafter referred to as “50/50”) was also prepared by mixing appropriate volumes of the dark and UV samples.

![Figure 3-1](image)

Figure 3-1. Results of compression studies using monolayers of adsorbed photosurfactant. Open and closed versions of each symbol indicate replicate experiments for the purposes of establishing reproducibility.

Figure 3-1 is rich in information about the adsorbed monolayers. First, for that portion of the plot where the available area per molecule is large (> about 40 Å²/molecule), it is seen that the surface pressure exerted by the film increases with increasing cis content of the sample. This is consistent with the physical conformations of the adsorbed isomers as proposed by Shang et al.
These are shown in Figure 3-2. When adsorbed at the air/water interface, the \textit{trans} surfactant is essentially normal to the interface with its tail extending out into the air phase. This occupies less of the interface than does the adsorbed \textit{cis} surfactant, for which the bent azobenzene group causes much of the tail to lie in the interfacial plane. Thus, for a fixed number of surfactant molecules adsorbed at the interface, the sample with a larger fraction of the \textit{cis} isomer will exert a larger surface pressure.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{surfactant_conformations.png}
\caption{Proposed conformations of surfactant adsorbed at the air/water interface. From Shang [5].}
\end{figure}

Secondly, the curve for the 50/50 sample lies between the curves for the visible and UV samples, which is to be expected since its isomeric composition lies between these photostationary state compositions. Thirdly, for the dark and UV samples, it is seen that, as the area available per molecule is reduced, eventually a point is reached at which further compression of the film no longer results in a substantial change in surface pressure. The point at which this transition occurs corresponds to the point at which the surface is saturated with surfactant and further compression of the interface results in expulsion of some of the adsorbed surfactant from the interface and into the subphase. For the dark sample, this transition occurs at an area of 21
Å²/molecule and a surface pressure of about 41 mN/m. These values are in good agreement with those estimated from equilibrium surface tension measurements by Shang et al. [5] for the “trans” state when the bulk concentration is equal to the CMC. Similarly, for the UV sample this transition corresponds to the formation of a saturated surface dominated by the cis isomer, and the surface pressure associated with this transition is in good agreement with the estimate given by Shang et al. for the “cis” state (about 30 mN/m). Lastly, the curves for the visible and 50/50 samples also show sharp discontinuities in slope, and the values of area at which these occur indicate that even a small amount of adsorbed cis isomer has a strong influence on the behavior of a surface. These saturation points for the dark, visible, 50/50, and UV samples occur at 21, 25, 28, and 29 Å²/molecule, respectively.

Thus, in proceeding from the dark sample to the UV sample, the effect of cis content on the saturation point is seen to be most profound when the cis content of the surface is small. With further compression beyond these saturation points, the visible and 50/50 mixtures first exhibit a fairly flat surface pressure response before eventually showing a rise in pressure with continued compression. Within the region of flat pressure response, the visible, 50/50, and UV samples all exhibit very similar surface pressures, despite having disparate isomer compositions (ranging from 15 to 90% cis). This suggests that the cis isomer dominates the surface pressure behavior. It is not until a substantial amount of the cis isomer has been squeezed from the interface by further compression that the curves become distinct again, as compression of the remaining trans-enhanced film results in increased surface pressure. This is seen most significantly in the visible sample, which has the largest trans content of these mixtures, and to a lesser degree in the 50/50 sample (and even the UV curve shows a slight increase in surface pressure with extensive
compression. Further evidence of the dominance of the cis isomer on the surface pressure behavior of the film can be seen by examining the curves at some fixed, large area (say, 60 Å²/molecule). When comparing adjacent curves at this area, it is seen that the effect of cis content on the surface pressure is most profound when the cis content of the surface is small.

Other Langmuir film studies focused on the effect of extensive compression on layers having a larger initial loading of surfactant on the interface and/or having a cis content less than 15%. Samples with a reduced cis content were obtained via illumination through optical longpass filters with cut-on wavelengths longer than 400 nm. (Figure 2-5b shows that the cis molar absorptivity increases relative to the trans value for increasing wavelengths beyond 400 nm, so that increasing the cut-on wavelength of the longpass filter used for illumination leads to an increase in the net conversion of cis isomer to trans at photostationarity.) The results of such monolayer experiments are shown in Figure 3-3a. Here it is seen that as the filter cut-on wavelength is increased and the cis content of the samples is decreased, the data series more closely resemble the dark-adapted sample, as expected. Also, extensive compression of these layers results in attainment of a surface pressure identical to that of the dark sample, owing to the removal of all cis from the interface. The cis content of the photostationary states corresponding to illumination from each of these filters was estimated from UV-Vis absorption measurements.

The surface pressure exerted by these films at an area near the trans saturation point (the reason for this particular choice of pressure will become more clear in Chapter 5) is plotted versus the cis content of the film in Figure 3-3b (previously collected data for the visible, 50/50, and UV states are included as well). This plot demonstrates that there is little difference in the surface pressure of these saturated films when the cis content lies between 15% and 90%, but that there
is a marked increase in the pressure when the cis content drops below about 10%. This is additional evidence of the strong impact of a small amount of cis present at the interface, a characteristic which affects the dynamic surface tension behavior of this surfactant, as will be shown in the next chapter.

Figure 3-3. (a) Results of compression studies using monolayers of adsorbed photosurfactant having isomeric compositions intermediate between the dark and visible states. The legend refers to the cut-on wavelength of the optical longpass filter used to illuminate samples prior to spreading. (b) The surface pressure of the film at the trans saturation point as a function of cis content.
3.3.2 Aggregation Studies

Estimates of the CMC of this surfactant under the different illumination conditions were obtained from fluorescence measurements [6]. Figure 3-4a is a plot of maximum emission intensity against surfactant concentration. At low surfactant concentrations, before aggregates are formed in any of the samples, the emission intensity is relatively low and the different illumination conditions display similar intensity values. At the highest concentrations shown, where aggregates are present, the intensity is much greater and is dependent upon the extent to which hydrophobic domains are present in solution. The CMC for each illumination state can be estimated from the intersection of the extrapolated linear fits for the low concentration and high concentration regions. The results indicate that the CMC for the dark state occurs around 1 μM, with the CMC values of the other illumination states increasing as trans content decreases. The value obtained for the dark state is in good agreement with the value previously reported by Shang et al. [5] for the “trans” state as obtained from equilibrium surface tension measurements.

![Figure 3-4a. Emission intensity for solutions containing a fixed amount of Nile Red and varying amounts of C₆ photosurfactant. Solid lines are best-fit lines used to estimate first (trans) CMC in these samples. Dashed lines are used to estimate second (cis) CMC.](image)
Additional insight can also be gained from the emission peak wavelength data shown in Figure 3-4b. In very dilute surfactant solutions, when Nile Red is exposed to an essentially aqueous environment, its emission peak occurs at a long wavelength (~ 655 nm) [3]. As aggregates are formed and Nile Red is able to incorporate itself into less polar domains, this peak wavelength diminishes. In the dark sample, a sharp decrease in peak wavelength occurs between 1 and 2 μM, which is consistent with the intensity data in indicating the onset of aggregation in this concentration range. The peak wavelength for the dark sample continues to decrease with increasing surfactant concentration before leveling off near 630 nm. The visible sample (~85% trans) shows a very similar behavior. The peak wavelengths of the cis-dominant samples (10 and 15% trans) remain at the high, water-like level for concentrations less than about 10 μM, after which they begin to drop. This is consistent with an increase in the emission intensity seen in the 15% trans sample in this range, but any intensity increase for the 10% trans sample is lost in the experimental noise. At higher concentrations, the peak wavelengths of the cis-dominant samples show no sign of leveling off (the solubility limit of these surfactants prevents further probing to higher concentrations). This difference in peak wavelength behavior between the trans-dominant samples and cis-dominant samples at the highest concentrations signifies a difference in the aggregation state of the system under these different conditions. The sample containing 40% trans shows behavior intermediate between the trans-dominant and cis-dominant samples, both in emission intensity and peak wavelength.
Figure 3-4b. Emission peak wavelength data for C₆/Nile Red samples.

The peak wavelength data are plotted against \textit{trans} concentration (product of \textit{trans} fraction and total concentration) in Figure 3-4c. It is seen that data from all five illumination conditions display the same drop in peak wavelength beginning at about 1 \textmu M, thereby indicating that aggregation begins at this critical concentration of \textit{trans} surfactant and that surfactant in the \textit{cis} form does not appreciably contribute to these aggregates. The data from the three UV samples eventually diverge from the \textit{trans}-dominant data and display shorter peak wavelength values. If these same wavelength data are plotted against \textit{cis} concentration as shown in Figure 3-4d, it is seen that data from all four mixtures intersect at a \textit{cis} concentration of around 65 \textmu M, beyond which any further increase in \textit{cis} concentration results in peak wavelengths shorter than those seen in the \textit{trans}-dominant samples. Even in the intensity data for the sample containing 10\% \textit{trans}, an appreciable increase in emission intensity is seen after this point. This value is then taken as an estimate of the critical \textit{cis} concentration at which \textit{cis}-dominant aggregation occurs. Presumably the reason that Figure 3-4d does not show more overlap between the different data
sets is that *trans*-dominant aggregates may form at much lower concentrations and dominate the environment seen by the Nile Red probe.

![Graph](image)

**Figure 3-4.** (c) Peak wavelength data for C$_6$/Nile Red samples plotted against *trans* concentration. (d) Peak wavelength data plotted against *cis* concentration.

In summary, these results suggest segregation of the two isomers into separate aggregate phases which can coexist in the photostationary state mixtures at high surfactant concentration. The first critical concentration, occurring at a *trans* concentration of about 1 μM, seems to
correspond to the formation of *trans*-rich micelles or vesicles. The second critical concentration, occurring at a *cis* concentration of about 65 μM, very likely corresponds to the formation of a *cis*-rich bicontinuous phase. The presence of vesicles in the dark state and of a bicontinuous phase in UV samples at high concentrations was demonstrated by Shang et al. [7] through Cryo-TEM imaging (shown in Figure 3-5) and neutron scattering experiments. The postulated coexistence of different aggregate populations in the isomeric mixtures at high concentrations and the presence of a single type of aggregate in all samples at compositions between the *trans* CMC and *cis* CMC are supported by dynamic light scattering studies (data shown in Appendix). Studies of a different azobenzene-containing surfactant system have reported this segregation of *cis* and *trans* aggregates and attribute it to simple packing considerations [8].

![Figure 3-5. Cryo-TEM images of 600 μM samples obtained by Shang et al. [7] (a) Vesicles formed in dark-adapted sample. (b) Bicontinuous phase formed in UV-illuminated sample.](image)

These extremely low CMC values illustrate the exceptional hydrophobicity of these surfactants. The fact that the *trans* aggregates form at a lower concentration than the *cis* aggregates is to be expected, as the *cis* isomer of the photosurfactant is known to have a higher dipole moment [5].
though it is interesting to note that the environment seen by the Nile Red probe once incorporated into the aggregates is actually less polar in the cis aggregates. This indicates that Nile Red is exposed to less water when incorporated into cis aggregates than when in trans aggregates [3].

3.4 Summary

The adsorption behavior of C₆ photosurfactant at an air/water interface and its aggregation behavior in aqueous solutions were examined for samples of various isomeric compositions. Langmuir film balance experiments indicate that surfactant adsorbed at an air/water interface occupies more area in the cis form than in the trans form. This is consistent with the physical conformations previously proposed for this surfactant, in which the bent tail of the cis isomer lies in the interfacial plane and the planar tail of the trans isomer extends away from the interface and into the air phase. These monolayer studies also indicate that any cis present in a saturated monolayer dominates the surface pressure behavior of the film. Fluorescence studies suggest the coexistence of two distinct aggregate phases, one rich in trans isomer and one rich in cis isomer, at high concentrations of the photostationary mixtures. The critical trans concentration associated with formation of trans-rich aggregates is about 1μM, while the cis-rich aggregates appear to form at a cis concentration of about 65 μM. The large difference in these CMC values, along with the structural differences in the aggregates formed by each isomer, reveals the impact of isomeric composition on the aggregation state of the surfactant. These monolayer and aggregation studies demonstrate that the conformation of the surfactant tail, which is dictated by the isomeric form of the surfactant, strongly affects the ability of the surfactant to pack into adsorbed monolayers at an air/water interface or into aggregates in solution.
3.5 References


4. Shang, T.G., *A New Class of Photoresponsive Surfactants*. Ph.D. Thesis. in Department of Chemical Engineering. 2005, Massachusetts Institute of Technology:Cambridge, MA 02139


Chapter 4
Dynamic Surface Tension: Relaxations

4.1 Introduction
As mentioned in Chapter 1, the dynamic behavior of surface properties is important in applications involving surfactants and the creation of fresh interfaces because these properties may not reach their equilibrium values quickly enough to be useful. In Chapter 3 it was seen that the isomeric composition of the photosurfactant solutions affects both the adsorption and aggregation behavior of the surfactant. Both of these characteristics influence the dynamic surface tension behavior of a surfactant system above the CMC after the creation of a new surface. Pendant bubble experiments were used to determine the evolution of surface tension over time in aqueous photosurfactant samples of varying isomeric composition. Simple theoretical models of the surfactant diffusion and adsorption process were developed to describe the resulting dynamic surface tension data.

4.2 Experimental/Methods

4.2.1 Axisymmetric Drop Shape Analysis Theory
Bashforth and Adams [1] pioneered the study of the shape of pendant drops of liquid hanging from a capillary as a means of determining the surface tension of the liquid. Such a method relies on the balance between gravitational and capillary forces acting on the drop to dictate the equilibrium shape of a drop of a given size. The generalized Young-Laplace equation, which dictates the equilibrium shape of the drop, cannot be solved analytically and requires numerical solution techniques. Bashforth and Adams (and later Andreas et al.[2] and Fordham [3] who extended their work) developed a system of estimating the surface tension by taking a
photograph of the drop and manually determining two of its dimensions: the maximum drop
diameter $d_e$ and the drop diameter $d_s$ at a distance $d_e$ from drop apex. This is shown
schematically in Figure 4-1, which is reproduced from Fordham [3].

![Diagram of pendant drop](image)

**Figure 1. Pendant drop.**

Figure 4-1. Figure 1 from Fordham [3], which illustrates the two pertinent drop dimensions used in early pendant
drop calculations.

From these two dimensions, the surface tension of the liquid is determined according to
prescribed relations [1, 2], and tabulated data for various drop shapes exist to aid these
calculations. This method is robust and allows not only for the determination of the surface
tension of a liquid drop surrounded by air, but also of the interfacial tension of two immiscible
liquids. Additionally, depending on whether the heavier fluid is inside the lighter, or vice versa,
the drop may be “pendant down”, as illustrated in Figure 4-1, or “pendant up”. The results of the
measurements are independent of the drop orientation [2].
As computational speed and efficiency have improved over the years, techniques have been developed which permit optical recognition of drops and automated numerical calculation of the surface tension [4, 5]. With sufficient contrast between the drop and the surrounding fluid, computer software invokes an edge detection algorithm to identify the drop contour. A best-fit value of surface tension is then calculated to match this contour. The user must specify a reference dimension (typically the diameter of the capillary or needle supporting the drop) and the densities of the two fluid phases, and the software calculates relevant quantities such as surface tension, drop volume, drop surface area, etc. These calculations can then be repeated at specified time intervals to track the temporal evolution of surface tension after creation of a new drop.

The mathematical expressions which describe the relationship between the drop profile and the surface tension can be developed by considering the expansion of a portion of curved interface, as shown in Figure 4-2. The two (perpendicular) radii of curvature of the surface are designated $R_1$ and $R_2$, and the lengths of the intercepted arcs are given by $x$ and $y$, respectively. Consider a slight outward displacement of the surface by a distance $dz$ normal to the interface. The area of the surface is then increased (from $A$ to $A'$) by a differential amount $dA$ given by

$$ dA = A' - A = (x + dx)(y + dy) - xy = xdy + ydx + dx dy = xdy + ydx $$

(4-1)

where $x + dx$ and $y + dy$ represent the new arc lengths, and the approximation arises from neglecting second-order differential quantities [6]. The increase in free energy associated with this increase in area is given by

$$ dG = \gamma dA = \gamma (xdy + ydx) $$

(4-2)
where \( \gamma \) is the surface tension. If ordinary pressure-volume work is responsible for the expansion of the surface, then the work required is given by

\[
dW = \Delta p dV = \Delta p x y dz
\]  

(4-3)

where \( \Delta p \) is the pressure difference between the exterior of the surface and its interior and \( dV \) is the volume swept by the moving surface [6].

![Figure 4-2](image)

**Figure 4-2.** Illustration of the expansion of an element of curved surface.

Equating the free energy change given by Eqn. 4-2 to the work required by Eqn. 4-3 yields

\[
\gamma (xdy + ydx) = \Delta p xy dz
\]  

(4-4)

The arc lengths \( x \) and \( x + dx \) in Figure 4-2 are related to the angle \( \alpha \) by

\[
x = R_1 \alpha
\]  

(4-5)

and

\[
x + dx = (R_1 + dz) \alpha
\]  

(4-6)

This allows for the following proportional relation:

\[
\frac{x + dx}{R_1 + dz} = \frac{x}{R_1}
\]  

(4-7)
Similarly,

\[ \frac{y + dy}{R_2 + dz} = \frac{y}{R_2} \tag{4-8} \]

Equations (4-7) and (4-8) simplify to

\[ \frac{dx}{xdz} = \frac{1}{R_1} \tag{4-9} \]

and

\[ \frac{dy}{ydz} = \frac{1}{R_2} \tag{4-10} \]

Equations 4-9 and 4-10 can be substituted into Eqn. 4-4 to relate \( \Delta p \), \( R_1 \), \( R_2 \), and \( \gamma \):

\[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tag{4-11} \]

This expression is the classic Young-Laplace equation, which allows for the calculation of the pressure difference across a curved interface based on the radii of curvature. This can be related back to the pendant drop calculations by revisiting the drop schematic shown in Figure 4-1. As illustrated in this figure, a coordinate system is chosen such that its origin is the apex of the drop. The \( z \) coordinate is the vertical coordinate extending away from the apex. The drop is assumed to be symmetric around this \( z \)-axis. The radial coordinate is denoted \( x \). The angle between the \( x \)-axis and a tangent line extending from a point on the drop contour with coordinates \((x,z)\) is given by \( \phi \). The arc extending from the apex to this point is denoted \( s \). The radii of curvature at this point are given by analytical geometry [6]:

\[ \frac{1}{R_i} = \frac{d\phi}{ds} = \frac{\frac{d^2z}{dx^2}}{\left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{\frac{3}{2}}} \tag{4-12} \]
Thus, the pressure difference across the interface at this point is given by

\[ \Delta p = \gamma \left( \frac{d^2 z}{dx^2} + \frac{dz}{dx} \right) \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right] \left( 1 + \left( \frac{dz}{dx} \right)^2 \right) \]  

This is a more generalized version of the Laplace equation for an axially symmetric drop. At the drop apex, the two radii of curvature are equal so that \( R_1 = R_2 = R_{\text{apex}} \). The pressure difference across the interface at the apex is then given by

\[ \Delta p_{\text{apex}} = \frac{2\gamma}{R_{\text{apex}}} \]  

The difference in pressure between the point \((x, z)\) on the drop contour and the drop apex is then represented by

\[ p(x, z) - p_{\text{apex}} = \gamma \left( \frac{d^2 z}{dx^2} + \frac{dz}{dx} \right) \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right] \left( 1 + \left( \frac{dz}{dx} \right)^2 \right) - \frac{2}{R_{\text{apex}}} \]  

This pressure difference can also be expressed hydrostatically as

\[ p(x, z) - p_{\text{apex}} = -\Delta \rho g z \]  

where \( \Delta \rho \) is the difference in fluid density between the drop phase and the surrounding phase and \( g \) is the acceleration of gravity. Equating the expressions in Eqns. 4-16 and 4-17 yields
This is the expression evaluated by the drop shape analysis software as a value of the surface tension is determined for a given drop profile.

4.2.2 Limitations of the Method

As described by Hoorfar and Neumann [7], a major limitation of current axisymmetric drop shape analysis routines is that inconsistent results are obtained for drops that are close to spherical in shape. Interestingly, the fitting routines appear to display a bias towards higher calculated surface tension values for these fairly spherical drops. An example of this is seen in Table 4-1, in which the surface tension of pure water was measured by the Krüss DSA10 drop shape analysis system (an apparatus described in more detail in the next section) for a series of drops of increasing volume. It is seen that the smaller and more spherical the drop, the higher and less reproducible the value of surface tension calculated by the software. The best agreement between the calculated value and the accepted literature value occurred when the drop was large and near the verge of detaching from the needle tip. Thus, whenever possible, the volume of liquid dispensed for a drop should be as large as possible (i.e. as large as can be supported by the surface tension of the liquid) for a measurement to ensure the best estimate of the surface tension. This is easily achieved for pure fluids, whose surface tension does not vary with time. But this poses a problem for solutions containing surface-active species, as these species diffuse and adsorb to the surface and lower the surface tension as time passes. In these systems, if the drop is initially at its optimal size (i.e. a large, elongated drop), subsequent
lowering of the surface tension will cause the drop to break. On the other hand, making a drop small enough to supported by the equilibrium tension of the drop will dictate that initially, just after the drop is formed and the tension value is still near the solvent value, the size of the drop is suboptimal and the tension will be overestimated by the software. The extent of this overestimation will depend on the difference between the initial surface tension value and the value at equilibrium. Determination of the exact drop size used for a given measurement requires consideration of the goals of the study and on which is of more importance: tension values at early times or the equilibrium value.

Table 4-1. Surface tension fitting results for pendant drops of water of varying volumes. Tension values reported are the average and standard deviation of four measurements taken over 3 s span.

<table>
<thead>
<tr>
<th>drop volume (µL)</th>
<th>4.3</th>
<th>7.4</th>
<th>10.6</th>
<th>15.4</th>
<th>22.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface tension (mN/m)</td>
<td>79.3 ± 1.3</td>
<td>75.4 ± 0.4</td>
<td>74.2 ± 0.4</td>
<td>73.1 ± 0.2</td>
<td>72.6 ± 0.1</td>
</tr>
</tbody>
</table>

Traditional pendant bubble experiments, in which a liquid drop hangs in air, require control of the air humidity to reduce evaporation of the drop during the course of a dynamic measurement. Evaporation of the drop causes a change in the concentration of any surface-active species present in solution, which can complicate an analysis of the adsorption process. If the tension equilibrates quickly enough, evaporation of the drop may be insignificant and not cause any problems to such a study. Also, if it is only desired to know the equilibrium tension of a solution above the CMC, then drop evaporation is unimportant. However, if accurate knowledge of the dynamic tension value over a long time span is required, then drop evaporation is a concern. As will be shown later in this chapter, experiments involving the C6 photosurfactant often needed hours to reach equilibrium tension values. It was difficult to control the humidity well enough to
prevent significant evaporation of a pendant drop over these time scales, so a pendant bubble approach was adopted instead. In these experiments a pendant bubble of air was created inside surfactant solution and the drop shape analysis was performed exactly as in the pendant drop case. In these studies, the bubble volume remained fairly constant over long periods of time and solution evaporation is less of a concern. An additional benefit of this method is that any modeling of the mass transfer of surfactant to the interface does not need to consider surfactant exchange between the drop and the contents of the needle and syringe, which can occur in the pendant drop case.

4.2.3 Pendant Bubble Method

Dynamic surface tension data were obtained with a Krüss DSA10 drop shape analysis system. A schematic of this system is shown in Figure 4-3. A pendant bubble of air was created in a surfactant solution contained in a quartz cuvette. A background light source was located behind the cuvette as a CCD camera captured the image of the bubble. The camera fed this image to a computer which displayed a magnified, digitized image of the bubble profile. Software then analyzed this profile and performed axisymmetric drop shape analysis [4, 5] to determine a value for the surface tension. This procedure was then repeated at specified time increments in order to track the evolution of surface tension in the system over time.

These dynamic surface tension measurements required background light to sharpen the contrast between the disperse phase and the continuous phase [8], so optical filters were placed on the background light source during these experiments. The visible and UV light filters shown in Figure 2-3 were used with the appropriate samples, while a 750 nm bandpass filter (Oriel 57661) was used with the dark-adapted sample to allow transmission of light at a high wavelength where
absorption by surfactant is not appreciable. Output intensity from this source (with UV filter in place), measured by a light meter in the UVA range, is only 1.7 $\mu$W/cm$^2$. For comparison, the Oriel lamp output (with UV filter) is 6.5 mW/cm$^2$. Thus, the background light from the Krüss instrument is so weak that the optical filters placed in its path during pendant bubble studies were merely precautionary, and no appreciable photoconversion was expected over the time scales of typical experiments.

Other than this background light, the experiments were performed in the dark. So, in these pendant bubble studies, the isomeric composition of the sample was initially dictated by the illumination state created before the experiment and it remained close to this value throughout the experiment, though some small amount of cis could have slowly reverted to trans. (In separate experiments, UV-Vis absorption was used to track the thermal reversion of mixtures back to a trans equilibrium in the absence of all light. The results exhibit first-order kinetics.

Figure 4-3. Schematic of drop shape analysis system. Krüss DSA10 Drop Shape Analysis system with DSA 1.8 software was used in pendant bubble studies. Note: Figure not drawn to scale.
with a time constant estimated at ~ 30 hours at 25° C.) Due to the extremely low CMC values of these surfactants and the resulting impractically long time scales needed for equilibration of interfacial properties (of order one day, as discussed later in the modeling section), all dynamic surface tension measurements were performed at concentrations well above the CMC.

4.3 Results

4.3.1 Dynamic Surface Tension Results

These experiments involve the creation of a fresh interface (via the formation of a pendant bubble of air inside an aqueous surfactant solution) and the tracking of the surface tension as a function of the age of this surface. The results of these studies are shown in Figure 4-4a. The curve for the dark sample is typical for these types of experiments: initially, when surfactant adsorption at the air/water interface is negligible, the surface tension remains high at a value near that of the pure solvent [9, 10]. As time passes and significant adsorption occurs, the surface tension decreases until eventually the interface becomes saturated with surfactant and the equilibrium surface tension is reached. The equilibrium surface tension found for the dark sample is in excellent agreement with the value previously reported for this surfactant in the “trans” state (29.5 mN/m) by Shang et al. [11] using the Wilhelmy plate method. The curves for the isomeric mixtures (the visible, 50/50, and UV samples), however, exhibit a rather different and interesting behavior. These curves show an intermediate plateau of nearly constant surface tension before ultimately reaching the same equilibrium tension as the dark sample. The surface tension value during this plateau is very near (and in the case of the UV sample, coincides with) the tension value (40.6 mN/m) identified by Shang et al. as the equilibrium value of the “cis” state. It is hypothesized that the behavior shown in the mixtures is due to competitive adsorption
between the *trans* and *cis* isomers present in solution. This type of behavior has been reported for other systems containing mixtures of nonionic surfactants [12, 13]. Presumably, in these C₆ samples, the air/water interface is first dominated by *cis* surfactant, leading to the onset of the intermediate plateau, but it eventually becomes saturated with *trans* surfactant as the more surface active *trans* isomer reaches the interface and displaces the adsorbed *cis* surfactant. A cartoon depiction of different stages of this adsorption process is shown in Figure 4-4b.

In the context of this competitive adsorption hypothesis, the isomeric composition of the air/water interface presumably changes throughout the duration of the intermediate plateau, beginning with a mostly *cis*-saturated interface at the onset of the plateau and proceeding to increase in *trans* content as *trans* surfactant continually reaches the interface and displaces the adsorbed *cis*. The fact that the surface tension changes only slightly during this process is consistent with the findings from the Langmuir film studies, which also suggest that *cis* present at an interface dominates the surface pressure/tension behavior and that a substantial amount of the *cis* must be removed from the interface (by compression with the Langmuir balance or by displacement in the pendant bubble studies) before significant surface tension changes are seen. This transition from a *cis*-dominant surface to a *trans*-dominant surface is comparable to the liquid-expanded (LE)/liquid-condensed (LC) surface phase transitions that are well documented [14. 15] for surfactant species that are capable of multiple adsorbed conformations. These systems with LE/LC (or gasesous to liquid-expanded, G/LE [16]) phase transitions also exhibit intermediate plateaus in their dynamic surface tension profiles during phase coexistence. In this photoresponsive system, the transition is caused by interchange of adsorbed isomer, rather than molecular re-orientation. The plateau ends when a significant amount of *cis* isomer has been
displaced from the interface and further adsorption of trans isomers (possible because the trans isomer packs more tightly and has a higher capacity for adsorption) allows for further reduction in the surface tension. As shown in Chapter 3, Langmuir film experiments involving the compression of monolayers indicate that the surface pressure of a saturated film increases sharply once its cis content drops below about 10%. Thus, the second tension relaxation that occurs in the isomeric mixtures seemingly corresponds to the point at which the cis composition of the surface drops below this threshold.

Some interesting trends can be noted from the dynamic surface tension curves. First, the initial rate of decline in surface tension increases as the cis content of the sample increases. Secondly, amongst the isomeric mixtures, the intermediate plateau becomes longer with increasing cis content and the time required to reach the final equilibrium state becomes much longer. It is worth noting that, in the case of the UV samples, relaxation to the final equilibrium state is slow enough that the thermal reversion of cis to trans in the sample is not insignificant. Since this relaxation can take as long as 8 hours, even at the slow reversion rate described earlier, the trans content of the sample can increase by almost 25% over this time. Thus, for these samples, the transition from a cis-dominated surface to a trans-dominated surface is augmented by an increase in the trans supply in bulk solution over time and possibly by thermal reversion of adsorbed cis surfactant to trans at the interface. For all other samples studied, the tension relaxations happen on time scale which is short compared to that for thermal reversion.
Figure 4-4. (a) Dynamic surface tension profiles of a 0.20 mM aqueous C₆ solution under various illumination conditions obtained using the pendant bubble method. Open and closed versions of each symbol indicate replicate experiments for the purposes of establishing reproducibility. Data points are shown in plots with less frequency than they were acquired during the experiment, for the purpose of clearly distinguishing the different symbols. (b) Cartoon illustration of competitive adsorption mechanism by which cis surfactant (bent tail) reaches the interface before the trans isomer (straight tail), but is eventually displaced by the trans isomer. In these depictions, only the air/water interface and sublayer (thin layer of solution adjacent to the interface) are shown. Numbers used to label sketch correspond to different surface ages for UV curve shown in (a).
4.3.2 Effect of Surfactant Concentration

These pendant bubble studies were repeated for various bulk surfactant concentrations, and the same qualitative behavior was observed. Quantitative differences resulted from faster relaxations occurring at higher concentrations. The impact of concentration on relaxation time scales is best demonstrated by separating the results for the two isomers. According to the competitive adsorption hypothesis, these dynamic surface tension plots contain information regarding the time needed for each of the isomers to adsorb to the interface: the time needed to reach the intermediate tension plateau gives an estimate of the cis adsorption time scale, and the time needed to reach the final equilibrium tension gives an estimate of the trans adsorption time scale.

Specifically, the time needed for \((1-e^{-1})(100\%) = 63\%\) relaxation to the intermediate tension plateau was chosen as the characteristic cis relaxation time scale. In Figure 4-5a, experimentally observed cis relaxation time scales are plotted against the cis concentration of samples from a variety of illumination states. The data points collapse onto one curve, indicating that the cis relaxation shows the same dependence on cis concentration for all illumination states. Half the time needed for \((1-e^{-2})(100\%) = 86\%\) relaxation to the final equilibrium state was used as an estimate of the characteristic trans relaxation time scale (this value is used instead of 63% to avoid choosing data from the intermediate plateau). Figure 4-5b is a plot of this trans relaxation time scale vs. trans concentration for various samples, and like the cis data, these trans data exhibit a common trend. These results suggest that the transport of trans and of cis to the interface occur independently (and at disparate rates), and that the same physical mechanism governs the transport of a given isomer in all samples.
Figure 4-5. (a) Characteristic cis relaxation time scale plotted as a function of cis concentration. (b) Characteristic trans relaxation time plotted as a function of trans concentration.

4.4 Modeling of Surfactant Diffusion and Adsorption

4.4.1 Development of Models which Account for Role of Aggregates

In order to interpret the dynamic surface tension data, it is useful to calculate the expected time scales for diffusion of surfactant to the interface. A pertinent length scale in these systems is the depletion thickness $\ell$ defined by
\[ \ell = \frac{\Gamma}{C_T} \]  

(4-19)

where \( \Gamma \) is the excess surface concentration and \( C_T \) is the bulk surfactant concentration [17].

This represents the depth of solution depleted by surfactant adsorption. Even at the lowest concentrations studied, the depletion layer is only on the order of 0.1 mm, which is significantly smaller than either of the physical length scales present in the experiment: the bubble radius (~1 mm) and the cuvette width (~10 mm). Thus, the depletion layer is the relevant length scale for diffusion calculations.

In surfactant systems containing aggregates, such as those under study in the pendant bubble experiments, the role of aggregates in the adsorption process must be considered. Aggregates can contribute to surfactant adsorption both by diffusion and by dissolution. In order to develop simple models, we assume limiting values for three aggregate properties: dissolution rate, mobility, and "fusibility" at the interface (to be explained momentarily). For dissolution rate, we examine extremely slow dissolution, for which aggregates are essentially "frozen" and there is no net monomer exchange between the aggregates and the bulk solution, and infinitely fast aggregate dissolution, for which aggregates break up to replenish the monomer supply in the bulk solution as rapidly as it is depleted. For aggregate mobility, the case of stationary, non-diffusing aggregates is contrasted with the case of aggregates diffusing with a finite diffusivity. And lastly, the ability or inability of the aggregates to "fuse" at the interface is considered. This "fusibility" refers to the availability of the surfactant contained in the aggregate for adsorption once the aggregate reaches the interface, either through direct adsorption of the aggregate [18] or by dissolution of the aggregate once it reaches the interface. These simple models focus on the transport of surfactant to the interface and do not, except via the fusibility criterion, consider
additional limitations to the adsorption process such as kinetic adsorption barriers. Consideration of two values for each of the three aggregate parameters yields eight limiting cases:

1. Fast-dissolving, diffusing, fusible aggregates
2. Frozen, diffusing, fusible aggregates
3. Fast-dissolving, non-diffusing, fusible aggregates
4. Frozen, non-diffusing, fusible aggregates
5. Fast-dissolving, diffusing, non-fusible aggregates
6. Frozen, diffusing, non-fusible aggregates
7. Fast-dissolving, non-diffusing, non-fusible aggregates
8. Frozen, non-diffusing, non-fusible aggregates

In developing diffusional time scale estimates for each case, some redundancy occurs among the results.

*Case 1.* In this case, aggregates break up infinitely quickly in order to maintain the monomer concentration equal to the CMC. This results in a thin layer of solution adjacent to the interface of thickness $\ell_1$ which is free of aggregates and over which the monomer concentration is depleted. Adjacent to this monomer depletion layer is an aggregate depletion layer of thickness $\ell_{agg}$ in which the monomer concentration is equal to the CMC but the aggregate concentration is depleted. This scenario is illustrated in Figure 4-6. Continuity of the surfactant flux at $x = \ell_1$, where $x$ is the coordinate extending away from the interface (since the depletion layer is much smaller than the bubble radius, curvature effects are ignored and the interface is treated as planar). requires that
where $D_I$ and $D_{agg}$ represent the diffusivities of the monomers and aggregates, respectively, and $c_I$ and $c_{agg}$ represent the concentrations of the monomers and aggregates, respectively. $N_{agg}$ is the aggregation number of the aggregates, which are assumed to be monodisperse. An order-of-magnitude estimate of the flux at $x = \ell_1$ is given by

$$D_1 \frac{C_I}{\ell_1} \sim D_{agg} N_{agg} \frac{(C_I - CMC)}{N_{agg}} \frac{(C_I - CMC)}{\ell_{agg}} = D_{agg} \frac{(C_I - CMC)}{\ell_{agg}}$$

(4-21)

**Figure 4-6.** Depiction of the depletion layers and corresponding concentration profiles assumed during development of surfactant diffusion models for the case of fast-dissolving aggregates.

The total amount of surfactant, $S$, per unit area contained between $x = 0$ and $x = L$, where $L$ is a fixed depth and $L > \ell_1 + \ell_{agg}$, is given by

$$S \approx \frac{1}{2} (C_{MC}) \ell_1 + \left[ C_{MC} + \frac{1}{2} (C_I - CMC) \right] \ell_{agg} + C_I (L - \ell_1 - \ell_{agg})$$

(4-22)

if linear concentration profiles of the monomers and aggregates are assumed within their respective depletion layers. The monomer concentration at $x = 0$ is assumed to be nearly zero.
This is certainly true at early times, but after significant adsorption has occurred, the concentration at \( x = 0 \) will increase. Nonetheless, the CMC serves as a reasonable order-of-magnitude estimate of the concentration difference across the monomer depletion layer. Eqn. 4-21 can be used to eliminate the aggregate depletion layer thickness from Eqn. 4-22:

\[
S \approx \left[ \left( \frac{1}{2} CMC - C_r \right) - \frac{1}{2} \frac{D_{agg}}{D_i} \frac{(C_r - CMC)^2}{CMC} \right] \ell_1 + C_r L \quad (4-23)
\]

The rate of change of surfactant contained within this region is related to the growth of the monomer depletion layer by

\[
\frac{dS}{dt} \approx \left[ \left( \frac{1}{2} CMC - C_r \right) - \frac{1}{2} \frac{D_{agg}}{D_i} \frac{(C_r - CMC)^2}{CMC} \right] \frac{d\ell_1}{dt} \quad (4-24)
\]

A material balance dictates that the rate of depletion of surfactant from this region must equal the rate of change in adsorbed surfactant concentration.

\[
\frac{dS}{dt} = \frac{d\Gamma}{dt} \quad (4-25)
\]

An order-of-magnitude estimate of these quantities shows that

\[
\left[ \left( C_r - \frac{1}{2} CMC \right) + \frac{1}{2} \frac{D_{agg}}{D_i} \frac{(C_r - CMC)^2}{CMC} \right] \frac{\ell_1}{\ell} \sim \frac{\Gamma_{\infty}}{\tau} \quad (4-26)
\]

where \( \Gamma_{\infty} \) is maximum surface packing parameter obtained from a Frumkin isotherm fit to the equilibrium surface tension data [17] (alternatively, \( \Gamma_{eq} = \Gamma_{CMC} = \Gamma_{sat} \) could be used) and \( \tau \) is the characteristic time scale for surfactant adsorption and surface tension relaxation. This expression then allows for an estimate of the monomer depletion layer thickness

\[
\ell_1 \sim \frac{\Gamma_{\infty}}{\left[ \left( C_r - \frac{1}{2} CMC \right) + \frac{1}{2} \frac{D_{agg}}{D_i} \frac{(C_r - CMC)^2}{CMC} \right]} \quad (4-27)
\]
Finally, the rate of change of adsorbed surfactant is also equal to the flux of surfactant monomer at the interface.

\[
\frac{d\Gamma}{dt} = D_1 \frac{\partial c_1}{\partial x} \Bigg|_{x=0}
\]  

(4-28)

An order-of-magnitude estimate of these terms is given by

\[
\frac{\Gamma_m}{\tau} \sim D_1 \frac{CMC}{\ell_i}
\]  

(4-29)

Rearranging Eqn. 4-29 and invoking Eqn. 4-27 for the monomer depletion layer thickness finally permits an estimate of the characteristic time scale for adsorption and illustrates the dependence of this time scale on the total surfactant concentration.

\[
\tau \sim \frac{\ell_i \Gamma_m}{D_1 (CMC)} \sim \frac{\Gamma_m^2}{D_1 (CMC) \left[ \left( C_T - \frac{1}{2} CMC \right) + \frac{1}{2} \frac{D_{agg}}{D_1} \frac{(C_T - CMC)^2}{CMC} \right]}
\]  

(4-30)

Song et al. [19] have performed a more detailed analysis of the adsorption process in a solution containing fast-dissolving aggregates but allow for finite adsorption kinetics at the air-water interface. Their conclusions are qualitatively similar to those reached here.

**Case 5.** Since the case of fast-dissolving, diffusing aggregates results in an aggregate-free region adjacent to the interface, the ability of the aggregate to fuse with the interface is irrelevant, and Case 5 is identical to Case 1, with a relaxation time given by Eqn. 4-30.

**Cases 3 and 7.** These are special cases of Case 1 in which the aggregates are stationary (and fusibility is immaterial when aggregates are non-diffusing), so that the characteristic time scale for adsorption can be found by setting \(D_{agg} = 0\) in Eqn. 4-30.
These analyses involving fast-dissolving aggregates employ a quasi-steady approximation. This is appropriate if the time scale associated with a change in the concentration is much slower than the time scale associated with surfactant flux through the fluid. This can be justified by examining the full transient diffusion equation governing surfactant monomer within the monomer depletion layer.

\[
\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \quad (4-32)
\]

The order-of-magnitude values of these terms are given by

\[
\frac{\partial c_i}{\partial t} \sim \frac{C_M}{\tau_D}, \quad D_i \frac{\partial^2 c_i}{\partial x^2} \sim D_i \frac{C_M}{\ell_1^2} \quad (4-33)
\]

so that the characteristic time scale for diffusion through the depletion layer is given by

\[
\tau_D \sim \ell_1^2 / D_i. \quad \text{If the relaxation time scale } \tau \text{ is much larger than this, one is justified in neglecting the transient term. Under typical experimental conditions for surfactant in the dark state } (C_T = 0.20 \text{ mM}), \ell_1 \sim 10^{-5} \text{ m, and } \tau_D \sim 1 \text{ s. Because the time scale } \tau \text{ for surface tension relaxation in a typical experiment is } \sim 10^2-10^4 \text{ s, a quasi-steady analysis is warranted. This result also validates the assumption of linear concentration profiles within the depletion layers.}
\]

\textbf{Case 2.} In this case, aggregates are frozen and no net exchange of surfactant occurs between aggregates and monomers. Transport of surfactant to the interface therefore takes place via the independent parallel processes of monomer diffusion and aggregate diffusion. This scenario involves overlapping monomer and aggregate depletion layers, and is illustrated in Figure 4-7.
The thicknesses of these depletion layers increase with time with order-of-magnitude estimates given by

\[ \ell_1 \sim \sqrt{D_1 t} \quad (4-34) \]

\[ \ell_{agg} \sim \sqrt{D_{agg} t} \quad (4-35) \]

**Figure 4-7.** Depiction of the depletion layers and corresponding concentration profiles assumed during development of surfactant diffusion models for the case of non-dissolving or “frozen” aggregates which are nonetheless fusible.

In this case, the flux of surfactant at the interface has contributions from both the monomers and aggregates, so that the analog of Eqn. 4-28 becomes

\[ \frac{d\Gamma}{dt} = D_1 \frac{\partial c_1}{\partial x} \bigg|_{x=0} + D_{agg} N_{agg} \frac{\partial c_{agg}}{\partial x} \bigg|_{x=0} \quad (4-36) \]

with order-of-magnitude estimates given by

\[ \frac{\Gamma_0}{\tau} \sim D_1 \frac{CMC}{\ell_1} + D_{agg} \frac{C_T - CMC}{\ell_{agg}} \quad (4-37) \]

This expression can be combined with Eqns. 4-34 and 4-35 (using \( \tau \) as the appropriate scale for \( t \)) to give an estimate of the characteristic time scale for adsorption in this case.
Cases 4, 6, and 8. These cases all involve aggregates that are unable to contribute to adsorption because they are frozen and either non-diffusing or unable to fuse at the interface. These are special cases of Case 2 with characteristic adsorption times that can be attained from the Case 2 estimate by making either of the following adjustments:

\[ D_{agg} = 0 \quad \text{(in non-diffusing Cases 4 and 8)} \]

\[ D_{agg} N_{agg} \frac{\partial c_{agg}}{\partial x} \bigg|_{x=0} = 0 \quad \text{(in non-fusible Cases 6 and 8)} \]

This results in adsorption which is completely dependent upon the monomer so that the diffusional time scale is independent of total concentration, and is given by

\[
\tau \sim \frac{\Gamma_\infty^2}{D_1 (CMC)^2}
\]

(4-39)

Because the CMC values of this photoresponsive surfactant system are so small, the time scale associated with diffusion of monomeric surfactant to the interface can be very long. To illustrate this, we compute the diffusional time scale appropriate for a dark sample at a bulk concentration equal to the CMC:

\[
\tau_D^{\text{dark}} \bigg|_{c=CMC} \sim \frac{\Gamma_\infty^2}{(CMC)^2 D_1} = \frac{(8 \times 10^{-6} \text{ mol/m}^2)^2}{(0.001 \text{ mol/m}^3)^2 (5 \times 10^{-10} \text{ m}^2/\text{s})} = 1.28 \times 10^5 \text{ s} = 35.6 \text{ hours}
\]

The value of \( \Gamma_\infty \) used (8x10^{-6} mol/m^2) was found by Shang et al. for this surfactant in the trans state [11], and the value of \( D_1 (5x10^{-10} \text{ m}^2/\text{s}) \) is typical of monomer diffusivities reported in the literature [17]. Here it is seen that a pre-micellar dark surfactant sample requires more than a
day for its surface properties to reach equilibrium. It is for this reason that experiments were generally performed at concentrations well above the CMC.

4.4.2 Model Predictions

For the dark samples, a comparison of the experimentally observed relaxation times to the predictions of the diffusion models is given in Figure 4-8a. The experimental data points correspond to the time needed for the tension to complete 63% of its relaxation to equilibrium. In the models, the value of $\Gamma_\infty$ used is $8 \times 10^{-6}$ mol/m$^2$, $D_1$ is $5 \times 10^{-10}$ m$^2$/s, and $D_{agg}$ is $2.6 \times 10^{-12}$ m$^2$/s (measured for this surfactant by dynamic light scattering at 0.10 mM [20]). The CMC value of 1 μM is used. The models for Cases 4, 6, and 8 (in which the aggregates do not contribute to adsorption) clearly do not describe the experimental data well, since the experimentally observed relaxation time scales do show a dependence on the total surfactant concentration and are much shorter than predicted by these models. The models in which the aggregates contribute to the adsorption process are all in reasonable agreement with the experimental data, despite widely different combinations of aggregate mobility and dissolution rate. This makes it difficult to infer the specific role of aggregates. Nonetheless, these simple diffusional arguments, which use only two diffusivity values (one measured and one estimated from literature) and two parameters fit from equilibrium experiments ($\Gamma_\infty$ and CMC), with no additional adjustable parameters, can be used to obtain reasonable estimates for the characteristic relaxation time scale for these dark samples, despite ignorance regarding the specific role of the aggregates.
Results for cis adsorption in UV samples were also compared with predictions obtained from the models for the eight limiting cases. These calculations were performed for a $\Gamma_c$ value of $5 \times 10^{-6}$ mol/m$^2$ (found by Shang et al. for this surfactant in the "cis" state [11]) and $D_1$ and $D_{agg}$ values identical to those used for the dark case (a reasonable assumption for the monomers, but harder
to justify for the aggregates, for reasons mentioned in Chapter 3). The critical concentration corresponding to the onset of a mostly cis aggregate phase, 65 µM, was used for the CMC value in the models. As shown in Figure 4-8b, the models in which aggregates contribute least to the relaxation process are in reasonable agreement with the experimental data. Except perhaps for the case of fast-dissolving aggregates, all of the models predict relaxation time scales of the same order of magnitude as the experimental data.

The simple diffusion models developed in this section are capable of describing the concentration dependence of the surfactant adsorption time scales as well as capturing the disparity of these time scales between the trans and cis isomers. These models are invoked for their simplicity, as they are simple algebraic equations and do not require any detailed knowledge regarding aggregate shape or aggregation number, and for the basic insight they offer concerning the potential roles of aggregates and the effect of total surfactant concentration on the adsorption process. They are intended only as order-of-magnitude estimates of the characteristic time scales needed for surfactant adsorption.

4.5 Summary
Dynamic surface tension studies have been performed on aqueous solutions of the C₆ photosurfactant. While all samples reach the same equilibrium state after creation of a fresh interface, the dynamic behavior of the surface tension during relaxation is highly dependent upon the isomeric composition of the sample. Samples containing significant amounts of the cis isomer display an intermediate plateau of nearly constant tension before finally relaxing to equilibrium. It is hypothesized that the presence of the plateau is due to competitive adsorption between cis and trans isomers present in solution, and that onset of the intermediate plateau
corresponds to a surface that is initially cis-dominated. The cis isomer adsorbed on the surface is eventually entirely displaced by the more surface active trans isomer and the final equilibrium state reached by all samples corresponds to a surface saturated with trans surfactant.

The large difference in the critical concentrations associated with the formation of separate trans-rich and cis-rich aggregate phases (discussed in Chapter 3) accounts for the large disparity seen in the time scales associated with adsorption of the trans and cis isomers. At high concentrations, cis monomer is much more abundant than is trans monomer, allowing the cis isomer to reach the surface more quickly in these isomeric mixtures. Simple diffusional time scale models which account for limiting cases of aggregate contributions to adsorption have been developed to describe the surface tension relaxation behavior of the two isomers and good agreement is found between the predictions and the experimentally observed time scales. Furthermore, the models show that the aggregates must play an important role in the relaxation to a trans-saturated equilibrium, though the specific role is unclear from these experiments alone. By contrast, due to the much higher CMC of the cis isomer, aggregates play little or no role in the adsorption process leading to a cis-dominated interface.

4.6 References

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Chapter 5
Dynamic Surface Tension: Response to Illumination

5.1 Introduction
The previous chapters described the results of various experiments performed on the C₆ photosurfactant, many of which involved studies of mixtures of the cis and trans photoisomers. For the purposes of most of these experiments, the two components of the mixtures behaved as unrelated species. In most of these studies, illumination of the surfactant had been used only to dictate the composition of the mixture (by bringing about a photostationary cis/trans ratio) prior to its use. In experiments discussed in this chapter, the responsiveness of the surfactant to light is exploited, as surfaces containing adsorbed surfactant were illuminated to drive photoisomerization of the surfactant. Specifically, high-intensity light was focused on the surface of a pendant bubble saturated with surfactant, and the change in the isomeric composition of the adsorbed surfactant layer was detected by monitoring the surface tension response of the system. Results from previous monolayer studies, along with consideration of the proposed conformations of the adsorbed surfactant isomers, were used to interpret the results.

5.2 Experimental Method
The experimental apparatus used for these experiments was identical to that described in Chapter 4 for the pendant bubble measurements. The only additional instrumentation was a Dymax Bluewave 200 high-intensity spot lamp. A single pole lightguide was used to focus high-intensity light on the bubble surface. Output intensity from this source (with UV filter in place), measured by a light meter in the UVA range, is greater than 300 mW/cm². The procedure was to allow the surface tension to relax and then illuminate the bubble surface.
5.3 Results

5.3.1 Response of Surface Tension to Bubble Surface Illumination

In these experiments, the dynamic surface tension of a surfactant solution was tracked using the pendant bubble method as described in Chapter 4, but when the tension reached a particular point, the bubble surface was illuminated by a focused, high-intensity light source to drive photoisomerization of the surfactant. In one such experiment, an air bubble was created inside a solution of C₆ surfactant initially in the visible state, and the surface tension was tracked over time. When the tension relaxed to its final equilibrium value, the bubble surface was illuminated with focused, high-intensity UV light and the surface tension quickly (<1 s) rose to a higher, cis-dominated value. This implies a fast surface photoconversion of trans to cis and a “squeezing out” of cis surfactant from the over-crowded interface and into the subphase. Two variations of the experiment were explored: in one case, the UV illumination lasted only 5 seconds, while in the other, the UV illumination was maintained indefinitely. The results are shown in Figure 5-1a, with a cartoon depiction of the photoconversion shown in Figure 5-1b. In the case of the 5 second illumination pulse, the surface tension remained at the higher, cis-dominated value for some time before eventually returning to the lower, trans-saturated value. In the case of sustained illumination, the surface tension remained at the higher value for as long as UV illumination was maintained. This indicates that photoconversion of the surfactant on the bubble surface was much faster than the rate of displacement of adsorbed cis surfactant by trans isomer.
Figure 5-1. (a) Dynamic surface tension studies of a 0.16 mM $C_6$ solution involving illumination of the bubble surface during the experiment. Surfactant solution was initially in the visible state, then illuminated with UV light. (b) Cartoon depiction of surfactant ($cis$: bent tail, $trans$: straight tail) adsorbed at the bubble surface just before (1) and just after (3) illumination with UV light.

Figure 5-2a shows the results of a similar experiment in which the surfactant solution was initially in the UV photostationary state and the tension was allowed to relax until, at a point on the intermediate tension plateau, the bubble surface was illuminated with focused, high-intensity visible light. A 5 second pulse of this visible light caused a rapid (again, on the order of 1 s) rise in surface tension before the tension eventually relaxed to the $trans$-saturated equilibrium value. The initial rise in surface tension is due to conversion of the adsorbed $cis$ surfactant to $trans$, so that the hydrophobic tail of the surfactant is raised out of the air/water interface and into the air.
phase, consistent with the proposed conformations of the adsorbed surfactant. Immediately after illumination, when the number of surfactant molecules on the surface is unchanged, this results in an increase in unoccupied surface and a rise in surface tension. This is depicted in Figure 5-2b. Trans surfactant then diffuses to the surface and adsorbs to these vacant sites, lowering the surface tension. Another 5 second pulse of visible light is delivered after the tension reaches the trans-saturated equilibrium. This causes another sudden rise in surface tension before the tension returns to the final equilibrium state. This rise in tension is caused by the conversion of a surface covered with only trans surfactant to a surface with the isomeric composition (15% cis) corresponding to the visible photostationary state. This is illustrated in Figure 5-2c.
Figure 5-2. (a) Dynamic surface tension studies of a 0.16 mM C₆ solution involving illumination of the bubble surface during the experiment. Surfactant solution was initially in the UV state. (b) Cartoon depiction of surfactant (cis: bent tail, trans: straight tail) adsorbed at the bubble surface just before (4) and just after (5) first illumination with visible light. (c) Depiction of surfactant adsorbed at the bubble surface just before (1) and just after (2) second illumination of visible light.

5.3.2 Interpretation of Results Using Film Balance Results

These findings are in very good agreement (even quantitatively) with the Langmuir film isotherm results reported in Chapter 3, as shown in Figure 5-3. In this plot, various points along the isotherms are labeled and numbered, and these numbers are used to identify the transition of
the monolayer state occurring during the surface illumination experiments shown in Figures 5-1 and 5-2. For example, in Figure 5-1a, the illumination of a *trans*-saturated surface with UV light is labeled as a transition from Point 1 to Point 3. In the surface pressure isotherm plot in Figure 5-3, Point 1 marks the saturation point of an all-*trans* monolayer, and Point 3 is located on the UV curve, vertically below Point 1. The surface pressure difference between Points 1 and 3 agrees with the observed surface tension change seen upon illumination of the bubble surface. In Figure 5-2a, the first pulse of visible light shows a transition from Point 4 to Point 5. The surface pressure isotherm shows Point 4 as the saturation point of a UV-illuminated sample, with Point 5 located directly below on the visible curve. The decrease in surface pressure seen in going from a saturated, *cis*-dominant surface (Point 4) to a surface with the same number of adsorbed molecules, but with an isomeric composition characteristic of the visible state (Point 5), is manifested in the pendant bubble studies as a rise in surface tension upon the first pulse of visible illumination in Figure 5-2a. The second pulse of visible light shows a transition from Point 1 to Point 2, with Point 2 being located on the visible curve directly below Point 1. The surface pressure difference between Points 1 and 2 is almost as large as the difference between Points 1 and 3, just as the surface tension rise obtained by illuminating a *trans*-saturated surface with visible light is almost as large as the rise obtained by illumination with UV light. Thus, the results of the bubble surface illumination studies are complementary to the adsorbed monolayer results obtained with the Langmuir film balance. These bubble surface illumination studies also show that surface photoconversion between the adsorbed isomers is very rapid under high-intensity illumination.
Figure 5-3. Langmuir film balance results used to explain results seen from experiments in Figures 5-1 and 5-2. Numbers associated with illumination in Figures 5-1 and 5-2 correspond to numbered points on surface pressure-area isotherms shown in Figure 5-3.

To further demonstrate the impact of a small amount of cis on the system, this type of experiment was repeated for a solution initially illuminated to photostationarity with light passed through a 455 nm longpass filter. The cis content of such a state was estimated by UV-Vis absorption to be about 9%. The results of the experiment are shown in Figure 5-4. The reduced cis content of this sample, compared to the other isomeric mixtures previously studied in dynamic surface tension experiments, is evidenced by the short duration of the intermediate tension plateau. This sample then eventually reached the same trans-saturated equilibrium state seen in all samples of this surfactant. The bubble surface was then illuminated with a 5 second pulse of high-intensity light passed through the same 455 nm longpass filter. This caused a rapid jump in surface tension before the surface tension returned to the equilibrium value. The magnitude of this rise in surface tension is smaller than for UV or visible illumination, which is to be expected as this illumination results in a surface with a lower percentage of adsorbed cis surfactant than in the UV or visible states. This small jump in surface tension upon illumination
using this optical filter is consistent with monolayer study results shown in Figure 3-3. This experiment demonstrates that, at equilibrium, the isomeric composition of surfactant at the interface is different from that in the bulk solution. This was already assumed in the competitive adsorption hypothesis, in which all samples reach a trans-saturated equilibrium regardless of their isomeric composition, but is clearly confirmed here, where forcing the surface composition to match the bulk composition results in a change from the equilibrium tension value.

![Graph showing dynamic surface tension studies](image)

**Figure 5-4.** Dynamic surface tension studies of a 0.4 mM C₆ solution involving illumination of the bubble surface during the experiment.

### 5.4 Summary

Dynamic surface tension studies in which the surface of a pendant bubble was illuminated with high-intensity light reveal that the conversion of *trans* to *cis* and vice versa on the bubble surface is rapid (seconds or less) under these conditions. This surface photoconversion results in rapid changes in the dynamic surface tension, with tension differences that can be rationalized on the basis of surfactant architecture. Specifically, an increase in the *cis* content of a surface saturated with adsorbed surfactant leads to overcrowding and desorption of surfactant from the interface,
resulting in an increase in surface tension. Interestingly, an increase in the trans content of a saturated surface initially also causes a rise in surface tension, due to the tail of the surfactant reconfiguring to occupy less of the interface. Both of these trends, including quantitative estimates of the magnitude of the resulting surface tension changes, can be predicted from the results of monolayer studies performed using a Langmuir film balance.
Chapter 6
Effect of Temperature

6.1 Introduction
The temperature of a surfactant solution is known to influence its properties. Specifically, the equilibrium and dynamic values of surface tension generally decrease with increasing temperature [1-3]. Additionally, for solutions containing surfactant aggregates, the temperature of the solution dictates the concentration at which these aggregates form [1, 4, 5] and the rate at which these aggregates can dissolve [6, 7]. The temperature dependence of these aggregate properties can influence the effect of temperature seen in dynamic surface tension studies of surfactant systems above the CMC. Understanding the effect of temperature on the behavior of a given surfactant is helpful in determining its range of applicability.

Pendant bubble experiments were performed to determine the effect of temperature on the rate of diffusion and adsorption for each isomer of the C₆ photoresponsive surfactant. These experiments were performed at surfactant concentrations which give rise to trans aggregates, but not to cis aggregates. Fluorescence studies were carried out to establish the role of temperature in the aggregation behavior of the surfactant. Further fluorescence studies were performed in which surfactant solutions containing aggregates were diluted rapidly and the rate of dissolution of these aggregates was inferred from fluorescence decay. The results of the dynamic surface tension experiments were interpreted by the application of diffusion models which include both the effect of temperature on the diffusivity and the effect of temperature on the supply of monomer via its effect on the CMC.
6.2 Experimental Methods

6.2.1 Dynamic Surface Tension

Dynamic surface tension data were obtained as described in Chapter 4. In these experiments, the surfactant solution was first illuminated at room temperature to the desired photostationary state, and vials containing the solution were immersed in a controlled-temperature water bath (in the absence of light). After the desired temperature was attained, the solution was transferred to the cuvette for surface tension measurement. This resulted in a solution which may not have been at the photostationary-state isomeric composition for this new temperature, but allowed for the isolation of the effect of temperature on the aggregation state of the system without the added complication of having a different isomeric composition. As soon as the sample was removed from illumination, the isomeric composition slowly changed as cis thermally reverted back to trans at a rate that increased with increasing temperature. (In separate experiments, UV-Vis absorption was used to track the thermal reversion of mixtures back to a trans equilibrium in the absence of all light. The results exhibit first-order kinetics with a time constant estimated at ~ 30 hours at 25 °C, 10 hours at 35 °C, and 5 hours at 40 °C.) Nonetheless, if the heating or cooling was performed rapidly and the measurement was completed on a much shorter time scale than the time scale associated with thermal reversion, the isomeric composition of the sample remained close to the room temperature photostationary equilibrium. During the measurement, the bottom face of the cuvette was in thermal contact with a stage connected to a circulating water bath. A temperature probe was inserted into the surfactant solution near the bubble surface, and the temperature was maintained within ± 0.5 °C during the measurement.
6.2.2 Fluorescence

Steady-state fluorescence spectra were obtained as described in Chapter 3. Samples containing varying amounts of C₆ surfactant and a fixed amount (1.8 μM) of the fluorescent probe Nile Red were excited at 575 nm, and the fluorescent emission spectrum was measured for each sample at several different temperatures. This allowed the peak intensities of the resulting spectra and the wavelengths at which these maxima occur to be determined as functions of concentration and temperature. The sample holder of the spectrophotometer was heated or cooled by a circulating water bath. Samples were stirred while being heated or cooled as well as during measurements. Attainment of the target temperature within ± 0.5 °C was verified by a thermocouple.

6.2.3 Rapid Dilution Studies

Experiments were conducted in which aqueous C₆ solutions containing aggregates and Nile Red were maintained at a fixed temperature, with stirring, before being added rapidly to a cuvette containing water maintained at the same temperature. The resulting diluted mixture was stirred and excited at 575 nm, and the fluorescent emission intensity at a given wavelength was tracked over time. The dilution ratio was ten. The rate of decay of the intensity gave an estimate of the rate of dissolution of aggregates, as the Nile Red once contained within an aggregate phase was expelled and exposed to an aqueous domain where its emission was much weaker. Simple time scale estimates were obtained by fitting a single exponential function to the dynamic response of the emission intensity. Control experiments performed with the water-soluble dye Methylene Blue exhibited a time constant of about 5 seconds. This is taken to be the characteristic time scale needed for a sample to become well-mixed and homogeneous. This mixing time scale did not vary significantly with changes in temperature. Thus, in samples containing surfactant and
probe, emission decays taking longer than this were presumably due to dissociation of the aggregates. Temperature control during these studies was achieved as described above in the Fluorescence section.

6.3 Results

6.3.1 Effect of Temperature on Surface Tension Relaxations

An aqueous solution of surfactant in the dark-adapted state was heated or cooled to a specified temperature, a pendant bubble of air was created inside this solution, and the surface tension was monitored as a function of the age of the bubble surface. The results for a 0.25 mM solution are shown in Figure 6-1. It is seen that, as the temperature of the solution is increased, the equilibrium surface tension reached by the surfactant system decreases, consistent with findings from other aqueous solutions [3, 8], and the time needed for the tension to reach this equilibrium value is reduced.

![Figure 6-1](image.png)

Figure 6-1. Dynamic surface tension profiles for aqueous 0.25 mM C₆ photosurfactant solutions at various temperatures. Sample in dark-adapted state.
This set of experiments was repeated with surfactant that was first illuminated to the visible photostationary state. The results are shown in Figure 6-2. As seen in Chapter 4 for samples in this state, these dynamic surface tension curves are qualitatively different from those of the dark samples, as they exhibit an intermediate plateau of nearly constant tension before eventually relaxing to a final equilibrium value. As discussed previously, the first relaxation (from the initial tension value to the value at the onset of the plateau) corresponds to adsorption of primarily \textit{cis} surfactant to the interface, while the final equilibrium tension value is achieved as \textit{trans} surfactant reaches the interface, displaces the adsorbed \textit{cis} surfactant, and eventually achieves domination. Thus, the dark samples and visible samples reach the same equilibrium state. Some interesting trends are seen in these curves. As temperature is increased, the time associated with the onset of the intermediate plateau decreases and the duration of the plateau diminishes. Also, as with the dark samples, an increase in solution temperature leads to a lower equilibrium tension value and a reduction in time needed to attain this equilibrium.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure6-2.png}
\caption{Dynamic surface tension profiles for aqueous 0.25 mM C$_6$ photosurfactant solutions at various temperatures. Sample in visible photostationary state.}
\end{figure}
Figures 6-1 and 6-2 then offer information about the effect of temperature on the rate of diffusion and adsorption of each isomer to the air/water interface. The time needed for \((1-e^{-1})(100\%) = 63\%\) relaxation to the intermediate tension plateau can serve as an estimate of the characteristic time scale for \(cis\) diffusion and adsorption. Half the time needed for \((1-e^{-2})(100\%) = 86\%\) relaxation to the final equilibrium state can be used as an estimate of the characteristic \(trans\) relaxation time scale. This value is used instead of 63% to avoid choosing data from the intermediate plateau. Both the dark and the visible samples give information about the \(trans\) relaxation time and the visible samples give additional information about \(cis\) relaxation. The linearity of the data on the Arrhenius-type plot in Figure 6-3 is evidence of the strong temperature dependence of these relaxation times. The solid lines are best-fit lines of the Arrhenius form [9]

\[
\tau = \tau_0 \exp \left( \frac{E_a}{RT} \right)
\]

where \(\tau\) represents the characteristic time scale for diffusion and adsorption, \(\tau_0\) is an intrinsic, high-temperature limit for this time scale, \(R\) is the gas constant, \(T\) is the absolute temperature, and \(E_a\) is an apparent "activation energy". The apparent activation energy for \(trans\) relaxation found from the dark and visible samples is 46 kJ/mol and 44 kJ/mol, respectively. The \(trans\) relaxations are slower in the visible samples than in the dark samples because the visible samples have a lower \(trans\) content (only 85-88% \(trans\)). The corresponding \(cis\) relaxation data yield an estimated apparent activation energy of 23 kJ/mol. The excellent agreement of the two values of the \(trans\) activation energy, as well as the large difference between the \(trans\) and \(cis\) energy values, supports the hypothesis that transport of \(trans\) surfactant to the interface is independent of transport of \(cis\) surfactant, and vice versa, as suggested by the results presented in Chapter 4.
Figure 6-3. Characteristic relaxation time scales from pendant bubble studies as a function of temperature. \textit{Trans} values taken as half the time needed for 86\% relaxation to equilibrium in dark and visible samples. \textit{Cis} values taken as time needed for 63\% relaxation to intermediate plateau in visible samples.

It should be noted that similar dynamic surface tension studies were not performed with surfactant in the UV-illuminated state because the long time scales associated with \textit{trans} adsorption in these samples pose difficulties to both procedure and data analysis. Experimental concerns such as bubble stability and temperature control over the extremely long \textit{trans} relaxation time scales anticipated for colder samples in the UV state (even samples at room temperature take $\sim$10 hours to equilibrate) discouraged such studies. Additionally, the thermal reversion of \textit{cis} surfactant to \textit{trans} in the warmer UV samples would be significant over the time scales needed for \textit{trans} adsorption, so that interpretation of \textit{trans} relaxation data would be convoluted for these hot UV samples.
6.3.2 Modeling of Diffusion and Adsorption

As mentioned earlier, because of the long time scales needed for equilibration of surface properties in pre-micellar C₆ solutions, the dynamic surface tension studies were performed at concentrations well above the trans CMC. Models developed in Chapter 4 permit estimates for the time scale associated with surfactant diffusion and adsorption in these samples and account for possible contributions from aggregates present in solution. These models were used to describe data from pendant bubble studies performed at room temperature with this surfactant at a variety of concentrations, and the model predictions were found to be in good agreement with the experimentally observed relaxation time scales. For trans relaxation, the results indicate that aggregates are important to the overall process, but are inconclusive concerning the precise role of the aggregates. In the case of cis relaxation, the results suggest that monomer diffusion is more important than any contributions from aggregates. The difference in the relative importance of aggregates to the adsorption process between the trans and cis isomers is due to the large difference in their CMC values.

To estimate the effect of temperature on the time required for surfactant to reach the interface, the temperature dependence of the diffusion coefficients and CMC values must be determined. The Stokes-Einstein equation is used to give an estimate of the effect of temperature on the diffusivity of surfactant, both in monomeric and aggregate-bound forms:

\[
D = \frac{RT}{6\pi\mu a}
\]  

(6-2)

where \(D\) is the diffusion coefficient, \(\mu\) is the viscosity of the solvent, and \(a\) is the radius of the diffusing species. If the size of a given species (monomer or aggregate) is assumed to be
independent of temperature, all of the temperature dependence is contained in the ratio $T/\mu$ [10].

To get estimates of the diffusivity values $D_i$ and $D_{agg}$, the room temperature values are simply scaled by this ratio, with viscosity values taken from tabulated data for water [11]. Fluorescence experiments were used to determine the temperature dependence of the CMC values. Additionally, rapid dilution studies were performed to assess the validity of the assumptions made in the diffusion models regarding aggregate dissolution rates.

6.3.3 **Effect of Temperature on Aggregation**

Estimates of the CMC of this surfactant at different temperatures were obtained from fluorescence measurements using Nile Red as the probe [12]. Figure 6-4a is a plot of maximum emission intensity vs. surfactant concentration for samples in the dark state. At low surfactant concentrations, before aggregates are formed in the samples, the emission intensity is fairly insensitive to surfactant concentration. The samples at higher temperatures (37 °C and 40 °C) have a stronger emission in this range. Control experiments performed with Nile Red in water, in the absence of surfactant, also showed an increase in emission intensity with increasing temperature at higher temperatures. As Nile Red is sparingly soluble in water, this effect is attributed largely to an increase in solubility. At the higher concentrations shown, the Nile Red emission intensity is seen to increase with increasing surfactant concentration, the onset of which indicates the formation of aggregates in solution and serves as an estimate of the CMC. The wavelength at which the emission intensity shows a maximum is also useful in determining the aggregation state of the surfactant. These peak wavelength data for the dark samples are shown in Figure 6-4b. In very dilute surfactant solutions, when Nile Red is exposed to an essentially aqueous environment, its emission peak occurs at a long wavelength (~ 655 nm) [13]. This is
seen for the low concentration data in Figure 6-4b at all temperatures. As aggregates are formed and Nile Red is able to incorporate itself into less polar domains, this peak wavelength diminishes. This decrease begins at different concentrations for solutions of different temperature. Figure 6-4b also shows that, at the higher surfactant concentrations where aggregates are present, the peak wavelength values for a given concentration generally increase with increasing temperature (indicating a reduction in the extent of aggregation in these samples). This is most pronounced at the extremes of the temperature range, where it is seen that, at the highest concentrations, the 7 °C samples exhibit the shortest peak wavelengths (indicating a larger extent of aggregation) and the 37 °C and 44 °C samples yield the longest wavelengths (indicating a smaller extent of aggregation).

For a given temperature, the CMC of the surfactant was estimated by extrapolating straight lines from the low concentration region and the high concentration region of the peak wavelength data. The data points at 2μM were not used in fitting these lines because these data seem to show systematic deviations from expected trends, in both intensity and wavelength. The results of the fitting estimates are shown in Figure 6-4c. It is seen that between 7 °C and 31.5 °C, the CMC of the trans surfactant increases slightly with increasing temperature, from a value of about 0.9 μM to a value of about 1.4 μM. The CMC value at 25 °C (about 1.3 μM) is consistent with previous findings for this surfactant at room temperature (as seen in Chapter 3 or in Shang et al. [14]). Above 31.5 °C, the increase in CMC with increasing temperature is more substantial, as the values at 37 °C and 44 °C are 1.8 and 2.3 μM, respectively.
Figure 6-4. (a) Maximum fluorescence emission intensity for dark solutions at different temperatures containing a fixed amount of Nile Red probe and varying amounts of C₆ photosurfactant. (b) Emission peak wavelength data for these samples. Solid lines used to fit data for CMC estimates are shown for the 7 °C, 25 °C, and 44 °C data series. (c) Trans CMC as a function of temperature, estimated from wavelength data.
Emission intensity and peak wavelength data for UV-illuminated samples are shown in Figures 6-5a and 6-5b. Interpretation of these results is not as straightforward as for the dark samples, as these samples contain a mixture of cis and trans isomers which can segregate into distinct aggregate phases (a behavior established for these surfactants in Chapter 3 and also reported for other azobenzene-containing photosurfactants [15, 16]). Each phase is potentially affected differently by temperature. Still, careful analysis of these UV results leads to an estimation of the effect of temperature on cis aggregation, which complements the information regarding trans aggregation obtained from the dark samples. The intensity results can be separated into three separate regions. First, below 10 µM, no aggregates are present, and the data are similar to the results of the dark case below 1 µM. Next, for concentrations greater than about 10 µM (the exact value varies with temperature), the emission intensity is seen to increase with increasing surfactant concentration. This indicates the formation of trans-dominant aggregates. Finally, for concentrations greater than about 75 µM, the intensity continues to increase with increasing surfactant concentration, but to an even greater degree, as evidenced by the steeper slope of the data in this region. This indicates the formation of cis-dominant aggregates, at a concentration consistent with previous room-temperature results. For a given temperature, the critical concentration associated with the onset of cis-dominant aggregates was taken to be the intersection of straight lines extrapolated from the “second” region (~10 µM to 75 µM) and from the “third” region (greater than ~75 µM). The results are shown in Figure 6-5c.
Figure 6-5. (a) Emission intensity for UV-illuminated solutions of different temperatures containing a fixed amount of Nile Red probe and varying amounts of C₆ photosurfactant. Solid lines used to fit data for CMC estimates are shown for the 7 °C data series. (b) Emission peak wavelength data for these samples. (c) Cis CMC as a function of temperature, estimated from intensity data. Note: The critical concentration reported is the cis concentration, not the total concentration.
Figure 6-5c shows that the cis CMC increases with increasing temperature, though the effect is more modest (a 30% increase in CMC over the temperature range studied) than in the trans case (a 150% increase over this range). In many other nonionic surfactant systems, particularly those of the C₆E₇ form, the CMC has been found to decrease with increasing temperature [1, 17-21], at least over the temperature range studied here. This has been attributed to a reduction in the hydration of the headgroup which results in an increase in the hydrophobic character of the molecules [4, 22]. The examination of larger ranges of temperatures or of molecules with smaller hydrophilic headgroups has led to observation of systems and temperature spans in which the CMC of a nonionic surfactant increases with increasing temperature [4, 22, 23], resulting in a minimum in the CMC-temperature curve in some cases. The temperature at which the CMC exhibits such a minimum is found to decrease with increasing hydrophobicity of the surfactant [24], so that surfactants with very large (or very small) hydrophilic portions relative to their hydrophobic portion can exhibit a strictly decreasing (or strictly increasing) trend in CMC value with increasing temperature over the temperature range examined in a given experiment. An increase in CMC with increasing temperature can be attributed to an enhanced solubility of the hydrophobic tails as the added thermal agitation disrupts the structured water cages encasing these hydrophobic moieties, with an accompanying reduction in the entropic penalty associated with this water structuring [4, 22]. Thus, the CMC behavior of a given surfactant over a given temperature span depends on the balance of the dehydration of its headgroup and the thermal solubility of its tail [22, 23]. It seems reasonable that the latter effect would be dominant for this C₆ photoresponsive surfactant, given the small size of its headgroup relative to its hydrophobic tail, so that its CMC would increase with increasing temperature, as observed. The more polar
(and less hydrophobic) nature of its tail when in the cis state [14], compared to the trans form, accounts for the less pronounced effect of temperature on the CMC of the cis isomer.

Crook et al. [23] have studied the effect of temperature on \( p,t \)-octylphenoxyethoxyethanols (OPEs). For the OPEs with the smallest headgroups, OPE\(_1\) and OPE\(_2\), which have CMC values very similar to the cis isomer of the C\(_6\) photosurfactant (about 50 \( \mu \)M and 75 \( \mu \)M at room temperature, respectively), an increase in CMC comparable to that of the cis surfactant (about 40% and 20%, respectively) was observed for increasing temperature over a range similar to that of the present study. Islam and Kato [22] report that C\(_{14}\)E\(_1\), which has a hydrophobicity similar to the trans C\(_6\) isomer (with a similar room temperature CMC of about 2.5 \( \mu \)M), exhibits a roughly 120% increase in CMC with increasing temperature, comparable to that seen in the trans surfactant. Finally, Yang et al. [25] have reported a cationic azobenzene-containing photosurfactant with a much larger room temperature trans CMC (~ 10 mM) than the surfactant described in this study, but which also shows an increase in trans CMC (though substantially smaller than seen here: ~ 40%) with increasing temperature over a similar temperature range (temperature dependence of cis CMC was not reported).

It is not surprising that the high-concentration data of Figure 6-5a show an increase in emission intensity with decreasing temperature. Clearly, the greatest extent of aggregation will occur at the lowest temperature and the least extent at the highest temperature. The peak wavelength data of Figure 6-5b offer additional support for the proposed behavior of the cis-dominant aggregates. As described in the discussion of the room temperature results in Chapter 3, the presence of cis-dominant aggregates is indicated by values of the peak wavelength which lie below the limiting
value associated with trans aggregates. Measurements of a 500 μM sample in the dark state (a sample which contains an abundance of trans-dominant aggregates) show that this limiting value of the peak wavelength varies only slightly (from 628 nm to 630 nm) as the temperature is varied over a wide range (7 °C to 44 °C). From Figure 5b, we see that the peak wavelength values first cross this threshold value at surfactant concentrations near 75 μM, consistent with the intensity data. Near this concentration, there is also an inversion of the temperature dependence of the peak wavelength for a given concentration: at concentrations below this value (and above ~10 μM, so that trans-dominant aggregates are present), the wavelength at a fixed concentration generally increases with increasing temperature, but at concentrations higher than this value, the peak wavelength is found to decrease with increasing temperature, despite the fact that the cis CMC was estimated to increase with increasing temperature. This appears to be due to the influence of the trans-dominant aggregates which coexist with the cis-dominant aggregates at these concentrations. The coldest samples contain greater amounts of cis-dominant aggregates, but the amount of trans-dominant aggregates increases even more. This skews the peak wavelength towards the 628 nm trans-associated value. Hence, the lowest peak wavelength values are seen at higher temperatures where relatively smaller amounts of trans-dominant aggregates are present.

6.3.4 Comparison of Model Predictions with Experimental Results

The diffusion coefficient and CMC data can be incorporated into the previously discussed diffusion models to predict the temperature dependence of surface tension relaxation. The different models exhibit different temperature behavior due to their different dependencies on these values. Results for the trans relaxations are shown in Figure 6-6 for the three models in
which aggregates contribute to the adsorption process. The apparent activation energy estimates range from 22 kJ/mol to 37 kJ/mol, with this value increasing as the relative importance of aggregate dissolution compared to aggregate diffusion increases in the model. All of the models provide an order-of-magnitude level of agreement with the experimental data. The model in which aggregates are considered to be fast-dissolving but non-diffusing exhibits the temperature dependence closest to that exhibited by the data. In the visible sample used for the surface tension relaxations, only about 37 μM of cis surfactant was present, which is insufficient to form the cis-dominant aggregate phase at any of the temperatures studied. Thus, all cis surfactant present in the sample was available as free monomer, and Eqn. 4-21 (with a concentration of 37 μM used in place of the CMC value) is the appropriate model for describing these data. The effect of temperature on the monomeric diffusion coefficient adequately describes the temperature dependence of the cis relaxation time scale. The estimate is 19 kJ/mol whereas the experimental value is 23 kJ/mol.
As mentioned earlier, the size of aggregates was assumed to be independent of temperature for these calculations. Available literature for nonionic surfactants indicates that the temperature dependence of aggregate sizes in such systems is strongly dependent on the nature of the particular surfactant [26-32]. For a given surfactant, aggregate size may be nearly independent of temperature [30], or it may increase with temperature [27, 29, 31], or both features may be present within different temperature ranges [26, 28, 32]. As suggested by Eqn. 6, an increase in the size of an aggregate will result in a decrease in its diffusion coefficient. This will in turn cause an increase in the estimated time scale for surfactant diffusion and adsorption given by Eqns. 2 and 4. The model in which aggregates are assumed to diffuse but not dissolve is more sensitive to the value of the aggregate diffusion coefficient than the model in which aggregates are diffusing and fast-dissolving, so that the former will be affected more strongly by an increase in aggregate size than the latter. For example, for an increase in aggregate size with increasing
temperature such as that reported for C₁₂E₆ (roughly, a 150% increase in aggregation number over a temperature range similar to that examined in the present study) [32], it is estimated that for aggregates of trans surfactant, the adsorption time scale predicted for frozen, diffusing aggregates would increase by about 50% while the adsorption time scale predicted for fast-dissolving, diffusing aggregates would only increase by about 10%. Such an increase in aggregate size with increasing temperature would lessen the apparent activation energy predicted by both models and worsen the agreement between the predicted adsorption time scales and the experimental data, though, as just calculated, less appreciably for the case of fast-dissolving aggregates. Given the order-of-magnitude nature of the diffusion model estimates, the assumption of temperature-independent aggregate size seems reasonable.

6.3.5 Rapid Dilution Studies

Experiments were performed in which aqueous surfactant solutions containing aggregates and the fluorescent probe Nile Red were diluted rapidly and the fluorescent emission was monitored as a function of time. Tracking the decay of the emission intensity over time allows for an estimate of the aggregate dissolution rate. In these studies, samples of dark surfactant initially at a concentration of 150 μM were diluted rapidly tenfold and the emission intensity at 630 nm was recorded. This resulted in a sample which still contained aggregates after dilution, so a strong fluorescent signal was maintained throughout the measurement without a significant shift in the emission peak. Results for such a measurement at 10 °C are shown in Figure 6-7a. This plot illustrates the weak signal given from the cuvette containing water before the surfactant solution is added, the subsequent spike in intensity when the surfactant solution is added (at ~ 40 s), and the resulting decay in intensity as aggregates dissolve and a new equilibrium state is reached.
These measurements were repeated at other temperatures and the resulting characteristic dissolution time scales are shown in Figure 6-7b. The results indicate that there is a finite time scale associated with dissolution of the trans-dominant aggregates and that this time scale increases as the temperature decreases, a trend observed in other systems [6, 7]. This time scale was seen to be as large as 35 seconds for samples at the lowest temperature (10 °C) and, at the highest temperature (44 °C), was found to approach the time constant associated with mixing in the samples. Even though these results provide evidence of finite aggregate dissolution kinetics, it is seen that, for a given temperature, the time scale associated with dissolution of these trans aggregates is an order of magnitude smaller than the time scale associated with diffusion and adsorption of the trans isomer. This appears to justify the assumption of infinitely fast aggregate dissolution used in some of the diffusion models, or at the very least, indicates that this is a better assumption than that of “frozen” or non-dissolving aggregates.
Figure 6-7. (a) Fluorescent emission intensity at 630 nm from an aqueous dark surfactant solution at 10 °C containing aggregates (initially 150 μM) and Nile Red which is diluted rapidly tenfold. Solid line represents exponential curve used to fit results. (b) Time scales needed for re-equilibration of sample intensity after rapid dilution, reported as a function of temperature. Shaded band near 5 seconds represents the range of time constants observed for mixing in control experiments.

6.4 Summary

Dynamic surface tension studies performed on the C₆ photoresponsive surfactant at varying temperatures demonstrate the effect of temperature on the rate of diffusion and adsorption of the
surfactant to a newly created interface. Both possible isomeric forms of the surfactant (cis and trans) are found to reach the interface more quickly as the temperature of the solution is increased. Temperature had a greater impact on the rate of trans adsorption in these studies than on cis adsorption, due to the formation of trans-dominant aggregates at lower concentrations. This temperature dependence of trans diffusion and adsorption is quantitatively consistent between samples containing trans isomer only and samples containing a mixture of the isomers. In these experiments, the cis isomer did not form aggregates and the effect of temperature on its rate of adsorption is adequately described by a simple diffusion model which estimates the effect of temperature on the diffusion coefficient of the monomer. The trans isomer, however, was mostly bound into aggregates during these measurements, and more detailed models which account for different potential roles of aggregates in the adsorption process and which incorporate the effect of temperature on the CMC were needed to describe the experimental trans data. Fluorescence studies were performed to estimate the temperature dependence of the CMC for each isomer, and each was found to increase with increasing temperature. The best agreement between trans surface tension relaxation data and the diffusion models is found for the case in which aggregates dissolve quickly but do not diffuse. This indicates that dissolution of the trans-dominant aggregates is more important to the adsorption process than their diffusion, a finding that was first suggested by earlier studies performed with this surfactant at room temperature for varying concentrations, but was inconclusive from these previous studies alone. Fluorescence studies involving rapid dilution of surfactant solutions reveal that dissolution of trans-dominant aggregates becomes more rapid with increasing temperature. These dissolution time scales, which are on the order of tens of seconds for the colder samples, are nonetheless very short when compared to the time scales associated with the adsorption process.
6.5 References


Chapter 7
Conclusions

7.1 Summary of Research

In this work, we have characterized the bulk and surface properties of a photoresponsive surfactant system. The surfactant under study was developed by Shang et al. [1, 2], and features the light-sensitive azobenzene group in its hydrophobic tail. The nonionic character of the hydrophilic headgroup allows for close packing of the surfactant in adsorbed monolayers, which can maximize the effect of conformational changes in the tail group brought on by cis-trans photoisomerization of the azobenzene present. UV-Vis absorption and NMR were used to characterize solutions of the surfactant, and it was found that, when removed from light for an extended period of time, the trans isomer of the azobenzene group is present almost exclusively. Upon prolonged exposure to visible light, solutions eventually reach an equilibrium state consisting primarily of the trans isomer, but with significant amounts of the cis isomer present. Prolonged exposure to UV light results in a solution dominated by the cis isomer, but with significant amounts of trans isomer present.

A Langmuir film balance was used to study the behavior of monolayers of the surfactant adsorbed at the air/water interface. When spread dilutely on the water surface, an adsorbed layer of the surfactant exerts a surface pressure which increases with its content of cis isomer. However, upon extensive compression, adsorbed layers containing greater amounts of trans isomer are able to be compacted more tightly and exert a greater surface pressure in these dense monolayers. Both of these findings are consistent with the physical conformations previously
proposed for this surfactant, in which the bent tail of the *cis* isomer lies in the interfacial plane and the planar tail of the *trans* isomer extends away from the interface and into the air phase [2]. The results of monolayer studies for films of various isomeric compositions also indicate that any *cis* present in a saturated layer tends to dominate the surface pressure behavior of the film.

Experiments involving the hydrophobic and fluorescent probe Nile Red were used to study the aggregation behavior of the surfactant in aqueous solution. The results suggest that the *trans* and *cis* isomers segregate into separate, co-existing aggregate phases and that the critical concentration associated with the onset of aggregation is very different for the two isomers. The *trans* isomer appears to form *trans*-rich aggregates at *trans* concentration of about 1 µM, while *cis*-rich aggregates form when the *cis* concentration reaches about 65 µM.

Pendant bubble studies were performed to determine the dynamic surface tension behavior of the surfactant at different concentrations and isomeric compositions. Samples containing significant amounts of the *cis* isomer show very different qualitative behavior from dark-adapted samples, though all samples reach the same equilibrium tension. Dark samples exhibit a simple relaxation in surface tension after the creation of a fresh interface, while isomeric mixtures display an intermediate plateau of nearly constant tension before eventually reaching the common equilibrium. The initial rate of decline in surface tension, the duration of the intermediate tension plateau, and the time needed to reach the final equilibrium state are all found to increase with increasing *cis* content. These findings support the hypothesis of competitive adsorption occurring between the two isomers when both are present in solution. In this scenario, the *cis* isomer reaches the interface more quickly than the *trans* isomer (because of its higher CMC and
larger monomer supply) and initially dominates the surface, leading to the onset of the plateau in tension. As *trans* isomer reaches the interface, it displaces adsorbed *cis* isomer from the interface and replaces it, due to its greater hydrophobicity. The surface tension of the system changes very little during most of this displacement process because of the dominance of the adsorbed *cis* isomer (as demonstrated in the monolayer studies). Eventually, after most of the *cis* has been removed from the interface, tighter packing of the adsorbed *trans* isomer leads to further reduction in surface tension until the surface becomes saturated with *trans* isomer and equilibrium is reached.

Repetition of these surface tension relaxation experiments at different surfactant concentrations indicates that the characteristic time scale for diffusion and adsorption of the *trans* isomer exhibits the same dependency on the *trans* isomer concentration in all samples, regardless of their illumination state. Likewise, the characteristic *cis* adsorption time scale exhibits the same dependency on the *cis* concentration in all illumination states. This suggests that *trans* and *cis* are transported to the interface independently and that the same physical mechanism governs the transport of a given isomer in all samples. Simple diffusion models were developed to interpret the observed relaxation time data. These models account for the possible roles of aggregates in the adsorption process by examining the limiting behavior of three aggregate properties: dissolution rate, mobility, and ability to incorporate into the interface. These models show that aggregates must play an important role in the adsorption of the *trans* isomer, though the specific role is unclear from these experiments alone. By contrast, because of the much higher CMC of the *cis* isomer, aggregates play little or no role in the *cis* adsorption process.
Dynamic surface tension studies were performed in which the surface of a pendant bubble was illuminated with high-intensity light to drive photoisomerization of adsorbed surfactant. These experiments reveal that the conversion of trans to cis and vice versa on the bubble surface is rapid (seconds or less) under these conditions. This surface photoconversion results in rapid, substantial changes in the dynamic surface tension, with tension differences that can be rationalized on the basis of surfactant architecture. The differences are consistent with the results of the Langmuir film studies.

The dynamic surface tension and aggregation experiments were also performed at various temperatures to determine the effect of temperature on these surfactant properties. Increasing the temperature of the solution increases the rate of diffusion and adsorption of both isomers of the surfactant to a newly created interface. Temperature had a greater impact on the rate of trans adsorption in these studies than on cis adsorption, because the trans isomer was mostly bound into aggregates during these measurements. The cis isomer did not form aggregates in these studies though, so the effect of temperature on its rate of adsorption is adequately described by estimating the effect of temperature on the monomeric diffusion coefficient. To describe the trans data, the effect of temperature on the CMC must be considered. The fluorescence experiments revealed that the CMC of each isomer increases with increasing temperature. When these data were incorporated into the previously developed diffusion models, so that these models then reflected the effect of temperature on both the diffusion coefficients and the monomer supply (via the CMC), the models adequately described the trans relaxation data. The results indicate that dissolution of the trans-rich aggregates plays a major role in the trans adsorption process. Further fluorescence studies involving rapid dilution of surfactant solutions
were carried out in order to estimate the rate of aggregate dissolution, and the results suggest that aggregate breakup in colder *trans* samples is slower than in warmer samples, but that these dissolution time scales are significantly shorter than those associated with the adsorption process.

### 7.2 Future Research Directions

Future research with these surfactants could focus on further study of the impact of photoisomerization of adsorbed surfactant, and on exploring potential applications where it could be useful. The experiments reported in Chapter 5 establish that rapid, substantial changes in surface tension are possible by illuminating a surface saturated with surfactant. It was seen that the largest change in surface tension occurred when an air/water interface saturated with *trans* surfactant was illuminated with UV light to drive conversion to surface containing mostly *cis* isomer (see Figure 5-1). It is worth noting, however, that although this particular change in surface state (from a saturated, all-*trans* surface to a saturated, mostly-*cis* surface) is reversible, it is not rapidly reversible, as there are diffusion limitations associated with the re-establishment of an all-*trans* surface. By contrast, tension changes caused by conformational adjustments of the surfactant tail which leave the number of molecules adsorbed at the surface essentially unchanged (such as the first tension jump shown in Figure 5-2) are capable of rapid reversal, though they are smaller in magnitude than the changes brought on by illumination events which additionally alter the number of adsorbed molecules (Figure 5-1 and the second tension jump of Figure 5-2). In the case where the number of molecules adsorbed at the surface remains unchanged, the adsorption capacity is dictated by the isomer which occupies the most area at the interface: in this case, the *cis* isomer. As discussed in Chapter 5, illumination of a *cis*-dominated surface with visible light causes considerable conversion of the adsorbed surfactant to the *trans*
state, thereby effectively lifting much of the hydrophobic tail out of the interfacial plane and into the air phase. Thus, the change in state is from a saturated, mostly-cis surface to an unsaturated, mostly-trans surface. UV illumination of this latter state should return the surface to a mostly-cis state, accompanied by an increase in the amount of hydrophobic domain residing at the air/water interface.

Since conversion from adsorbed cis isomer to trans (and vice versa) was found to be fast (order 1 s), illumination which alternates rapidly between UV and visible wavelengths could, in theory, be used to rapidly cycle between surfaces of different isomeric compositions which exhibit very different coverage of the air/water interface and thus very different surface tension values. It was determined by monolayer studies presented in Chapter 3 that any adsorbed cis present at a surface dominates its tension, so the key to maximizing the magnitude of the tension change achievable by this illumination scheme is to minimize the cis content of the visible state. To this end, it was also found that increasing the cut-on wavelength of the optical filter used for visible illumination beyond 400 nm results in a reduced cis content at photostationarity. For extremely long cut-on wavelengths, this can come at the cost of reducing the molar absorptivity of the surfactant, which can slow the photoresponse to illumination. Thus, in choosing an appropriate optical filter for a given application and a given illumination source intensity, a balance must be struck between the desired isomeric selectivity and the desired speed of photoconversion.

Such dynamic monolayer behavior of photoresponsive surfactants has been studied and reported before [3], whereby conformational changes on a molecular level have been used to bring about surface pressure modulation. These techniques could be potentially useful in any application
where the ability to rapidly and reversibly change the interfacial properties of a surface would be advantageous. Another potential application of these surfactants involves spatially non-uniform illumination of a liquid/gas interface where the surfactants are adsorbed. Having a spatial gradient in the characteristic wavelength of the light shining on the surface will cause a spatial gradient in the isomeric composition of adsorbed surfactant, which can in turn cause a spatial gradient in surface tension capable (in theory, at least) of driving surface flow (the Marangoni phenomenon [4, 5]). Again, the key for developing substantial surface tension differences across a surface saturated with the C₆ surfactant seems to be in minimizing the amount of cis present in the areas illuminated with visible light. Basic, proof-of-concept flow visualization experiments to demonstrate light-induced Marangoni flows using this surfactant were attempted without success. (Calculations which motivated these experiments and details of attempted experiments are outlined in the Appendix.) Still, given the potential utility of such an application, more sophisticated experiments aimed at determining the feasibility of using these surfactants for surface tension-driven flows seem justified.

It could also be interesting to examine the role of surfactant architecture on all of the properties reported in the previous chapters, though whether changes to the surfactant design would be considered improvements depends on the desired application. Maximizing surfactant performance on the basis of one property can come at the cost of performance in another. For example, one could imagine that increasing the size of the hydrophilic head group would reduce the hydrophobicity of the surfactant and result in a higher CMC value. This larger CMC would reduce the time needed for surfactant diffusion and adsorption at high concentrations (due to a larger supply of monomeric surfactant) and result in faster equilibration of interfacial properties.
However, this bulkier head group would cause the surfactant to occupy more area when adsorbed at an interface and reduce the packing density of the adsorbed layer, which would likely reduce the effect of tail conformation changes caused by photoisomerization. Shang et al. [2] have studied the effect of tail length of these surfactants on the equilibrium properties of the system. In these studies, the surfactants all had the same head group and the same azobenzene-containing tail structure; the only difference was in the length of the carbon spacer connecting the headgroup to the rest of the tail: this spacer was varied between two and eight methylene groups in length (with C₆ being the six methylene group moiety). Interestingly, trends that were observed for the values of the CMC and equilibrium surface tension with increasing spacer length in going from two to six methylene groups ceased to hold when proceeding from six methylene groups to eight. The very different adsorption behavior seen in going from six to eight carbon spacers is explained by a fundamental change in the conformation of the adsorbed surfactant isomers. For spacer lengths of six carbons or fewer, the adsorbed trans isomer appears to adopt a conformation in which its tail extends away from the interface and into the air phase, while the bent tail of the cis isomer causes much of the tail to lie in the interfacial plane. In these cases, the trans isomer packs more tightly and has a greater surface excess concentration upon saturation, which results in a lower surface tension. For the eight carbon spacer, it is proposed that even the tail of the trans isomer lies mostly in the interfacial plane and takes up more room than the bent cis tail. Thus, in this case, the adsorbed trans isomer packs more loosely than the cis, and results in a higher tension upon saturation. These two examples illustrate the types of considerations to be taken into account when attempting to optimize surfactant design.
7.3 References

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Appendix

A.1 Introduction

Many additional experiments were carried out in addition to the ones discussed in the previous chapters. Several of these offer support for findings established from the previously described experiments, while some represent efforts to determine the feasibility of potential applications of the surfactant. The purpose of this Appendix is to report the data and findings from these auxiliary experiments and discuss their significance. The body of work compiled here does not necessarily share a common theme, so each section may be treated independently without loss of context. Experiments recounted here include dynamic light scattering studies aimed at further understanding the aggregation behavior of the surfactant, unconventional Langmuir trough studies to probe the nature of the intermediate tension plateau seen in dynamic surface tension studies, examination of the tension response of pendant drops to perturbations from equilibrium, and rough-and-dirty attempts to demonstrate light-driven Marangoni flows.

A.2 Dynamic Light Scattering

Dynamic light scattering (DLS) was used to establish the effect of isomeric composition and concentration on the aggregation state of the surfactant. DLS measurements are a well-established means of determining the diffusion coefficient of large particles [1, 2], which is usually reported in terms of a hydrodynamic diameter by assuming a spherical shape and applying the Stokes-Einstein relation. These studies were conducted using a light scattering apparatus from Brookhaven Instruments, which consists of a motor driven goniometer (BI-200SM), a digital autocorrelator (BI-9000AT), and a photon counter (BI-9025AT). The laser
light was provided by an Argon ion laser (Spectra-physics 2017-055) operated at a wavelength of 514 nm. Aqueous surfactant solutions were illuminated to the desired photostationary state prior to measurements. Because of the polydispersity of aggregates expected for the isomeric mixtures, the exponential sampling (ExpSam) method was used to fit these data.

The results for 600 μM samples are shown in Figure A-1. Figure A-1a illustrates the size distributions seen in the samples after a five minute scan (a time sufficiently long to obtain statistically significant scattering results). Here it is seen that the dark-adapted sample has an average (more precisely, a number average) aggregate size of about 85 nm. This is in good agreement with the size measured by Shang et al. for the trans vesicles using Cryo-TEM imaging (~ 70 nm) [3]. The visible sample appears to exhibit two populations of aggregates of disparate sizes. The most prevalent aggregate size for this sample occurs within the population of smaller size. Based on the fluorescence studies reported in Chapter 3, two separate aggregate phases are expected for isomeric mixtures at high concentrations. Trans isomer is expected to preferentially form trans-rich micelles or vesicles, while the cis isomer is anticipated to form a cis-rich bicontinuous phase. The fact that two populations are seen in the DLS results is consistent with these expectations, but caution should be used before attempting any quantitative interpretation of these DLS results, as a scenario involving coexisting vesicles and bicontinuous phase presents an unusual and complicated aggregation scheme for which any existing correlation function models are inappropriate. Figure A-1a also shows that the UV sample is dominated by aggregates which appear in the same size range as the larger aggregate population seen in the visible sample. This is consistent with the findings from the visible sample, if the larger aggregate population can be interpreted as indicative of a cis-rich bicontinuous phase.
Extended exposure to the laser can alter the aggregation state of these photoresponsive samples, especially in the localized region near the illumination path, as the laser provides a high-intensity, focused light source. At the wavelength of light provided by this particular laser, 514 nm, absorption by the cis isomer is more than ten times stronger than absorption by the trans isomer (see Figure 2-5b). Thus, illumination of an isomeric mixture by this laser will drive a net conversion of cis isomer to trans isomer and lead to an increase in the trans content of the sample. The two photostationary mixtures used for the studies shown in Figure A-1a were allowed to remain in the path of the laser for an additional span of time, and the samples were re-examined after about 30 minutes of exposure to the laser. The results are found in Figure A-1b. Here it is seen that the visible sample displays a single population, occurring in a size range slightly smaller than the smaller of the two populations seen after 5 minutes of laser exposure (and close in size to the dark sample results seen in Figure A-1a). This is consistent with the idea of cis surfactant being converted to trans and leaving the cis-rich bicontinuous structure to form trans-rich vesicles. This hypothesis also explains the behavior seen in the UV sample, where the relative abundance of aggregates in the larger aggregate population is reduced after prolonged exposure to the laser, and a population of smaller aggregates becomes prominent in a size range very similar to that of the visible sample. The qualitative findings from Figure A-1 offer support for the proposition of segregation of the two photoisomers when aggregates are formed in solution at high surfactant concentrations.
Figure A-1. Dynamic light scattering (DLS) results for aqueous C₆ solutions at a concentration of 600 µM. (a) After 5 minutes of laser exposure. (b) After 30 minutes of laser exposure.

The hypothesis of isomer segregation was further tested using DLS by examining samples under conditions where trans aggregates were expected to be formed, but not cis aggregates. Solutions at a concentration of 37 µM were measured, and the results are shown in Figure A-2. At this concentration, the trans concentration of the sample under each of the illumination conditions exceeds the trans CMC, but the cis concentration falls short of the cis CMC in all states. Indeed,
it is seen that each illumination state displays a single aggregate population, and that the populations of the three states overlap to a great degree. This is the type of behavior expected if all samples solely contain \textit{trans}-rich vesicles. Thus, the results from the DLS studies complement the findings from the fluorescence-based aggregation studies of Chapter 3.

![Graph showing hydrodynamic diameter vs. number](image)

\textbf{Figure A-2.} Dynamic light scattering (DLS) results for aqueous C₆ solutions at a concentration of 37 μM after a 5 minute scan.

\section*{A.3 Langmuir Trough Experiments}

In addition to the surface pressure-area isotherms generated for Chapter 3, the Langmuir film balance was also used in experiments to examine the intermediate plateau seen in dynamic surface tension studies.

\subsection*{A.3.1 Wilhelmy Plate Experiment}

It was desired to know whether the strange inflection seen in the dynamic surface tension profile of the isomeric mixtures after the creation of a fresh interface in the pendant bubble studies was influenced by the geometry of the system. To test whether this was the case, the same
measurement was performed with a planar air/water interface for comparison with results from
the curved interface of the bubble. In this experiment, only the Wilhelmy plate of the Langmuir
trough apparatus was used. About 20 mL of aqueous 0.16 mM C₆ solution previously
illuminated to the visible photostationary state was poured into a dish and placed under the
Wilhelmy plate, and the plate was lowered down until it touched the free surface of the solution.
The surface pressure was then continuously measured with results shown in Figure A-3. The
absolute value of the surface pressure shown in this plot should be disregarded, as the crude
nature of this particular experiment prevented the interface from being clean of surfactant at the
time that the instrument was “zeroed” and measurement began. Nonetheless, two important
features of this plot offer insight: first, it is seen that this dynamic pressure profile exhibits the
same intermediate plateau that was seen in the pendant bubble studies. Secondly, the pressure
difference between the two plateaus (intermediate and final), about 12 mN/m, is the same as in
the pendant bubble case, which indicates that these are indeed indicators of the same physical
phenomena. Thus, it appears that the interesting dynamic behavior seen in the isomeric mixtures
is not due to the curved interface of the bubble, since this same behavior is seen for the planar
interface studied in this Wilhelmy plate experiment. This was to be expected because, as
calculated in Chapter 4, at the concentrations under study in this work, the thickness of the
depletion layer caused by surfactant adsorption is sufficiently small so that (i) it becomes the
relevant length scale for diffusion and (ii) curvature effects can be ignored. This experiment
offers support for this assumption.
Figure A-3. Dynamic surface pressure profile for an aqueous 0.16 mM C₆ solution measured by a Wilhelmy plate after sample was loaded into a dish.

A.3.2 Kinetic Barrier Experiment

Another experiment was aimed at trying to determine whether adsorption of the trans isomer to the interface during the intermediate tension plateau was limited by transport of surfactant to the interface or if additional barriers to the adsorption process existed. The basic idea behind the experiment can be summarized as follows: a mixture of photoisomers is allowed to diffuse and adsorb to a surface, and after significant adsorption of the cis isomer has occurred, the surface is rapidly compressed. The surface pressure response of the system to this compression could then potentially offer insight concerning the nature of this adsorption: if the surface pressure rapidly rose from the value associated with a cis-dominated surface to the value associated with a trans-saturated surface during this compression, then this would suggest that trans isomer was present at or near the interface and that compression of the surface helped to accelerate the displacement of adsorbed cis isomer by trans isomer. If instead the surface pressure did not change significantly during the compression, then this might indicate that significant amounts of the trans isomer had not yet reached the interface. This latter case admittedly provides less
conclusive evidence, as there is no guarantee that surface compression actually reduces an adsorption barrier for the *trans* isomer, but the experiment was worthwhile to determine which response the system shows. To carry out this experiment, the subphase of the Langmuir film balance was filled with water, the movable barriers were opened to a wide degree, the surface was aspirated, the surface pressure reading was “zeroed”, etc., as in a typical film balance study. But instead of spreading surfactant on the surface using chloroform, 1 mL of 0.50 mM aqueous C₆ solution (previously illuminated to the UV photostationary state) was injected into the water subphase, and, with the barriers remaining stationary, the surface pressure was continuously monitored as surfactant adsorbed to the interface. After it became clear from the surface pressure reading that the intermediate plateau region had indeed commenced (though very early in the lifetime of the plateau, as these plateaus can last for hours in UV samples, as shown in Chapter 4), the barriers were rapidly closed to compress the surface.

As seen in Figure A-4, the surface pressure rises modestly (~ 2 mN/m) during this compression, consistent with the rise seen in Chapter 3 for compression of a *cis*-dominated (UV state) surface. This seems to suggest that adsorption of the *trans* isomer is transport-limited, though as mentioned above, evidence from this experiment alone is not convincing proof. However, taken together with the findings reported in Chapter 4, in which (i) the *trans* adsorption time scale was found to exhibit the same dependency on *trans* isomer concentration for a variety of illumination states over a large span of concentrations, and (ii) these *trans* adsorption time scales were described well by diffusion models which did not consider additional barriers to the adsorption process, the findings from this experiment strongly suggest that adsorption of the *trans* isomer is diffusion-limited.
A.4 Pendant Drop Perturbation Experiments

The drop shape analysis system first described in Chapter 4 was used in another set of experiments in which pendant drops of surfactant solution were created and the surface tension was monitored as time passed. Once the surface tension reached an equilibrium value, the volume of the drop was rapidly changed by manual turning of the micrometer used to depress the plunger of the syringe containing the surfactant solution. This caused a rapid change in the surface area of the drop and, consequently, the relative surface coverage of the adsorbed surfactant. The response of the system to this sudden change was studied by examining the subsequent dynamic surface tension profile. Expansions and contractions of the drop surface were both performed over a span of compression ratios and bulk surfactant concentrations.

Results for surfactant solutions in the dark-adapted state are shown in Figure A-5. Figure A-5a shows the drop volume and surface tension behavior of a typical drop contraction experiment. The time needed for the surface tension to achieve 63% return to equilibrium was taken as the characteristic re-equilibration time. These time scales are plotted as functions of the ratio of the surface coverage just after the perturbation to the surface coverage at equilibrium in Figure A-5b.
This ratio, $\Gamma^*/\Gamma_{eq}$, is assumed to be equivalent to the ratio $A_{eq}/A^*$, where $A_{eq}$ is the drop surface area at equilibrium, just before the perturbation, and $A^*$ is the area just after the perturbation. The drop surface area values measured by the drop shape analysis instrument allow calculation of these ratios. Thus, $\Gamma^*/\Gamma_{eq}$ values greater than one correspond to drop contractions, while values less than one correspond to drop expansions. Drop contractions result in a decrease in surface tension, while expansions result in a tension increase.

Figure A-5. (a) Typical drop volume and surface tension behavior for an experiment involving rapid contraction of a pendant drop of aqueous $C_6$ solution in the dark-adapted state. (b) Re-equilibration time scales for drop expansion and contraction experiments of varying magnitudes of perturbation.
It is seen in Figure A-5b that for the drop contractions, the re-equilibration response is rapid (~ 1-2 s) and seemingly independent of bulk surfactant concentration. This is consistent with a picture of a surface that is saturated with surfactant suddenly becoming compressed, causing the surface to become overcrowded with surfactant so that surfactant must be “squeezed out” from the interface to re-attain an equilibrium state. In such a physical mechanism, one would expect the response of the system to be rapid and not dependent upon the concentration of the bulk solution. For the drop expansions, it is seen that the re-equilibration time scales are much longer and somewhat dependent upon the bulk concentration, with samples of higher concentration exhibiting slightly faster responses. This is indicative of a different mechanism for re-equilibration. In this case, a surface that is saturated with surfactant is suddenly expanded so that new vacancies are created at the air/water interface and the surface is no longer saturated. To re-obtain equilibrium, surfactant must diffuse to the interface and adsorb to the vacant sites and re-saturate the surface. Thus, given the diffusional limitations that are present in this case (which are largely absent from the contraction case), it is sensible that the re-equilibration time scales for drop expansions are longer than for drop contractions, and that these time scales show some dependency on bulk surfactant concentration. Note that these re-equilibration time scales are significantly shorter than the tension relaxation time scales reported in Chapter 4. This, of course, is because the latter case involves diffusion to a fresh, initially-clean interface, while the former case involves only a slight perturbation from equilibrium, so that less adsorption is needed to reach equilibrium and the regions of solution adjacent to the interface already contain significant amounts of surfactant.
Diffusion models used to describe these expansion re-equilibrations were obtained by slightly modifying the models developed in Chapter 4 for the tension relaxations. The adsorption driving force for diffusion in these systems is given by the difference in adsorption states

\[ \Delta \Gamma = \Gamma_{eq} - \Gamma_0 \]  

(A-1)

where \( \Gamma_0 \) is the initial surface excess concentration. For the case of diffusion to a fresh interface, \( \Gamma_0 = 0 \), since the interface is initially free of surfactant. Thus, in these cases, the driving force is simply \( \Gamma_{eq} \) (equivalently, \( \Gamma_\infty \) can be used). For a system perturbed from equilibrium, \( \Gamma_0 = \Gamma^* \) so that the driving force becomes

\[ \Delta \Gamma = \Gamma_{eq} - \Gamma^* \]  

(A-2)

In this way, the diffusion models developed in Chapter 4 for relaxations can be applied the perturbations by making the following substitution:

\[ \Delta \Gamma : \Gamma_{eq} \rightarrow \Gamma_{eq} - \Gamma^* \]  

(A-3)

For example, Eqn. 4-21, which examines the case in which aggregates do not contribute to adsorption (due to being non-dissolving and either non-diffusing or not fusible with the interface) goes from

\[ \tau \sim \frac{\Gamma_{eq}^2}{D_i (CMC)^3} \]  

to

\[ \tau \sim \frac{(\Gamma_{eq} - \Gamma^*)^2}{D_i (CMC)^3} \]  

(A-4)

which can be recast to explicitly show the dependence on the ratio \( \Gamma^*/\Gamma_{eq} \):

\[ \tau \sim \frac{\Gamma_{eq}^2}{D_i (CMC)^3} \left( 1 - \frac{\Gamma^*}{\Gamma_{eq}} \right)^2 \]  

(A-5)

In a similar manner, the other diffusion models from Chapter 4 (Eqns. 4-12, 4-13, and 4-20) can be adjusted to describe the perturbation experiments by multiplying by the factor \( (1 - \Gamma^*/\Gamma_{eq})^2 \).
These diffusion models have been applied to the data from the drop expansion/contraction experiments performed on the dark-adapted samples, and the results are shown in Figure A-5b (parameters used in the models are the same as used in Chapter 4). Here it is seen that, for each concentration, the experimental data fall somewhere between the curve representing the slowest of the cases in which aggregates contribute to adsorption and the “monomer only” curve representing the case in which aggregates do not contribute to adsorption. This is an interesting contrast to the relaxation studies of Chapter 4, where it is clear from Figure 4-8a that aggregates contribute to the adsorption of *trans* isomer to an initially clean interface. In that case, the experimentally-observed relaxation time scales happen much faster than predicted by the “monomer only” model, and are described fairly well by the models which consider contributions from aggregates to the adsorption process (results from varied temperature studies reported in Chapter 6 further suggest that dissolution of the aggregates is more important to the adsorption process than their diffusion). In the perturbation studies, the relative importance of the role of aggregates compared to the role of free monomer is not as clear. It seems plausible that this is related to the results of the aggregate dissolution studies discussed in Chapter 6. In those studies, it was found that the time scale associated with dissolution of *trans*-rich aggregates after perturbation of the monomer-aggregate equilibrium (which, in the case of the drop expansion experiments, is caused by depletion of the monomer population due to adsorption) is on the order of tens of seconds. This is substantially shorter than the time scales associated with tension relaxations, and thus aggregate dissolution kinetics did not seem to influence the adsorption kinetics in those experiments. But the aggregate dissolution time scales are of the same order-of-magnitude as many of the re-equilibration time scales seen in the perturbation studies, so that contributions of the aggregates to adsorption could be at least partially limited by
the rate that the aggregates can dissolve to replenish the monomer supply. This would explain the increased relative importance of monomeric surfactant to the adsorption process that is implied by the experimental data. Additionally, the greatest discrepancy between the models which account for aggregate contributions and the data occurs for the 0.43 mM samples. Since these samples have the greatest fraction of surfactant bound in aggregates, it is sensible that limitations from aggregate dissolution kinetics would impact them the most.

These perturbation experiments were also performed on samples initially illuminated to the UV photostationary state. In this case, perturbations were from the pseudo-equilibrium surface tension associated with the intermediate plateau in tension. Expansions and contractions were performed shortly after the onset of the tension plateau so that the surface was presumably dominated by cis surfactant. In this way, the re-equilibration of a saturated, mostly cis surface could be studied. The results are shown in Figure A-6, with Figure A-6a demonstrating typical volume and surface tension responses to a drop expansion. As seen in Figure A-6b, the responses to drop contractions are rapid (occurring within a few seconds), as seen in the trans samples, consistent with the physical mechanism described earlier for surface contractions. Interestingly, in this cis-dominant case, the re-equilibration time scales associated with surface expansions are equally short. It is not surprising that these time scales are shorter than in the trans case, since the cis CMC is much larger than the trans CMC and monomeric surfactant is much more abundant, leading to faster diffusion rates. In the cis relaxation studies of Chapter 4, it was established that aggregates likely played little or no role in the adsorption of cis isomer to a fresh interface. Thus, aggregates would not be expected to make significant contributions to adsorption after a slight perturbation to the adsorption state. When applied to the perturbation
analysis, all of the cis diffusion models (using the cis parameters of Chapter 4), including the “monomer only” models, predict re-equilibration time scales shorter than one second for all bulk concentrations studied. Responses on the order of 0.1 s or 0.01 s exceed the temporal resolution of the instrument and software (limiting frequency of measurement of about 0.5 s) and thus could not be detected even if real, though they do not seem supported by the experimental data. Nonetheless, the rapid response of the cis isomer to surface expansions and the fact that these responses are in better agreement with the “monomer only” models than with those models which account for aggregate contributions are credited as consequences of the large cis CMC and the dominance of monomeric surfactant in the cis adsorption process.
Figure A-6. (a) Typical drop volume and surface tension behavior for an experiment involving rapid expansion of a pendant drop of aqueous C₆ solution in the UV state. (b) Re-equilibration time scales for drop expansion and contraction experiments of varying magnitudes of perturbation.

A.5 Marangoni Flow Experiments

One potential application of these photoresponsive surfactants involves using light to create surface tension gradients across an air/water interface in order to drive surface flow. A cartoon depiction of this type of surface tension-driven (Marangoni) flow using these surfactants is
shown in Figure A-7. The basic premise is that if an interface saturated with photoresponsive surfactant is illuminated non-uniformly such that the surface is exposed to a spatial gradient in the characteristic wavelength of the light, a spatial gradient in the isomeric composition of the adsorbed surfactant will result. This gradient in composition should cause a gradient in the tension of the surface, which could in turn drive surface motion. This type of flow has been demonstrated using surfactants which are responsive to reduction/oxidation reactions [4, 5], but it is believed that light would be a superior stimulus to trigger this phenomena, as it is non-invasive and can be readily focused and patterned to provide excellent spatial and temporal resolution.

Figure A-7. Cartoon depiction of surface tension-driven flow using photoresponsive surfactants and non-uniform illumination of the surface. (a) Visible and UV light shining on different ends of a surface. (b) UV light shining in the middle of a surface otherwise illuminated with visible light.

A simple model was developed in order to perform some order-of-magnitude calculations aimed at determining the feasibility of using these surfactants for this purpose. A sketch of the system under consideration in this model is shown in Figure A-8. A rectangular trough of length $L$ and semi-infinite width is filled with water to a depth $h$. Considering only two-dimensional, nearly unidirectional flow in the $x$-direction (along the length of the trough), the Navier-Stokes equation simplifies to
\[
\frac{\partial^2 V_x}{\partial z^2} = \frac{1}{\mu} \frac{dP}{dx} \tag{A-6}
\]

where \( V_x \) is the fluid velocity in the \( x \)-direction, \( P \) is the pressure, and \( \mu \) is the fluid viscosity.

The two boundary conditions associated with this equation are the no-slip boundary condition at the bottom of the trough:

\[
V_x \big|_{z=0} = 0 \tag{A-7}
\]

and the tangential stress balance at the free surface:

\[
\tau_n \big|_{z} - \tau_n \big|_{1} + L \cdot \nabla_y \gamma = 0 \Rightarrow \mu \frac{\partial V_x}{\partial z} \bigg|_{z=h, \text{air}} - \mu \frac{\partial V_x}{\partial z} \bigg|_{z=h, \text{water}} + \frac{d\gamma}{dx} = 0
\]

\[
\mu_{\text{water}} \gg \mu_{\text{air}}
\]

Figure A-8. Diagram of the system considered when developing model for Marangoni flow.

Equation A-8 then provides a means of obtaining an order-of-magnitude estimate for the surface velocity possible for a given surface tension gradient.

\[
\mu \frac{\partial V_x}{\partial z} \bigg|_{z=k} = \frac{d\gamma}{dx} \Rightarrow \mu \frac{U}{h} - \frac{\Delta \gamma}{L} \tag{A-9}
\]

where \( U \) is the characteristic surface velocity and \( \Delta \gamma \) is the difference in surface tension across the length of the trough. Substituting typical values for length scales and fluid parameters permits calculation of the velocity. If the trough is 10 cm long, the fluid depth is 1 mm, water viscosity is \( 10^{-3} \) \( Pa \cdot s \), and the surface tension difference is 10 mN/m (the difference between a
trans-saturated surface and a cis-dominated surface is about 12 mN/m), then the velocity is estimated as

\[ U \sim \frac{h \Delta \gamma}{L \mu} \left( \frac{10^{-3} m}{s^2} \right) \left( \frac{10^{-2} kg}{s^2} \right) = 10^{-1} \frac{m}{s} \]  

This is significantly faster than the velocities typically reported for surface tension-driven flows in responsive surfactant systems (~ 1 mm/s) [4, 6]. Thus these surfactants appear capable of providing substantial flow which can be directed with light, a possibility with enormous potential.

Basic, quick-and-dirty experiments were attempted in order to demonstrate light-induced surface tension-driven flows using these surfactants, but without success. The details of these experiments are outlined here, to provide a means of reference for any additional, more-sophisticated experiments. The first major consideration in these studies was to determine how any surface flow would be detected. In an effort to maintain simplicity, flow visualization was attempted by powdering the surface with a fine particulate. Sulfur powder has been used for this purpose by other researchers [4], but in separate Langmuir film balance studies, sulfur powder was found to alter the surface pressure behavior of C\textsubscript{6} photosurfactant films. Talc powder, however, did not affect the C\textsubscript{6} surface pressure behavior and was used instead for these flow visualization tests. The next consideration was the method of illumination used to try to create the gradient in isomeric composition. A few different light sources and configurations were tried, but ultimately the illumination was provided by the same high-intensity light source used for the surface illumination experiments of Chapter 5 (the Dymax Bluewave 200 lamp). Two
separate lightguides were used to illuminate different regions of the interface, with appropriate optical filters employed to create one region of visible light and one region of UV light.

The first experiments that were attempted involved filling a small trough or dish with water to a fluid depth of about 1-3 mm, then spreading C₆ surfactant in the dark-adapted state on the water surface using chloroform. (The volume of chloroform solution added was determined by calculating the amount of surfactant needed to saturate the entire area of the free surface, based on previous estimates of the molecular area of the trans isomer at saturation. An amount of surfactant about 20-30% in excess of this required amount was added to try to ensure saturation of the surface.) After the chloroform was allowed to evaporate, talc powder was sprinkled on the surface. Then, regions of the surface were illuminated by using the Dymax lightguides and optical filters. The 320 nm bandpass filter was used for UV illumination and a longpass filter with a cut-on wavelength of at least 475 nm was used for visible illumination to try to minimize the amount of cis present at photostationarity (and hence maximize the composition difference between the two regions). The talc was then visually monitored for movement, but no definitive surface motion was observed. It should be noted that discernment of surface motion caused by illumination was often complicated by slight motion of the talc which occurred even without illumination, caused either by convection in the surrounding air or by the tendency of the talc to agglomerate into clumps.

The next iteration of these experiments involved spreading the surfactant/chloroform solution on top of a water subphase contained in the Langmuir trough, just as done when establishing a surface pressure-area isotherm. After the chloroform evaporated, talc was added to the surface,
and the barriers of the tough were slowly closed while the surface pressure was monitored. As soon as the surface pressure began to level off (in this way guaranteeing that the surface was saturated with surfactant), the barriers were stopped and the surface was illuminated as described above. Again, no definitive surface motion was observed. Thus, none of the experiments were able to provide the proof-of-concept demonstration of light-induced Marangoni flow that was desired. If the photosurfactants are capable of producing surface velocities of the magnitude calculated above, one would imagine that the effect would be fairly pronounced and easily noticed. Perhaps the attempted experiments were inherently flawed, and more careful and sophisticated experiments would be capable of establishing surface tension-driven flow. A different flow-visualization technique may prove more useful: the tendency of the talc to agglomerate and the possibility that the talc might inhibit the photoresponse of the adsorbed surfactant could make it a poor choice for this purpose. A different flow cell or method of illumination might also improve the results. The potential applicability of photo-controllable flow is impressive enough that use of these surfactants for this objective should not be discouraged based on the results of these attempted experiments alone.

A.6 References

2. Shang, T.G., *A New Class of Photoresponsive Surfactants*. Ph.D. Thesis. in Department of Chemical Engineering. 2005, Massachusetts Institute of Technology:Cambridge, MA 02139