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A

**Study of Adsorption of Trisiloxane Surfactants on Air-Water
and Hydrophobic Solid-Water Interface: An Attempt to
Explain the "Super-Spreading" Behavior**

by

Nitin Kumar

*A Dissertation submitted to the Graduate Faculty in Engineering in partial
fulfillment of the requirements for the degree of Doctor of Philosophy,
The City University of New York*

2001

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Abstract

Study of Adsorption of Trisiloxane Surfactants on Air-Water and Hydrophobic Solid-Water Interface: An Attempt to Explain the "Super-Spreading" Behavior

**By
Nitin Kumar**

Advisors: Professor Alexander Couzis and Professor Charles Maldarelli

The exceptional ability of the trisiloxane surfactants to enhance spreading of water on highly hydrophobic surfaces has been the focus of many recent studies. The reason behind their "super-spreading" ability is not yet clear. In this work, we explain the reason of their "super-spreading" ability by comparing their adsorption characteristics on air-water and hydrophobic solid-water interfaces with that of alkyl poly-ethoxylate surfactants ($C_{12}E_j$).

In the first part, we have developed model hydrophobic surfaces using self-assembled silane monolayers. These surfaces have been used for surfactants' adsorption experiments. Using Atomic Force Microscope as a tool to study the morphology of the partial silane monolayers, we have developed a protocol to prepare mixed silane monolayers by sequential adsorption of different silanes. In these mixed monolayers, domains of one-chemical functionality are surrounded by another chemical functionality. The size and morphology of the domains can be controlled from nanometer to micrometer scale by controlling the deposition conditions.

The adsorption characteristics of trisiloxane surfactants on air-water interface have been investigated by pendant bubble technique and compared with that of $C_{12}E_j$

surfactants. Due to the peculiar "T" structure of the hydrophobic groups, the trisiloxane surfactants have larger driving force to adsorb on the air-water interface. Consequently, they pack more densely than $C_{12}E_j$, and reduce the surface tension faster and to values lower than that of $C_{12}E_j$ surfactants.

The adsorption of the trisiloxane and $C_{12}E_j$ surfactants on hydrophobic silane monolayers has been investigated using FTIR spectroscopy in attenuated total internal reflection mode. We have observed the changes induced in the hydrogen bonding structure of water near hydrophobic surfaces, as a result of surfactants' adsorption, and the effect of surfactant structure on the hydrogen bonding of the interfacial water. The trisiloxane surfactants reduces the hydrophobic-solid water surface energy to lower values because of their ability to remove free OH present near the hydrophobic surface. This is again attributed to their "T" structure. In conclusion, the super-spreading ability of the trisiloxane surfactants is due to their ability to reduce hydrophobic solid- and air-water surface tensions, which in turn is attributed to the structure of their hydrophobic group.

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List of Symbols:**Chapter 2**

- S : Spreading coefficient
- γ_{SL} : Surface tension/ energy of solid-liquid interface
- γ_{SV} : Surface tension/ energy of solid-vapor interface
- γ_{LV} : Surface tension of liquid
- θ : Contact angle
- θ_w : Contact angle with water

Chapter 3

1. : Contact angle

Chapter 4

- γ_e : Equilibrium surface tension
- C_0 : Bulk concentration
- D : Diffusion Coefficient
- t : Time (sec)
- A : Area of the bubble
- Γ : Surface Concentration
- Γ_{ref} : Relative Surface Concentration
- Γ_{60} : Surface Concentration at surface tension of 60 mN/m
- A_{60} : Area of the bubble at surface tension of 60 mN/m
- α : Desorption coefficient

β	: Adsorption coefficient
C_s	: Sub-layer concentration
K	: Frumkin interaction parameter
Γ_∞	: Parameter for maximum surface concentration
a	: α/β
R	: Ideal gas constant
T	: Temperature
γ_c	: Surface tension of pure liquid
R'	: Bubble radius
τ_{diff}	: Diffusion time scale
τ_{kin}	: Kinetic adsorption and desorption time scale
Φ^2	: τ_{diff} / τ_{kin}
δ	: Time step size
E_D	: Activation energy of desorption
E_D^0	: Activation energy of desorption at infinite dilution
Π	: Surface pressure
A_{min}	: Minimum area per molecule
Γ_{CAC}	: Surface concentration at CAC
α'	: Molecular desorption frequency factor
β'	: Molecular adsorption frequency factor
E_A	: Activation energy for adsorption
E_A^0	: Activation energy for adsorption at infinite dilution
ΔG^0	: Standard free energy change

Chapter 5

γ_{SL} : Surface tension / energy of solid-liquid interface

γ_{SV} : Surface tension / energy of solid-vapor interface

γ_{LV} : Surface tension of liquid

A : Area of absorbance peak

ϵ : Integrated molar absorptivity

b : Thickness

C : Bulk concentration

η_1 : Refractive index of medium 1

η_2 : Refractive index of medium 2

η_{21} : η_2 / η_1

θ : Angle of incidence

ϕ : Angle of refraction

E : Electric field intensity

E_0 : Electric field intensity at interface

z : Distance from interface

d_p : Penetration depth

λ : Wave length

R : Reflectivity

I : Intensity of beam

I_0 : Initial intensity of beam

N : Number of reflections

α	: Molar absorptivity
D	: Dichroic ratio
$A_{\parallel}$	: Area of absorbance peak in parallel polarization
$A_{\perp}$	: Area of absorbance peak in perpendicular polarization
$\vec{P}$	: Chain axis vector
$\vec{N}$	: Surface normal vector
$\vec{M}$	: Transient dipole moment vector
Φ	: Angle of chain inclination
$d_{e\parallel}$	: Effective depth in parallel polarization
$d_{e\perp}$	: Effective depth in perpendicular polarization
Γ	: Surface Concentration
*	

Chapter 1

Introduction

1.1 Background

Spreading of water on hydrophobic surfaces is important many technological applications as well as in our daily lives. A common method to achieve this is by the addition of surface-active agents to water, called surfactants. Surfactants adsorb on the air-water and solid-water interfaces and reduce the corresponding interfacial tensions. The development of effective surfactants that aid spreading is a priority in a number of industries, such as, coatings¹, cosmetics²⁻⁴, heat transfer^{5,6}, and agriculture⁷. Conventional ionic and non-ionic surfactants are used extensively in these industries. A large number of ionic and non-ionic surfactant systems are available, which can enhance the spreading on moderately hydrophobic surfaces. For highly hydrophobic surfaces, with a large water contact angle, there are not many surfactants, which can enhance the spreading of an aqueous drop. During 1960's a class of surfactants, called siloxane surfactants was identified^{8,9}. These surfactants were found to be very effective in spreading of water on highly hydrophobic surfaces. Due to the unusually rapid spreading of the aqueous solutions of the siloxane surfactants, these are called super-spreaders. Among the siloxane surfactants, the surfactants containing a trisiloxane group as the hydrophobic groups are found to be the most effective^{9,10}.

The structure of a common structure of the trisiloxane surfactants is shown in Figure 1.1. The hydrophobic part of the surfactant molecule consists of seven methyl

groups attached to a trisiloxane group (-Si-O-Si-O-Si-). The seven methyl groups attached to the silicon atom form a spatially compact hydrophobic group. This trisiloxane hydrophobic group is linked to the hydrophilic part of the surfactant molecule through a three carbon atom hydrocarbon chain. The hydrophilic part consists of a poly-ethoxylate chain (E_j), consisting of 4-12 ethoxylate ($(CH_2CH_2O)_j$) units. The terminal group (R) of the poly-ethoxylate chain can be methoxy, or hydroxy or acetyl group¹¹. A common abbreviation for the trisiloxane surfactants is $M(D'E_jR)M$, where M: $(CH_3)_3SiO$, D': $-CH_3Si(CH_2)_3-$, E_j : $(CH_2CH_2O)_j$, R: $-H$, $-OH$, $-CH_3$ or $-C(O)CH_3$. The trisiloxane surfactants are non-ionic surfactants. The structure of the trisiloxane surfactants is partly similar to the structure non-ionic alkyl poly-ethoxylate surfactants (Figure 1.1), which are commonly used and have been extensively studied¹². The trisiloxane surfactants differ from the alkyl poly-ethoxylate surfactants only in the structure of the hydrophobic group. The hydrophobic group of the alkyl poly-ethoxylate surfactants consists of a linear hydrocarbon chain of 8-16 carbon atoms. The hydrophilic part is same as that of the trisiloxane surfactants. The alkyl poly-ethoxylate surfactants are not super-spreaders. In the literature, the alkyl poly-ethoxylate surfactants are denoted as C_iE_j , where i is the number of the carbon atoms in the hydrocarbon chain, and j is the number of the ethoxylate units in the hydrophilic part.

The effectiveness of the trisiloxane surfactants is illustrated in Figure 1.2. This figure shows snapshots of aqueous drops impact experiments on hydrophobic surfaces. The contact angle of a static drop of pure water on the hydrophobic surface is $\sim 107^\circ$. A drop of pure water strikes the surface, and spreads because of the kinetic energy. Then, the drop retracts and rebounds from the surface. When $C_{14}E_6$ and $C_{12}E_0$ are added to

water, the drops strike the surface, spread because of the kinetic energy, retract, and finally stay on the surface with some positive contact angle. When a trisiloxane surfactant ($M(D'E_sOH)M$) is added to water, the drops strike the hydrophobic surface and immediately spread to form a thin water layer on the hydrophobic surface. This demonstrates the super-spreading ability of the trisiloxane surfactants.

Due to their exceptional spreading ability, the trisiloxane surfactants are used in many industrial applications. We will describe only one major potential application of the trisiloxane surfactants in the agrochemical industry^{7,13,14}. In the agriculture industry, many organic formulations, (such as, herbicides and pesticides) are emulsified in water and sprayed on plants and soil. The efficacy of the sprays depends on the amount of the pesticide solution which is retained on the leaves. Due to the hydrophobic character of plant leaves, most of the drops roll off or rebound from the leaves' surfaces. The spray drops, which are not retained by the plant leaves, are a waste and end up in soil, causing environmental pollution. Because of this reason, the agrochemical and agriculture industry is under immense pressure to reduce the usage of agrochemicals. An effective way to increase the efficacy of the sprays is by increasing the spreading of the agrochemical solutions on plant leaves. Addition of surfactants to the agrochemical solutions increases the effectiveness of the pesticide and herbicides sprays. Among many available surfactants systems, the trisiloxane surfactants are the most effective in increasing the potency of the sprays by increasing the spreading of impacting drop on plant leaves and soil^{7,13,14}. Figure 1.3A shows the effect of the addition of surfactants to a drop of water placed on a hydrophobic leaf. Pure water does not spread on the surface, and forms a drop with large contact angle. On the addition of a non-super-spreading non-

ionic surfactant, the contact angle reduces, but the spreading is still not effective. On addition of Silwet L-77® (a trisiloxane surfactant), the water drop spreads on the leaf to form a thin layer. This again demonstrates the super-spreading ability of the trisiloxane surfactant. Figure 1.3B shows the effect of the addition of the Silwet L-77® on the penetration of water in soil.

Increased spreading of the spray drops on plants, increases the effectiveness of agrochemical sprays, thereby reducing their usage. In this multi billion-dollar industry, reductions of even a fraction of a percent in usage of agrochemical can lead to savings of millions of dollars. Apart from the monetary value, this will also help to reduce soil and water pollution.

In spite of the excellent spreading characteristics of the trisiloxane surfactants, their industrial use has been limited, especially in the agricultural sprays. The reason of the limited use of the trisiloxane surfactants is their degradation in acidic and basic environment^{3,15} by hydrolysis of the siloxane bond. The hydrolysis strongly depends on pH of the solutions. We have also observed that trisiloxane solutions, kept in acid-cleaned glass containers, tend to degrade even in few hours.

An understanding of the super-spreading ability of the trisiloxane surfactants is important not only for the fundamental surface science, but also it will help in developing other super-spreading surfactants, which do not suffer from the disadvantages of the trisiloxane surfactants. In this thesis, the author has attempted to explain the reason behind the super-spreading behavior of the trisiloxane surfactants. This knowledge, which is of fundamental importance in surface science, attempts to relate the structure of

the trisiloxane surfactant molecules to their ability to reduce the air-water and hydrophobic solid-water surface tensions.

1.2 Literature Survey

Some early patents, regarding the super-spreading ability of the trisiloxane surfactants were filed in 1960's^{16,17}. A current search of the US patent database containing key words " trisiloxane surfactant", yielded approximately 150 patents. The applications ranged from hair care products ¹⁸ to anti-foaming agents¹⁹. During the period from 1960's to 1990, not much literature is available, which has focused on understanding the super-spreading ability of the trisiloxane surfactants, in spite of the widespread applications. In one of the early works on the trisiloxane surfactants, Schwartz et al⁹ studied the spreading behavior of many surfactants, which included siloxane surfactants, fluorocarbon surfactants, and some other non-ionic and ionic surfactants. They measured the interfacial tension of surfactants' solutions in contact with air and organic liquids. The siloxane surfactants were found to be better spreaders of water on polyethylene than the fluorocarbon surfactants, even though the fluorocarbon surfactants reduce the air-water surface tension to values lower than that of the siloxane surfactants. In 1990, Ananthapadmanabhan et al¹⁰ carried out a systematic study of the wetting behavior of three siloxane surfactants. They observed that the trisiloxane hydrophobe based surfactants ($M(D'E_{7.5}OCH_3)M$) exhibit the best spreading characteristics. They attributed the super-spreading properties of the trisiloxane surfactants to a variety of factors, such as, the peculiar 'T' or umbrella shape of the molecule, ability of the trisiloxane surfactants to reduce the air-water and hydrophobic solid-water interfacial tensions, high affinity of the trisiloxane surfactants for low energy surfaces, and favorable orientation and structure of the adsorbed molecules. However, these were only suggested reasons and no concrete experimental or theoretical evidence

was provided. The critical aggregation concentration (CAC) of the trisiloxane surfactant $M(D'E_8OCH_3)$ was measured to be ~ 0.007 wt%. Among numerous ways to define the CAC, the most commonly used definition is the concentration above which the surface tension of the surfactant aqueous solution reaches a plateau without any significant further decrease. The concentrations, at which the trisiloxane surfactant exhibits super-spreading on Parafilm®, are 5-10 times above the CAC. The authors strongly believed that the unique ability of the trisiloxane surfactant solutions to spread on the hydrophobic surfaces is related to the compact structure of the trisiloxane hydrophobe. In comparison, the conventional "non super-spreading" ionic and non-ionic surfactants have a long hydrocarbon chain as the hydrophobic group. Later, Zhu et al²⁰ used video microscopy to measure the spreading rates and the extent of spreading of water droplets containing various trisiloxane surfactants. Parafilm® was used as the hydrophobic surface. It was observed that the super-spreading trisiloxane solutions were slightly turbid. The solutions did not spread in dry atmosphere. The authors speculated that the water vapors provide a thin high-tension water film at the leading edge of the spreading drop, which leads to Marangoni force driven spreading. The maximum initial rate of spreading was observed at 0.16% w/w concentration of $M(D'E_8OCH_3)M$. The equilibrium spreading area was found to be proportional to the concentration, indicating that the drops spread until the inventory of the surfactant in the drops is exhausted. The turbid dispersions, prepared by sonicating the solutions, were found to spread faster than the dispersions prepared by shaking the solutions with hand. The authors emphasized on two requirements for super-spreading, (1) presence of water vapors, and (2) turbid solutions. It should be noted even though the rate of spreading was maximum at 0.16 % w/w ($\sim 22 \times CAC$), significant

equilibrium spreading occurred at concentrations as low as 0.02 %w/w ($\sim 3 \times \text{CAC}$). A 2.5 mm diameter spherical drop containing 0.02 % trisiloxane surfactant solution, spread to an area of $\sim 80 \text{ mm}^2$ ($\sim 10 \text{ mm}$ in diameter). Zhu et al²⁰ have also provided a raw definition of super-spreaders. According to them, "As a working definition, we say a surfactant is a super-spreader if the addition of a small amount, say less than 0.1%, to a small droplet of water enables it, when placed on a hydrophobic surface, to spread into a thin, wetting film within tens of seconds." However this definition is very crude and the spreading properties of the surfactants are highly dependent on the hydrophobicity of the surface.

The observations of Zhu et al²⁰, that the initial spreading rate was maximum at concentration much higher than the CAC, and the super-spreading solutions were turbid, led to some studies about the phase behavior of the trisiloxane and other surfactants. Gradzielski et al²¹ investigated the phase behavior of various siloxane surfactants in water. The surfactants used in this study were trisiloxane hydrophobe based, and with non-ionic poly-ethoxylate and ionic hydrophilic groups. From the CAC data, the authors concluded that for the hydrophobicity of the hydrophobic part of the trisiloxane surfactants ($\text{M}(\text{D}')\text{M}$) is similar to the hydrophobicity of a linear $\text{C}_{12}\text{H}_{25}$ hydrocarbon chain. He et al²² investigated the phase behavior of various trisiloxane surfactants and compared their phase behavior with the alkyl poly-ethoxylate (C_iE_j) surfactants. Hill et al²³ studied the phase behavior of $\text{M}(\text{D}'\text{E}_8\text{OCH}_3)\text{M}$, $\text{M}(\text{D}'\text{E}_8\text{OH})\text{M}$, and $\text{M}(\text{D}'\text{E}_8\text{OAc})\text{M}$. All the three surfactants exhibit super-spreading. The end group affects the phase behavior, but not the super-spreading ability. At low concentrations ($\sim 0.1\text{-}1\%$), the three surfactants form unilamellar and multilamellar vesicles coexisting with the particles of

much smaller size and of uncertain identity. Hill et al²³ speculated that these small particles of uncertain identity might be the reason for the super-spreading behavior. Some other investigations were carried out for the phase behavior of the trisiloxane and alkyl poly-ethoxylate surfactants^{24,25 25-31}. An important point to note is that the trisiloxane surfactants do not behave as super-spreaders at high concentrations ($>2\text{-}3\%$ w/w)²⁰.

The above mentioned phase behavior studies did not shed much light on the question why the trisiloxane surfactants are super spreaders, while other alkyl poly-ethoxylate surfactants (C_iE_j) are not super-spreaders, in spite of the fact that the phase behavior of some alkyl poly-ethoxylate surfactants is similar to that of the super-spreading trisiloxane surfactants. As a result, attention was diverted from the bulk phase behavior to various interfaces involved in spreading. In a significant work, using video microscopy, Stoebe et al^{32,33} measured the spreading rate of various trisiloxane and alkyl poly-ethoxylate surfactants at various concentration and on surfaces with varying hydrophobicity. They used mixed self-assembled thiol monolayers of varying hydrophobicity, with water contact angle from 24° to 112° . The trisiloxane surfactants $M(D'E_4OH)M$ and $M(D'E_8OH)M$ exhibited super-spreading on the surfaces with water contact angle as large as $\sim 95^\circ$, whereas the turbid solutions of $C_{10}E_3$, $C_{12}E_3$, and $C_{12}E_4$ did not spread on such surfaces. The spreading rate was found to depend on the surface hydrophobicity. The maximum spreading rate for the trisiloxane surfactants occurred on surfaces with moderate hydrophobicity (water contact angle $\sim 66^\circ$). The spreading rate was also found to depend on the number of ethoxylate units. The alkyl poly-ethoxylate surfactants (C_iE_j) also exhibited rapid spreading, but on surfaces with reduced hydrophobicity (water contact angle $\sim 50^\circ$). Furthermore, the authors observed that the

turbidity of the solutions was not a requirement for the super-spreading, which is in contrast with the observations of Zhu et al²⁰. The humidity effects, as observed by Zhu et al²⁰, were not significant. On a similar theme, Lin et al^{34,35} measured the spreading rates using quartz crystal microbalance. Wagner et al²⁵⁻²⁸ have investigated the spreading behavior of various trisiloxane surfactants at various temperatures. The maximum spreading rate was observed to depend on temperature and the number of ethoxylate units. At 6°C, M(D'E₄CH₃)M had the maximum initial spreading rate, whereas at 26°C M(D'E₆CH₃)M was found to have the maximum initial spreading rate. At 40°C, only M(D'E₈CH₃)M and M(D'E₉CH₃)M were observed to exhibit super-spreading. The authors attempted to relate these effects to the presence of a two-phase state in the bulk solution. The spreading of ionic surfactant solutions on surfaces with varying hydrophobicity was studied by Stoebe et al³⁶. Similar to the alkyl poly-ethoxylate surfactants^{32,33}, the ionic surfactants solutions spread only on surfaces with reduced hydrophobicity. The dependence of spreading rate on surface hydrophobicity and concentration was similar in the case of the trisiloxane, alkyl poly-ethoxylate and ionic surfactants. Based on these results Stoebe et al^{32,33,36,37} suggested an explanation of the surfactant enhanced spreading. This explanation is based on Marangoni flow and illustrated in Figure 1.4. This mechanism can explain the spreading rate dependence on humidity, concentration of surfactants, phase behavior, and surface hydrophobicity. But still does not explain the peculiarity of the trisiloxane surfactants, makes them "super-spreaders".

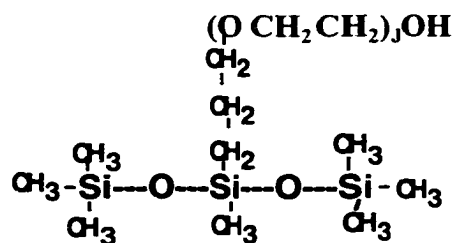
In a recent study, Svitova et al³⁸ studied the behavior of water drop containing M(D'E₆OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M on various hydrophobic surfaces with

concentrations below and above CAC. They measured surface tension and contact angles of the trisiloxane surfactant's solutions on hydrophobic surfaces, such as Parafilm®, polyethylene and Teflon. They proposed a critical wetting concentration (CWC), at which the transition from partial wetting to complete wetting occurs. The values of CWC are 5-10 times the CAC. The authors, using the contact angle data, have calculated the interfacial tensions at solid-liquid surfaces, both below and above the CAC. They speculated the formation of aggregates of unknown identity on hydrophobic surfaces at concentration near and above CWC. In a more recent paper, Svitova et al³⁹ have used AFM to image the surface aggregates of the trisiloxane and alkyl poly-ethoxylate surfactants ($C_{12}E_3$) on graphite.

Most of the studies mentioned above, are related to the observations of the super-spreading behavior of the trisiloxane surfactants under different conditions. Some studies have been carried out to investigate the surface and interfacial tensions of the trisiloxane surfactants. Svitova et al⁴⁰ investigated the dynamic surface tension of trisiloxane and alkyl poly-ethoxylate surfactants at concentrations above CAC. In an attempt to understand the unusually low surface tensions of the trisiloxane surfactants solutions, Gentle et al⁴¹ measured equilibrium surface tension below CAC, and evaluated the surface concentrations of different trisiloxane surfactants on air-water interface. Rosen et al⁴² unsuccessfully attempted to relate the super-spreading with Draves Skein wetting. Ruckenstein⁴³ suggested that a short range attractive interaction between the hydrophobic moiety of the trisiloxane surfactants and the hydrophobic surface is the reason for super-spreading. Churaev et al^{44,45} included disjoining pressure effect in the hydrodynamic equation to explain the super-spreading behavior. Churaev et al⁴⁶

investigated the application of the trisiloxane surfactants to remove oil from hydrophobic surfaces. Svitova et al⁴⁷ and Stoebe et al³⁷ have studied the spreading of the trisiloxane surfactant solution on hydrophobic liquids. Nikolov et al⁴⁸ have tried to explain the super-spreading behavior as a result of enhanced Marangoni effect. Hill^{11,49} has reviewed some of this literature.

In conclusion, many explanations have been proposed to explain the super-spreading behavior of the trisiloxane surfactants, such as, the molecular structure of the surfactants, Marangoni force driven spreading on water film on surfaces, presence of certain phases in solution, and short range attraction between the hydrophobic. The reason for the super-spreading ability of the trisiloxane surfactants is still unclear. The objective of this thesis is to find an explanation of the super-spreading ability of the trisiloxane surfactants by comparing their adsorption characteristics on air-water and hydrophobic solid-water surfaces with that of the alkyl poly-ethoxylate surfactants, and to relate the super-spreading ability with the peculiar molecular structure of the trisiloxane surfactants.

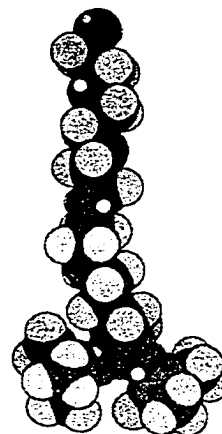


M: $(\text{CH}_3)_3\text{SiO}$

D': $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3$

E: $(\text{OCH}_2\text{CH}_2)$

R: $-\text{OH}$, $-\text{OCH}_3$, $-\text{H}$, $-\text{OAc}$



Trisiloxane Surfactant $\text{M}(\text{D}'\text{E}_j\text{R})\text{M}$



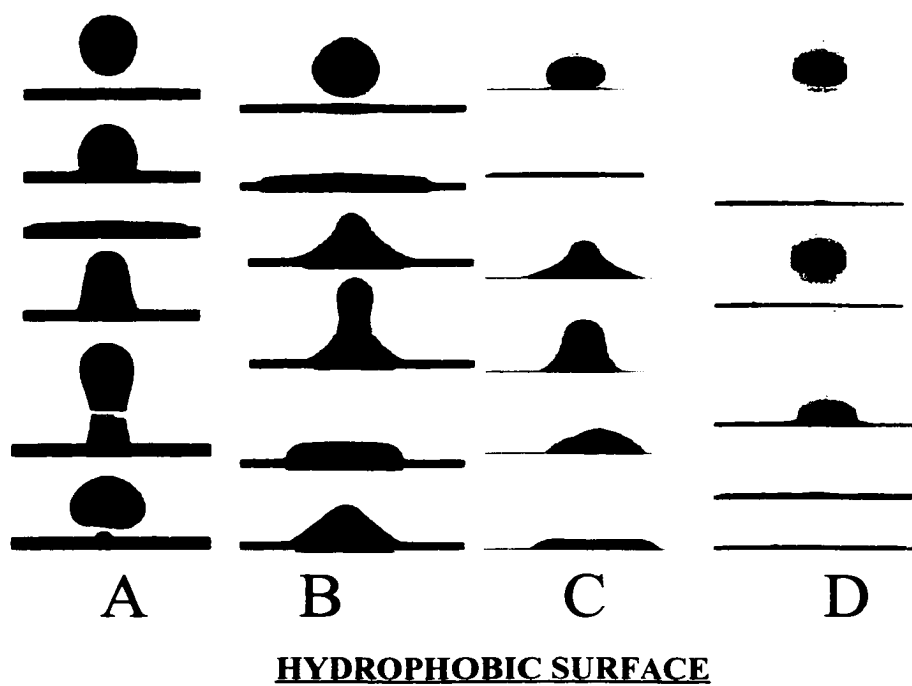
C_iE_j

Alkyl poly-ethoxylate Surfactant

C_iE_j



Figure 1.1: Structure of Trisiloxane and Alkyl poly-ethoxylate surfactants



Reference: Subramanayam⁵⁰

Figure 1.2: Aqueous drop impact experiments on hydrophobic surfaces demonstrating the super-spreading ability of the trisiloxane surfactants. (A) pure water, (B) containing $C_{12}E_0$, (C) containing $C_{14}E_6$, (D) containing trisiloxane surfactant $M(D'E_8OH)M$

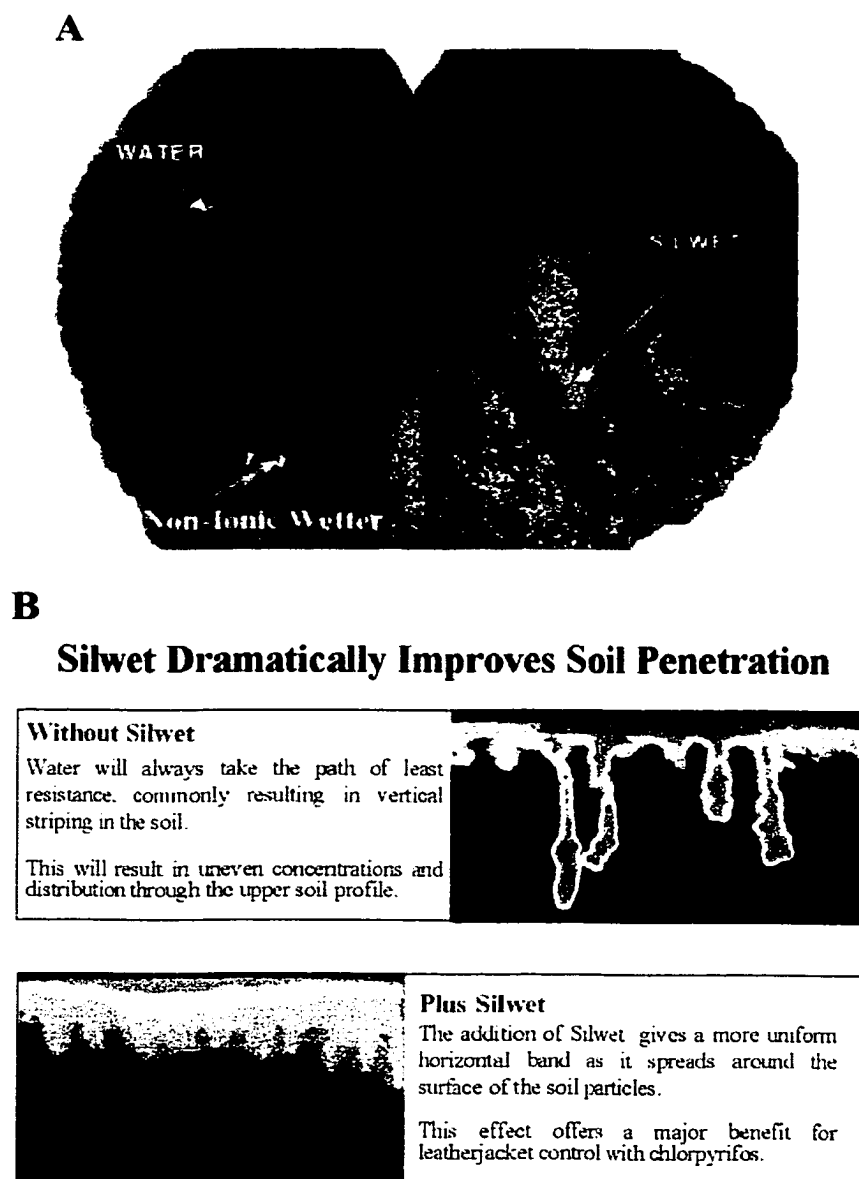
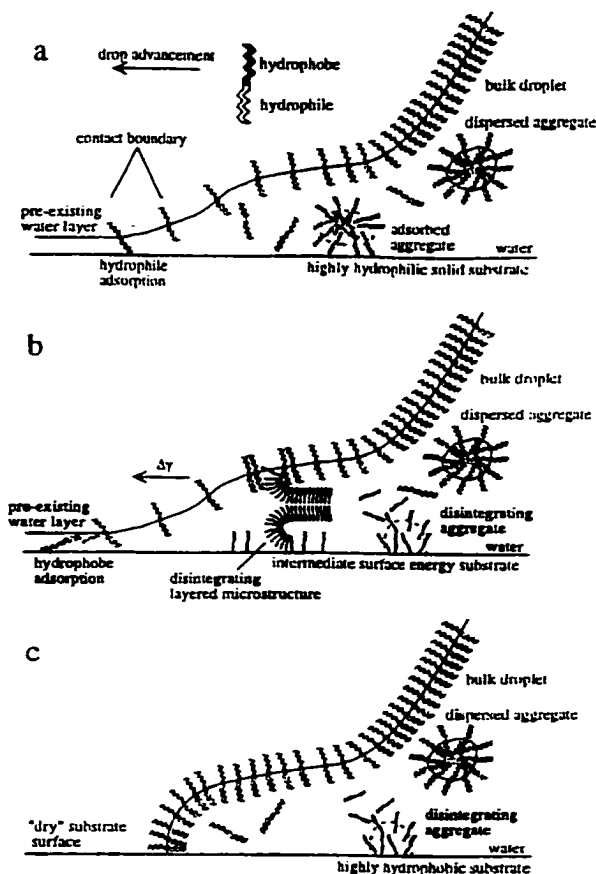


Figure 1.3: Application of trisiloxane surfactants in agrochemical industry. Taken from <http://www.loveland.co.uk/adjuvants/Silwet.html> on April 30, 2001



"Schematic representation of the processes that may be responsible for surfactant-enhanced spreading. In (a) and (b) the drop introduced to the surface actually is in contact with a pre-existing water layer. The contact line defining the boundary of the leading edge of the droplet and the pre-existing water layer is continuous and may not be very distinct. However, the surfactant concentrations at the air-water interfaces of the droplet and the region just beyond this contact line will differ throughout the spreading event due to continuous advancement of the contact line across the pre-existing water layer, which initially is devoid of surfactant. A surface tension gradient ($\Delta\gamma$) between a pre-existing water film and the surfactant/water droplet favors Marangoni flow and rapid spreading of the aqueous droplet. (a) On highly hydrophilic substrates the pre-existing water layer will be present. However, spreading on these surfaces is observed to be slow. This can be attributed to adsorption of the surfactant hydrophiles on the substrate, which forces the hydrophobe to point away from the substrate surface and resents a hydrophobic barrier to drop advancement. The surfactant molecule, with its hydrophile bound to the substrate, may pin the drop at the contact line joining the leading edge of the drop and pre-existing water film. The kinetics of desorption of the surfactant hydrophile from the substrate may govern the spreading rate. Surfactant aggregates may adsorb on hydrophilic substrates intact as there is no driving force to adsorb the hydrophobes on these surfaces. Consequently, aggregate disintegration may be slower than on

hydrophobic substrates. (b) On surfaces of intermediate surface energy a pre-existing water film necessary for Marangoni flow is still likely, but the tendency for the hydrophobe of the surfactant to adsorb on the substrate will increase. This can instigate aggregate disintegration, resulting in the efficient delivery of surfactant to the air-water interface when this occurs in the vicinity of the leading edge of the advancing drop. This is illustrated here for a flat-layered microstructure unraveling at the leading edge, although the specific microstructure of the aggregates responsible for enhanced spreading have not been identified. Direct surfactant adsorption on the substrate in the region just beyond the leading edge of the drop, depicted here by the arrow, will also reduce the concentration of surfactant at the opposing air-water interface and augment the surface tension gradient. The difference in thickness of the pre-existing water layer in (a) and (b) is only for clarity. (c) On a highly hydrophobic substrate a pre-existing water layer is considerably less likely, prohibiting the creation of the surface tension gradient necessary for Marangonic flow. Very hydrophobic surfaces do not favor formation of a continuous water film, which prevents the creation of the surface tension gradient necessary for Marangoni flow and accounts for the negligible spreading on these surfaces. Spreading on these surfaces also is less thermodynamically favorable owing to a less positive spreading coefficient."

Figure 1.4: Explanation of surfactant enhanced spreading by Stoebe et al³³.

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Chapter 2

Scope and Direction of Research

2.1 Scope

When a drop of liquid is placed on a solid surface, the liquid either spreads and forms a thin layer on the surface, or remains as a discrete drop⁵¹⁻⁵³. The former behavior is described as complete wetting and the later as incomplete or partial wetting. The wetting behavior depends on the interfacial surface energies of solid-vapor(γ_{sv}), solid-liquid(γ_{sl}) and liquid-air(γ_{lv}) interfaces. Spreading coefficient (S) is used to characterize this wetting behavior. S is defined as:

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (2.1)$$

If $S > 0$, the drop forms a thin layer of liquid on the solid surface and complete wetting occurs. In case of partial wetting, $S < 0$, and the liquid forms a drop with a certain contact angle (θ) as illustrated in Figure 2.1. This relationship is valid for any liquid. In the special case, when the liquid is water, the surfaces are divided in two classes, hydrophilic and hydrophobic surfaces. On hydrophilic surfaces, a water droplet completely wets the surface or achieves a small contact angle. On a hydrophobic surface, the contact angle of is relatively large. There is no clear demarcation between the hydrophilic and hydrophobic surfaces in terms of the water contact angle. Vogler⁵⁴ has classified surfaces based on the value of water contact angle (θ_w). A surface is named hydrophobic if $\theta_w > 65^\circ$, and hydrophilic if $\theta_w < 65^\circ$. The term highly hydrophobic surfaces can be used for surfaces with water contact angle greater than 90° . The contact

angle depends on γ_{SV} , γ_{SL} , and γ_{LV} . Their relationship is described by Young-Laplace equation.

$$\cos(\theta) = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \quad (2.2)$$

Addition of surfactants to the water drop reduces the interfacial tension of air-water (γ_{LV}) and solid-water (γ_{SL}) interfaces. Reduction in contact angle on surfaces, with $\theta_w < 90^\circ$, can be achieved by a reduction in γ_{LV} alone. On highly hydrophobic surfaces, with $\theta_w > 90^\circ$, a reduction in γ_{LV} only increases the contact angle, as $\cos(\theta)$ becomes more negative. Therefore, on such highly hydrophobic surfaces, it is necessary to reduce γ_{SL} .

Addition of the trisiloxane surfactants to water causes complete wetting on highly hydrophobic surfaces ($\theta_w > 90^\circ$). Other non-ionic alkyl poly-ethoxylate surfactants do not cause spreading on such surfaces, even though the hydrophilic group of these two classes of surfactants is similar. The necessary condition for complete wetting is a positive spreading coefficient⁵¹. If the spreading coefficient is negative, then there is no driving force for complete wetting and the solution stays as a drop on the surface. By comparing the spreading behavior of the trisiloxane and alkyl poly-ethoxylate surfactants, it is obvious that the addition of the trisiloxane surfactants to water drops, increases the spreading coefficient from negative to nearly zero or positive values. On the other hand, the addition of the alkyl poly-ethoxylate surfactants makes the spreading coefficient less negative, but still not close to zero. Once the necessary condition of positive spreading coefficient is satisfied, then the surfactant solution drop can spread on the surface.

The spreading of a drop is driven mainly by the interfacial tensions. The spreading rate and other characteristics of spreading depend on the many factors, such as, adsorption kinetics of the surfactant, the ability of the surfactant to reduce the interfacial

tensions, surface tension gradients which drive the Marangoni flows, viscosity of the solution, roughness of the surface, presence of pre-existing fluid layer, etc. For the solutions with concentrations above CAC, the adsorption kinetics depends on the kinetic rates of adsorption of monomeric surfactant molecules, break-up kinetics of the bulk aggregates (e.g. micelles, vesicles, etc.), diffusion coefficients of the monomeric surfactant and aggregates, and convective transport of the surfactant to the edge of the spreading drop. Some authors have suggested that vesicles structure can supply surfactant to the spreading drop edge more efficiently and rapidly than micellar structures. They attribute this as the reason behind the super-spreading ability of the trisiloxane surfactants⁵⁵. The shape and type of bulk phase aggregates can be can change the viscosity of surfactants solutions²⁰, break up kinetics of aggregates, and transport properties of the aggregates⁵⁶. The Marangoni flow driven spreading on solid surfaces depends on the kinetics of adsorption, hydrodynamic flow field, and the presence of pre-wetting film on the surface. A positive or nearly zero spreading coefficient is again necessary and main requirement for Marangoni flows to occur during spreading of a drop.

From the above arguments, it is obvious that the super-spreading ability of the trisiloxane surfactants is related to their ability to reduce the contact angle on highly hydrophobic surfaces to zero or close to zero, and thus changing the spreading coefficient from negative values to nearly zero or positive values. The changes in the spreading coefficients are a result of the reduction in the interfacial tensions. The reduction in the interfacial tensions is a consequence of the adsorption of surfactants. The adsorption of surfactant from bulk to the surface is driven by the chemical potential of surfactant in the

bulk. The chemical potential of the surfactant molecules in the bulk increases as the concentration increases, till CAC. At concentrations above CAC, there is no *significant* increase in the chemical potential of the surfactant in the bulk⁵⁶. As a result, the spreading coefficient does not change significantly for concentrations above the CAC. Therefore, the ability of a surfactant to increase spreading on a surface can be judged by the value of the spreading coefficient, S , at CAC. For the partial wetting case, S , can be calculated from surface tension and contact angle. Using Equations 2.1 and 2.2, the spreading coefficient can be expressed as $S = \gamma_{LV}(\cos(\theta) - 1)$. On Parafilm®, the values contact angle of pure water^{38,57}, M(D'E₆OH)M (at CAC)³⁸, and C₁₂E₅ (at CAC and above CAC)⁵⁷ are 107°, ~24°, and ~60°, respectively. The respective surface tensions at the air-water interface are, ~72.4, 21, and 30 mN/m. Using these values, the spreading coefficient on Parafilm® for water, M(D'E₆OH)M, and C₁₂E₅ are -93, -15, and -2.1 mN/m, respectively. This proves that the trisiloxane surfactants bring the spreading coefficient much closer to zero. (A positive spreading coefficient cannot be measured by contact angle techniques.)[§]

The change in the spreading coefficient depends on surfactants' ability to reduce the air-water and the hydrophobic solid-water interfacial tensions. The trisiloxane

[§] Svitova et al³⁸ observed that the contact angle of a M(D'E₆OH)M solution at CAC is ~24°. They suggested a critical wetting concentration (CWC) at which the wetting occurs. The CWC is a few times higher than the CAC. However, this result can be explained by the fact that at low contact angles, due to large increase in surface area, the surfactant from the bulk is depleted, thereby changing the bulk concentration. For a spherical shape drop of contact angle θ , surface area (S) to volume (V) ratio varies as $\frac{1}{1 - \cos\theta} + \frac{1}{\sin^2\theta + 1 - \cos\theta}$. Therefore, at small contact angles, the depletion of the surfactant should be accounted for. Using the contact angle, CAC, and the surface concentration data, (Svitova et al³⁸), it was calculated that approximately 20 % of the surfactant was depleted from the bulk to

surfactants reduce the air-water surface tension to values as low as 21 mN/m⁹. Only few other surfactants, such as fluorocarbon surfactants, have the ability to reduce the air-water surface tensions below 21mN/m. However, the fluorocarbon surfactants are not super-spreaders^{9,10}, even though the Zisman's critical surface tension on Parafilm® is 25mN/m⁵⁷. The alkyl poly-ethoxylate surfactants reduce the air-water surface tension to values >28 mN/m^{12,41}. The difference in the contact angle of solutions of M(D'E₆OH)M (~24°) and C₁₂E₅ (60°) at CAC, cannot be explained merely by reduction in γ_{LV} . Assuming, $(\gamma_{SV} - \gamma_{SL})$ to be the same for the two surfactants, a reduction in the surface tension from 30mN/m to 21mN/m reduces the contact angle from 60° to ~44° ($= \cos^{-1}[\frac{\cos(60^\circ) * 30}{21}]$). This does not account for low contact angle of 24° for M(D'E₆OH)M.

The difference $(\gamma_{SV} - \gamma_{SL})$ for M(D'E₆OH)M and C₁₂E₅ can be calculated, for known values of θ and γ_{LV} . The values of $(\gamma_{SV} - \gamma_{SL}) (= \gamma_{LV} \cos \theta)$ for M(D'E₆OH)M and C₁₂E₅ are 15 and 19.2 mN/m respectively. The value of γ_{SV} is same for both the surfactants, implying that the trisiloxane surfactant not only reduce the air-water surface tensions, but also reduce the hydrophobic solid-water tension (γ_{SL}) to values lower than that of the alkyl poly-ethoxylate surfactants (C₁₂E₅).

In conclusion, the trisiloxanes surfactants somehow reduce the air-water and hydrophobic solid-water surface tensions to values lower than to other non-ionic surfactants. This is the reason behind their super-spreading ability on highly hydrophobic

the surfaces. This, to some extent, explains why the complete wetting concentrations are a few times higher than the CAC.

surfaces. The trisiloxane surfactants have a very peculiar structure of the hydrophobic group compared to other common "non-super-spreading" ionic-and non-ionic surfactants³⁶, such as $C_{12}E_j$, sodium dodecyl-sulphate(SDS), didodecyldimethyl ammonium bromide (DDAB), etc. The hydrophobic group in these "non-super-spreading" surfactants is a long linear hydrocarbon chains, compared to very compact, "T" shaped trisiloxane hydrophobe in the trisiloxane surfactant. The surface activity of both ionic and non-ionic surfactants has been observed to increase by increasing the branching of the hydrocarbon chain⁵⁸⁻⁶². This suggests that the extraordinary surface properties of the trisiloxane surfactants may be due to the peculiar structure of its hydrophobic group. In this thesis, the author has studied the adsorption characteristics of the trisiloxane and alkyl poly-ethoxylate surfactants' solutions on air-water and hydrophobic solid-water interfaces. All the experiments were carried out at concentrations below the CAC. By comparing the two classes of surfactants, we conclude that the structure of the trisiloxane hydrophobe is the reason behind the exceptional spreading abilities of the trisiloxane surfactants.

2.2 Direction of Research

Three main aspects of the problem can be identified, based on the pervious section. In the first part (Chapter 3), model hydrophobic surfaces are developed, whose morphology and hydrophobicity could be controlled. In the second part (Chapter 4), the adsorption of three different trisiloxane surfactants, $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$, on air-water interface has been studied using pendant bubble technique. This is an attempt to explain the unusual low surface tensions of the trisiloxane surfactants. In the third part (Chapter 5), Fourier Transform Infrared (FTIR) spectroscopy in Attenuated Total Internal Reflection (ATR) mode is used to investigate the adsorption of the trisiloxane and $C_{12}E_j$ surfactants on the model hydrophobic surfaces, prepared in the first part. This section briefly describes these three parts. The experimental techniques and related literature of the three parts are very different from each other. Therefore, they are discussed in the respective chapters.

2.2.1 Formation of Model Hydrophobic Surfaces.

Usually the spreading of surfactant solutions is carried out on hydrophobic and hydrophilic polymer surface. Many such surfaces have been used for the spreading study of the trisiloxane and other surfactants, including Parafilm®^{20,38}, polystyrene⁴⁸, polyethylene³⁸, carbon film³⁸, and Teflon³⁸. The polymer surfaces are much more readily available. However, they have many drawbacks. These surfaces are usually very rough. Careless handling can cause more roughness and stretching of polymer films, which has been found to affect spreading²⁰. The surface morphology of commercial polymer surfaces is unknown. There may be regions of different chemical and crystal

structure. This can generate patches of hydrophilic and hydrophobic regions, which lead to non-uniform adsorption of surfactants, contact angle hysteresis and pinning of drops⁶³. The hydrophobicity of the polymer surfaces cannot be modified as the hydrophobicity of the polymer surfaces is intimately linked to the chemical structure of the polymer. This is a major drawback, because the effect of the surface hydrophobicity on spreading cannot be investigated. In addition, surface spectroscopy techniques, such as, infrared spectroscopy, cannot be used. Usually polymers contain some surfactant additives, which are added to aid processing. The presence of these surfactants on polymers surfaces can affect the adsorption from the solutions. Information about the topography of the polymer surface is difficult to obtain. Techniques, such as Atomic Force Microscopy (AFM), cannot be used easily, owing to the fact that polymer surfaces are too rough to be imaged by AFM.

Due to these difficulties, we decided not to use the polymer surfaces for the adsorption experiments. Instead we use self-assembled silane monolayers (SAM) deposited over silica surfaces. The preparation of the SAMs is described briefly in Figure 2.2. Octadecyltrichlorosilane(OTS) is used as the silanizing agent. Chlorine in the trisilane group is hydrolyzed by water present in the solvent and on silica surface. The hydrolyzed OTS molecules adsorb on the silica surface and interact with the surface and other adsorbed OTS molecules to form a dense monolayer. The hydrophilic silica surface is transformed into a hydrophobic surface due to the methyl groups of the OTS monolayers. AFM study of the partial monolayers of OTS revealed the formations of condensed domains of OTS, whose morphology and size (tens of nanometer to few micrometers) could be controlled by controlling the deposition conditions. In this manner

we are able to fabricate mixed silane monolayers, in which domains of controlled size and morphology are surrounded by another chemical functionality.

The SAMs have numerous advantages over the polymer surfaces. The SAM's can be deposited over glass surfaces or polished silicon wafers, which have roughness of $\sim 1\text{\AA}$. The chemical homogeneity of the SAM surface is ensured, if only one silane is used. Angstrom level smoothness and chemical homogeneity eliminates many problems associated with the polymer surfaces, such as, non-uniform adsorption, contact angle hysteresis, pinning of drops, etc. Surface hydrophobicity can be controlled by using mixed silane monolayers. The surface morphology can be controlled from nanometer to micrometer scales. The deposition of SAM does not significantly affect the optical properties of silica and glass surfaces. Therefore, infrared spectroscopy and other microscopy techniques can be used. The procedure to prepare SAMs is easy and fast. The SAM's can be prepared fresh, thus eliminating the problems associated with storage, such as deposition of dust and vapors from air.

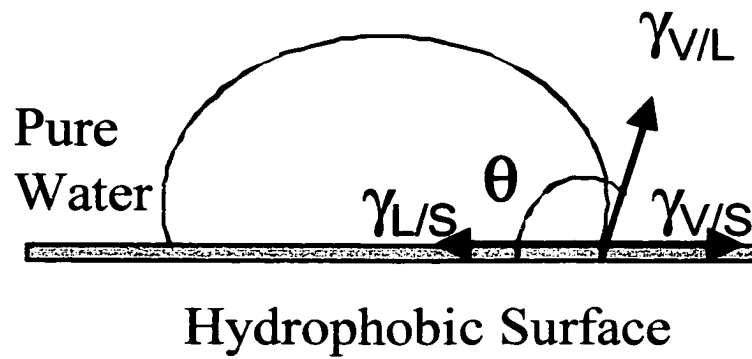
2.2.2 Adsorption on Air-Water Interface

The adsorption characteristics of the three trisiloxane surfactants are investigated using pendant bubble technique. This technique has been used by Pan et al^{64,65}, Subramanyam⁵⁰ and Lin et al⁶⁶⁻⁶⁸ to evaluate the kinetic adsorption constants, diffusion coefficients, and equations of state for many alkyl poly-ethoxylate surfactants. The desorption constant of the trisiloxane surfactants $(M(D'E_jOH)M)$ is found to be lower than the comparable $C_{12}E_j$ surfactants. This is attributed to the structure of the trisiloxane group. The trisiloxane surfactants pack more densely on the air-water surface. These

results throw some light on the reason behind the unusually low surface tension of trisiloxane surfactants.

2.2.3 Adsorption on Hydrophobic Solid-Water Interface

FTIR-ATR spectroscopy has been used extensively to study interfaces⁶⁹. We have used this technique to study the adsorption of trisiloxane and alkyl poly-ethoxylate surfactants. Silicon ATR element is made hydrophobic by coating with OTS monolayer. The surfactant's solution is passed over the ATR element in a flow cell. The amount of the adsorbed surfactant is calculated from the IR spectra. The trisiloxane surfactants pack more tightly on the hydrophobic surface than the alkyl poly-ethoxylate surfactants. For the first time (known to the author) we have observed the changes in the hydrogen bonding structure of water induced by surfactants' adsorption. The trisiloxane surfactants, due to the peculiar shape of the hydrophobe, modify the hydrogen bonding to more favorable configurations, thus reducing the surface energy to values lower than that of the alkyl poly-ethoxylate surfactants.



γ : Surface tension or surface energy

Spreading Coefficient $S = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(\cos\theta - 1)$

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Figure 2.1: Partial wetting of a liquid drop on a surface.

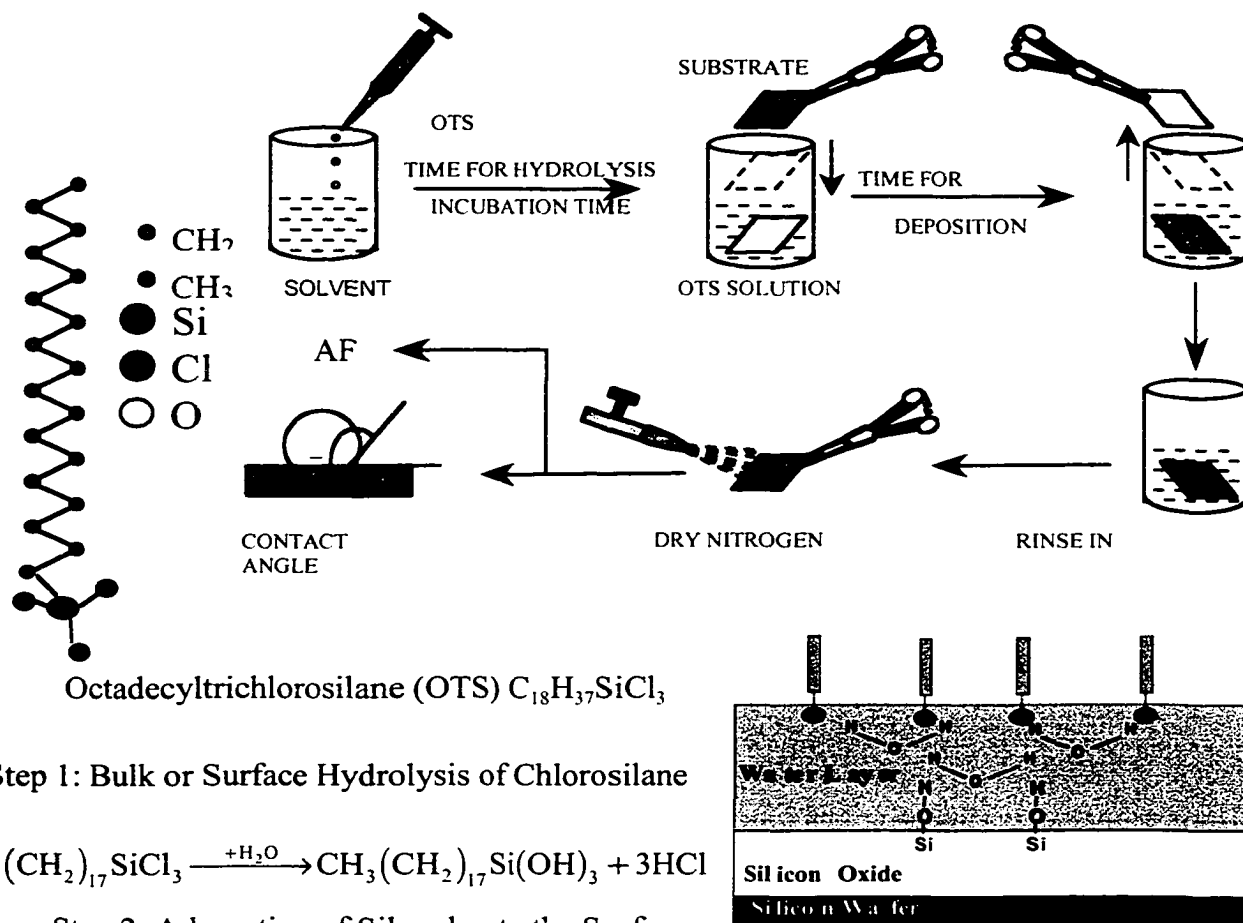


Figure 2.2: Formation of Self assembled monolayer of OTS

Chapter 3

Formation of Nanometer Domains of One Chemical Functionality in a Continuous Matrix of a Second Chemical Functionality by Sequential Adsorption of Silane Self-Assembled Monolayers

3.1 Introduction

In recent years, there has been a great deal of interest in the development of molecularly engineered surfaces that have regions of one chemical functionality with sizes ranging from the nanometer to the micrometer in a continuous matrix of a second functionality. Such surfaces can be used for molecular recognition applications, such as the arraying and immobilization of proteins⁷⁰, cells⁷¹ and DNA⁷², the localization of crystal growth^{73,74}, and phase separation of polymer mixtures^{75,76}. Methods for patterning micrometer features on surfaces are well developed, and include micro-contact printing⁷⁷⁻⁷⁹ and micro-lithography of self-assembled units^{73,80}. On the other hand methods for developing nanometer scale features, such as nano-writing^{81,82}, phase separated Langmuir-Blodgett (LB) films^{83,84}, and block copolymers⁸⁵ are time consuming and cumbersome. Additionally, there are concerns that the LB film transfer process does not preserve the phase separated structure of the air-water interface. Methods involving sequential adsorption^{86,87} or competitive co-adsorption^{86,88} of self-assembling monolayers (SAMs) have been suggested as an alternate and simpler

route for making such surfaces. In this paper, we focus our study on the sequential adsorption approaches.

Self-assembled monolayers (SAMs) consist of amphiphiles, which spontaneously adsorb onto a solid surface from solution to form a densely packed two-dimensional ordered monolayer. These amphiphiles consist of a head group, which anchors the molecule to the solid surface by a specific interaction, an intermediate hydrocarbon chain, and a functional group attached to the opposite end of the chain. Upon adsorption, the functional group dangles off the surface and thereby changes the surface chemistry of the substrate. For the most part, SAMs have been formed by the adsorption of alkylthiols on gold surfaces, long chain carboxylate acids on alumina surfaces, and alkylsilanes on silica surfaces (as described by Ulman⁸⁹). In our study we use the silane based SAMs.

Sagiv et al.⁹⁰⁻⁹³ were the first to show that when a hydrophilic surface, such as silica, is immersed in a solution of octadecyltrichlorosilane ($\text{CH}_3\text{-(CH}_2\text{)}_{17}\text{-SiCl}_3$, OTS) in a non-competing solvent, an organized monolayer of OTS is spontaneously formed on the solid surface. Originally, Sagiv et al. proposed that upon adsorption the OTS molecules covalently bond to the surface silanol groups and to the other neighboring OTS molecules in the monolayer, resulting in a robust and strongly anchored two-dimensional structure. The results of later experiments have modified this picture. Firstly, no evidence of the formation of an OTS-surface silanol covalent bond has been found⁹⁴⁻⁹⁷. Instead there is strong evidence that suggests that the OTS based SAM is formed on top of a water layer, which typically exists on hydrophilic surfaces. The OTS molecules are hydrolyzed by either this water layer or by water present in the solvent to form silanols. These silanols hydrogen bond to the water layer⁹⁴. Because of this water layer, the adsorbed

molecules are mobile and can diffuse on the surface. This mobility allows OTS molecules to aggregate into islands, which can be exploited to form nanometer size domains by sequential adsorption. In what follows below, we discuss the current state of understanding of this mechanism. Understanding and controlling this growth mechanism will allow us to tune the structure of the aggregates on the solid surfaces.

These islands, which are formed by aggregation, have been imaged by atomic force microscopy (AFM)^{96,98-102} and have been found to be "fractal" like in structure. This is the result of a adsorption - surface diffusion - aggregation mechanism¹⁰³, in which surface diffusion is rate determining. The OTS molecules, diffusing on the surface, become immobilized on the perimeter of an existing island or aggregate. During studies of complete monolayers, Rondelez et al ^{104,105} and Rye ¹⁰⁶ found that below a critical deposition temperature ($28 \pm 4^\circ\text{C}$), the monolayers formed condensed ordered phases resembling the liquid condensed (LC) states analogous to Langmuir monolayers. A complete monolayer prepared above this critical temperature, showed regions of chain disorder, which can be interpreted as a "melting" to a liquid state resembling the liquid expanded (LE) state of the Langmuir monolayers. The authors drew an analogy to the LE-LC phase coexistence of Langmuir films and therefore interpreted this critical deposition temperature as the triple point temperature. Increasing the deposition temperature resulted in more disorder, until the monolayers were in a completely LE state.

AFM measurements of partial monolayers at room temperature ($\sim 22^\circ\text{C}$) have shown a two-step growth mechanism ^{96,99,102}. In the first step, fractal islands of constant height, $\sim 21\text{\AA}$,^{96,99,102} relative to the background, appear and grow on the

surface. This step is referred to as the primary growth step. The tilt angle of the OTS molecule in a complete monolayer was measured by infrared spectroscopy and its value was about 11 degrees from the normal to substrate^{105,107}. Given the fact that the fully extended OTS molecule is 26.4Å long¹⁰⁴, a tilt angle of $\sim 11^\circ$ leads to a monolayer height of $\sim 25\text{Å}$. This value agrees well the thickness of about $25 \pm 1\text{Å}$ measured by ellipsometry¹⁰⁸⁻¹¹⁰. Comparison of these values with the height of a primary island ($\sim 21\text{Å}$ in AFM images), implies that the primary fractal islands are in fact liquid-condensed (LC) phases surrounded by a low-density liquid phase. In the second step, the growth of the primary fractal islands stops, and the difference of height between the islands and the background begins to decrease^{99,101,102}. Both these facts indicate that the surrounding is a liquid expanded phase whose density, and therefore height, are increasing. With increasing concentration of the LE phase, the surface diffusion to the primary islands is reduced, thereby arresting the primary growth. Finally, nucleation and growth of smaller islands of the same height (as the primary islands) occur in the regions surrounding the primary fractal islands. This second step is referred to as the secondary growth step and it continues until a complete monolayer of uniform height is formed. Following Rondalez's^{104,105} analogy, the secondary nucleation and growth occurs as the density of the surrounding LE state reaches the value for its condensation to the LC phase. However, the appearance of the LE phase in monolayers deposited at room temperature ($\sim 22^\circ\text{C}$)^{99,101} suggests that the critical temperature (analogous to the triple point temperature for Langmuir monolayers) as inferred by Rondalez et al^{104,105}, maybe too high.

AFM imaging of partial monolayers deposited at temperatures well below room temperature ($<16^{\circ}\text{C}$) shows a different growth mechanism^{96,99,101}. In this case it is observed that the height of the primary island domains does not change over time and remains constant at a height of $\sim 21\text{\AA}$. This suggests that during growth the surrounding phase is either gaseous (G) (if the deposition temperature is below the triple point as supposed by Carraro et al⁹⁹) or a low-density liquid phase, if the deposition temperature is above the triple point (as suggested by Davidovits et al¹⁰¹). This phase is less dense than the LE phase at room temperature as dictated by the phase diagram. Finally, at temperatures exceeding 40°C , all AFM studies show a uniform monolayer without any islands^{96,99,101}. This can be inferred as a pure LE phase.

The morphology of the monolayer is affected by the amount of water present on the substrate. A thinner water layer on the surface reduces the surface mobility of the OTS molecules, affecting their ability to form large condensed aggregates. On a dehydrated mica surface, for partial monolayers, OTS clusters of about 50-80 nm have been observed, instead of the primary fractal islands⁹⁶. Based on infrared measurements, the monolayers on dehydrated substrates are disordered^{94,109-111}.

From the above discussion, it is clear that the ability of the partial monolayers to form island-like aggregates offers a route to fabricate nano-meter scale domains of one chemical functionality in a continuous phase of a different functionality. In sequential adsorption, first a partial monolayer of one silane consisting of islands of a desired size and functionality is formed. In the second step, a second silane is deposited on the area surrounding the islands of the first silane. Ideally, the islands in the first step should be in a condensed state so that they cannot be diluted in the second step. In addition, the area

surrounding the islands should be devoid of the first silane, so that the second silane can deposit without any competition, ensuring that the surrounding matrix contains only the second silane.

Despite its potential, this sequential adsorption procedure has not been utilized to form nano-meter scale chemical functionalities on surfaces. Mauthauer et al⁸⁷ were the first to attempt this technique. However, this investigation did not study the domain formation of the mixed monolayers.

The specific goals of our study are to demonstrate, using atomic force microscopy, that nano-meter scale domains of a specific functionality surrounded by a matrix of another chemical functionality can be obtained by sequential deposition or back-filling. We show that the domain size can be varied in a controlled manner from tens of nano-meters up to a few micro-meters. We will use OTS as the first silane to form domains of desired size, and 11-bromo undecyltrichlorosilane (BrUTS) and decyltrichlorosilane (DTS) as the back-filling silanes.

3.2 Experimental Section

3.2.1 Materials

Octadecyltrichlorosilane (OTS, 95 % purity) was purchased from Sigma Aldrich Company. Decyltrichlorosilane (DTS, 97% purity) and 11-bromo undecyltrichlorosilane (BrUTS, 95% purity) were purchased from Gelest, Inc. HPLC grade hexadecane, chloroform, and carbon tetrachloride were obtained from Sigma-Aldrich Co. Nochromix® and sulfuric acid (98%) were purchased from Fischer Scientific. All chemicals were used as received without any further purification. Deionized water, with a resistivity of 18M Ω cm from a Millipore® system, was used. Double side polished (n type, <111>) single crystal silicon wafers were purchased from Montco Silicon Technologies Ltd.

3.2.2 Monolayer Preparation

We have used a procedure⁹⁴, in which amount of water in the solvent can be controlled. A solvent mixture containing hexadecane, carbon tetrachloride and chloroform (30:5:3 by volume, respectively) was used for making the silane solutions. Chloroform was saturated with water by keeping it overnight in contact with water. Amount of water in the solvent mixture was estimated to be 4 - 6 mM and was verified using Karl-Fisher titration.

The polished silicon wafers (with roughness of ~ 1 Å as measured by AFM) were cleaned by sonicating in a mixture of Nochromix® and 98% sulfuric acid for about 30

minutes, followed by successive water rinsing. The cleaned substrates were stored under water and dried in a stream of dry nitrogen just before use. These substrates are hydrated with a water layer of thickness of a few nanometers¹¹²⁻¹¹⁵. Partially dehydrated substrates were prepared by heating clean silicon wafers at 100 and 150°C for an hour and then cooling under vacuum in a desiccator. The vacuum was broken using dry nitrogen. Maximum care was taken to prevent the dehydrated substrates from exposure to sources of moisture.

Silane solutions were prepared by adding OTS, DTS or BrUTS in the required quantities to freshly prepared solvent mixtures. The substrates were immersed in the silane solutions after 30-60 seconds of silane addition to solvent mixture, so that the silanes could hydrolyze by the water present in the bulk. If silane solutions are kept for a longer time, then bulk polymerization occurs. Partial OTS monolayers were prepared by immersing clean the substrates in OTS solution for varying deposition times (Figure 2.2). The deposition was terminated by rinsing the samples in chloroform for about 15 minutes. Excess chloroform was dried with a stream of dry nitrogen.

The back-filling experiment procedure is as follows. In the first step, OTS islands of desired size are formed by immersing a hydrated or dehydrated substrate in a 1mM OTS solution for varying deposition times at 10°C. The substrates are then removed from the OTS solution and immersed in chloroform at 10°C for approximately one second to rinse the OTS solution. Then, immediately the substrates with partial OTS monolayer are immersed in 1 mM DTS or BrUTS solution for one hour at 10°C followed by rinsing in chloroform at 10°C. The analysis of the sample with AFM and contact angle goniometry was carried out within one to two hours after the monolayer preparation.

3.2.3 AFM Imaging

Atomic force microscopy images were obtained using Nanoscope III (Digital instruments, Inc.). Silicon nitride sharpened tips with a force constants of 0.58N/m, (purchased from Digital Instruments, Inc.) were used for height and friction images in contact mode. A normal force of approximately 116nN was used in the contact mode experiments. Tapping mode images were obtained using silicon tips. At least three images were acquired for each sample at various locations. Height and friction differences between the various phases on the samples were obtained by taking cross sections at random locations. The surface area coverage was calculated using the bearing analysis mode of AFM software. In-situ experiments were conducted using a quartz flow cell purchased from Digital Instruments, Inc. Water contact angles on the monolayers were measured using a contact angle goniometer (Rame-Hart, Inc) by placing a 2 μ l water drop on the sample. The contact angle values of at least six different locations were averaged.

3.3 Results and Discussion

3.3.1 Partial OTS Monolayers on Hydrated Substrates at Room and Reduced Temperatures

We begin with a reference set of experiments in which fractal shaped islands of OTS are formed on hydrated substrates at room and reduced temperatures. As we explain below, we observe in the AFM images, the primary and secondary growth at room temperature as discussed in the Introduction. Using lateral force microscopy we further confirm this growth mechanism. At temperatures below room temperature, we observe the same primary growth as detailed by Carraro et al.⁹⁹, however we also see evidence of a secondary nucleation at high surface coverage when the primary islands are about to merge.

Partial OTS monolayers are prepared by immersing clean and fully hydrated silicon substrates in 2 mM OTS solutions for different deposition times at $22 \pm 1^\circ\text{C}$. Height and friction images of these samples are shown in Figure 3.1. Water contact angles, height differences, friction differences, and area coverages are summarized in Table 3.1.

The AFM image of a sample with a one second deposition time, shown in Figure 3.1A, exhibits the onset of the formation of the primary islands. The islands appear diffuse with a height $\sim 11 \text{ \AA}$ compared to $\sim 21 \text{ \AA}$ ⁹⁹ for a condensed (LC) island, suggesting that the islands have not yet condensed. In the friction image, the regions covered by OTS exhibit lower friction than the surroundings. OTS monolayers are known to reduce friction on solid substrates¹¹⁶. The friction difference between the islands and the

surrounding regions is approximately 0.76V. These friction measurements suggest that at this early stage, the region surrounding the islands can be either a G or LE phase.

As the deposition time is increased, more OTS adsorbs on the water layer present on the hydrated substrate and diffuse towards the primary islands. On reaching the perimeter of an existing island, they become immobilized and aggregate with the island. This leads to the growth of the fractal features. The surface coverage of the primary islands grows rapidly during the primary growth. An image of such a sample, with a deposition time of five seconds, is shown in Figure 3.1B. The islands are much larger in size, between 4 and 8 μm and cover approximately 30% of the surface. The height of these islands is $\sim 21\text{\AA}$, which suggests that they have condensed into a LC phase. The friction difference between the primary fractal islands and the surrounding phase has decreased from 0.76 V to 0.26V, which suggests an increase in OTS density in the surrounding phase. After five seconds of OTS deposition, the water contact angle has increased to about 67 degrees compared to 44 degrees for the one second deposition time sample. On increasing the deposition time further, we observe that the rate of growth of the primary islands is reduced. An image of a sample with a fifteen seconds deposition time is shown in Figure 3.1C. The surface coverage of the primary islands is approximately 50 %, compared to 30% for the five-second-deposition time sample. Also, we observe that the height and friction difference between the primary island and surrounding area has decreased to 16.9 $\text{\AA}$ and 0.1 V respectively. This indicates that the phase surrounding the primary islands is becoming denser and starting to increase in height. Surface diffusivity of the OTS molecules in the area surrounding the islands is

reduced because of the increase in density of the surrounding phase. The reduction in surface diffusivity reduces the growth of primary islands.

Upon further adsorption, the primary islands cease to grow, but the surrounding liquid phase becomes progressively denser, leading to a further reduction in the friction and the height difference between the primary islands and the surrounding liquid phase. For a sample with 30 seconds deposition time (Figure 3.1D), the height difference is further reduced to $\sim 15\text{\AA}$. The friction difference between the primary islands and the surrounding liquid phase is approximately 0.03 V. The primary islands cover $\sim 66\%$ of the surface. After 45 second of deposition, we observe a new growth regime (Figure 3.1E). The height difference between the primary islands and the surrounding phase is now reduced to $11.4\text{\AA}$. Small islands of dimension less than $0.5\text{ }\mu\text{m}$ are observed in the liquid phase surrounding the primary islands. The height of these islands is the same as that of the primary fractal islands. This growth regime is referred to as the secondary nucleation and growth step, in which small condensed islands nucleate and grow in the surrounding liquid phase. As we noted in the Introduction, several studies have drawn an analogy between this secondary growth and the formation of an LC phase from an LE phase in Langmuir films.

In the friction image, shown in Figure 3.1E, the condensed primary and secondary islands exhibit slightly higher friction (-0.01 V) than the surrounding liquid phase. In all the earlier samples (Figure 3.1 A, B, C, and D), the LC primary islands exhibit lower friction than the surrounding phase. This observation suggests that the OTS monolayer in the liquid phase surrounding the islands, as it approaches a "LE-LC phase transition", has a lower friction than the corresponding the denser LC phase. Upon continued adsorption,

the secondary condensed islands continue to nucleate and grow from the liquid phase, until all the substrate is covered with a condensed monolayer. An image of a 120-second deposition time sample (Figure 3.1F) shows almost a uniform monolayer. The water contact angle on this sample is approximately 105° , which increases to 108° when the deposition time is increased to 5 minutes.

During this complex growth mechanism, the primary islands grow rapidly to their fractal like morphology via adsorption, surface diffusion and aggregation. During the primary growth, the regions surrounding the islands are lean and have a high affinity for the hydrolyzed OTS molecules present in the bulk. As the density of the area surrounding the primary islands increases, the OTS adsorption rate from the bulk is reduced. As a consequence, the initial rapid increase of the area covered by the primary islands is attenuated. On the other hand, the secondary islands grows from the phase surrounding the primary fractal islands as the density of OTS in this phase increases.

AFM images of hydrated substrates, with deposition time of (a) 5 second (b) 10 second, and (c) 30 second, in 2mM OTS solution at 10°C are shown in Figure 3.2. At this reduced temperature, the primary fractal islands grow at nearly constant height of $\sim 21\text{\AA}$ in agreement with Carraro et al⁹⁹. However, at later stages (Figure 3.2C), we note the appearance of very small islands in the region between the primary islands (see the inset of Figure 3.2C). These small islands are similar to the secondary islands nucleating in an liquid phase as observed at room temperature (Figure 3.1E). The height difference between the primary fractal islands and the surrounding phase is $15\text{-}16\text{\AA}$ compared to $\sim 11.4\text{\AA}$ (Figure 3.1E) at room temperature. This implies that the region surrounding the primary islands is leaner at 10°C , compared to the surrounding region at room

temperature, but not necessarily a G phase as suggested by Carraro et al⁹⁹. The fact that a liquid phase exists at even at 10°C, implies that the triple point of the OTS monolayers may be lower than surmised by Carraro et al⁹⁹ or no triple point exists for the OTS self-assembled monolayers. In any case, we observe that at low temperatures, OTS forms condensed fractal islands on a hydrated surface, which are surrounded by a lean liquid phase. This surrounding phase is denser when the depositions are carried out at higher temperatures ($\sim 22^{\circ}\text{C}$) compared to a monolayer prepared at low temperature ($\sim 10^{\circ}\text{C}$).

3.3.2 Effect of Bulk Concentration on Island Size

As discussed in the previous section, condensed islands with dimensions ranging in the range of a few micrometers are formed in a couple of seconds from a 2mM OTS solution at temperatures ranging from 10 to 22°C. We have also conducted experiments at lower concentrations. The results of these experiments suggest that reduced concentrations lead to reduced aggregation rate. Thus, in order to form nanometer size islands in a reasonable time scale of a couple of seconds, our data suggests reducing the concentration of OTS in the solutions. We immerse a hydrated substrate in a 0.2 mM OTS solution for a deposition time is approximately one second. This concentration is 1/10 of the concentration used for samples described in Figures 3.1 and 3.2. An AFM height image of this sample is shown in Figure 3.3. Very small OTS clusters of about 50-100 nm in diameter and 15-20 Å in height are distributed almost randomly on the surface. Upon increasing the deposition times further, the OTS monolayer exhibits various phases (as observed at higher concentrations, Figure 3.1) until a uniform coverage is attained.

However, adsorption times are longer at lower concentration. Thus, by reducing the concentration, we are able to obtain nanometer scale islands of OTS.

3.3.3 Effect of Substrate Hydration on Island Size

Many researchers have shown that good OTS monolayers are not formed on dehydrated substrates^{96,97,109-111}. Britt et al⁹⁶ have reported the formation of very small islands of OTS on partially dehydrated mica surfaces. The thickness of the water layer determines the diffusivity of the OTS molecules on the surface. This in-turn controls the morphology of the OTS monolayer. We will use this concept to control the primary and secondary growth.

The preparation of substrates with varying degrees of hydration is described in the Experimental Section. Under ambient conditions, a water layer is adsorbed on the native silica surface^{94,109-111,117}. The thickness of this water layer depends on the ambient humidity and can have values of a few nanometers¹¹²⁻¹¹⁵. Upon heating the substrate at 100°C, some of the physisorbed water is removed^{94,104,109-111}. We refer to these surfaces as partially dehydrated. Upon further heating to 150°C, most of the physisorbed water is removed and we refer to these substrates as dehydrated. Partial OTS monolayers are deposited on the fully hydrated, partially dehydrated and dehydrated substrates by immersing in a 2mM OTS solution for 30 seconds at 22±1°C. AFM images of these substrates are shown in Figure 3.4.

Image of the OTS monolayer on a hydrated substrate is shown in Figure 3.4A. As expected, on a hydrated substrate, primary fractal islands and secondary islands are observed. The water contact angle is ~ 93°. On a partially dehydrated substrate (Figure

3.4B), we still observe primary fractal and secondary growth. But the area occupied by the primary fractal islands is reduced and so is their size, when compared to the hydrated substrate (Figure 3.4A). The presence of the smaller primary fractal islands suggests that the surface mobility of the OTS molecules on the partially dehydrated substrate is reduced compared to the hydrated substrate, but still high enough to initiate the primary growth. The water contact angle is ~ 90 degrees, which does not differ substantially from the hydrated substrate.

A different morphology is observed on the dehydrated substrate. Using AFM in contact mode, we observed that the AFM tip could move the OTS clusters, resulting in the images which were not stable during successive scans. Therefore, the samples were imaged in tapping mode, which overcame this difficulty. Such an image is shown in Figure 3.4C. A large number of randomly placed "dots" are observed instead of the primary and secondary islands. These "dots" are about 100nm in diameter and 17-18Å in height. They are clusters of adsorbed OTS molecules, which are unable to form large condensed primary islands due to the reduced surface mobility on the dehydrated substrate. These OTS clusters or "dots" are not strongly adhered to the substrate, and therefore they are swept away by the AFM tip when imaged in contact mode as seen in our experiments. The water contact angle is only 78 degrees compared to 93 and 90 degrees for a hydrated and partially dehydrated substrate respectively. This suggests that a smaller amount of OTS adsorbs on a dehydrated substrate, which is in agreement with earlier studies^{94,109-111}. Upon further increase in the deposition time, the number of random "dots" increases, but no condensed fractal islands are observed. The number of these "dots" continues to grow, until they begin to touch each other to form a disordered

monolayer. On a dehydrated substrate, deposition times of about 15 minutes are required in order to get a monolayer with water a contact angle of $\sim 105^\circ$, compared to a deposition time of 2 minutes for a hydrated substrate. Similar results are obtained, when OTS depositions are carried on dehydrated substrates at 10°C .

On a dehydrated surface, OTS molecules are unable to form large condensed islands, even when the thermodynamic requirement of low temperatures is satisfied. Therefore, the thermodynamic conditions, such as temperature etc., are not the only factors governing the monolayer morphology. The inability of the OTS molecules to diffuse on the surface restricts the formation of condensed islands. We utilize this property to form nanometer scale islands of OTS, which we use in the back filling experiments.

3.3.4 In-Situ Experiments

One possible criticism of our results can be that various morphologies observed can be the result of processing of the substrate, such as rinsing and drying. Such effects and the resulting fractal morphology has been observed on some Langmuir-Blodgett monolayers¹¹⁸. In order to establish that the primary and secondary growths are indeed formed during adsorption, we conducted in-situ AFM experiments, using a quartz flow cell, in which the partial OTS monolayers are formed and imaged under liquid, without rinsing or drying. To study the adsorption on a hydrated substrate, a 2 mM OTS solution is flowed over a clean fully hydrated substrate for 40 seconds. The adsorption is terminated by flowing pure solvent mixture over the substrate for approximately 20 minutes and then the AFM images are acquired in contact and tapping mode. The flow of

pure solvent is continued and AFM images are acquired after 20 minutes. The AFM image of this substrate is shown in Figure 3.5A. The primary and secondary growths, similar to the ex-situ experiments (Figure 3.1), are observed.

In following experiment, first the pure solvent mixture is passed over the substrate in the flow cell for about 20 minutes. In this step, some water from the substrate is extracted into the solvent, resulting in partially dehydrated substrate. OTS is then deposited by passing a 2mM solution for about 40 seconds. The deposition is terminated by passing the pure solvent mixture. The flow is continued and images are acquired after about 20 minutes. In the AFM image of this sample (Figure 3.5B), we do not observe any primary islands, instead only small random "dots" are observed. These are similar to the "dots" observed on a dehydrated substrate shown in Figure 3.4C. These two in-situ experiments conclusively confirm that the various monolayer morphologies observed in the ex-situ experiments are indeed formed during adsorption and they are not a result of rinsing and drying.

3.3.5 Formation of Mixed Monolayers with Controlled Morphology by Back-filling

In the previous four sections, we have described how the morphology of the partial OTS monolayers can be controlled by various experimental conditions during deposition. Low density in regions surrounding condensed islands is required for successful back-filling experiments. We have shown in the previous sections that the phase surrounding the primary islands in OTS monolayers prepared at 10⁰C, is a lean phase and these conditions are ideal for conducting the back-filling experiments. Partial

OTS monolayers are prepared by immersing hydrated and dehydrated substrates in OTS solutions for varying amount of deposition times.

In the first sample, a hydrated substrate is immersed in a 1mM OTS solution for ~ 0.5 seconds. It is then back-filled with BrUTS as described in the Experimental Section. The height and Friction images of this sample are shown in Figure 3.6. The AFM image shows small islands with a height of $9\text{\AA}$ and diameter in the range of 30-100nm. These are OTS islands surrounded by BrUTS. The friction of the OTS islands is lower compared to the region covered by BrUTS. Thus, we are able to obtain nanometer scale islands of methyl functionality surrounded by silanes with bromine functionality. This result is expected because partial OTS monolayers with short deposition times exhibit small clusters of OTS, as shown in Figure 3.3. The water contact angle on this sample is ~ 81 degrees. The area covered by the OTS islands is approximately 5.2%. We can use the Cassie equation ¹¹⁹ (Equation 3.1) to predict the water contact angle on this mixed monolayer.

$$\cos\theta_{mix} = A_{OTS} \cos\theta_{OTS} + A_{BrUTS} \cos\theta_{BrUTS} \quad (3.1)$$

where A_{OTS} and A_{BrUTS} are fractional coverages of OTS and BrUTS respectively, θ_{OTS} and θ_{BrUTS} are water contact angles for full OTS and BrUTS monolayers, which are 108 and 75 degrees respectively. Using these values, the predicted value of water contact angle on the mixed monolayer is 77 degrees, which is in agreement with the observed value of 81 degrees, considering the errors involved in measuring the contact angle.

In another experiment, we aimed for larger aggregates of OTS surrounded by BrUTS. A hydrated substrate is immersed in a 1mM OTS solution for about 3 seconds and then it is back-filled with BrUTS. Under these conditions, we expect larger fractal

primary islands to form. Height and friction images of this sample are shown in Figure 3.7. Fractal islands of OTS are surrounded by BrUTS. No secondary islands of OTS are observed. This proves our hypothesis that low deposition temperatures are required for successful back-filling.

The height difference between the fractal OTS islands and surrounding BrUTS phase is $12.1\text{\AA}$. Assuming the thickness of OTS islands to be $24.4\pm 1\text{\AA}$ ¹⁰⁴, the average thickness of the BrUTS region is calculated to be $12.3\pm 1\text{\AA}$. The length of a fully stretched BrUTS molecule is $17.6\text{\AA}$ (calculated using Chem3D® software), which implies that the average tilt angle of BrUTS chains is $45\pm 4^\circ$ from the normal to the surface, compared to 11° for a condensed OTS region¹⁰⁴. This suggests that the BrUTS regions are in a disordered state. OTS islands on this sample are more condensed compared to the "nano" islands in Figure 3.6. This conclusion is derived from the fact the fractal islands in Figure 3.7 are $12.1\text{\AA}$ above the surrounding region, compared to the value of $9\text{\AA}$ for the "nano" islands in Figure 3.6. The friction of the BrUTS region is less than that of the OTS islands. The difference is about 0.02V .

Approximately 48 % of the substrate is covered with fractal OTS islands. Again, using Cassie equation (Equation 3.1), the water contact angle on this mixed monolayer is predicted to be 89 degrees, which is in excellent agreement with the experimentally observed value of 91 degrees.

Mixed monolayers of DTS and OTS are also prepared by immersing a hydrated substrate in 1mM OTS solution for 3 seconds and subsequent back-filling with 1mM DTS solution. Friction and height images of this sample are shown in Figure 3.8. As expected, fractal islands of OTS surrounded by DTS are observed. Similar to the

OTS/BrUTS mixed monolayer (Figure 3.7), no secondary OTS islands are observed. The height difference between the OTS islands and the surrounding phase is $11.4\text{\AA}$ compared to $12.1\text{\AA}$ for the OTS/BrUTS mixed monolayer of Figure 3.7. The thickness of the DTS region can be calculated to be about $13\pm 1\text{\AA}$. By carrying out a similar analysis for the DTS layer, the average tilt angle of the DTS molecules is found to be $32\pm 6^\circ$ from the normal, (length of a fully stretched DTS molecule $\sim 15.6\text{\AA}$ from Chem3D® software) suggesting that the DTS regions is also in a disordered state. The critical temperature of DTS is about 0°C ¹⁰⁴, therefore at 10°C , DTS is expected to form a disordered state. Another interesting result is obtained when the thickness of the DTS and BrUTS regions, 13 ± 1 and $12.3\pm 1\text{\AA}$ respectively, are compared. The DTS monolayer is thicker and less tilted compared to the BrUTS monolayer in spite of the fact that DTS molecule is about $2\text{\AA}$ shorter than the BrUTS molecule. This is a result of the presence of bromine as the end group in BrUTS, which prevents denser packing.

The friction image of the mixed monolayer of DTS and OTS exhibits another interesting feature. Friction of the DTS region is less than that of the OTS islands. The DTS monolayer exists as a disordered phase, whereas the OTS islands are in condensed state. This result is similar to the results shown in Figure 3.1E, where we observed that a dense liquid phase of OTS exhibits lower friction than the condensed phase. The water contact angle on this substrate is ~ 106 degrees compared to 108 degrees on a full OTS monolayer. The small difference may be attributed to the disordered regions of DTS.

An alternate method to form nanometer scale islands of OTS surrounded by DTS or BrUTS is to use a dehydrated substrate. OTS deposits as small "dots" or clusters on a dehydrated substrate as shown in Figure 3.4C. We have also investigated this alternative.

The silicon substrates are dehydrated at 150°C as described in the Experimental Section. They are then immersed in 1mM OTS solution for 3 seconds and then back-filled with DTS and BrUTS. Contact mode AFM images do not show any features, but tapping mode images show "nano" islands of OTS in surrounded by DTS or BrUTS. One such image for a BrUTS sample is shown in Figure 3.9. The islands of OTS have a height of $\sim 7.3\text{\AA}$. The diameter the OTS islands are about 50-100nm. AFM images for the OTS/DTS samples also show similar nanometer scale islands of OTS with average heights of about $7.6\text{\AA}$. These mixed monolayers are not strongly adhered to the substrate. The AFM tip in contact mode is able to remove the monolayer from the surface. The water contact angle on mixed monolayers containing OTS/DTS and OTS/BrUTS is 101 and 88° respectively. In conclusion, we are able to form nanometer scale islands of OTS on the dehydrated surfaces, but the monolayers are not strongly adhered to the substrates.

3.4 Conclusion:

In this work, we have presented a procedure to fabricate nanometer scale islands of OTS surrounded by monolayers of DTS or BrUTS. In the first four sections, we have described how various deposition conditions, such as temperature, concentration, deposition time, and substrate hydration affect the morphology of partial OTS monolayers. Various morphologies of the partial monolayers are formed during adsorption and they are not a result of processing. Size of the OTS domains can be controlled by varying the deposition conditions. OTS depositions are conducted at 10°C, so that the region surrounding the OTS islands is covered by a lean OTS phase, which can then be back-filled by either BrUTS or DTS by sequential adsorption. Low OTS deposition times result in the formation of almost circular OTS islands of about 30-100nm in diameter. Large fractal condensed islands of OTS are prepared by increasing the OTS deposition time. The region surrounding the OTS islands is a disordered DTS or BrUTS phase. Adsorption of OTS on dehydrated substrates also results in the formation of nanometer scale islands of OTS, but the monolayers are not strongly adhered to the substrate.

Deposition time (sec)	~ 1	5	15	30	45	120	300
Height Difference (Å)*	11.6	20.9	16.9	15.2	11.4	-	-
Friction Difference (V)*	0.76	0.26	0.1	0.03	-0.01	-	-
Area Coverage (%)	11.1	30.7	52.1	66.5	65.3	100	100
Water Contact angle (deg.)	44	67	78	94	97	105	108

*: Between islands and surrounding region

TABLE 3.1: Partial Monolayers of OTS on hydrated substrates at $22 \pm 1^\circ\text{C}$

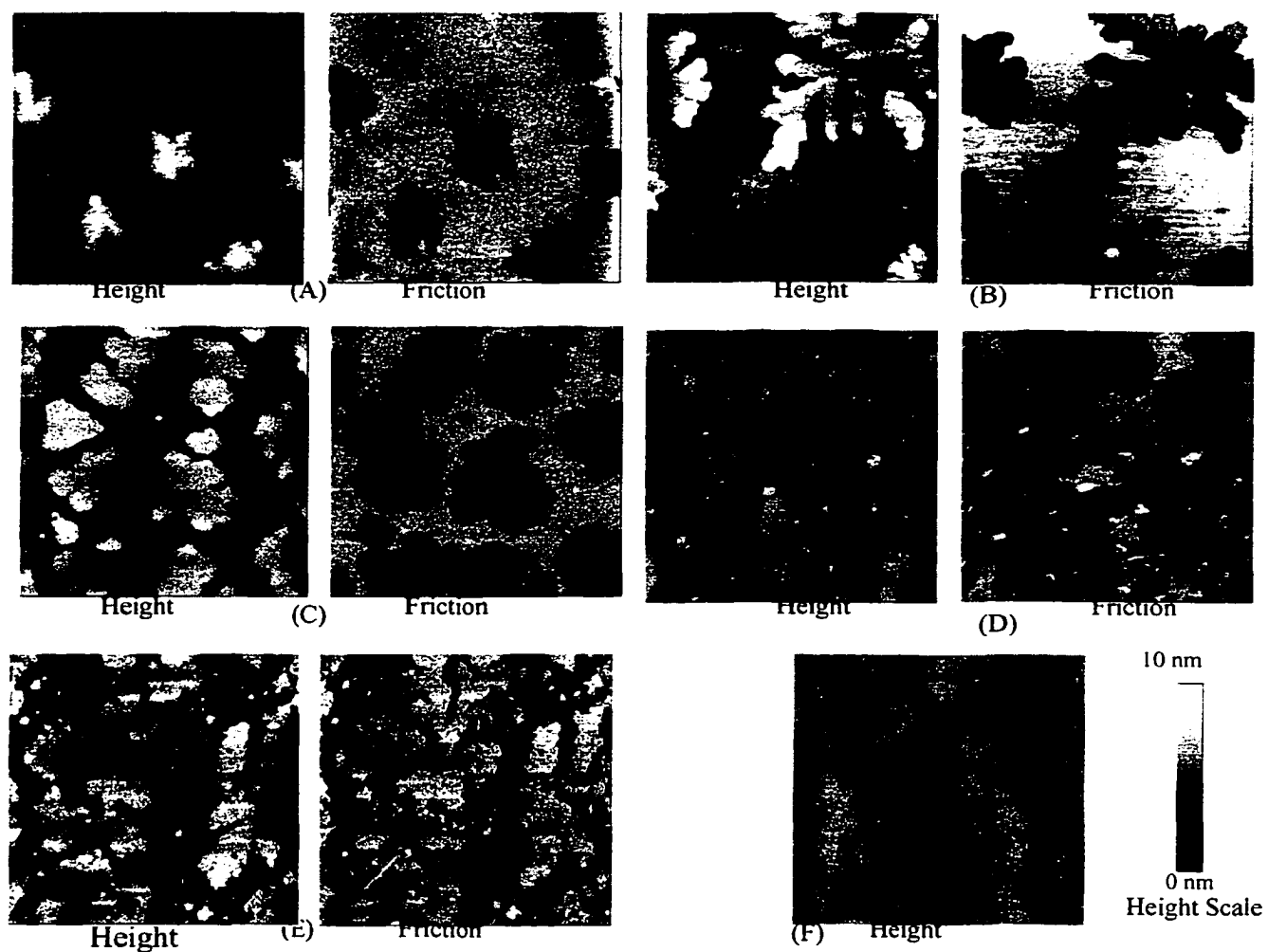


Figure 3.1: Height and friction images of partial OTS monolayers deposited at 22 ± 1 °C on fully hydrated substrates; Image size: $10 \mu\text{m} \times 10 \mu\text{m}$; OTS concentration: 2mM; Deposition times: (A) ~1sec, (B) 5 sec, (C) 15 sec, (D) 30 sec, (E) 45 sec, (F) 120 sec; In the friction images, brighter regions indicate regions with higher friction

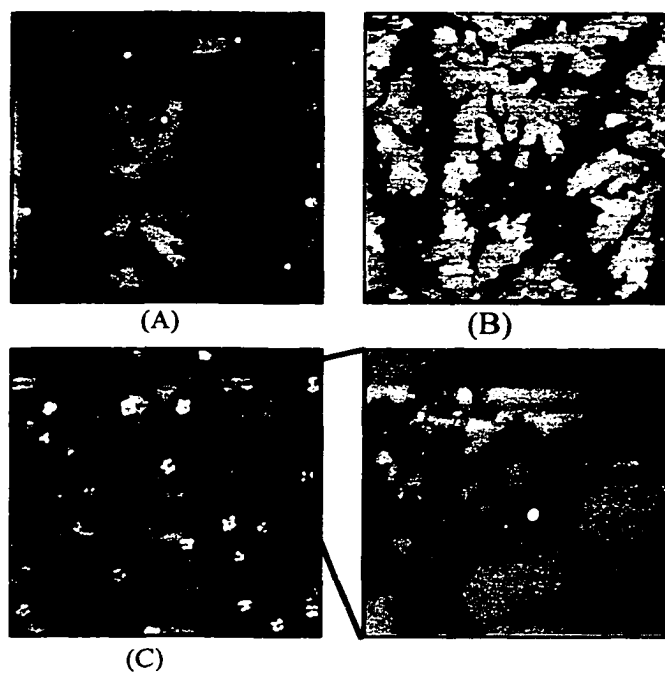


Figure 3.2: Contact mode height images of partial OTS monolayers prepared at 10⁰C on hydrated substrates. OTS concentration: 2mM; Image size 10 μ m x 10 μ m image; Height scale: 0-10nm; Deposition times: (A) 5 seconds (B) 10 seconds (C) 30 seconds.



Figure 3.3. Contact mode height image of a hydrated substrate immersed for 1 second in a 0.2 mM OTS solution at 22⁰C. Image size: 5 μ m x 5 μ m; Height scale 0-10 nm

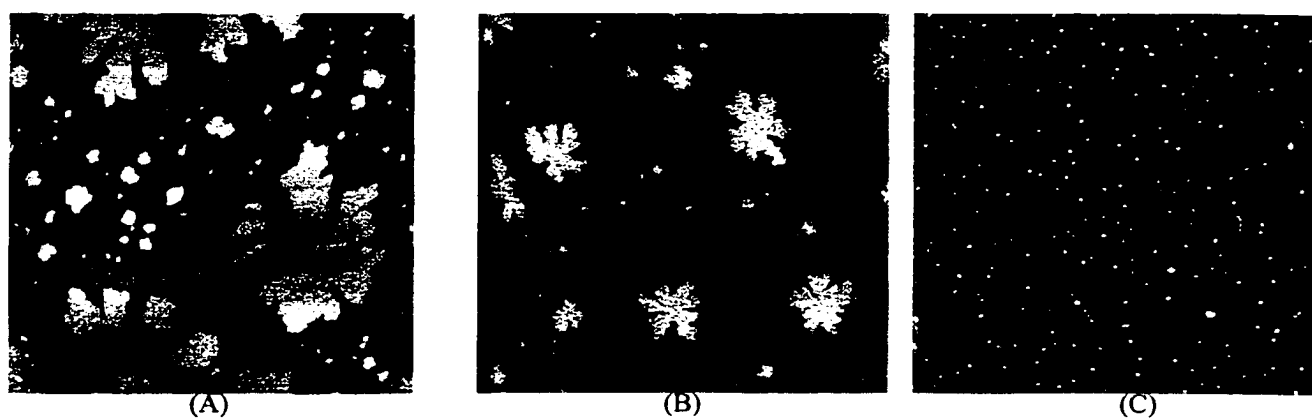


Figure 3.4: Height images of partial OTS monolayers on substrates with different degrees of hydration. Image size: $10\mu\text{m} \times 10\mu\text{m}$; Temperature $22\pm 1^\circ\text{C}$; OTS concentration: 2mM; Deposition time: 30 seconds; Height scale: 0-10nm; (A) Fully hydrated substrate (B) Partially dehydrated substrate, heated at 100°C (C) Dehydrated Substrate, heated at 150°C

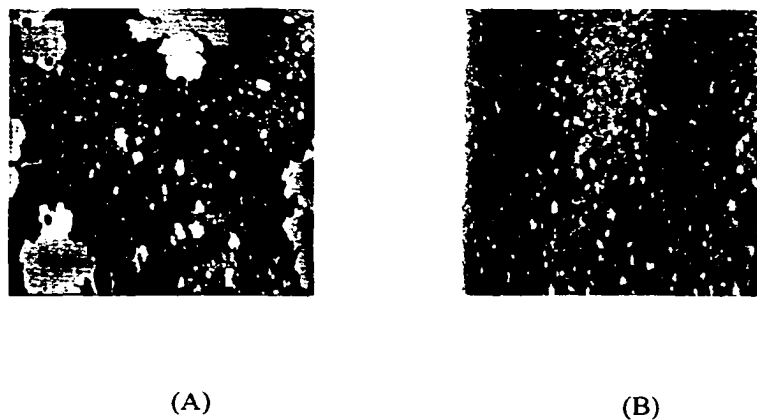


Figure 3.5: Contact mode height images of in-situ experiments. Temperature: $22\pm 1^{\circ}\text{C}$, OTS concentration: 2mM; Image size $10\mu\text{m} \times 10\mu\text{m}$; Height scale: 0-10nm; (A) OTS solution flow for 40 seconds, followed by pure solvent flow (B) Pure Solvent flow for 20 minutes, followed by OTS solution flow for 40 seconds and then again pure solvent flow. Both images were acquired under pure solvent flow

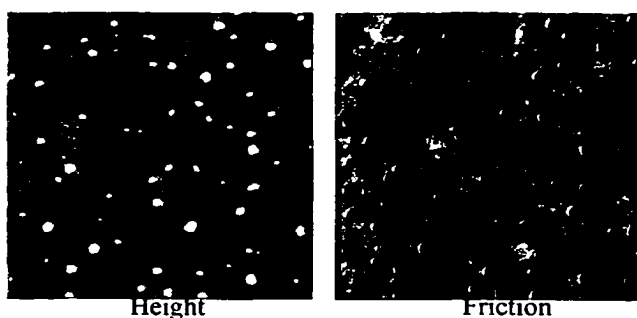


Figure 3.6: Height and friction images of an OTS/BrUTS mixed monolayer showing "nano" islands of OTS surrounded by BrUTS. The procedure is described in the Experimental Section. OTS deposition time ~ 0.5 seconds; Hydrated substrate, Image size: $2\mu\text{m} \times 2\mu\text{m}$; Height scale: 0-10nm.

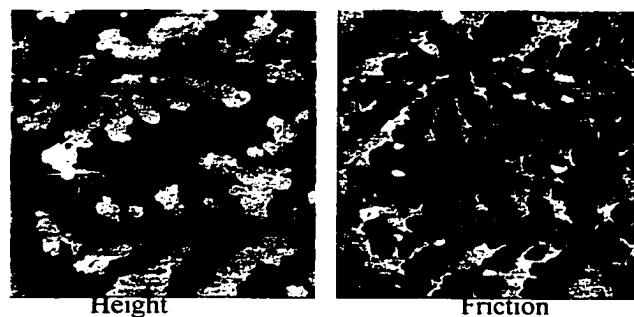


Figure 3.7: Height and friction images of an OTS/BrUTS mixed monolayer showing large condensed fractal islands of OTS surrounded by BrUTS. The procedure is described in the Experimental Section. OTS deposition time: 3 seconds; Hydrated substrate; Image size: $10\mu\text{m} \times 10\mu\text{m}$; Height scale: 0-10nm.

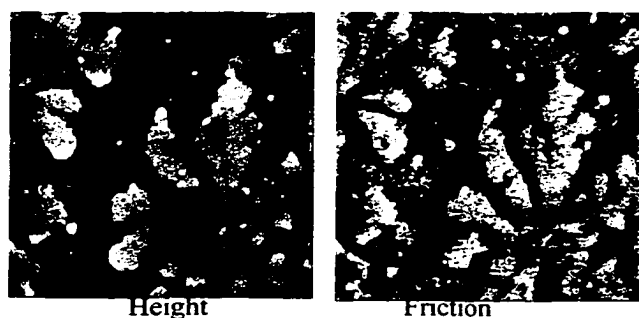


Figure 3.8: Height and friction images of an OTS/DTS mixed monolayer showing large condensed fractal islands of OTS surrounded by DTS. The procedure is described in the Experimental Section. OTS deposition time: 3 seconds; Hydrated substrate; Image size: $10\mu\text{m} \times 10\mu\text{m}$; Height scale: 0-10nm.

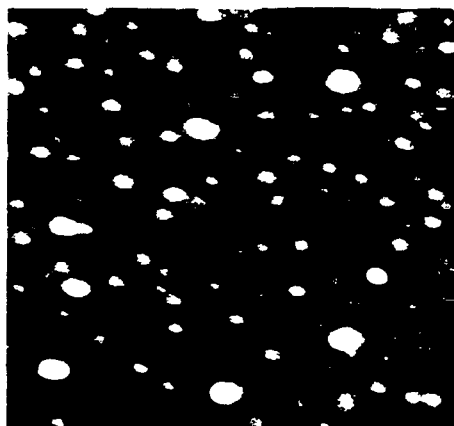


Figure 3.9: Tapping mode image of an OTS/BrUTS mixed monolayer showing "nano" islands of OTS surrounded by BrUTS on a dehydrated substrate. The procedure is described in the Experimental Section. OTS deposition time ~ 3 seconds; Image size: $2\mu\text{m} \times 2\mu\text{m}$; Height scale: 0-10nm

Chapter 4

Adsorption of Trisiloxane and Alkyl Poly-ethoxylate

Surfactants on Air-Water Interface: (1) Measurement of Kinetic Constants and Equation of State (2) Explanation of Unusual Surface Properties of Trisiloxane Surfactants at Air-Water Interface

4.1 Introduction

In Chapter 1 and 2, we discussed the unusual spreading properties of the trisiloxane surfactants. One unusual aspect of the interfacial behavior of the trisiloxane surfactants is that they reduce the air-water surface tension to values as low as 21 mN/m. Very few surfactants, other than the trisiloxane surfactants, have the ability to reduce the air-water surface tension to so low values. These include fluorocarbon surfactants and double chain hydrocarbon surfactants, such as didocyl dimethylammonium bromide³⁸. However, the double hydrocarbon chain and the fluorocarbon surfactants are not super-spreaders³⁸. The alkyl poly-ethoxylate surfactants (C_iE_j) differ from the trisiloxane surfactants only in the structure of the hydrophobe (Figure 1.1), but the minimum surface tension that can be achieved by the alkyl poly-ethoxylate surfactants is only ~27 mN/m and above¹². The reason behind this exceptional ability of the trisiloxane surfactants to reduce the air-water surface tension is not yet clear. This prompted us to undertake the present study. Using pendant bubble technique and Frumkin adsorption model, we have

investigated the adsorption characteristics of the trisiloxane surfactants on the air-water interface, and compared them with the adsorption characteristics of the alkyl poly-ethoxylate surfactants. For reasons mentioned in Chapter 2, all experiments are carried out at concentrations below the critical aggregation concentrations (CAC).

The adsorption characteristics of the alkyl poly-ethoxylate surfactants on the air-water interface have been studied extensively^{120,121} and recently reviewed by Lu et al¹²². The dynamic surface tension and adsorption mechanism has been recently reviewed by Eastoe et al¹²³. In order to compare the adsorption characteristics of the trisiloxane and alkyl poly-ethoxylate surfactants, it is important to judiciously choose the alkyl poly-ethoxylate surfactants. We have chosen $C_{12}E_j$ series of surfactants. The reason behind this choice is that the hydrophobicity of the hydrophobic group of the trisiloxane surfactants is similar a $C_{12}H_{25}$ linear hydrocarbon chain^{21,32}. In the $C_{12}E_j$ series, based on the number of ethoxylate units, we have specifically chosen $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$ to compare with the three trisiloxane surfactants, $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$. Lin and co-workers have used the pendant bubble technique to obtain the equation of state (relating the surface concentration and the surface tension) and kinetic parameters of the Frumkin adsorption model for $C_{12}E_4$ ⁶⁷ and $C_{12}E_8$ ⁶⁸. Using a rapidly expanding and compressing pendant bubble, Pan et al⁶⁵ have developed a technique to directly measure the equations of state for the soluble surfactants. They have used this technique to measure the equation of state and kinetic constants for $C_{12}E_6$.

Compared to the C_iE_j surfactants, there are very few studies for the trisiloxane surfactant adsorption on the air-water interface. The maximum surface concentrations of the trisiloxane surfactants have been evaluated from the equilibrium surface tension (γ_e)

vs. bulk concentration (C_θ) data. But there is large disagreement in the available literature. For example, the values of the maximum packing for M(D'E₈OH)M as measured by Gentle et al⁴¹ and Svitova et al³⁸ are 32.6 and 49 Å²/molecule, respectively. For a similar surfactant, M(D'E₈OCH₃)M, Ananthapadmanabhan et al¹⁰ have measured a value of 70 Å²/molecule. The dynamics of the trisiloxane surfactant adsorption has been studied by Rosen et al⁴², Ananthapadnabhan et al¹⁰, and Svitova et al⁴⁰. In all these studies, the concentration of the surfactant solution was above the critical aggregation concentration (CAC). The dynamics adsorption characteristics at concentrations above the CAC, depend not only on the adsorption kinetics of the surfactant on the interface, but also on the break-up kinetics and transport of the aggregates the bulk. Therefore, these studies do not provide significant information about the kinetic adsorption of the surfactants on the air-water interface. The γ_e vs. C_θ data does not provide the kinetic adsorption characteristics of surfactants. The kinetic adsorption characteristics, including the adsorption, desorption, and diffusion constants are obtained from the dynamic surface tension data¹²³. The dynamic adsorption characteristics are important not only how fast the surface tension reduces, but also to in the drop impact and Marangoni driven spreading. In the drop impact experiments, (Figure 1.2), in order to retain the drop on the surface, it is necessary that the surfactant adsorbs on the interfaces fast enough to compensate for the increase in the area caused by the impact. The Marangoni driven spreading is also greatly influenced by the adsorption kinetics of the surfactants. If the surfactant does not adsorb rapidly enough at the leading edge of the drop, the surface tension gradients will diminish, leading to a slower spreading.

In this work, we have evaluated the kinetic adsorption constants and equation of state for the three trisiloxane surfactants, $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$, using the pendant bubble technique. The equations of state are obtained by the technique developed by Pan et al⁶⁵. The Frumkin adsorption model parameters and diffusion coefficient (D) are obtained from the equilibrium surface tension and the dynamic surface tension measurements. In contrast with the previous studies^{10,40,42}, we have used surfactants concentrations which are below the CAC's. Therefore these results truly represent the adsorption kinetics of the surfactant molecules. Finally, by comparing various kinetic constants of the Frumkin model, we observe that the desorption constants of the trisiloxane surfactants are much smaller than the desorption constant of corresponding $C_{12}E_j$ surfactants. As a result, the surface activity of the trisiloxane surfactants is much higher than the $C_{12}E_j$ surfactants, due to which they pack more densely on the air-water interface, thereby reducing the surface tension to values as low as 21mN/m. These special adsorption characteristics of the trisiloxane surfactants are attributed to the trisiloxane hydrophobe.

4.2 Background:

Surface equation of state (EOS) is a relationship between the surface concentration of surfactant and the reduction in the surface tension of the air-water interface caused by the adsorption of the surfactant. It is a 2-dimensional analogue of the 3-D equations of state used for gases and liquids, such as, ideal gas EOS, van der Waal's EOS, etc. The experimental data for surface EOS can be obtained experimentally and fitted to obtain model parameters. For the insoluble surfactants, Langmuir Trough is extensively used to obtain surface tension and surface concentration data. The surface concentration is measured simply by mass balance. Various phase transitions, analogous to the gas-liquid and liquid-solid phase transitions for 3-D fluids, have been observed for the insoluble surfactants⁵⁶. Some EOS's are able to account for the phase transition in the surfactant monolayers.

In comparison, there are no direct and simple techniques to measure the EOS of soluble surfactants. Neutron reflectivity, X-ray reflection, ellipsometry, IR, and Raman spectroscopy have been used to quantify the amount of surfactant on the air-water interface¹²². The use of these techniques has been limited because of elaborate experimental procedure. The surface tension techniques have been used extensively to indirectly evaluate the surface concentration and EOS. The EOSs are obtained by fitting the equilibrium surface tensions vs. bulk concentration data, measured at sub-CAC concentrations.

The adsorption of soluble surfactants is intimately connected with the behavior of the surfactants in the bulk. The surfactants are packed more densely on the air-water interface than in the bulk. As a result, by adsorbing on the interface, the entropy of the

surfactant molecules is reduced drastically. Therefore, there has to be an additional factor, which provides sufficient driving force to the surfactant to adsorb on the surface. This driving force results from the fact that hydrophobic part of the surfactant molecule does not want to stay in water, surrounded by water molecules. Water is a hydrogen bonding liquid. When a hydrophobic solute is forced in water, the hydrogen-bonding network of water is broken. Due to the peculiar structure of water molecules, they are forced to arrange around the solute in a more ordered fashion, providing mostly an entropic penalty to the free energy of the system¹²⁴. Due to the amphiphilic nature of surfactants, the hydrophobic part of the surfactants comes out of water into air, when they adsorb on air-water interface. As a result, the hydrophobic part is freed from the structured water. This mainly contributes to the driving force of adsorption of the surfactants from the bulk to the surface.

The relatively high surface tension of water is due to its hydrogen bonding characteristics. Water molecules near the air-water interface are forced to lose some of the hydrogen bonds. As a result, they are in energetically more unfavorable configuration. The surfactant molecules, on their adsorption at the air-water interface replace some of the water molecules, which are present at the interface. This can also contribute to the driving force for the adsorption of surfactant from bulk. These two effects (i.e. surfactant molecule freeing itself from the structured water and replacement of the water molecules present on the interface) primarily provide the driving force of adsorption of surfactant (i.e. high surfactant's entropy configuration in dilute solutions to a higher concentration and lower surfactant entropy configuration on the surface)

A surfactant molecule adsorbing from the bulk to the interface faces an adsorption activation energy barrier^{††}. The rate of adsorption depends on this adsorption activation energy barrier. Similar to the adsorption activation energy, there is desorption activation energy barrier for surfactants to desorb from the surface into the bulk. In order to desorb from the surface into the bulk, the surfactant molecule has to form structured water around itself. In addition, some water molecules may be required to replace the surfactant on the surface. The desorption and adsorption activation energy barriers affect the rates of desorption and adsorption.

The kinetic rates as well as the activation energies of adsorption and desorption are affected by some other factors, such as the nature of surfactant monolayer. The interaction between the surfactant molecules also affects the kinetic rates. The attraction can be due to the van der Waals interaction among the hydrophobic groups of the adsorbed surfactants. The repulsive interaction can be caused by the repulsion among the poly-ethoxylate chains or by the repulsion among the ionic hydrophilic groups. The attractive interactions are thought to be the reason for the existence of certain phase transitions in surfactant monolayers. The repulsive interactions among the poly-ethoxylate chains are thought to be the reason for the dependence of maximum packing of C_iE_j on the number of ethoxylate units in C_iE_j ^{12,125}.

At equilibrium, the net rate of adsorption is zero. Therefore, the net driving force for adsorption at equilibrium adsorption can be calculated from the ratio of the adsorption and desorption rates, i.e. the difference of the activation energies of desorption

^{††} Pan et al⁶⁵ have shown that adsorption activation energy barrier for C_iE_j surfactants is nearly zero, if $i > 10$.

and adsorption⁶⁵. This results in a relationship between the surface concentration and bulk concentration, (at equilibrium and at a certain temperature), called adsorption isotherm. As a result, the adsorption isotherm and kinetic rate expressions are not independent of each other. Therefore, any model for adsorption isotherm should be able to account for the kinetic expressions and vice-versa. The adsorption isotherm can not be measured directly from the surface tension vs. bulk concentration data. The Gibbs-Duhem equation, using Gibbs's adsorption model, provides a differential equation relating surface tension, surface concentration and chemical potential of the surfactant molecule in the bulk. At dilute concentrations, the chemical potential of the surfactant in bulk can be easily evaluated. Using this equation, in combination with the adsorption isotherm, relationships between surface tension - bulk concentration and surface tension - surface concentration (EOS) are obtained. The values of the model parameters are obtained by fitting the equilibrium surface tension vs. bulk concentration data. Pan et al⁶⁵ have shown that this data is not sensitive to the choice of the EOS model, and therefore does not provide much insight into the adsorption characteristics of the surfactants. They have developed a new technique using pendant bubble to directly measure the EOS of soluble surfactants. This technique can be considered analogous to the Langmuir Trough under certain experimental conditions. We have used this technique to directly obtain the equation of state for the soluble the trisiloxane surfactants. The adsorption isotherms for the trisiloxane surfactants are obtained directly from the EOSs. The additional parameters of the kinetic model, including the adsorption, desorption, and diffusion coefficients are obtained from the dynamic surface tension measurements. The maximum packing of the surfactants are obtained from the adsorption isotherms.

4.3. Experimental Section

4.3.1 Materials

Commercial samples of the trisiloxane surfactants $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$ were provided by Dr. Randall Hill of Dow Corning Corp. The purity of these samples are approximately 85%, and the remaining 15 % are non-surface-active glycols. The trisiloxane part is approximately 98% mono-disperse¹²⁶. The glassware are cleaned by successive rinses with acetone and deionized water. Deionized water, with a resistivity of 18M Ω cm, is obtained from a Millipore® system.

4.3.2 Measurement of the Dynamic and the Equilibrium Surface Tensions

The pendant bubble technique is used to measure the dynamic and equilibrium surface tensions. A brief description of this technique is presented here. We have used an apparatus similar to the one used by Subramanayam^{50,127} and Pan⁶⁵. This apparatus is developed in-house. An illustration of the apparatus is shown in Figure 4.1. A light beam is produced from a tungsten bulb. It is collimated by passing through a series of lenses and pinholes. A transparent quartz cell (2.5x4x4 cm) is filled with the surfactant solution and placed in the path of the collimated beam. An inverted stainless steel needle is immersed in the surfactant solution. A motor driven syringe is connected to the inverted needle through a solenoid valve. A pendant bubble is formed on the edge of the needle by pushing air through the valve, tubing, and the inverted needle. The collimated light forms a silhouette on a CCD array video camera placed on the other side on the quartz cell. The images of the pendant bubble are captured electronically using Scion

imaging software and an image capturing board. The X-Y coordinates of the bubble profile are obtained using the Scion software. This apparatus has the capability to capture images as fast as 30 frames/second.

The dynamic surface tension data are obtained by rapidly forming a pendant bubble on the inverted needle. The images of the bubble are acquired at various time intervals. The profiles of the pendant bubble are obtained from the captured images. The surface tensions at various times are obtained by integrating the Young-Laplace equations and fitting the resulting profile to the bubble profiles. After some time, the dynamic surface tension of the pendant bubble reaches an equilibrium value. This value is taken to be the equilibrium surface tension at that concentration.

4.3.3 Determination of the Equation of State

Pan et al⁶⁵ have devised a new technique to determine the equations of state for the soluble surfactant systems. In this method, a bubble of diameter of $\sim 1-3$ mm is created in a dilute surfactant solution and it is allowed reach equilibrium. Then, the bubble is rapidly expanded or compressed in approximately two to five seconds. The profile of the bubble is captured during the expansion or compression process. The surface tension, $\gamma(t)$, and the area of the bubble, $A(t)$, are evaluated from the bubble profiles. The surface tension is a unique function of the surface concentration (Γ). We assume a reference surface tension (γ_{ref}), to be 60 mN/m. Corresponding to this tension, there is a unique surface concentration, Γ_{60} . The experiments are conducted in such a way that the surface tension profiles during every compression or expansion passes through the reference surface tension. In a particular experiment, the area of the bubble,

corresponding to the surface tension of 60 mN/m is evaluated from the $A(t)$ vs. $\gamma(t)$ data, and this value is called A_{60} . If the expansion and compression of the bubble is rapid enough, then we can assume that $A(t) \cdot \Gamma(t) = S$, where S is the total amount of the surfactant on the bubble surface. We define a relative surface concentration Γ_{rel} ($= \Gamma/\Gamma_{60}$). With the assumption of S being constant during the compression or expansion, we can write $\Gamma_{rel}(t) = \Gamma(t)/\Gamma_{60} = A_{60}/A(t)$. Thus, we obtain experimental plots of the surface tension γ vs. Γ_{rel} . The γ vs. Γ_{rel} data is obtained for many compression and expansion experiments carried out at various bulk concentration and varying expansion and compression rates. If the assumption of S being constant, is valid, then the γ vs. Γ_{rel} data from various experiments should collapse onto a single curve. Many experiments are carried out for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M. The γ vs. Γ_{rel} data for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M are shown in Figures 4.2, 4.3 and 4.4 respectively. In these plots, we observe that the data from various experiments collapses onto a single curve. This justifies our assumption that the amount of surfactant on the expanding or compressing bubble is constant. The equations of states of the three trisiloxane surfactants are obtained from the γ vs. Γ_{rel} plots.

4.4 Analysis and Results

4.4.1 Model Formulation

Many equations of states are available in the literature. Lin et al¹²⁸ have discussed some of the equation of states. We have chosen the Frumkin model for the following reasons:

- 5 The adsorption-desorption kinetics are intrinsic to the model. Therefore, no separate formulation of the kinetics of adsorption and desorption is required. This is an important factor, since one of the main objectives of this work is to evaluate the kinetic adsorption constants of the trisiloxane surfactants.
- 6 Langmuir adsorption model is also developed from the kinetics of adsorption and desorption. However, it does not take into account the interaction among the surfactant molecules adsorbed at the interface. In next sections, we will show that the Langmuir model does not fit the experimental data. Therefore, it is not a good representative for the equation of state.

In the Frumkin model, the expression for the surfactant adsorption on an interface is given by:

$$\frac{d\Gamma}{dt} = \beta\Gamma_{\infty}C_S\left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) - \alpha\Gamma e^{K\Gamma/\Gamma_{\infty}} \quad (4.1)$$

where Γ is surface concentration; C_S is sub-layer concentration; Γ_{∞} is maximum surface concentration parameter; α and β are desorption and adsorption coefficients respectively. K is a non-dimensional Frumkin parameter, which accounts for the interaction between

the adsorbed surfactant molecules. At equilibrium, the LHS of Equation 4.1 is zero. After rearrangement, an expression of the Frumkin adsorption isotherm relating the equilibrium surface concentration (Γ_e) and the bulk concentration (C_0) is obtained.

$$\frac{\Gamma_e}{\Gamma_\infty} = \frac{1}{1 + (a / C_0) e^{(K\Gamma_e - \Gamma_\infty)}} \quad (4.2)$$

where $a = \alpha/\beta$. Using Gibbs-Duhem equation, ($d\gamma = -RT\Gamma d \ln(C)$, for dilute solutions) an equation of state, relating the surface tension (γ) and the surface concentration (Γ), is obtained. The expression of Frumkin equation of state is:

$$\gamma(\Gamma) = \gamma_c + RT\Gamma_\infty \left(\ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - \frac{K}{2} \left(\frac{\Gamma}{\Gamma_\infty}\right)^2 \right) \quad (4.3)$$

where γ_c is the surface tension of clean air-water interface, and its value is ~ 72.5 mN/m.

4.4.2 Evaluation of Γ_∞ , K , and a

Usually the parameters Γ_∞ , K , and a are determined from the equilibrium surface tension (γ_e) vs. $\log(C_0)$ data. Pan et al⁶⁵ have shown that this method is not sensitive to the choice of the adsorption model. The γ_e vs. $\log(C_0)$ plots are almost linear except at low surface pressures and low bulk concentrations. In our experiments, we do not use the γ_e vs. $\log(C_0)$ data to evaluate all the three parameters. Instead, we use the γ vs. Γ_{rel} to obtain two parameters, Γ_∞ and K , by fitting the Frumkin equation of state (Equation 4.2) to the γ vs. Γ_{rel} data. The Frumkin model fits for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M, along with the experimental data are shown in Figures 4.2, 4.3, and 4.4 respectively. The values of Γ_∞ and K obtained in this manner are shown in Table 4.1. The third parameter in the Frumkin model, a ($= \alpha/\beta$), is obtained by fitting Equations 4.2 and 4.3 to the γ_e vs. $\log(C_0)$ data, using the values of Γ_∞ and K evaluated from the γ vs. Γ_{rel}

data. The experimental data and fitted curve for γ_e vs. $\log(C_0)$ for the three trisiloxanes, M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M are shown in Figures 4.5, 4.6, and 4.7, respectively. The values of Γ_∞ , K , and α for these three surfactants are also shown in Table 4.1.

4.4.3 Evaluation of α , β and Diffusion Coefficient (D)

The value of a ($=\alpha/\beta$), is obtained from the γ vs. Γ_{rel} and γ_e vs. $\log(C_0)$ data, as described in the previous section, but the individual values of α and β cannot be obtained from this data. The individual values of α and β are obtained by comparing the dynamic surface tension data with the simulation of dynamic surface tension. The simulations of the dynamic surface tension are carried out in a manner described below.

The simulations are carried out for known values of Γ_∞ , K , α , β , and D . Values of β , and D are assumed, and remaining parameters are obtained as described previously. In these simulations, the pendant bubble is assumed to be a spherical air bubble of radius R . The bubble is created instantaneously in the surfactant solution of concentration C_0 and at time $t=0$. The surface of the bubble is clean at $t=0$, i.e. $\Gamma(t=0) = 0$. The surfactant adsorbs on the air-water interface from the sub-layer present beneath the interface, leading to a reduction in C_s . The reduced sub-layer concentration creates a concentration gradient in the bulk, which drives the diffusive mass transport of the surfactant from the bulk to the sub-layer. The convective mass transport is assumed to be negligible. As the surfactant adsorbs on the air-water interface, the surface tension is reduced according to the equation of state. We also assume that the volume of the bubble remains constant as the surface tension of the bubble decreases. The governing equations for the surfactant

mass transport are as follows.

Diffusion of the surfactant from the bulk to the surface is given by the Fick's law.

$$\frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} \quad (r > R, t > 0) \quad (4.4)$$

Boundary and initial conditions are:

$$C(r, t) = C_0 \quad (r > R, t = 0) \quad (4.5a)$$

$$C(r, t) = C_0 \quad (r \rightarrow \infty, t > 0) \quad (4.5b)$$

$$\Gamma(t) = 0 \quad (t = 0) \quad (4.5c)$$

The diffusive flux at the bubble interface results in the accumulation of the surfactant, thereby increasing the surface concentration.

$$d\Gamma / dt = D(\partial C / \partial r) |_{r=R} \quad (r = R, t > 0) \quad (4.5d)$$

Using Laplace transform, the above set of equation can be transformed into well known Ward and Tordai equation.

$$\Gamma(t) = \Gamma_0(t=0) + \frac{D}{R} \left[C_0 t - \int_0^t C_s(\tau) d\tau \right] + 2\sqrt{\frac{D}{\pi}} \left[C_0 \sqrt{t} - \int_0^{\sqrt{t}} C_s(t-\tau) d\sqrt{\tau} \right] \quad (4.6)$$

where $C_s(t)$ is the sub-layer concentration at time t . However, this equation cannot be solved without knowing the sub-layer concentration. Another relationship between $\Gamma(t)$ and $C_s(t)$ is required in order to solve for $\Gamma(t)$ or $C_s(t)$. This relationship depends on the relative rates of diffusion and adsorption. The time scale of diffusion⁶⁵ (τ_{diff}) is defined as $\tau_{diff} = \pi \Gamma_\infty^2 / 4DC_0$. The time scale of kinetic adsorption and desorption⁶⁵ (τ_{kin}) is defined as $\tau_{kin} = (\alpha + \beta C_0)^{-1}$. The ratio of the diffusive to kinetic time scale (Φ^2) becomes $\Phi^2 = \tau_d / \tau_{kin} = \{\pi \Gamma_\infty^2 \beta^2 (1 + C_0 / a)\} / \{4D\alpha(C_0 / a)^2\}$. The value of a for the trisiloxane surfactants are of the order of 10^{-6} mol/m³, considering the values of CAC, the value of

$\beta C/\alpha \gg 1$. As a result, the expression of Φ^2 simplifies to (neglecting factor of $\pi/4$):

$$\Phi^2 = \frac{\tau_d}{\tau_{kin}} = \frac{\Gamma_{\infty}^2 \beta^2}{D\alpha(C_0/a)} \quad (4.7)$$

At low concentrations, the diffusive time scale is large compared to the kinetic time scale and the interface is always in equilibrium with the sub-layer. This regime is called the diffusion controlled (DC) regime. On increasing concentration, the diffusion time scale reduces faster than the kinetic time scale. As a result the surface is not always in equilibrium with the sub-layer at high concentrations. This regime is called mixed-diffusion-kinetic controlled (MDC) regime.

In the DC regime, an equilibrium relationship between the surface concentration and sub-layer concentration can be used. Equation 4.2 can be written as:

$$\frac{\Gamma(t)}{\Gamma_{\infty}} = \frac{1}{1 + (a/C_s(t))e^{(k\Gamma_{\infty}/\Gamma_{\infty})}} \quad (4.8)$$

In the MDC regime, the surface is no longer in equilibrium with the sub-layer. Therefore, a kinetic expression, relating $\Gamma(t)$ and $C_s(t)$ has to be used. Equation 4.1 can be used in the following form for this purpose:

$$\frac{d\Gamma(t)}{dt} = \beta\Gamma_{\infty}C_s(t)\left(1 - \frac{\Gamma(t)}{\Gamma_{\infty}}\right) - \alpha\Gamma(t)e^{k\Gamma(t)/\Gamma_{\infty}} \quad (4.9)$$

Equations 4.8 and 4.9 provide the additional relationship required for solving Equation 4.6. However, this is not a trivial procedure, because of the presence of convolution integrals in Equation 4.6. Lin et al⁶⁶ have described the technique to solve Equation 4.6 together with Equation 4.8 or 4.9. We will briefly describe this procedure. The time interval $(0, t)$ is divided in time steps of size δ . At any time step, t_n , Equation 4.6, after slightly elaborate procedure, can be transformed into a simple form ⁶⁶.

$$C_s(t_n) = b_1 \Gamma(t_n) + b_2 \quad (4.10)$$

where b_1 and b_2 are functions of D , C_0 , R and the sub-layer concentrations in the previous time steps ($C_s(0)$, $C_s(\delta)$, $C_s(2\delta)$... $C_s(t_{n-1})$). The values of b_1 and b_2 are evaluated at each time step. In the DC regime, Equation 4.8 and 4.10 are solved numerically to obtain $C_s(t_n)$ and $\Gamma(t_n)$. In the MDC regime, Equations 4.9 and 4.10 are solved numerically using Simpson's one-third rule to obtain $C_s(t_n)$ and $\Gamma(t_n)$. Thus, in this way we obtain the surface concentration, ($\Gamma(t)$), for the DC and MDC regimes. The dynamic surface tension, ($\gamma(t)$) is obtained from $\Gamma(t)$ using the Frumkin equation of state.

Pan et al⁶⁶ have reviewed the available literature concerning the evaluation of the kinetic and diffusion constants in the two regimes. At low bulk concentrations, the diffusion of the surfactant to the interface is in DC controlled regime. The dynamic surface tension simulations, for the DC regime are carried out for the known values of Γ_∞ , K , and α/β . A value for D is assumed. The simulated dynamic surface tension is compared with the experimental data to check the validity of the assumed value of D . The value of D should be in the range predicted by Stokes-Einstein relation. The experimental dynamic surface data at a higher concentration is again compared with the DC simulations. If the comparison is satisfactory, then the value of D is taken to be the value of diffusion coefficient. The dynamic surface tension data for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M are shown in Figures 4.8, 4.9, and 4.10, respectively. Plot 1 of Figure 4.8 is compared with the DC simulation with $D=11 \times 10^{-10}$ m²/sec. The simulations are in very good agreement with the experimental data. The DC simulation, using the same value of D agrees well with the experimental data at higher concentration (plot 2, Figure 4.8). Thus, the value of D for M(D'E₄OH)M is 11×10^{-10} m²/sec. Figure 4.9 shows the dynamic

surface tension data for $M(D'E_8OH)M$. Using the same value of D , i.e. $11 \times 10^{-10} \text{ m}^2/\text{sec}$, the DC simulation agree well with the experimental data for plot 1 (Figure 4.9). Therefore, the value of D for $M(D'E_8OH)M$ is also $11 \times 10^{-10} \text{ m}^2/\text{sec}$. Similarly, the same value of D , predicts the dynamic surface tensions of $M(D'E_{12}OH)M$ at three concentrations, as shown in plot 1,2 and 3 in Figure 4.10.

On further increase in the surfactant concentration, the DC simulation can predict faster relaxation in surface tension than the experimental values. This is observed for the three trisiloxane surfactants, and shown as plots 3,2, and 4 in Figures 4.8, 4.9, and 4.10, respectively. At these concentrations, the DC simulations predict faster drop in the surface tension. This suggests that the adsorption process is no longer controlled by diffusion only, thus, necessitating the use of mixed-kinetic-diffusion controlled model. MDC simulations are carried out for the three surfactant with some values of β . The results of the MDC simulations, for different values of β , are compared with the experimental data and DC simulations in plots 3, 2, and 4 in Figures 4.8, 4.9, and 4.10, respectively. The values of β , which provide the best agreement of the experimental data with the MDC simulations, are 3, 5, and $10 \text{ m}^3/(\text{mol}.\text{sec})$ for $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$, respectively. At higher concentrations, these values of β provide excellent agreement of the MDC simulations with the experimental data, as shown in Figures 4.8, 4.9, and 4.10. In this manner, we obtain, the values the kinetic coefficients of the Frumkin adsorption model. The values of various kinetic coefficients for the three trisiloxane surfactants are summarized in Table 4.1.

Now, with the values of the kinetic coefficients known, using Equation 4.7, we can calculate the values of Φ^2 for the three trisiloxane surfactants, at all the

concentrations for which the dynamic surface tension experiments are carried out. These results are shown in Table 4.2. For convenience, a reduced concentration (C_R) has been defined as $C_R = C_0/CAC$. The values of C_0/a are also calculated. Pan et al⁶⁵, using numerical simulations have shown that the crossover from the DC regime to the MDC regime occurs when the value of Φ^2 is $\sim O(10)$. They showed that only the value of Φ^2 determines the crossover from DC to MDC regime, irrespective of the value of C_0/a . However, they were unable to provide conclusive experimental evidence of their results. In Table 4.2, we observe that the crossover from DC to MDC regime occurs when the values of Φ^2 are ~ 37 -100 for the three trisiloxane surfactants, which is exactly in the range predicted by Pan et al⁶⁵. Also note that the values of C_0/a range from 42 to 5000 when the crossover in the diffusion mechanism occurs. This confirms that the transition from the DC to MDC regime depends only on the value of Φ^2 . These results are true for three different surfactants with very different adsorption characteristics. Therefore, our results provide a conclusive experimental evidence of the validity of predictions of Pan et al⁶⁵.

In the dynamic surface tension experiments, an important thing to notice is that D and β are the only two parameters used to fit five to seven plots each for every trisiloxane surfactant, at concentrations varying by few orders of magnitude. The fact that only two parameters can predict so much dynamic surface tension data, proves the validity of the diffusion-adsorption model, as well as validity of the Frumkin model as the adsorption isotherm and equation of state.

4.5 Discussion.

In this work, we have obtained the values of the various parameters of the Frumkin adsorption model, and diffusion coefficients for the three trisiloxane surfactants, $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$. These values are shown in Table 4.1. In order to compare the trisiloxane surfactants with alkyl poly-ethoxylate surfactants, we have chosen three alkyl poly-ethoxylate surfactants, namely $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$. As mentioned in the Introduction (Section 4.1), the motive behind choosing the $C_{12}E_j$ series is that the hydrophobicity of hydrophobic group of the trisiloxane surfactants is similar to the hydrophobicity of a linear $C_{12}H_{25}$ hydrocarbon chain²¹. The Frumkin parameters for these three alkyl poly-ethoxylate surfactants are available in the literature. The values of the Frumkin parameters for $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$, obtained by the pendant bubble technique, are taken from the references cited in Table 4.1 and Table 4.3. In this section, we compare adsorption characteristics of the trisiloxane and alkyl poly-ethoxylate surfactants and discuss the effect of the surfactant's molecular structure on adsorption characteristics of the surfactants. Finally, we explain the reason why the trisiloxane surfactants are able to reduce the surface tension to lower values compared to the alkyl poly-ethoxylate surfactants.

4.5.1 Intermolecular Interaction

The parameter K , in the Frumkin model, accounts for the interaction among the surfactant molecules adsorbed on the interface. It also relates the activation energy of desorption (E_D) with the surface concentration (Γ). The relationship between E_D and Γ is given by: $E_D / RT = E_D^0 / RT - K * (\Gamma / \Gamma_\infty)$, where E_D^0 is the activation energy for

desorption at infinite dilution (C_0 and $\Gamma \rightarrow 0$). The value of $K=0$ results in the Langmuir model, implying that there is no interaction among the adsorbed surfactant molecules and E_D does not change with Γ . A positive value of K implies that the net interaction between surfactant molecules on the interface is repulsive. And as a result, as the surface concentration increases, it becomes easier for a surfactant molecule to desorb from the surface into the bulk. This effect manifests as reduction in E_D^0 as the surface concentration of the surfactant increases. On the other hand, a negative value of K implies that the net interaction among the surfactants on the interface is attractive and it becomes progressively more difficult to desorb a surfactant with increasing surface concentration. The activation energy for desorption increases with an increase in the surface concentration. The dominant interactions among the surfactant molecules consist of attractive van der Waals interaction between the hydrocarbon chains and the repulsive interaction between the ethoxylate groups. The value of K signifies the summation of the attractive or repulsive interaction. As a result the value of K can be negative or positive. Hsu et al¹²⁹ have discussed the effect of the intermolecular interactions on the adsorption kinetics of surfactants.

Any changes in the molecular structure of the surfactant leads to variations in the intermolecular interactions. As a result, the value of K depends on the molecular structure. For example, the value of K for 1-decanol ($C_{10}E_0$) and 1-octanol (C_8E_0) are -3.71 and -2.66 respectively¹³⁰. This implies that increase in the length of hydrocarbon chain increases the attractive interaction, which results in more negative value of K for 1-dodecanol. The values of K for $C_{12}E_4$ and $C_{12}E_8$ are 1.87 and 5.19 respectively¹³⁰(Table

4.1), suggesting that the repulsion between the surfactant molecules increases on increasing the number of ethoxylate groups.

The values of K for the three trisiloxane surfactants $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$ are 5, 7.26, and 10 respectively, as shown in Table 4.1. We compare these values with the values of K for $C_{12}E_4$ and $C_{12}E_8$. Similar to the C_iE_j , the value of K for the trisiloxane surfactants increases with an increase in the number of the ethoxylate groups. The attractive interaction among the trisiloxane groups is not expected to be same as the interaction between the C_{12} hydrocarbon chains. Therefore, we do not expect the same value of K for $C_{12}E_j$ and $M(D'E_jOH)M$ with same number of ethoxylate groups (j). The values of K for $C_{12}E_4$ and $M(D'E_4OH)M$ are 1.87 and 5 respectively. Assuming that the repulsion induced due to the ethoxylate units is same in the two surfactants, we can conclude that the interaction among the trisiloxane groups is not as attractive as it is for C_{12} hydrocarbon chains. Similar conclusion is drawn from the values of K for $C_{12}E_8$ and $M(D'E_8OH)M$.

4.5.2 Evaluation of the Equation of State

The equation of state for a soluble or insoluble surfactant system is the relationship between the surface tension (γ) and the surface concentration (Γ). As described previously, experimental techniques, such as Langmuir Trough cannot be used for the soluble surfactants. This limitation is because the surfactant, being soluble, either adsorbs or desorbs, whenever the surface concentration is perturbed from its equilibrium value corresponding to the bulk concentration (C_0). The equation of state and the adsorption isotherms are usually evaluated from the $\gamma_e - \log(C_0)$ data, which is very simple

to obtain. However, this method has some limitations. It is observed that the $\gamma_e\text{-log}(C_0)$ data for most of the common non-ionic surfactant systems is almost linear. As a result, many different adsorption models can be used to fit the experimental data with similar accuracy. Thus, this does not provides much understanding of the adsorption process. The $\gamma_e\text{-log}(C_0)$ data begins to show some non-linear behavior only at small surface pressures ($\Pi = \gamma_{\text{water}} - \gamma_e$). These values of surface pressures are achieved only at very low concentrations. Two main problems begin to appear at such low concentrations. Firstly, the surfactant solutions become very sensitive to the presence of impurities. Secondly, the system takes long time to reach equilibrium. In some experimental techniques, the long adsorption time can result in some unwanted effects, such as, evaporation of water, adsorption of impurities from air to the on air-water interface. The technique developed by Pan et. al⁶⁵ overcomes these limitations. We have used this technique to evaluate the equation of state for the trisiloxane surfactants. An important advantage of this technique is that all the experimental γ vs. Γ_{rel} data can be obtained by conducting experiments at only one concentration (low or high). The reproducibility and validity of the data is verified by varying the expansion or compression rates. The problems associated with the impurities adsorbing from air are not encountered, because the air bubble is always surrounded by the solution. The remaining parameter of the adsorption isotherm (a) can be obtained from only one equilibrium surface tension data point, which can be evaluated at the same concentration at which the compression-expansion experiments are carried out.

We have mentioned earlier that we have used the Frumkin model against the Langmuir model, because the Langmuir model does not takes into account the interaction

between the surfactants. The Frumkin parameter, K , represents the overall interaction among the surfactants molecules adsorbed on the interface. The trisiloxane surfactants adsorbed on the interface have a net repulsive interaction. The Langmuir and Frumkin models which provide the best fit to the γ vs. Γ_{rel} and γ_e vs. C_0 data for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M are shown in Figures 4.2 to 4.7. The best fitting parameters are shown in the captions. There is almost no significant difference between the Langmuir and the Frumkin model in the γ_e vs. $\log(C_0)$ data as shown in Figures 4.5 to 4.7. Some difference are observed when the equilibrium surface tension is above 60 mN/m. However, in Figures 4.2 to 4.4, the Langmuir model fails to fit the γ vs. Γ_{rel} data. For C₁₂E₄, the Langmuir model is in a reasonable agreement with the experimental γ vs. Γ_{rel} data for M(D'E₄OH)M, above $\gamma \sim 60$ mN/m. At low surface concentrations, the effect of interactions between the surfactants is insignificant. Therefore, the at low surface concentrations of M(D'E₄OH)M, the Langmuir model fits reasonably well. As the surface concentration increases, the effect of the interaction among the surfactant molecules on the surface tension increases. Consequently, the Langmuir model fails at higher surface concentrations. For M(D'E₈OH)M and M(D'E₁₂OH)M, the Langmuir model fails even at low surface concentrations (Figures 4.3 and 4.4), even though the γ vs. $\log(C_0)$ data can be fitted with the Langmuir model (Figure 4.7 and 4.8). The difference between experimental values and the Langmuir model increases with an increase in the interaction parameter K , as observed in Figure 4.3 and 4.4. In comparison, the Frumkin Model, which takes into account the intermolecular interactions, fits both the γ_e vs. $\log(C_0)$ and γ vs. Γ_{rel} data reasonably well for all the three trisiloxane surfactants (Figures 4.2 to 4.7). These results show that even though the Langmuir model fits the γ_e vs. $\log(C_0)$ data, it is

not a good representative of the adsorption isotherm and the equations of state for the three trisiloxane and the γ vs. $\log(C_v)$ data alone is not adequate to model the surfactant adsorption isotherms and equation of states.

The inadequacy of the Langmuir model is also evident from the values of minimum area per molecules ($A_{min} = 1/\Gamma_{CAC}$) or maximum packing, evaluated at CAC. The values of A_{min} as predicted by the Langmuir and Frumkin model are compared with the values of A_{min} obtained from neutron reflectivity measurements for $C_{12}E_4$, $C_{12}E_6$, $C_{12}E_8$ and $C_{12}E_{12}$ (Table 4.3). The values of A_{min} predicted by the Langmuir model are much larger than the values obtained from the neutron reflectivity measurements. On the other hand, the predictions of the Frumkin model are in excellent agreement with the values obtained from the neutron reflectivity measurements. In conclusion, the Langmuir model does not accounts for the interactions among the surfactant molecules adsorbed on the air-water interface. The interactions among the trisiloxane and alkyl poly-ethoxylate surfactant, adsorbed on air-water interface are significant. As a results, the Langmuir model does not agree with all the experimental data. In comparison, the Frumkin model, which takes into account the intermolecular interaction, is able to describe all the experimental data to a very large accuracy, and agrees well with the results obtained from other techniques.

4.5.3 Maximum Packing of Surfactant at the Air-Water Interface

The maximum packing of a surfactant adsorbed on the air-water interface is the interfacial area occupied by the surfactant molecule at the CAC. It is the inverse of the surface concentration (Γ_{CAC}) at the CAC. The value of Γ_{CAC} is evaluated by numerically solving the Frumkin adsorption isotherm, with values of model parameter taken from

Table 4.1. The values of the maximum packing or the minimum area per molecule (A_{min}) for the trisiloxane and the alkyl poly-ethoxylate surfactants are shown in Table 4.3. The maximum packing is not the inverse of Γ_{∞} . For example, in case of $C_{12}E_6$, $1/\Gamma_{\infty}$ is $47.7 \text{ \AA}^2/\text{molecule}$, compared to the packing at CAC ($1/\Gamma_{CAC}$), which is $56 \text{ \AA}^2/\text{molecule}$. The values of A_{min} for the alkyl poly-ethoxylate surfactants¹²², obtained using neutron reflectivity measurements are also shown in Table 4.3.

For the alkyl poly-ethoxylate surfactants (C_iE_j), it is well known that A_{min} increases with an increase in the number of the ethoxylate groups(j)¹². A large amount of literature is available on this subject. This literature has been reviewed recently^{122,125}. On the other hand, A_{min} decreases with an increase in the hydrocarbon chain length, because of the increased cohesion between the hydrocarbon chains. The values of A_{min} for $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$ are 38, 56, and $64.9 \text{ \AA}^2/\text{molecule}$, respectively. There is a very large effect of the number of ethoxylate units (j) on the value of A_{min} for $C_{12}E_j$. In comparison, there is little effect the value of j on A_{min} for the trisiloxane surfactants. The values of A_{min} for $M(D'E_4OH)M$ and $M(D'E_8OH)M$ are 53.4 and $54.3 \text{ \AA}^2/\text{molecule}$, respectively. The value of A_{min} for $M(D'E_4OH)M$ and $M(D'E_8OH)M$ are almost equal to the cross section area of the trisiloxane group ($\sim 52 \text{ \AA}^2$ calculated using Chem3D® software). The value of A_{min} for $M(D'E_4OH)M$ and $M(D'E_8OH)M$ is also close to the value of A_{min} for $C_{12}E_6$. The value of A_{min} for $M(D'E_{12}OH)M$ is $69.2 \text{ \AA}^2/\text{molecule}$, suggesting that the packing of the trisiloxane surfactants reduces slightly when the number of ethoxylate units is increased from eight to twelve, still $M(D'E_{12}OH)M$ packs more densely than $C_{12}E_{12}$.

An illustration, comparing $M(D'E_4OH)M$ and $C_{12}E_8$ adsorbed on the air-water interface at their maximum packing, is shown in Figure 4.11. The trisiloxane surfactants are packed on the interface to their physically maximum possible packing, which is the cross sectional area of the trisiloxane group. It is physically impossible to increase the packing further, as because of the steric effects. The air-water interface is fully covered by the trisiloxane hydrophobic groups, leaving negligible air-water contact. As a result most of the water molecules which are present on clean air-water interface are replaced by the trisiloxane surfactants. This result is also supported by the fact that the surface energy of low molecular weight poly-dimethylsiloxanes (PDMS) is approximately $\sim 20 \text{ mN/m}^{63}$, which is close to the minimum surface tension of the trisiloxane surfactant solutions. The trisiloxane group is essentially a low molecular weight PDMS, with three siloxane groups. In the case of the $C_{12}E_8$, the value of A_{min} is $64.9 \text{ \AA}^2/\text{molecule}$, whereas the cross sectional area of the hydrocarbon chain is approximately $20 \text{ \AA}^2/\text{molecule}$. This implies that in the case of $C_{12}E_8$, even at the maximum packing, a large fraction of the interfacial water is still in contact with air. As we will show in the next section, that denser packing of the trisiloxane surfactants is due to the ability of the trisiloxane hydrophobe to replace water molecules present on the air-water interface.

4.5.4 Adsorption and Desorption Rate Coefficients

In the Frumkin model, the adsorption rate constant is given by $\beta\Gamma_\infty$, which is equal to $\beta' \exp(-E_A^0 / RT)$, where β' is proportional to the collision frequency of the adsorption. The value of β' may vary with the molecular weight, but this variation can be assumed to be small⁶⁵. Therefore, any variations in the value of $\beta\Gamma_\infty$ are suggestive of

changes in E_A^0 . The values of $\beta\Gamma_\infty$ for the trisiloxane and alkyl poly-ethoxylate surfactants are shown in Table 4.4. These are calculated from the Frumkin adsorption coefficients as shown in Table 4.1. The values of $\beta\Gamma_\infty$ for $C_{12}E_4$, $M(D'E_4OH)M$, $C_{12}E_8$, $M(D'E_8OH)M$ and $M(D'E_{12}OH)M$ are 5.37×10^{-5} , 0.96×10^{-5} , 3.19×10^{-5} , 1.63×10^{-5} , and 2.4×10^{-5} m/sec respectively (Table 4.4). These values are of the same order of magnitude, though there are small differences. The adsorption rate constant of $M(D'E_4OH)M$ is less than that of $C_{12}E_4$. Similarly, the adsorption rate constant of $M(D'E_8OH)M$ is also slightly less than that of $C_{12}E_8$. These small differences can be attributed to the peculiar structure of the trisiloxane surfactant molecules. As the number of ethoxylate groups (j) in the trisiloxane surfactants increases, the adsorption rate constant ($\beta\Gamma_\infty$) increases. The ratio of the $\beta\Gamma_\infty$ for the $M(D'E_jOH)M$ and $C_{12}E_j$ (for same j) seems to approach one on increasing the value of j . This suggests that an increase in the number of ethoxylate groups, diminishes the effect of the structure of the hydrophobic group on the value of $\beta\Gamma_\infty$.

Pan et al⁶⁵ have suggested that for the C_iE_j surfactants ($i > 10$), the negative free energy change associated with the removal of the hydrophobe from water can adequately compensate for the energy required for breaking hydrogen bonds, which are destroyed in order to accommodate the surfactant on the air-water interface. Therefore, there is no activation energy of adsorption, i.e. $E_A^0 = 0$. The values of the adsorption rate constant $\beta\Gamma_\infty$ for $M(D'E_jOH)M$ and $C_{12}E_j$ are of the same order of magnitude, suggesting that the trisiloxane surfactants also do not face any adsorption activation energy barrier, i.e. $E_A^0(M(D'E_jOH)M) \approx E_A^0(C_{12}E_j) \approx 0$.

The expression of the desorption rate constant in the Frumkin model is: $\alpha' \exp(-E_D / RT) = \alpha' \exp(-E_D^0 / RT + K\Gamma / \Gamma_\infty)$, where α' is proportional to the

molecular desorption frequency. E_D^0 is the activation energy of desorption at infinite dilution ($\Gamma \rightarrow 0$). For positive values of K , the net activation energy for desorption (E_D) decreases with Γ . The desorption rate at dilute concentrations ($\Gamma/\Gamma_\infty \rightarrow 0$) is equal to α ($=\alpha' \exp(-E_D^0 / RT)$). The values of α for $C_{12}E_4$, $C_{12}E_8$, $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$ are shown in Table 4.4. There may be some differences in the value of α' for $M(D'E_jOH)M$ and $C_{12}E_j$ depending on their molecular weights. However, these differences can be assumed to be negligible⁶⁵. As a result, the variations in the value of α represent the variations E_D^0 . The value of α also depends on the number of the ethoxylate units (j) in the surfactant molecule.

An important observation is made when the values of α for $M(D'E_jOH)M$ and $C_{12}E_j$, with same j , are compared. The value of α for $C_{12}E_4$ is approximately 140 times larger than that of $M(D'E_4OH)M$. Similarly, the value of α for $C_{12}E_8$ is approximately 14 times larger than the value of $M(D'E_8OH)M$. Compared to this, the ratio of the adsorption rate constant ($\beta\Gamma_\infty$) of $C_{12}E_4$ and $M(D'E_4OH)M$ is approximately 5.5, while this ratio for $C_{12}E_8$ and $M(D'E_8OH)M$ is ~ 1.9 . This suggests that the presence of the trisiloxane hydrophobe in the surfactant affects the desorption rate constant much more than the adsorption rate constant.

The ratio $\alpha/\beta\Gamma_\infty$ can be written as $\alpha / \beta\Gamma_\infty = (\alpha' / \beta') e^{-\Delta G^0 / RT}$, where ΔG^0 , ($=E_D^0 - E_A^0$) is the standard free energy change when a molecule is taken from the surface into the bulk at infinite dilute concentrations ($\Gamma \rightarrow 0$). As mentioned earlier, the values of α' , and β' for $C_{12}E_j$ and $M(D'E_jOH)M$ can be assumed to be the same. Thus, the differences in the value of $\alpha/\beta\Gamma_\infty$ represent the differences in value of ΔG^0 . As mentioned previously, $E_A^0 (M(D'E_jOH)M) \approx E_A^0 (C_{12}E_j) \approx 0$. Therefore, $\Delta G^0 \approx E_D^0$. By comparing

the values of α for $C_{12}E_j$ and $M(D'E_jOH)M$ it is clear that it is more difficult to desorb a trisiloxane surfactant from the surface into the bulk. There is a larger increase in (positive) free energy required to take a trisiloxane surfactant molecule from the surface into the bulk. This free energy change can be estimated for linear alkyl chains. As mentioned in Section 4.2, two main factors contribute to this free energy change, which provides the necessary driving force for adsorption. The first factor ($\Delta G''_{(1)}$), is associated with the water molecules, which are required to replace the interface area vacated by the surfactant molecule on its desorption. The second factor, ($\Delta G''_{(2)}$), is associated with the water molecules, which are required to structure around the hydrophobic part, when the surfactant molecule is forced into the bulk. The value of $\Delta G''_{(2)}$ has been estimated for CH_2 and CH_3 groups present in the hydrocarbon chain of the alkyl poly-ethoxylate surfactants. Using these values ($1.1RT$ and $3.3RT$ for CH_2 and CH_3 respectively) for eleven CH_2 and one CH_3 , $\Delta G''_{(2)}$ for $C_{12}H_{25}$ is $15.4RT$. The value of $\Delta G''_{(2)}$ for the trisiloxane hydrophobic group is not available in literature. However, it can be estimated from the product of interfacial energy and the area of the molecule when exposed to solvent or air^{124,131,132}. The interfacial energy of the trisiloxane group in contact with air can be taken to be the surface energy of PDMS ($\sim 20 \text{ mN/m}^{63}$). When the trisiloxane group is forced in water, its interfacial energy can be approximated to be $\sim 45 \text{ mN/m}$ (PDMS-water interfacial energy). The area of the trisiloxane group, which is accessible to the solvent is estimated to be $\sim 120 \text{ \AA}^2$ (using Chem3D®). As a result the free energy required for bringing the trisiloxane group from surface (in contact with air) to water, is $\approx (45 - 20) \text{ mN/m} * 120 \text{ \AA}^2$, which is $\sim 7.24RT$. In addition there are three CH_2 groups between the trisiloxane group and the poly-ethoxylate chain (Figure 1.1), which

contribute $\approx 3.3RT$. Thus, $\Delta G_{(2)}^0(M(D')M) \approx 10.54RT$. The value of $\Delta G_{(1)}^0$ can also be estimated for the hydrophobic group for the trisiloxane and alkyl poly-ethoxylate surfactants. The surface area vacated by the hydrophobe has to be replaced by water molecules, thereby forming a new air-water interface. The free energy required for this process can be estimated from the cross section area of the hydrophobe, multiplied by the surface energy of air-water interface. It was mentioned in Section 4.5.3 that the area of cross-section of hydrocarbon chain is much smaller than the packing of the surfactant molecule, suggesting that $\Delta G_{(1)}^0(C_{12}E_j) \approx 0$. However, for the trisiloxane group, this contribution is not insignificant, because of the "T" structure with a much larger cross-section area of the trisiloxane group (Figure 4.11). The cross-section area of the trisiloxane group is $\sim 52\text{\AA}^2$ (Figure 4.11). Thus, $\Delta G_{(1)}^0(M(D')M) \approx 52\text{\AA}^2 \cdot 72\text{mN/m}$ per molecule $\approx 9RT$. Therefore, the value of $\Delta G^0 (= \Delta G_{(1)}^0 + \Delta G_{(2)}^0)$ for the trisiloxane hydrophobe and $C_{12}H_{25}$ chain are $\sim 19.54RT$ and $15.4RT$, respectively. The difference in the value of ΔG^0 for the trisiloxane surfactant's hydrophobic group and $C_{12}H_{25}$ is $\sim 4.1RT$, which can account for a factor of ~ 60 ($= e^{4.1}$) in the ratio of the values of α for the trisiloxane and $C_{12}E_j$ surfactants. This value is in excellent agreement with the ratio of experimentally observed values of α for $C_{12}E_j$ and the trisiloxane surfactants (14 to 140, see Table 4.4).

The value of ΔG^0 signifies the driving force of adsorption which compels the surfactant to adsorb from the bulk to the interface. The trisiloxane surfactants have larger driving force to adsorb on the air-water interface than the $C_{12}E_j$ surfactants. This is a result of the peculiar "T" shape structure of the trisiloxane hydrophobe. The repulsion between the poly-ethoxylate chains can limit the maximum packing, as in case of alkyl

poly-ethoxylate surfactants (Table 4.3). However, in case of the trisiloxane surfactants, the additional driving force for adsorption (i.e. larger $\Delta G''$) compensates for the repulsion among the poly-ethoxylate chains. As a results, the trisiloxane surfactants pack much more densely (limited by the size of the trisiloxane hydrophobe) than the corresponding alkyl poly-ethoxylate surfactants. Consequently, the trisiloxane surfactants reduce the air-water surface tension to values as low as 21mN/m.

4.5.5 Comparison of the Dynamic Surface Tension of the Trisiloxane and the Alkyl poly-ethoxylate Surfactants

The surface activity of a surfactant ($\beta\Gamma_\infty/\alpha$) signifies the ability of a surfactant to absorb on the interface. Higher the surface activity, lower is the bulk concentration required to achieve a certain surface concentration. The values of surface activity of the trisiloxane and $C_{12}E_j$ surfactants are shown in Table 4.4. The surface activity of the trisiloxane surfactants is 8 to 26 times more than the corresponding $C_{12}E_j$ surfactants. As a result, the trisiloxane surfactants achieve a certain surface concentration at lower bulk concentration. The higher surface activity of the trisiloxane surfactants is due to lower values of α . It is not obvious how and why the dynamic surface tension behavior can be affected by the desorption coefficient and surface activity of the surfactant. To demonstrate this, we have chosen two surfactants, $M(D'E_8OH)M$ and $C_{12}E_6$. These two surfactants are similar in many respects. The respective values of various parameters for $M(D'E_8OH)M$ and $C_{12}E_6$ are - (I) Γ_∞ : 3.25×10^{-6} and 3.48×10^{-6} mol/m², (II) K : 7.26 and 6.65, (III) β : 5 and 4.02 m³/(mol.sec), (IV) D : 11×10^{-10} and 6.4×10^{-10} m²/sec, (V) CAC: 0.07 and 0.09 mol/m³ (VI) A_{min} : 54.3 and 56 Å²/molecule. The values of adsorption rate

constants ($\beta\Gamma_\infty$) are close to each other. However, the desorption coefficient of these two surfactants are different from each other (see Table 4.4). Using the values of K and Γ_∞ , the equations of state for $M(D'E_8OH)M$ and $C_{12}E_6$ are generated. These plots are shown in Figure 4.12. The equation of states for $C_{12}E_6$ and $M(D'E_8OH)M$ are very close to each other, implying that the same amount of adsorbed surfactant produces almost identical reduction in the surface tension, especially at low surface concentrations. We have carried out the simulations of a spherical air bubble, created in the solutions of these two surfactants, at time, $t=0$ (as described in the Section 4.4.3). The bulk concentration (C_0) of both the surfactants are taken to be 0.0004 mol/m^3 . The values of C_0/a for $C_{12}E_6$ and $M(D'E_8OH)M$ are 11.4 and 102 respectively. Therefore, the assumption of $C_0/a \gg 1$ is valid in Equation 4.7. The values of Φ^2 for $C_{12}E_6$ and $M(D'E_8OH)M$ at this concentration are 189 and 120 respectively. Therefore, we can use the diffusion-controlled (DC) model for the simulations of $\gamma(t)$, $\Gamma(t)$, and $C_s(t)$. The results of $\Gamma(t)$, $\gamma(t)$, and $C_s(t)$ are shown in Figures 4.13, 4.14, and 4.15, respectively.

The $C_s(t)$ for $C_{12}E_6$ and $M(D'E_8OH)M$ (Figure 4.15) are almost identical. But $\Gamma(t)$ (Figure 4.13) and $\gamma(t)$ profiles (Figure 4.14) for the two surfactants are very different from each other. The value of $\Gamma(t)$ of $M(D'E_8OH)M$ at any time is higher than that of $C_{12}E_6$, even though the sub-layer concentrations, $C_s(t)$, are almost the same. This is a result of higher surface activity of $M(D'E_8OH)M$ compared to $C_{12}E_6$. The equations of states of the two surfactants are similar. As result, the surface tension of $M(D'E_8OH)M$ is lower than the surface tension of $C_{12}E_6$ at any time and $M(D'E_8OH)M$ shows a faster reduction in the dynamic surface tension. From these simulations, we conclude that the faster reduction in the dynamic surface tension of $M(D'E_8OH)M$ is not a result of faster

adsorption rate or faster diffusion coefficient. Instead, this is a result of higher surface activity of the trisiloxane surfactants.

In the Introduction (Section 4.1), we described that the ability of a surfactant to rapidly reduce the surface tension, affects the spreading behavior of a drop in impact experiments (Figure 1.2). In a similar fashion, spreading of a water drop containing surfactants and driven by Marangoni flow, depends on the ability of the surfactant to rapidly reduce the air-water surface tension. The trisiloxane surfactants have exceptional ability to rapidly reduce the surface tension to very low values. Therefore, they are expected to have much better spreading ability in drop impact as well as Marangoni driven spreading.

4.6 Conclusion.

In this work, we have used a pendant bubble technique to measure the equation of state, and other adsorption parameters for the trisiloxane surfactants $M(D'E_4OH)M$, $M(D'E_8OH)M$, and $M(D'E_{12}OH)M$. The kinetic parameters of the Frumkin adsorption model are obtained from the dynamic and equilibrium surface tension measurements. The exceptional abilities of the trisiloxane surfactant at the air water interfaces area attributed to their "T" shape trisiloxane hydrophobe. Due to the peculiar structure of their hydrophobe, the trisiloxane surfactants require larger energy to desorb from the surface into the bulk. As a result, They have higher surface activity and lower desorption rate coefficients than the $C_{12}E_j$ surfactants. As a consequence, they pack more densely on the air water interface, thereby reducing the surface tension to much lower values than $C_{12}E_j$ surfactants. The higher surface activity of the trisiloxane surfactants is also manifested in faster reduction in the dynamic surface tensions.

Molecule	C ₁₂ E ₄	C ₁₂ E ₆	C ₁₂ E ₈	C ₁₂ E ₁₂
Min. Surface Tension at CAC, mN/m	29	32	34	38
CAC Mol/m ³	5.0x10 ⁻²	6.8x10 ⁻²	10.2x10 ⁻²	12.5x10 ⁻²
Γ_{∞} Mol/m ²	4.88x10 ⁻⁶	3.48x10 ⁻⁶	2.66x10 ⁻⁶	
Frumkin Interaction Parameter, K	1.87	6.62	5.19	
Adsorption coefficient, β , m ³ /(mol.sec)	11	4.02	12	
Desorption coefficient, α sec ⁻¹	390x10 ⁻⁵	14.0x10 ⁻⁵	29x10 ⁻⁵	
$a=\alpha/\beta$, mol/m ³	354x10 ⁻⁶	34.9x10 ⁻⁶	24.2x10 ⁻⁶	
Diffusion Coefficient, D m ² /sec	6.4x10 ⁻¹⁰	6.4x10 ⁻¹⁰	11x10 ⁻¹⁰	
Reference:	Hsu et al	Pan et al	Lin	Lu et al
Interaction parameter K/Γ_{∞} m ² /mol	0.417x10 ⁶	1.47x10 ⁶	1.95x10 ⁶	

Molecule	M(D'E ₄ OH)M	M(D'E ₈ OH)M	M(D'E ₁₂ OH)M
Min. Surface Tension at CAC, mN/m	22	22	23
CAC Mol/m ³	11.0x10 ⁻²	9.1x10 ⁻²	15.2x10 ⁻²
Γ_{∞} Mol/m ²	3.20x10 ⁻⁶	3.25x10 ⁻⁶	2.40x10 ⁻⁶
Frumkin Interaction Parameter, K	5	7.26	10
Adsorption coefficient, β , m ³ /(mol.sec)	3	5	10
Desorption coefficient, α sec ⁻¹	2.7x10 ⁻⁵	1.95x10 ⁻⁵	0.29x10 ⁻⁵
$a=\alpha/\beta$, mol/m ³	9.16x10 ⁻⁶	3.9x10 ⁻⁶	0.29x10 ⁻⁶
Diffusion Coefficient, D m ² /sec	11x10 ⁻¹⁰	11x10 ⁻¹⁰	11x10 ⁻¹⁰
Reference:	Present work	Present work	Present work
Interaction parameter K/Γ_{∞} m ² /mol	1.56x10 ⁶	2.23x10 ⁶	4.16x10 ⁶

References: Hsu et al⁶⁷, Pan et al⁶⁵, Lin et al⁶⁸, Lu et al¹²²

Table 4.1: Frumkin model parameters for trisiloxane and alkyl poly-ethoxylate surfactants

Plot #	M(D'E ₄ OH)M				M(D'E ₈ OH)M			
	C_R	C_0/a	Φ^2	Transport Regime	C_R	C_0/a	Φ^2	Transport Regime
1	0.00239	29	106.2	DC	0.00048	11	1100.3	DC
2	0.00343	42	74.1	DC	0.00490	114	107.7	MDC
3	0.00522	64	48.6	MDC	0.00917	214	57.5	MDC
4	0.00941	115	27.0	MDC	0.02311	539	22.8	MDC
5	0.03746	458	6.8	MDC	0.03787	884	13.9	MDC
6	0.14188	1734	1.8	MDC	0.17547	4094	3.0	MDC

Plot #	M(D'E ₁₂ OH)M			
	C_R	C_0/a	Φ^2	Transport Regime
1	0.00033	174	1037.0	DC
2	0.00079	412	436.8	DC
3	0.00413	2158	83.4	DC
4	0.00971	5073	35.5	MDC
5	0.01918	10020	18.0	MDC
6	0.03462	18085	9.9	MDC

DC : Diffusion controlled adsorption

MDC : Mixed diffusion-kinetic controlled adsorption

C_0 : Bulk concentration

C_R : Reduced concentration = C_t/CAC

a : Surface activity coefficient = α/β

Table 4.2 Value of various coefficients in the dynamic surface tension data for M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M

	Frumkin Model	Langmuir Model	Neutron Reflectivity Measurements
$C_{12}E_4$	38 †	62 †	44±3 #
$C_{12}E_6$	56 ⊕	68 ⊕	55±3 #
$C_{12}E_8$	64.9 ††	81.2 ††	62±3 #
$C_{12}E_{12}$	-	85.2 #	72±3 #
$M(D'E_4OH)M$	53.4	66 *	-
$M(D'E_8OH)M$	54.3 *	70.6	-
$M(D'E_{12}OH)M$	69.2 *	84.2 *	-

References: *: This work; †: Hsu et al⁶⁷; †† :Lin et al⁶⁸; #: Lu et al¹²²; ⊕ Pan et al⁶⁵

Table 4.3. The Maximum packing or the minimum area per unit molecule(A_{min} , Å²/molecule) evaluated at the critical aggregation concentration

	Desorption rate, α , sec ⁻¹	Adsorption rate constant $\beta\Gamma_{\infty}$ m.sec ⁻¹	$\alpha/\beta\Gamma_{\infty}$ m ⁻¹	Surface Activity $1/(\alpha/\beta\Gamma_{\infty})$, m
C₁₂E₄	390x10⁻⁵	5.37x10⁻⁵	72.7	0.013
C₁₂E₆	14x10⁻⁵	1.x10⁻⁵	10	0.10
C₁₂E₈	29x10⁻⁵	3.19x10⁻⁵	9.09	0.11
M(D'E₄OH)M	2.7x10⁻⁵	0.96x10⁻⁵	2.81	0.35
M(D'E₆OH)M	1.95x10⁻⁵	1.63x10⁻⁵	1.2	0.83
M(D'E₁₂OH)M	0.29x10⁻⁵	2.4x10⁻⁵	0.12	8.3

Table 4.4. Kinetic rate constants.

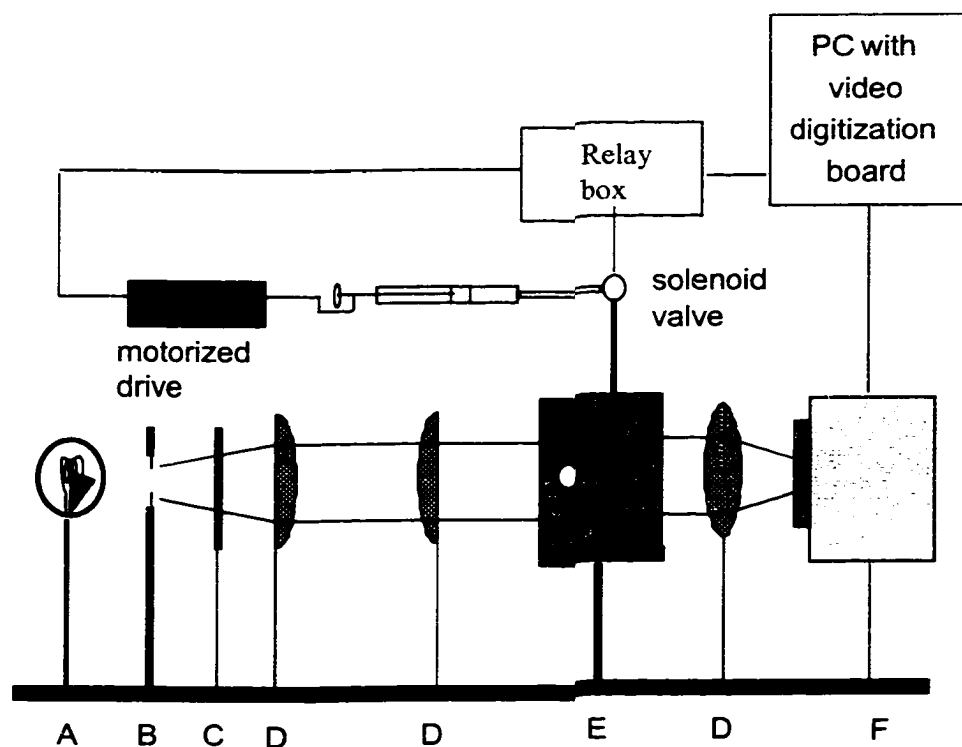


Figure 4.1: Apparatus for pendant bubble shape technique: (A) light source, (B) pin hole, (C) filter, (D) lens, (E) cuvette, (F) video camera

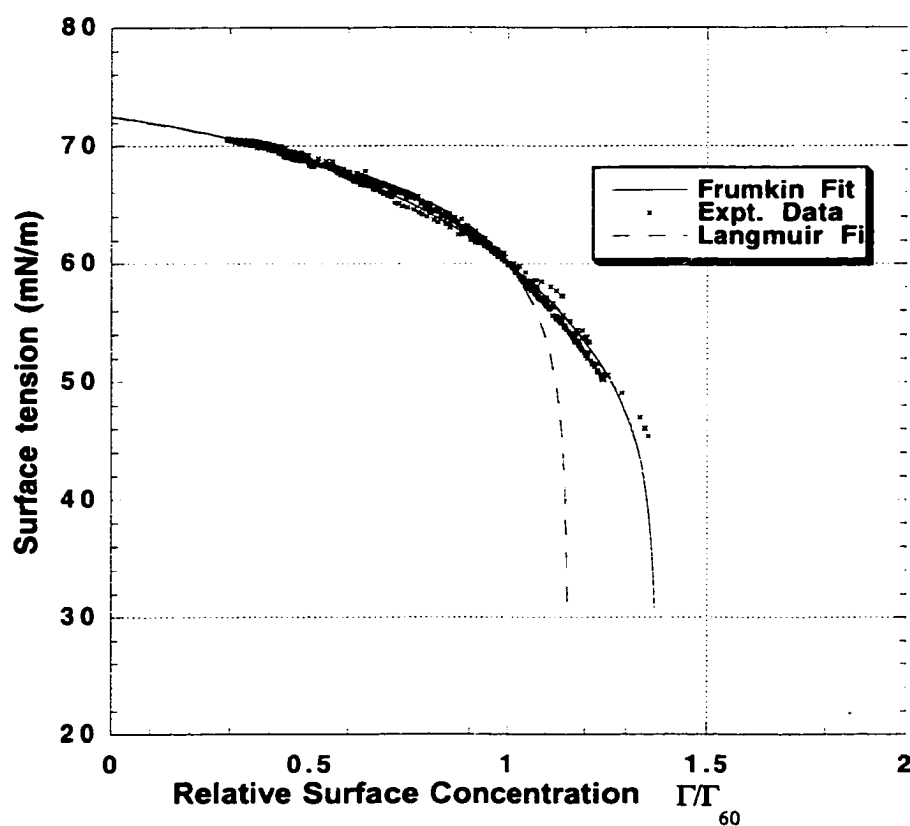


Figure 4.2: Surface tension vs. relative surface concentration ($\Gamma_{rel} = \Gamma/\Gamma_{60}$) for M(D'E₄OH)M. Parameters for the Frumkin model: $\Gamma_{\infty} = 3.2 \times 10^{-6}$ mol/m², $K = 5$; Parameter for the Langmuir model: $\Gamma_{\infty} = 2.5 \times 10^{-6}$ mol/m².

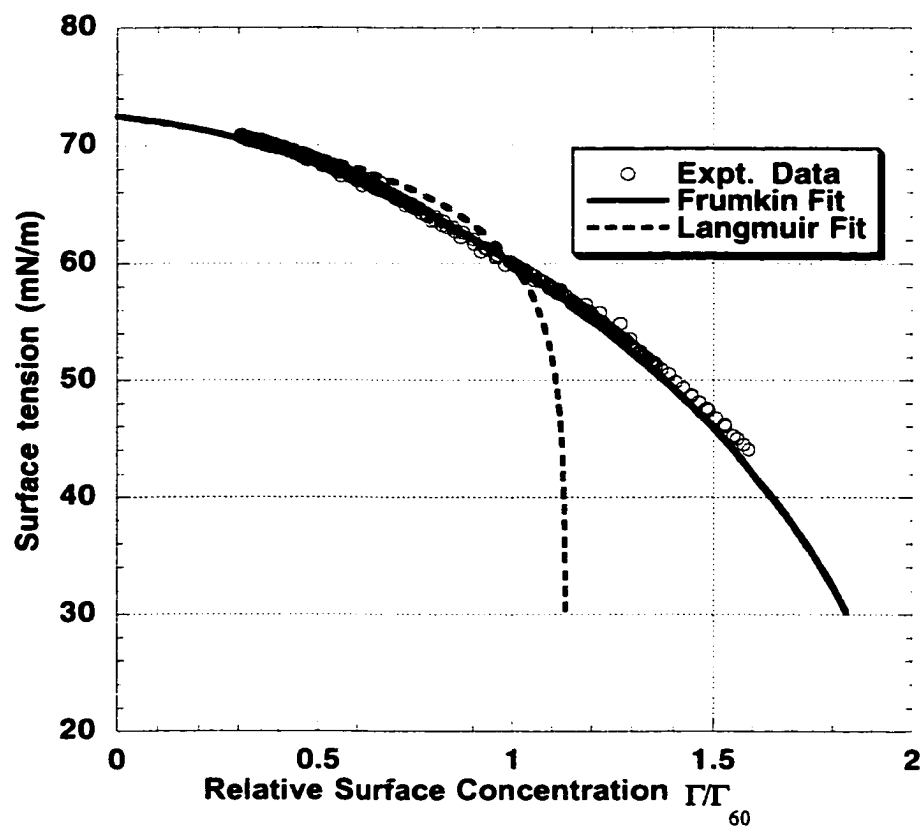


Figure 4.3: Surface tension vs. relative surface concentration ($\Gamma_{rel} = \Gamma/\Gamma_{60}$) for M(D'E₈OH)M. Parameters for the Frumkin equation of state: $\Gamma_{\infty} = 3.25 \times 10^{-6} \text{ mol/m}^2$, $K = 7.26$; Parameter for the Langmuir equation of state: $\Gamma_{\infty} = 2.35 \times 10^{-6} \text{ mol/m}^2$.

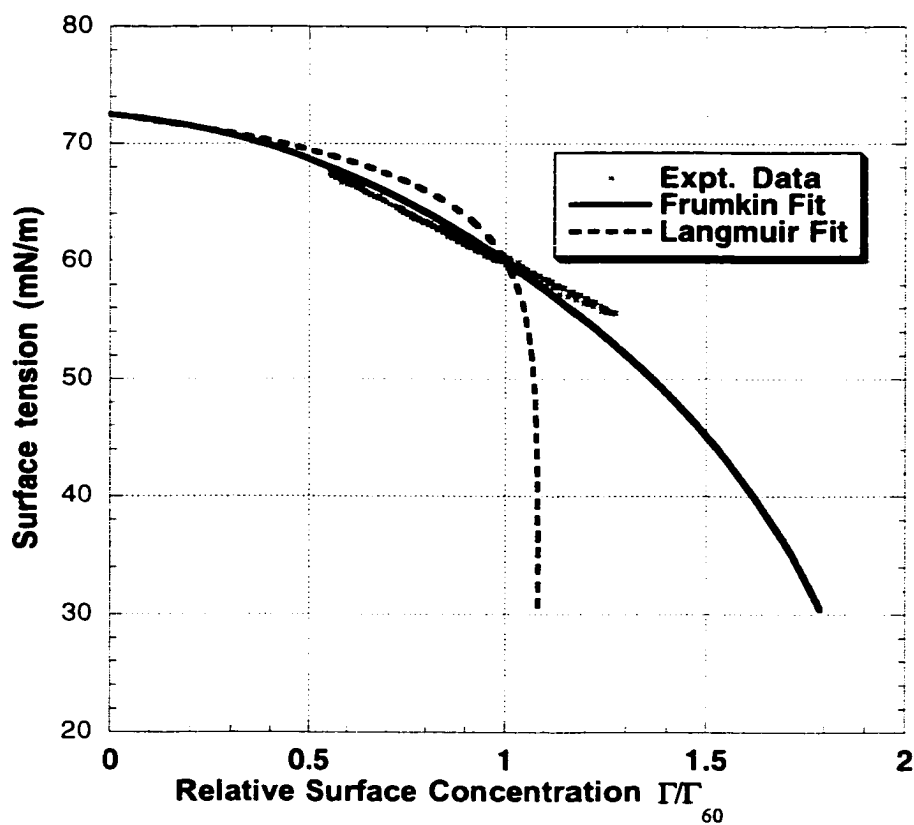


Figure 4.4: Surface tension vs. relative surface concentration ($\Gamma_{rel} = \Gamma/\Gamma_{60}$) for M(D'E₁₂OH)M Parameters for the Frumkin equation of state: $\Gamma_{\infty} = 2.4 \times 10^{-6}$ mol/m², $K = 10$; Parameters for the Langmuir equation of state: $\Gamma_{\infty} = 1.97 \times 10^{-6}$ mol/m².

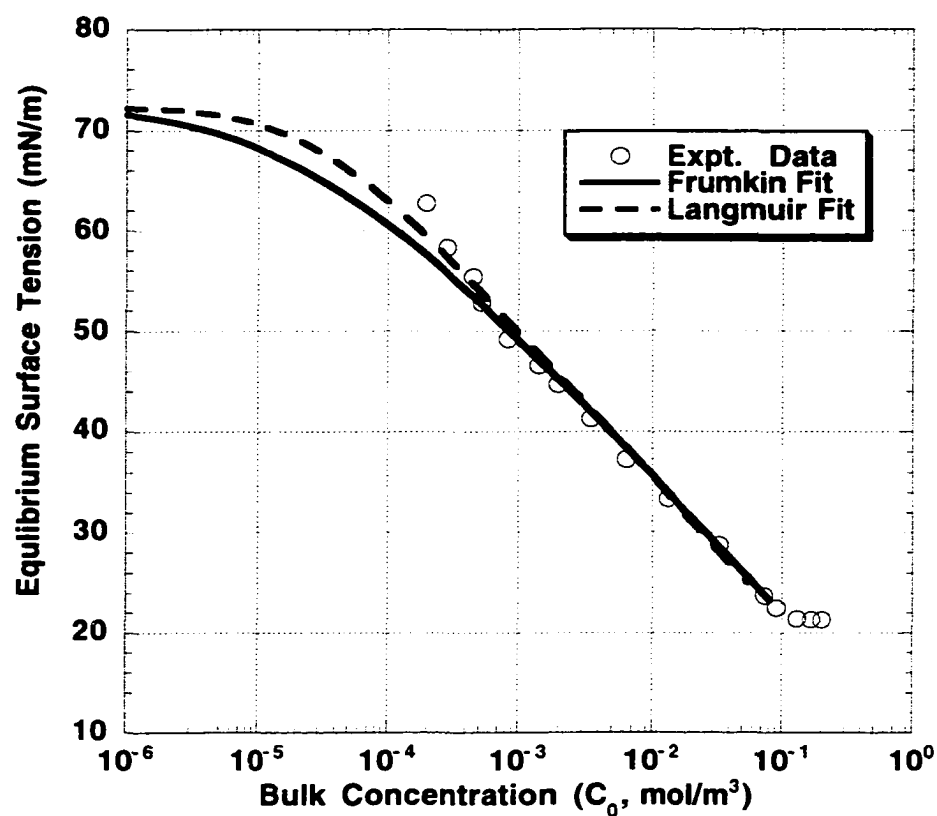


Figure 4.5: Equilibrium surface tension vs. bulk concentration for M(D'E₄OH)M.

Parameters for the Frumkin model: $\Gamma_{\infty} = 3.2 \times 10^{-6}$ mol/m², $K = 5$; $a = \alpha/\beta = 9.1 \times 10^{-6}$ mol/m³. Parameters for the Langmuir model: $\Gamma_{\infty} = 2.5 \times 10^{-6}$ mol/m², $a = \alpha/\beta = 2.8 \times 10^{-5}$ mol/m³.

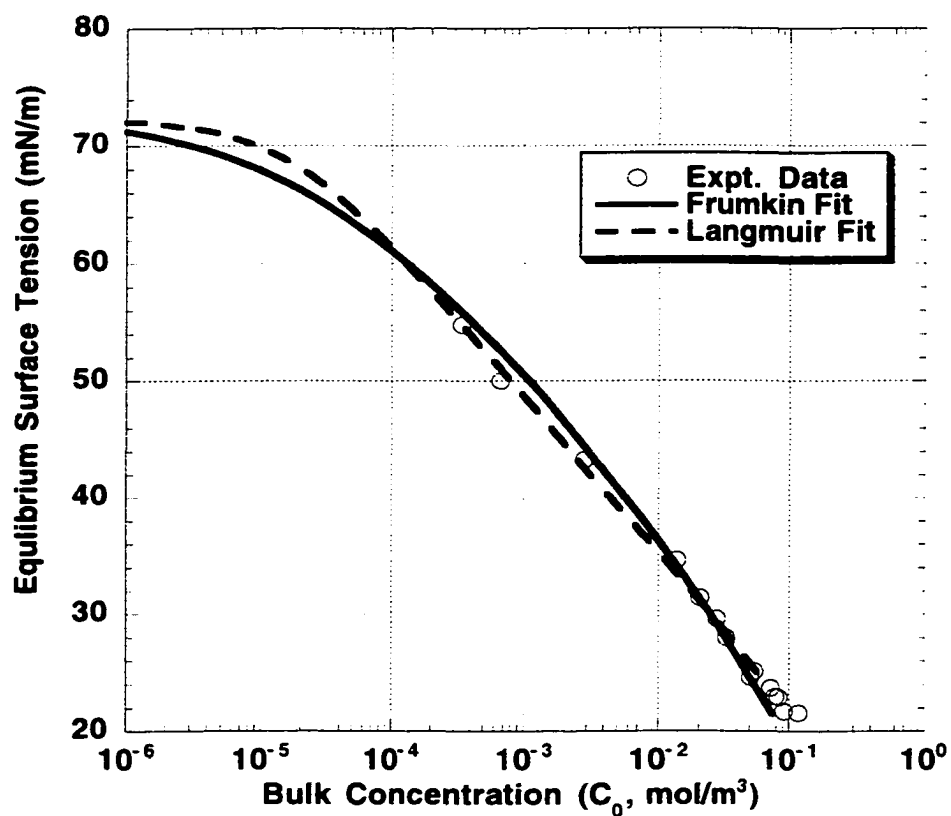


Figure 4.6: Equilibrium surface tension vs. bulk concentration for M(D'E₈OH)M.

Parameters for the Frumkin model: $\Gamma_{\infty} = 3.25 \times 10^{-6}$ mol/m², $K = 7.26$; $a = \alpha/\beta = 3.9 \times 10^{-6}$ mol/m³. Parameters for the Langmuir model: $\Gamma_{\infty} = 2.35 \times 10^{-6}$ mol/m², $a = \alpha/\beta = 1.75 \times 10^{-5}$ mol/m³.

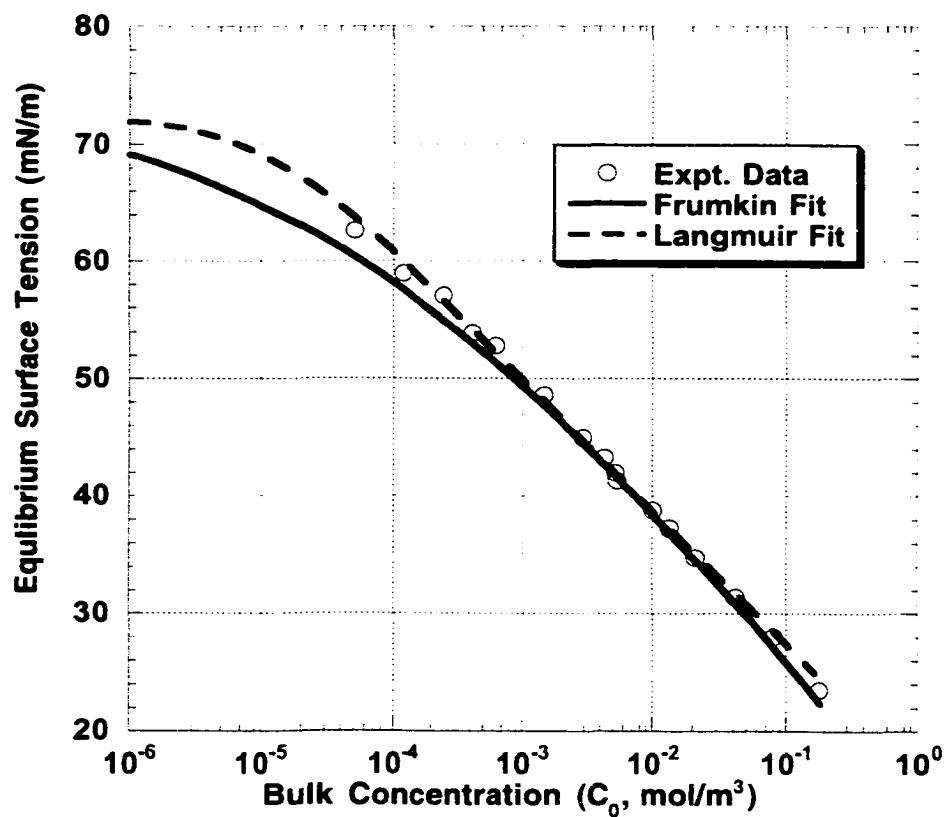


Figure 4.7: Equilibrium surface tension vs. bulk concentration for M(D'E₁₂OH)M. Parameters for the Frumkin model: $\Gamma_\infty = 2.4 \times 10^{-6}$ mol/m², $K = 10$; $a = \alpha/\beta = 0.29 \times 10^{-6}$ mol/m³. Parameters for the Langmuir model: $\Gamma_\infty = 1.97 \times 10^{-6}$ mol/m², $a = \alpha/\beta = 1. \times 10^{-5}$ mol/m³.

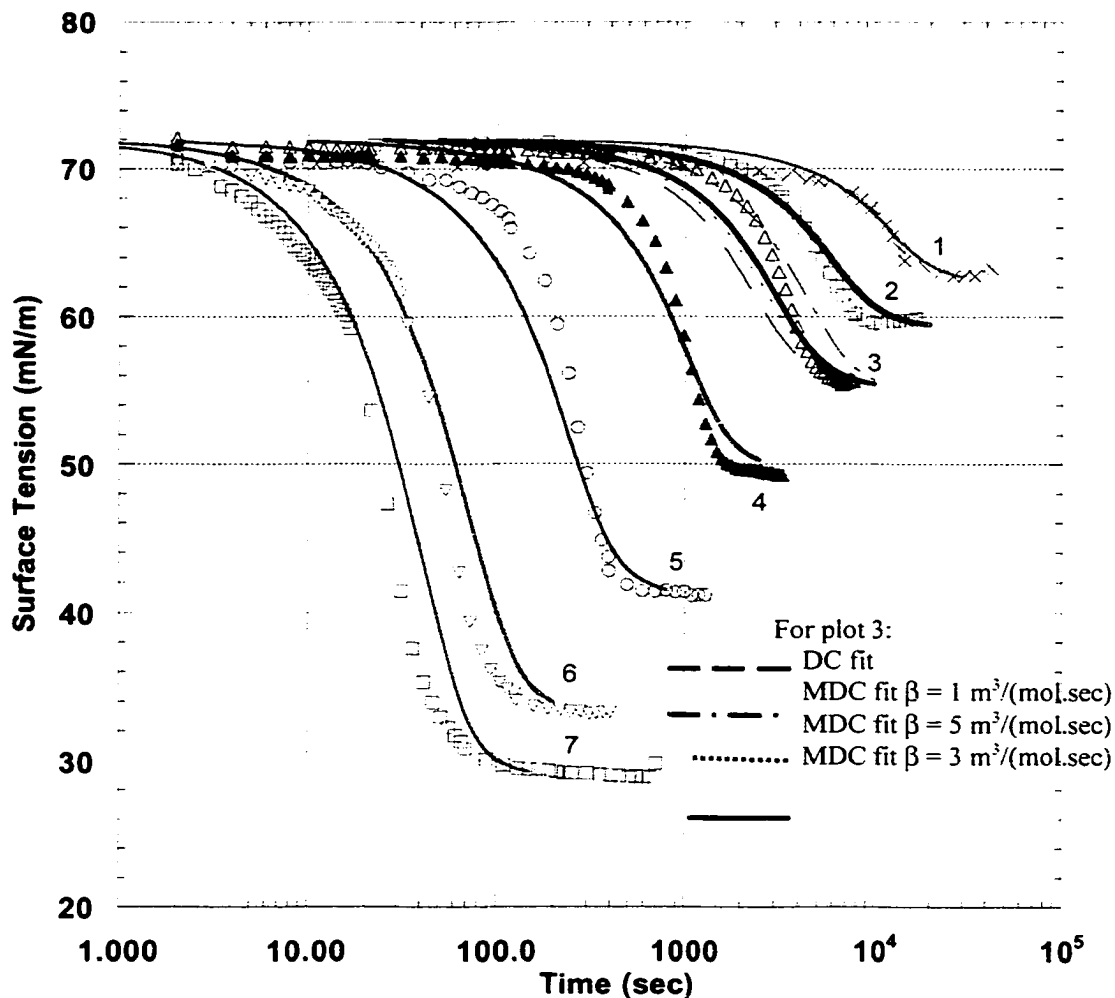


Figure 4.8: Dynamic Surface tension plots for M(D'E₄OH)M at various concentrations, C_R (C_0/CAC). (1) 0.00239, (2) 0.00343, (3) 0.00522, (4) 0.00941 (5) 0.0374, (6) 0.142 (7) 0.358; For all plots $D=11 \times 10^{-10} \text{ m}^2/\text{sec}$; Plots 1 and 2 are fitted using DC simulations. Plots 4 to 7 are fitted using MDC simulations with $\beta = 3 \text{ m}^3/(\text{mol}.\text{sec})$. Plot 3 is simulated by (i) DC (ii) MDC with $\beta = 1 \text{ m}^3/(\text{mol}.\text{sec})$. (iii) MDC with $\beta = 5 \text{ m}^3/(\text{mol}.\text{sec})$ (iv) MDC with $\beta = 3 \text{ m}^3/(\text{mol}.\text{sec})$

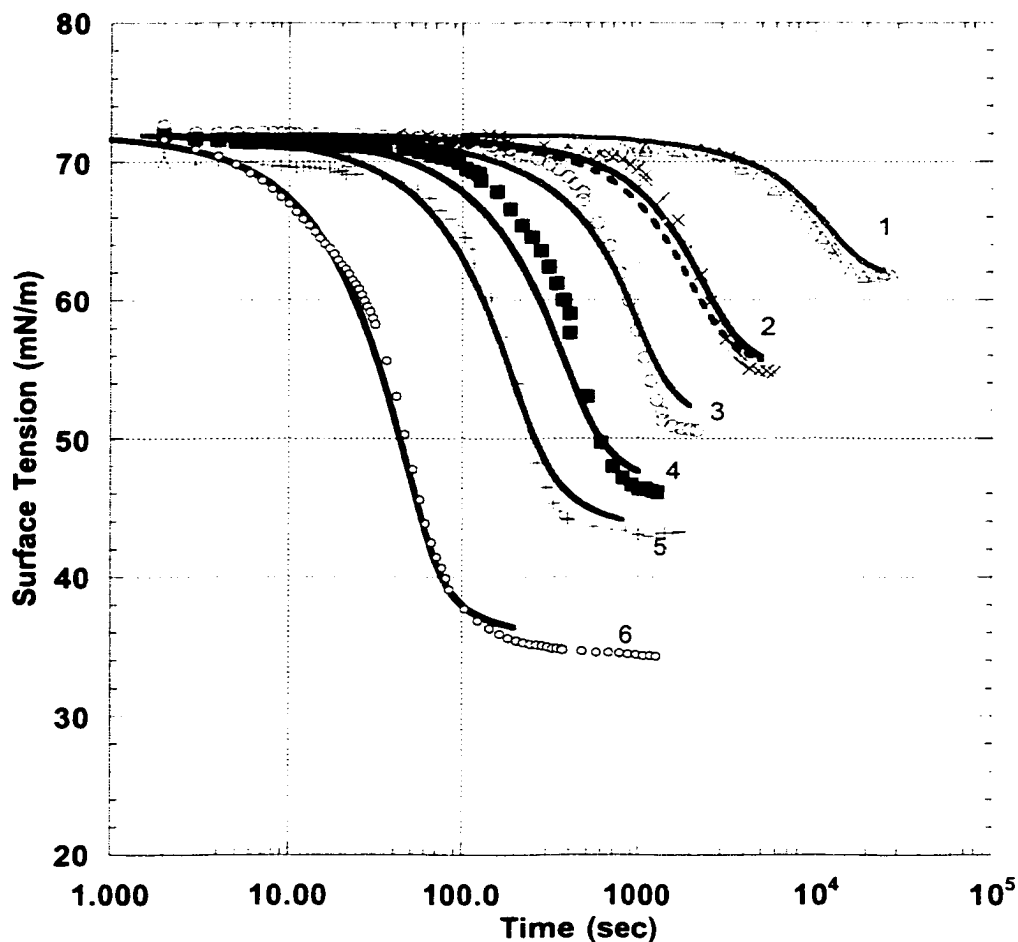


Figure 4.9: Dynamic Surface tension plots for M(D'E₈OH)M at various concentrations, C_R (C_0/CAC). (1) 0.00048 (2) 0.0049, (3) 0.00917, (4) 0.00231 (5) 0.0378, (6) 0.175 ; For all plots $D=11 \times 10^{-10} \text{ m}^2/\text{sec}$; Plots 1 is fitted using DC simulations. Plots 3 to 6 are fitted using MDC simulations with $\beta = 5 \text{ m}^3/(\text{mol}.\text{sec})$. Plot 2 is simulated by (i) DC plotted as dotted line (ii) MDC with $\beta = 5 \text{ m}^3/(\text{mol}.\text{sec})$, plotted as solid line

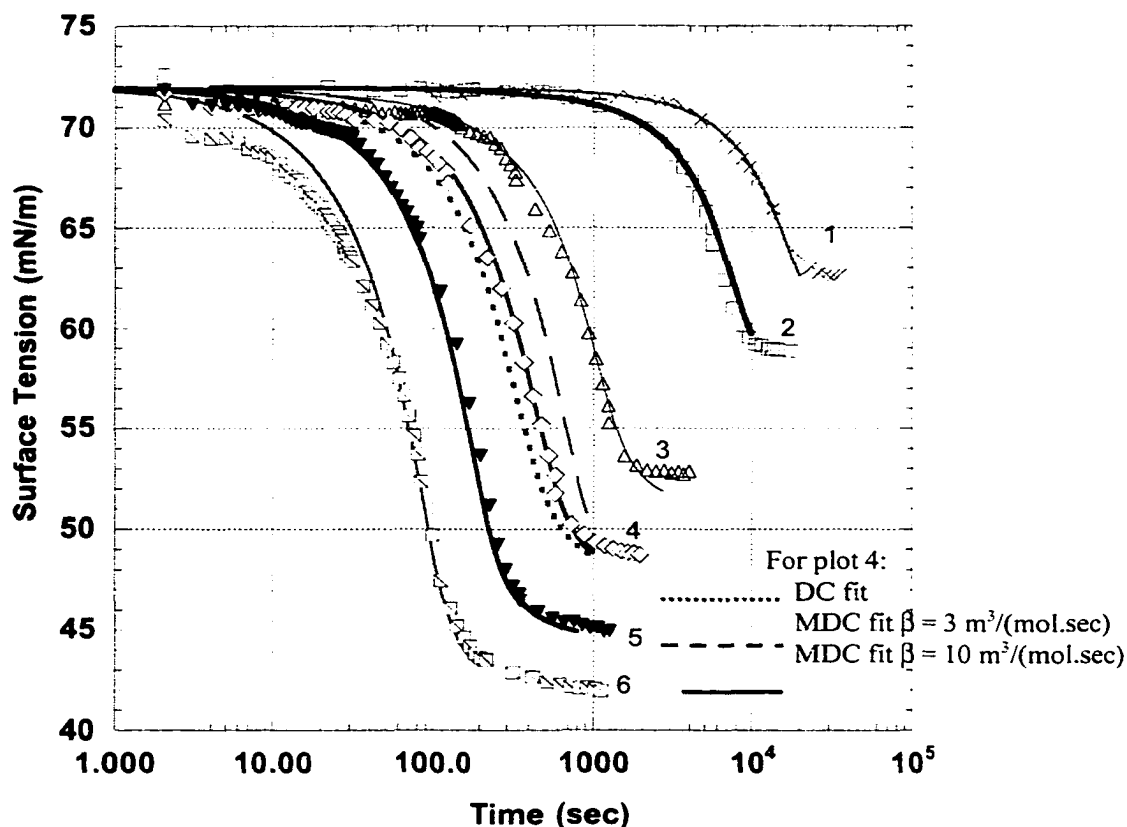


Figure 4.10: Dynamic Surface tension plots for M(D'E₁₂OH)M at various concentrations, C_R (C_0/CAC). (1) 0.00033 (2) 0.00079, (3) 0.00413, (4) 0.00971 (5) 0.0191, (6) 0.0346 ; For all plots $D=11 \times 10^{-10} \text{ m}^2/\text{sec}$; Plots 1,2 and 3 are fitted using DC simulations. Plots 5 and 6 are fitted using MDC simulations with $\beta = 10 \text{ m}^3/(\text{mol}.\text{sec})$. Plot 4 is simulated by (i) DC plotted as dotted line (ii) MDC with $\beta = 3 \text{ m}^3/(\text{mol}.\text{sec})$ and (iii) MDC with $\beta = 10 \text{ m}^3/(\text{mol}.\text{sec})$

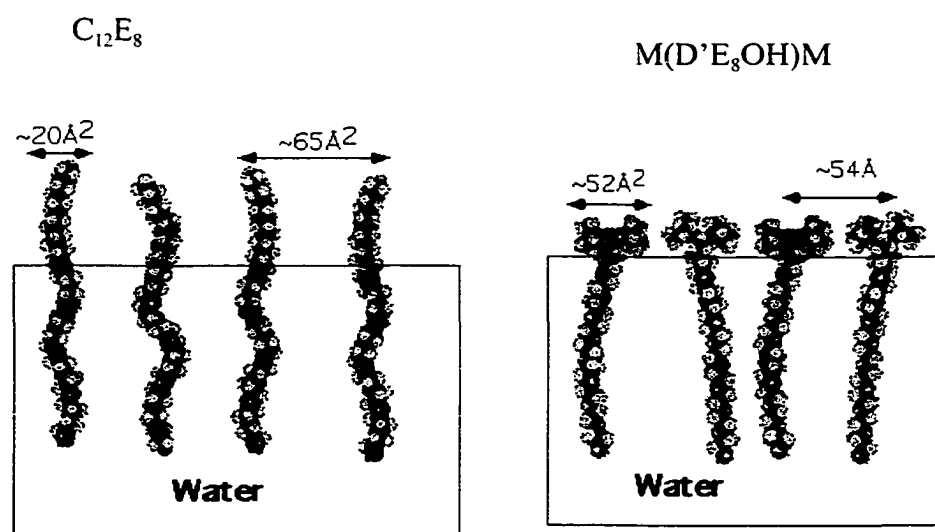


Figure 4.11: An illustration of $M(D'E_8OH)M$ and $C_{12}E_8$ adsorbed on the air-water interface at their maximum packing.

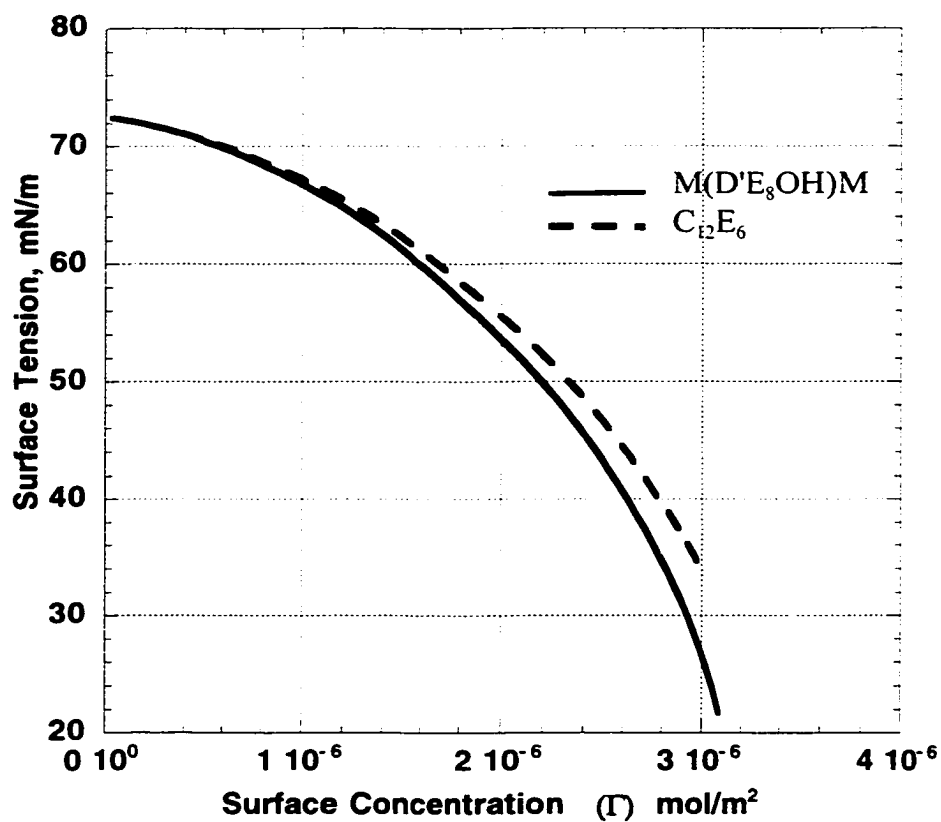


Figure 4.12: Frumkin equation of state for M(D'E₈OH)M and C₁₂E₆.

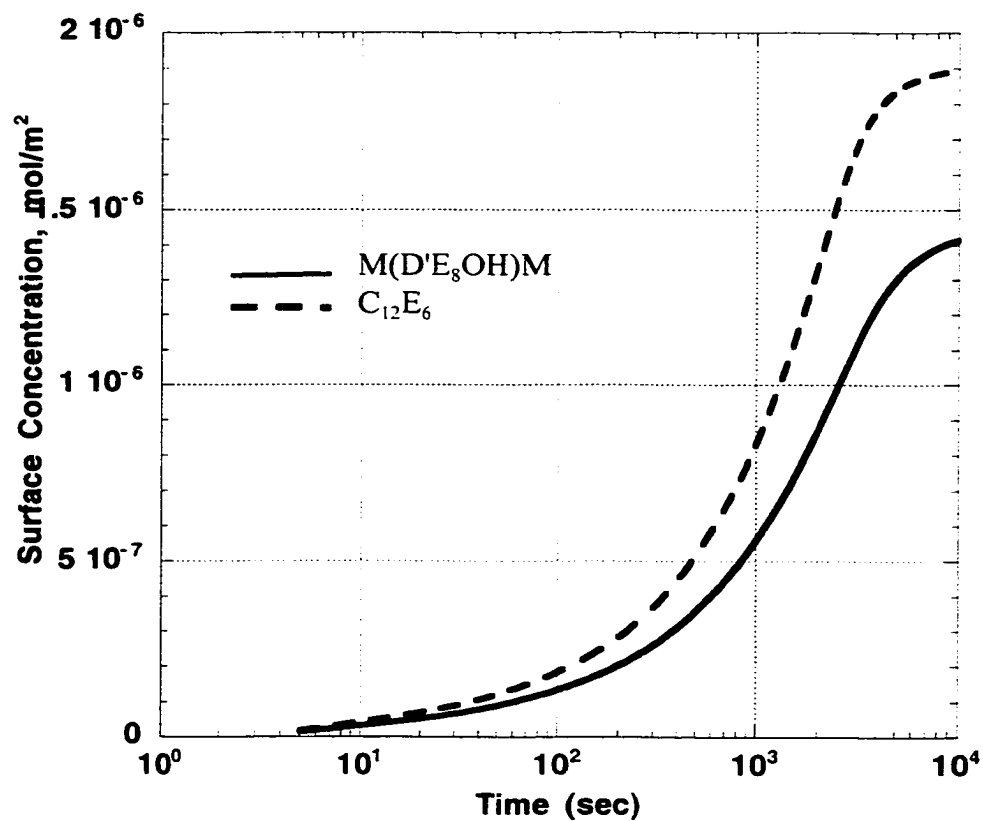


Figure 4.13: Simulated surface concentration profile for a spherical bubble created in 0.0004 mol/m³ surfactant solution.

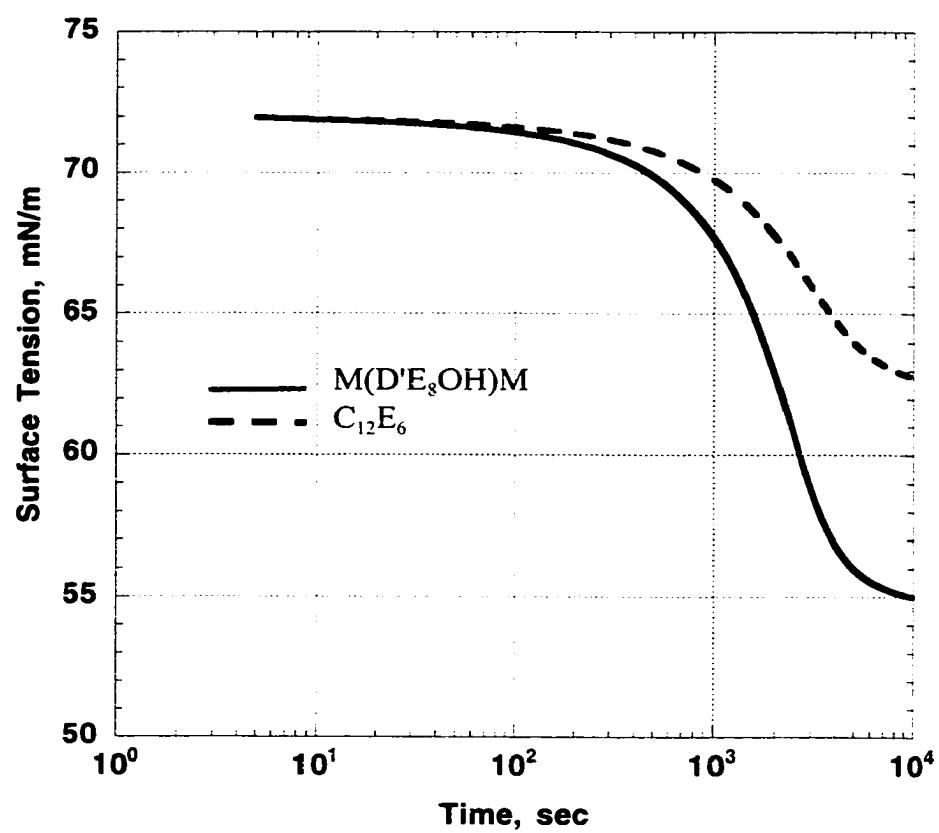


Figure 4.14: Simulated surface tension profile for a spherical bubble created in 0.0004 mol/m³ surfactant solution

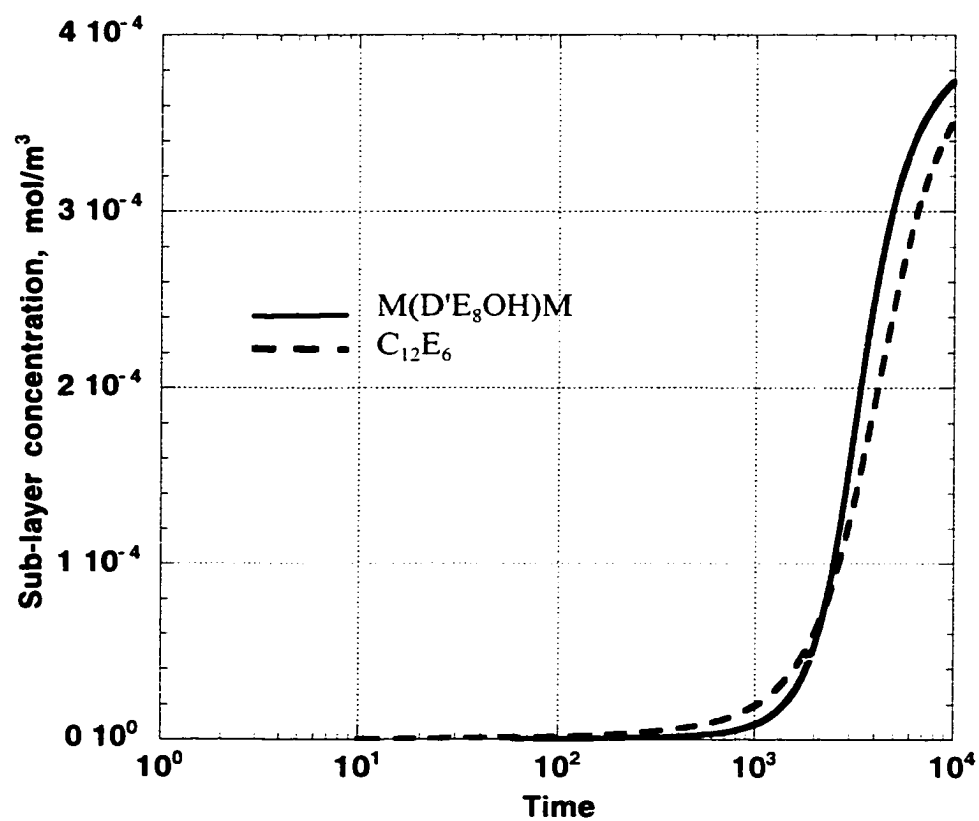


Figure 4.15: Simulated sub-layer concentration profile for a spherical bubble created in 0.0004 mol/m³ surfactant solution

Chapter 5:

A FTIR-ATR Study of Adsorption of Trisiloxane and Alkyl Poly-Ethoxylate Surfactants on Hydrophobic Silane Monolayers: Explanation of Super-spreading Characteristics of Trisiloxane Surfactants

In chapter 2, we described that it is important to study the adsorption the surfactants on hydrophobic solid water interfaces, in order to understand the super-spreading behavior of the trisiloxane surfactants. In this chapter, we investigate the adsorption characteristics of the trisiloxane and the alkyl poly-ethoxylate surfactants using Fourier Transform Infrared (FTIR) Spectroscopy in Attenuated Total internal Refection (ATR) mode.

5.1 Introduction

In comparison to the surfactant adsorption on solid surfaces, the adsorption on air-water interfaces has been extensively studied. The adsorption characteristics of the surfactants on air-water interface, such as, surface concentration, surface activity, dynamic adsorption characteristics, can be obtained from surface tension experiments. In the past few decades, many experimental techniques have been used to study the surfactant adsorption on the air-water interface. These include, neutron reflectivity, ellipsometry, second harmonic and sum frequency generation, Infrared and Raman

spectroscopy, X-ray Reflection, disjoining pressures in thin films, computer simulations etc. Lu et al¹²² have reviewed these techniques.

The literature regarding the surfactant adsorption on the solid water interface is limited compared to the adsorption on the air-water interface. Unlike the measurement on the air-water interface, there are no direct methods to evaluate the surface energies of solid-water interfaces. Contact angle measurements have been extensively used to evaluate the surface energetic and surface concentration on solids surfaces¹³³⁻¹³⁶. Some major limitations of this technique are¹³³ (1) contact angle hysteresis, which is the difference between the advancing and receding contact angle, (2) other data required to evaluate the surface energy and surface concentrations, such as, surface energy of the solid-vapor interface (γ_{sv}), is difficult to obtain, (3) controversy regarding the interpretation of the surface energetic, contact line, (4) limited knowledge of the contact line region. Some other experimental techniques have been developed in last few decades, which directly measure the surfactant concentration on the surface. These include, ellipsometry¹³⁷⁻¹⁴³, neutron reflectivity^{144,145}, FTIR-ATR¹⁴⁶⁻¹⁴⁸, sum-frequency spectroscopy^{149,150}, etc.

Fourier Transform Infrared spectroscopy has the ability to examine matter at molecular scale. In addition to the identification and quantification of chemical species, IR spectroscopy is also used to investigate intermolecular interactions and molecular orientation. FTIR in the ATR mode is very useful and widely used to study interfaces. FTIR-ATR is capable of probing the interfaces from angstrom to micrometer scales. FTIR-ATR is a very versatile technique. This technique has been used to quantify the amount of surfactants adsorbed on surfaces, to study orientation of molecules¹⁵¹ on

surfaces, structure of water near surfaces^{152,153}, interaction of water molecules in polymers¹⁵⁴⁻¹⁵⁶, etc.

The surface concentration and structure of the alkyl poly-ethoxylate surfactants on hydrophobic surfaces has been estimated by neutron reflectivity^{144,145}, ellipsometry^{142,143}, and contact angle^{57,157}. The studies regarding the adsorption of trisiloxane surfactants on hydrophobic solid surfaces are relatively rare. Ananthapadmanabhan et al¹⁰, using solution depletion techniques, estimated the maximum packing of $M(D'E_{7.5}OCH_3)M$ on polyethylene surfaces to be $50 \text{ \AA}^2/\text{molecule}$. Using contact angle, Svitova et al³⁸ estimated the maximum packing of $M(D'E_{12}OH)M$, on a Teflon surface, at CAC, to be $207 \text{ \AA}^2/\text{molecule}$. Using neutron reflectivity, Thritle et al and Fregnato et al, have measured the maximum packing of $C_{12}E_4$, $C_{12}E_8$, and $C_{12}E_{12}$ on hydrophobic self-assembled silane monolayers to be 51^{145} , 75^{144} , and $92^{144} \text{ \AA}^2/\text{molecule}$, respectively. Due to the lack of information about the adsorption of trisiloxane surfactants on hydrophobic surfaces, we have carried out the present work in order to study the adsorption of $M(D'E_4OH)M$, $M(D'E_8OH)M$, $M(D'E_{12}OH)M$, $C_{12}E_4$, and $C_{12}E_8$ on hydrophobic self-assembled monolayers(SAM) of octadecyltrichlorosilane(OTS) . The reasons for choosing OTS SAM as hydrophobic surfaces, are described in Chapter 2. We have evaluated the surface concentration, orientation of surfactants, and changes in the hydrogen bonding structure of the interfacial water.

In Chapter 2, we showed that the trisiloxane surfactants are very effective in increasing the spreading on hydrophobic surfaces, such as Parafilm® surfaces. The difference in the interfacial surface tensions, $\gamma_{SV} - \gamma_{SL}$, (γ_{SV} is the surface energy of

Parafilm®-air interface, γ_{SL} is the surface energy of surfactant solution in contact with the Parafilm® surface) for the trisiloxane surfactant (M(D'E₆OH)M) and alkyl polyethoxylate surfactant (C₁₂E₅) are 18.9 and 15 mN/m, respectively. The value of γ_{SV} for Parafilm® (or paraffin wax) reported in literature are 18.7³⁸, 25.4¹⁵⁸, and 32¹⁵⁸ mN/m. However, in spite of the uncertainties in the value of γ_{SV} , the difference in the value of $\gamma_{SV} - \gamma_{SL}$ for M(D'E₆OH)M (18.9 mN/m) and C₁₂E₅ (15 mN/m) is significant. Even with the uncertainty about the exact values of γ_{SV} and γ_{SL} , we can definitely conclude that $\gamma_{SL}(\text{M(D'E}_6\text{OH)M solution}) < \gamma_{SL}(\text{C}_{12}\text{E}_5 \text{ solution})$ on Parafilm® surface. In this Chapter, based on the FTIR-IR experiments, we explain the reason behind the ability of the trisiloxane surfactants to reduce γ_{SL} to lower values. Due to the peculiar molecular structure, the trisiloxane surfactants pack to the maximum limit physically possible, determined by the size of the trisiloxane hydrophobe. The trisiloxane surfactants are also able to change the hydrogen bonding structure of the interfacial water in an energetically more favorable configurations. This effect, combined with the dense packing of the trisiloxane surfactants, explains the low values of γ_{SL} compared to that of the alkyl polyethoxylate surfactants. These results explain the super-spreading behavior of the trisiloxane surfactants.

In the next section, we describe the experimental procedure. Section 5.3 reviews the literature regarding the structure of water near hydrophobic surfaces. In Section 5.4, we present the results the FTIR-ATR experiments and finally provide the conclusions in Section 5.5.

5.2 Experimental Section

5.2.1 Materials:

Octadecyltrichlorosilane (95%), chloroform (>99.9%, HPLC) and carbon tetrachloride (>99.9%, HPLC grade), octamethyltrisiloxane (purity >95%) and hexadecane(HPLC grade) were purchased from Aldrich Chemicals. Acetone (AR grade), Sulfuric acid (95-98%) and Nochromix® crystals (GODAX labs Inc.) were purchased from Fisher Scientific. Research samples of the trisiloxane surfactants, M(D'E₄OH)M, M(D'E₈OH)M, and M(D'E₁₂OH)M, were provided by Dr. Randall Hill of Dow Corning, Inc. The purity of these samples is approximately 85%, and the remaining 15% are non-surface active polyethylene glycols. The trisiloxane part is approximately 98% monodisperse¹²⁶. The alkyl poly-ethoxylate surfactants, C₁₂E₄ and C₁₂E₈ (purity > 99.0 %) were obtained from Nikko Chemicals, Japan. All chemicals were used as received without further purification.

Water used in our experiments was purified by passing tap water through a Milli-Q filter system that is fitted with an Organex-Q column to remove trace surface active impurities (Millipore®, Malborough, MA). Argon and industrial grade N₂ gases were purchased from T.W. Smith Corporation, New York.

The silicon ATR element IRE, (50 x 10 x 3 mm³, with the beveled edge cut at 45°), transmission mode cell, and NaCl windows were obtained from International Crystal Laboratories, NJ. The stainless steel ATR flow sell was purchased from Harrick Scientific Corporation, NJ. Teflon tubing (Nalgene 890 Teflon FEP), used for flowing the

solutions, were purchased from Fisher Scientific. Three way valve was purchased from Hamilton, Inc. Polypropylene connectors, which are used to connect syringe, valve and the flow cell, were purchased from Value Plastics, Inc. O-rings used in the flow cell were chosen for their flexibility and minimal contamination of water. The O-rings complied with EP 70 NSF 61 clean water standards. The O-rings (size dash 025) were purchased from Sealing Devices, Inc. Disposable polypropylene syringes, used to for flowing the solution, were purchased from Sigma Aldrich.

5.2.2 Cleaning Protocol

It is important to ensure that the substrates and other surfaces, which come in contact with water during the flow experiments, are clean and devoid of any organic impurities. This sub-section details the cleaning protocol adopted during all experiments. The silicon ATR element is cleaned in a multi step process. It is sonicated in water, followed by sonication in acetone for 30 minutes each. In the next step, both sides of the ATR element are cleaned for 15 minutes each, using argon gas plasma, created in a plasma cleaner (Harrick Scientific Corporation, model PDC - 32G). Further cleaning is done by sonicating the ATR element in a solution of sulfuric acid and Nochromix®, which is followed by rinsing with water. The ATR element is again cleaned in argon gas plasma as described above.

The stainless steel ATR cell is cleaned thoroughly with water, by sonication and by flowing water through the inlet and outlet ports. It is followed by sonication in acetone. The final cleaning of the ATR cell is done using argon gas plasma.

The valve is cleaned by flowing water through the inlet and outlet ports, followed by sonication in water and acetone. Teflon tubing, syringe, and connectors are cleaned with acetone and water, before connecting with the flow cell. The O-ring is sonicated in water for one hour, followed by many rinses of water. The exposure of the cleaned surfaces with ambient air is minimized by keeping them under water or in a dust-free environment.

5.2.3 Preparation of Hydrophobic Surface

The OTS SAM is deposited on the clean silicon ATR element to make it hydrophobic. The procedure is described in detail in Chapter 3 and Figure 2.2. A 2mM OTS solution is prepared in a 80:12:8 (by volume) mixture of hexadecane, carbon tetrachloride and chloroform, respectively. The clean silicon ATR element is immersed in the OTS solution for 30 minutes. The excess OTS solution is removed from the ATR surface by sonicating twice in chloroform. The hydrophobized ATR is then heated at 70°C for 60 minutes. Water contact angle on the hydrophobic OTS monolayer is measured to be 105-108°.

5.2.4 Procedure of Flow Experiments

The IR spectra are collected using Bio-Rad FTS 175 spectrometer. Highly sensitive, liquid nitrogen cooled Mercury-Cadmium-Telluride (MCT) detector is used to detect the IR beam. The spectra are collected at a resolution of 2cm⁻¹. Each spectrum was averaged over at least 100 scans. The hydrophobized ATR element is assembled in the ATR cell assembled using a standard procedure (Harrick Scientific Corporation). An

illustration of the ATR flow cell is shown in Figure 5.1 and 5.2. The assembled ATR cell is kept in the spectrometer and purged with nitrogen to remove water vapors. Water used in the flow experiments is degassed by boiling, followed by rapid cooling to room temperature. The degassed water is passed through the ATR cell at a flow rate of 0.25 ml/min. The water flow is continued for approximately five hours. Unpolarized IR spectra are collected at regular intervals during the water flow. A background spectrum (polarized and unpolarized) of pure water in contact with the OTS monolayer is collected just before the flow of the surfactant solution is started. The surfactant solution flow is continued for few hours, during which unpolarized spectra are collected at regular intervals (5-15 minutes). Polarized spectra are also collected at intervals of one to two hours.

5.2.5 Calculation of Molar Absorptivity

The absorptivity of the hydrocarbon peaks are calculated from transmission mode experiments, using a transmission flow cell with NaCl windows. Solutions of surfactants, at various concentrations, are prepared in CCl_4 . Spectra of the solutions at various concentrations are collected using standard procedures. The resulting absorbance spectra are a summation of various hydrocarbon peaks. The CH stretch region ($\sim 3050\text{-}2800\text{ cm}^{-1}$) is dominated by five peaks. The approximate positions of the five peaks have been described by Hill et al¹⁵⁹. The approximate position of five peaks are: CH_3 asymmetric stretch ($\sim 2965\text{ cm}^{-1}$), CH_2 symmetric stretch ($\sim 2925\text{ cm}^{-1}$), CH_3 symmetric stretch in Fermi resonance with overtone of CH_3 asymmetric deformation ($\sim 2894\text{ cm}^{-1}$), overtone of CH_3 asymmetric deformation in Fermi resonance with CH_3 symmetric stretch (~ 2873

cm^{-1}), and CH_2 symmetric stretch ($\sim 2856 \text{ cm}^{-1}$). The absorbance spectra of the surfactant solutions, in CCl_4 , is fitted using these five Lorentzian shape peaks to obtain various peak parameters, which include total area of the peak (A), peak intensity, peak width, and peak position. Figure 5.3 shows a spectrum of a solution of C_{12}E_4 in CCl_4 , which is fitted using the five Lorentzian peaks, as described above. Bio-Rad® peak fitting software is used for the peak fittings analysis.

It is very important to choose a peak, particular to a certain CH stretching mode, which represents the surfactant molecule in the most unique way. For the alkyl poly-ethoxylate surfactants, the CH_2 asymmetric CH stretch ($\sim 2925 \text{ cm}^{-1}$) is used for the evaluation of the surfactant concentration. This is chosen because of a large number of CH_2 groups in the alkyl poly-ethoxylate surfactants, as a result this peak dominates the absorbance spectra. For the trisiloxane surfactants, CH_3 asymmetric CH stretch ($\sim 2965 \text{ cm}^{-1}$) is used for quantifying the trisiloxane surfactants concentration. This choice is guided by the fact that the trisiloxane surfactant molecule contains a large number of CH_3 groups and this peak dominates the absorbance spectrum of the trisiloxane surfactant.

The data of peak area at various concentrations is collected from the fitted spectra. The integrated molar absorptivities (ϵ) of various peaks are evaluated by fitting the peak area (A) vs. concentration (C) data to Beer's law:

$$A = \epsilon b C \quad (5.1)$$

where b is the transmission cell thickness. The peak area vs. concentration data for $\text{CH}_2^{\text{asym}}$ of C_{12}E_4 and C_{12}E_8 are shown in Figure 5.4. By fitting Equation 5.1, the value of $\epsilon(\text{CH}_2^{\text{asym}})$ are evaluated. These values are: $42.3 \times 10^6 \text{ cm/mol}$ of C_{12}E_4 , $42.5 \times 10^6 \text{ cm/mol}$ of C_{12}E_8 . Note that these values are almost same, in spite of the fact that the number of

total CH_2 groups in the two surfactants is different. This can be explained by the fact that the contribution to the $\epsilon(\text{CH}_2^{\text{asym}})$ peak comes entirely from the CH_2 groups in the 12-carbon hydrocarbon chain, which comprises the hydrophobic part. The contribution to the $\epsilon(\text{CH}_2^{\text{asym}})$ peak from CH_2 groups in the poly-ethoxylate part is negligible. Matsuura et al¹⁶⁰ have shown that the $\text{CH}_2^{\text{asym}}$ peak is negligible for poly-ethoxylate polymer chains, with more than three ethoxylate units. This explains the reason why the molar absorptivity of the $\text{CH}_2^{\text{asym}}$ peak is same for C_{12}E_4 and C_{12}E_8 .

The $\text{CH}_3^{\text{asym}}$ peak ($\sim 2956 \text{ cm}^{-1}$) is used for the trisiloxane surfactants. However, the commercial samples of the trisiloxane surfactants are not used for the evaluation of $\epsilon(\text{CH}_3^{\text{asym}})$. The value of $\epsilon(\text{CH}_3^{\text{asym}})$ is evaluated using octamethyltrisiloxane $((\text{CH}_3)_3\text{Si}(\text{CH}_3\text{SiCH}_3)\text{Si}(\text{CH}_3)_3)$, which is essentially the trisiloxane part of the trisiloxane surfactants. The value of $\epsilon(\text{CH}_3^{\text{asym}})$ is evaluated to be $96 \times 10^5 \text{ cm/mol}$ of octamethyltrisiloxane.

5.2.6 Calculation of the Surface Concentration from the ATR-IR Spectra.

In this section, we discuss the analysis for the evaluation of the surface concentration of the surfactant from the ATR-IR spectra. The total internal reflection phenomenon is not uncommon in Nature and has been known for centuries. Harrick¹⁶¹ used this phenomena to develop the ATR-IR techniques to study interfaces. In past few decades, the ATR-IR technique has become a standard analytical tool in surface science^{69,162}. The details of theory and analysis are provided by Mirabella^{69,162} and Harrick¹⁶¹. Here, we will briefly describe the derivation of formulae used in the calculation of the surface concentration.

The ATR technique uses familiar properties of light. When a light beam (a general term used for electromagnetic waves) propagating in an optically transparent medium of refractive index η_1 , strikes the surface of another material with refractive index η_2 , then a part of the beam is reflected back in the first medium and the remaining is refracted into the second medium (Figure 5.5A). Snell's law relates the angle of incidence and angle of refraction.

$$\eta_1 \sin \theta = \eta_2 \sin \phi \quad (5.2)$$

In the special case, when the first medium is denser than the second medium, i.e. $\eta_1 > \eta_2$, and if the angle of incidence (θ) is greater than a certain angle called critical angle ($\theta_{critical}$), the incident beam is reflected back into the first medium, with out any refraction into the second medium (Figure 5.5B). This phenomenon is called Total Internal Reflection. The value of $\theta_{critical}$ is:

$$\sin \theta_{critical} = \eta_2 / \eta_1 \quad (5.3)$$

During total internal reflection, a standing wave is generated in the denser medium (medium 1) near the interface, as shown in Figure 5.5C. No propagating wave is transmitted in the second medium, instead an exponentially decaying evanescent wave is generated. The electric field amplitude of the light wave ($E(z)$) is given by:

$$E = E_0 e^{-z/d_p} \quad (5.4)$$

where E_0 is the amplitude of the electric field at the interface, z is the distance from the interface in medium 2, d_p is a decay length factor, called penetration depth.

$$d_p = \frac{\lambda_1}{2\pi(\sin^2 \theta - \eta_{21}^2)^{1/2}} \quad (5.5)$$

where, $\eta_{21} = \eta_2 / \eta_1$, λ_1 is the wavelength in the first medium, ($=\lambda/\eta_1$). The electric field amplitude, in direction x , y and z , (Figure 5.5) at the interface are given as:

$$E_{y0} = \frac{2 \cos \theta}{(1 - \eta_{21}^2)^{1/2}} \quad (5.6a)$$

$$E_{x0} = \frac{2(\sin^2 \theta - \eta_{21}^2)^{1/2} \cos \theta}{(1 - \eta_{21}^2)[(1 + \eta_{21}^2) \sin^2 \theta - \eta_{21}^2]^{1/2}} \quad (5.6b)$$

$$E_{z0} = \frac{2 \sin \theta \cos \theta}{(1 - \eta_{21}^2)[(1 + \eta_{21}^2) \sin^2 \theta - \eta_{21}^2]^{1/2}} \quad (5.6c)$$

During a normal total internal reflection, there is no net transfer of energy to medium 2. However, if the medium 2, absorbs light at that particular wavelength, then there is a loss of energy and not all of the light is reflected back into the first medium. This results in a loss of reflectivity. The reflectivity (R) is defined as the ratio of intensity of the reflected light (I) to the intensity of the incident beam (I_0).

$$R = \frac{I}{I_0} \quad (5.7)$$

For small absorption losses in medium 2, the strength of interaction can be expressed in terms of an effective thickness, d_e , in a manner similar to the path length used in the transmission spectroscopy. For N successive reflections, the reflectivity can be written as:

$$R = \frac{I}{I_0} = e^{N\alpha d_e} \approx 1 - N\alpha d_e \quad (5.8)$$

where d_e is effective thickness, and α is absorptivity. The values of d_e for parallel ($d_{e\parallel}$) and perpendicular ($d_{e\perp}$) polarization are given by:

$$\frac{d_{e\parallel}}{\lambda_1} = \frac{\eta_{21} \cos \theta}{\pi(1 - \eta_{21}^2)(\sin^2 \theta - \eta_{21}^2)^{1/2}} \quad (5.9a)$$

$$\frac{d_{e\perp}}{\lambda_1} = \frac{\eta_{21} \cos \theta (2 \sin^2 \theta - \eta_{21}^2)}{\pi (1 - \eta_{21}^2) [(1 + \eta_{21}^2) \sin^2 \theta - \eta_{21}^2] (\sin^2 \theta - \eta_{21}^2)^{1/2}} \quad (5.9b)$$

$$d_e = \frac{d_{e\parallel} + d_{e\perp}}{2} \quad (5.9c)$$

These equations have been used to evaluate the surface concentration of species adsorbed on the interface^{146,147,163-166}. Area of the absorbance peak, corresponding to a certain vibration mode, is related to the surface concentration (Γ) and bulk concentration (C_b) as :

$$A / N = \varepsilon_b C_b d_e + 2\varepsilon_s (d_e / d_p) \Gamma \quad (5.10)$$

where A is integrated area of the peak under analysis, N is the number of reflection, ε_b and ε_s are the integrated molar absorptivities for the molecules on the surface and in the bulk, respectively. For the ATR cell used in this study, Krishnan¹⁴⁷ has experimentally evaluated the value of N to be $\sim 6.5 \pm 0.5$. In the present study we have used a value of 7 (calculated from the geometry of the cell). The value of θ is 45° . The value of ε_s and ε_b can be assumed to be the same. The values of refractive index are: $\eta_1 = \eta_{\text{silicon}} = 3.42$ ¹⁶⁷, η_2 (solution) = 1.46. The refractive index of the solution and the adsorbed layer is assumed to be the same. The refractive index of water at $\sim 2900 \text{ cm}^{-1}$ is 1.42¹⁶⁸. Assuming that the refractive index of the hydrocarbon is 1.5, the refractive index of the solution and the surfactant film can be assumed to the average of two, i.e. 1.46. The errors induced in the calculation of the surface concentration because of this approximation, are calculated to be $\sim \pm 6\%$.

The absorbance spectra of the adsorbed surfactants are obtained using background spectrum of pure water on the ATR, taken just before the surfactant solution flow.

Therefore, the resultant absorbance spectra describe the changes in the structure of the interface, when the surfactant solution is flown through the cell. A example of such a spectrum of the adsorbed $C_{12}E_8$ is shown in Figure 5.6. The CH stretch region is fitted with five peaks, as described previously. The surface concentration of the surfactants is obtained by substituting the peak area of the corresponding peak in Equation 5.10. The surface concentration and area per unit molecules of the trisiloxane and alkyl polyethoxylate surfactants, at their respective CAC, are shown in Table 5.1.

5.2.7 Orientation of adsorbed surfactants

Parallel and perpendicular polarized IR beams, in combination with FTIR-ATR, are used to determine the orientation of the surfactant molecules. Dichroic ratio (D) for a particular peak is defined as the ratio of the absorbance peak area in perpendicular ($A_{\perp}$) and parallel polarization ($A_{\parallel}$) mode.

$$D = \frac{A_{\perp}}{A_{\parallel}} \quad (5.11)$$

The dichroic ratio for CH_2^{asym} and CH_2^{sym} peaks can be used to determine the orientation of a hydrocarbon chain normal to the ATR. This method has been used to determine the orientation of lipid bilayers¹⁶⁹, Langmuir-Blodgett films¹⁷⁰ and surfactant^{171,172} adsorbed on solid surfaces. The formulae used for this purpose have been developed and their physical interpretation is very well described. We will use formulae used by Singh et al¹⁷¹. More details can be found in the references mentioned above. The dichroic ratio of a linear all-trans hydrocarbon chain inclined the surface (Figure 5.7) can be evaluated. The chain axis ($\vec{P}$) is inclined to the normal to the surface ($\vec{N}$) with angle Φ .

The transient dipole moment ($\vec{M}$), specific for $\text{CH}_2^{\text{asym}}$ and CH_2^{sym} is at angle δ from the chain axis. The chain is assumed to be fixed with one end on the surface, but still free to rotate about $\vec{P}$ and $\vec{N}$ axis. Averaging the absorbance for all position of the hydrocarbon chain, while rotating along $\vec{N}$ and $\vec{P}$ axis, a relationship for the dichroic ratio can be obtained. The value of δ for both $\text{CH}_2^{\text{asym}}$ and CH_2^{sym} stretch is 90° . Using this value of δ , following relationship between D and Φ can be obtained.

$$\langle \cos^2 \Phi \rangle = 1 - \frac{2}{1 + \frac{2E_{z0}^2 D}{E_{y0}^2 - E_{x0}^2 D}} \quad (5.12)$$

The values of E_{x0} , E_{y0} , and E_{z0} can be obtained from Equations 5.6a, 5.6b and 5.6c.

5.3 Structure of water near hydrophobic surfaces.

Water is one of the most important molecule and liquid. Water is omnipresent around us many as liquid, steam, and ice. The structure of water is of immense importance and focus of research and discussion over past few centuries. It is almost next to impossible to compile all the literature regarding the structure of water. Frank has compiled the literature relating to water in a series of six volumes¹⁷³. Origin of many usual properties of water, such as, unusually high boiling point, high melting point, high heat of vaporization, low density of ice, are a result of the ability of water molecules to hydrogen bond with other water molecules and other hydrogen bond forming molecules¹²⁴. Water molecules are unable to hydrogen bond with air and other non-hydrogen bonding molecules. Because of this reason, the surface energy or surface tension of water in contact with air or other non-polar liquids or solids is relatively higher than the values predicted using continuum theories. Water molecules hydrogen bond with each other in liquid or solid form, but when a non-hydrogen bonding molecules is forced to come in contact with water, some hydrogen bonds need to be broken in order to accommodate the non-hydrogen bonding molecule. This increase in the free energy of the system can be compensated, to some extent, by the ability of water molecules to restructure around the non-hydrogen bonding molecules^{124,174}. This restructuring of water leads to the formation of "clathrate cages" around small solute molecules and structured water near hydrophobic surfaces. The formation of clathrate cages and structures water is entropically very unfavorable because it disturbs the existing water structure to impose a new and more *ordered* structure around the hydrophobic solute or surface¹²⁴. There is a possibility of some reduction in the free energy due to increased

hydrogen bonding in the structured water, but it is insignificant compared to the reduction in entropy of water molecules¹²⁴. The continuum theories cannot account for this restructuring of water. The concept of disjoining pressure, to some extent accounts for such restructuring and explain the unusual properties of thin films of water on hydrophilic and hydrophobic surfaces, which cannot be explained by the continuum theories⁵⁴. The restructuring effect of water molecules near non-hydrogen bonding molecules results manifest itself as in many forms, such as hydrophobic effect, and hydration forces^{56,124,174}. Thermodynamically it is observed as a decrease in solubility of hydrocarbons in water with an increase in temperature⁵⁶.

A part of the enthalpic penalty of breaking the hydrogen bonds between the water molecules to accommodate the non-hydrogen bonding solute can be compensated by the uncanny ability of water molecules to hydrogen bond with each other in many configurations around the solute. This result increased ordering of the water molecules around the solute molecule. For small solute molecules, due to their size it is possible for the water molecules to arrange around the solute so that the hydrogen bonding groups (-OH) can avoid pointing in a direction towards the non-hydrogen bonding solute molecule. However, on extended hydrophobic surfaces, (such as self-assembled silane monolayers), or in case of large non-hydrogen bonding solute molecules, it may not be possible for water molecules to totally avoid pointing the OH group in the direction of the non-hydrogen bonding surface or molecule. Some water molecules, closest to the surface are forced to lose a hydrogen bond and point a -OH group towards the non-hydrogen bonding surface. Hydrogen bonding in water is relatively strong, therefore, the presence

of some non-hydrogen bonded OH can contribute significantly to the surface energy of a hydrophobic water interface.

Information about the structure of water around small hydrocarbon molecules can be obtained from thermodynamic properties, such as solubility of hydrocarbons¹²⁴. However, water structure near hydrophobic surfaces has not been studied extensively due to the lack of experimental techniques capable of probing interfaces. Variation in the thermodynamic properties, such as, solubility, can not be used to for the case of hydrophobic surfaces. (Vogler⁵⁴ has recently reviewed the literature regarding structure of water near hydrophobic and hydrophobic surfaces. No single review can compile all the available literature of water structure in contact with surface. However, this review covers almost all the relevant literature related to this thesis.). In the absence of the experimental techniques, capable of probing the interfacial region, molecular dynamics studies were carried to understand the structure of water in contact with air¹⁷⁵ and extended hydrophobic surfaces^{176,177}. The molecular dynamics simulations suggested that the some water molecules in the layer nearest to the hydrophobic surface have some OH bonds, which are directed toward the hydrophobic surface and are not hydrogen bonded¹⁷⁶ The subsequent layers of water are more structured in an "ice like" manner. This structuring of water molecules extends to 7-10 Å and beyond that water molecules have "liquid" structure with no preferred orientation.

Infrared spectroscopy is a useful tool to investigate hydrogen bonding. The OH stretching frequency of water molecules is highly dependent on the extent of hydrogen bonding. However, this technique is difficult to use for the air-water and hydrophobic solid-water interfaces, because of very small thickness of the interfacial region (few

angstroms). The spectrum of bulk water in liquid form is dominated by a wide band at $\sim 3400\text{ cm}^{-1}$, whose assignment is still controversial^{152,173,178}. In general, it represents the bond disorder in liquid water¹⁷³. Water in form of ice, has an IR band near 3200 cm^{-1} , which characterizes the OH stretch in fully hydrogen bonded water molecules. Water molecules which are not hydrogen bonded, such as in gas phase, have a OH stretch band near 3600 cm^{-1} . Recently, with the development of second harmonic generation and sum frequency generation (SFG) techniques, it has become possible to obtain the vibration spectrum of molecules only in the interfacial region. Du et al have used the SFG technique to obtain the vibration spectrum of water molecules in the interfacial region in contact with air¹⁷⁹ and a hydrophobic SAM of OTS¹⁷⁸. Their results are shown in Figure 5.8. The SFG IR spectra of water molecules in the interfacial region adjacent to a hydrophobic OTS surface, is dominated by two main peaks. A peak at $\sim 3600\text{ cm}^{-1}$, experimentally demonstrates the presence of free non-hydrogen bonded OH groups in the water layer next to the surface. The presence of the other peak at $\sim 3200\text{ cm}^{-1}$, confirms that presence of more hydrogen bonded, ice-like, structured water in subsequent layers of water. These results experimentally confirm the results of the molecular dynamics simulation of Lee et al¹⁷⁶. An illustration of the suggested picture of the water structure near highly hydrophobic surface, such as OTS monolayer, is shown in Figure 5.8. Water layers, till a depth of $\sim 7\text{-}10\text{ \AA}$ are more structured or ordered or ice like, than the water in the bulk. Similar, SFG results are also obtained for the air-water interface¹⁷⁹. As mentioned above, that the restructuring of water molecules at the-air water and hydrophobic solid-water interfaces is thought to account for the difference in the values of interfacial tensions predicted using the continuum theories and the experimental

values⁵⁴. But no acceptable molecular scale theory has been developed to account for the restructuring of water.

The interfacial surface energy contains both enthalpic and entropic contributions. Around a small hydrophobic solute, water molecules restructure around the solute, which results in mainly an entropic contribution to the free energy¹²⁴. However, on an extended highly hydrophobic surface, due to the presence of free non-hydrogen bonded water, there is a significant enthalpic contribution to the interfacial surface energy. Some other studies related to the structure of water in contact with hydrophobic surfaces and solute molecules have been carried out^{152,180-212}.

5.4 Results and Discussion

5.4.1 Packing on the Hydrophobic Solid-Water Interface

The surfactant absorption experiments, at CAC, are carried out as described in the Experimental Section (Section 5.2). The hydrophobicity of the OTS monolayers, as measured by water contact angle, is same as Parafilm®. Water contact angle on both the surfaces is approximately 107° . The maximum packing of the surfactants on the hydrophobic solid water interface is expected to occur their respective CAC. The results of the FTIR-ATR experiments are shown in Table 5.1. This table details the minimum area per unit molecule (A_{min}) of the surfactants adsorbed on OTS monolayer from the surfactant solutions at CAC. In the present study, we obtained the data for $M(D'E_4OH)M$, $M(D'E_8OH)M$, $M(D'E_{12}OH)M$, $C_{12}E_4$, and $C_{12}E_8$. The evolution of the surfactant adsorption is shown in Figure 5.9. For the trisiloxane surfactants' adsorption on hydrophobic surfaces, the comparative data available is provided by Ananthanpadmanabahn et al¹⁰, who using the depletion technique, estimated the packing of the trisiloxane surfactant, $(M(D'E_{7.5}CH_3)M)$ on polyethylene surface. In comparison, there are a larger number of studies regarding the adsorption of alkyl poly-ethoxylate surfactants on surfaces. We have chosen only a few neutron reflectivity studies dealing with the adsorption of alkyl poly-ethoxylate surfactants on self-assembled hydrophobic silane monolayers. These results are shown in third column of Table 5.1 and are chosen because of the similarity of the hydrophobic surfaces with the present study. In the fourth column, we report the results of the adsorption on air-water interface. The results of the

trisiloxane surfactants are obtained in this thesis and described in Chapter 4. The data for the alkyl poly-ethoxylate surfactants has been taken from the cited references.

The value of A_{min} for $M(D'E_4OH)M$ is same as the value of A_{min} for $M(D'E_8OH)M$. This value, $49 \pm 3 \text{ \AA}^2/\text{molecule}$, is very close to the cross sectional area of the trisiloxane hydrophobic group, $\sim 53 \text{ \AA}^2/\text{molecule}$ (calculated using Chem3D® software). The values of A_{min} for $M(D'E_8OH)M$ are also in excellent agreement with the results of Anathapadmanabhan et al for $M(D'E_{7.5}CH_3)M$. This shows that the packing of the trisiloxane surfactants is not affected by increasing the number of ethoxylate units from 4 to 8. $M(D'E_4OH)M$ and $M(D'E_8OH)M$ are packed to the maximum possible packing as determined by the size of the molecular structure of the trisiloxane surfctant. On increasing the number of the ethoxylate units to 12, the value of A_{min} increases to $59 \pm 3 \text{ \AA}^2/\text{molecule}$ suggesting that the effect of the number of ethoxylate units in the hydrophilic part is significant only for longer poly-ethoxylate chains hydrophilic group.

Compared to the trisiloxane surfactants, the alkyl poly-ethoxylate surfactants do not pack as densely on hydrophobic surface. The value of A_{min} for $C_{12}E_4$ and $C_{12}E_8$ are 73 ± 4 and $75 \pm 4 \text{ \AA}^2/\text{molecule}$, respectively. These values are also very close to each other, which suggest that the number of ethoxylate units does not significantly affect the packing of the alkyl poly-ethoxylate surfactants on hydrophobic solid surfaces. The value of A_{min} for $C_{12}E_8$, on hydrophobic solids, (see Table 5.1) is in excellent agreement with the value obtained by Thritle et al using neutron reflectivity technique. Also, the value of $A_{min}(C_{12}E_4)$ obtained is in reasonable agreement with the results of Fragnato et al.

The comparison of the packing density the trisiloxane and alkyl poly-ethoxylate surfactants on the air-water and the hydrophobic solid-water interface surface exhibit

some interesting and new results. The packing of the trisiloxane on the hydrophobic OTS monolayer is equal or denser than the air-water interface. $M(D'E_4OH)M$ and $M(D'E_8OH)M$ pack almost to the same value of A_{min} on these two interfaces, because they can not pack more due to the size of the trisiloxane hydrophobe ($52\text{\AA}^2/\text{molecule}$). $M(D'E_{12}OH)M$ packs more densely on the hydrophobic solid-water interface than the air-water interface. In comparison, the alkyl poly-ethoxylate surfactants show entirely reverse trend. They tend to pack more densely on the air water interface than the hydrophobic solid water interface. The values of A_{min} for $C_{12}E_4$ on the hydrophobic solid water and air-water interface are 73(present study) and $36\text{\AA}^2/\text{molecule}$, respectively. Similar trend is also observed for $C_{12}E_8$ and $C_{12}E_{12}$, both of which pack more densely on the air-water interface, than the hydrophobic solid-water interface. In brief, the trisiloxane surfactants tend to pack more densely on the hydrophobic solid-water interface, while the alkyl poly-ethoxylate surfactants pack more densely on the air-water interface. This peculiarity of the trisiloxane surfactant can be attributed to the structure of their hydrophobic group, due to which, the trisiloxane surfactants pack more densely on the hydrophobic solid water interface than the air-water interface.

5.4.2 Orientation of Surfactants on the Surface.

FTIR-ATR spectra is obtained using parallel and perpendicular polarized light as shown in Figure 5.5. The area of the absorbance peak for a certain CH stretching mode is obtained in the parallel ($A_{||}$) and perpendicular ($A_{\perp}$) polarization mode. The dichroic ratio (D), as described in Equation 5.11 is evaluated for CH_3^{asym} , CH_2^{asym} , and CH_2^{sym} peaks for $M(D'E_4OH)M$, $M(D'E_8OH)M$, $M(D'E_{12}OH)M$, $C_{12}E_4$, and $C_{12}E_8$. The dichroic

ratio for a particular CH vibration mode depends on the arrangement of the CH_2 and CH_3 groups in the molecule and on average orientation of the molecule relative to the surface. It is not a trivial task to separate these two effects. The dichroic ratio of the $\text{CH}_3^{\text{asym}}$ peak in the trisiloxane surfactants cannot provide any unambiguous information about the orientation of the trisiloxane group. The seven CH_3 groups in the trisiloxane group are oriented in seven different directions. The dichroic ratio of the CH_2^{sym} peak is not useful in a simple and direct manner. This is because the contribution to this peak comes from the CH_2 groups present in the poly-ethoxylate chain as well as from the CH_2 groups from the hydrocarbon chain in the hydrophobic part. The relative contribution from these two types of CH_2 group is not necessarily equal. However, some useful and conclusive information about the orientation of the hydrophobic hydrocarbon chain of C_{12}E_4 and C_{12}E_8 can be obtained from the dichroic ratio of the $\text{CH}_2^{\text{asym}}$ peak. As mentioned in Section 5.2.5, the contribution to this peak comes only from the CH_2 groups present in the hydrophobic hydrocarbon chain part of C_{12}E_4 and C_{12}E_8 . Using the dichroic ratio for $\text{CH}_2^{\text{asym}}$ peak and Equation 5.12, an average value of Φ (Figure 5.7) for the hydrocarbon chain part of C_{12}E_4 and C_{12}E_8 can be evaluated to be $34\text{-}37^\circ$. Fragnato et al¹⁴⁵ have also evaluated the hydrocarbon chain tilt angle for C_{12}E_4 adsorbed on hydrophobic silane SAM, using neutron reflectivity. Their values are $\sim 49\text{-}56^\circ$. The value of hydrocarbon chain tilt obtained in the present study and by Fragneto et al are in reasonably good agreement, considering that these two techniques are totally different, and also a model of orientation of the hydrocarbon chain is assumed.

5.4.3 Changes in the Structure of Water on the Adsorption of Surfactants

The structure of water near a hydrophobic surface, such as OTS monolayer is discussed in the Section 5.3 and illustrated in Figure 5.8. In brief, results the SFG spectrum of water near a hydrophobic OTS monolayer (Figure 5.7) shows two main peaks, at $\sim 3200\text{ cm}^{-1}$ and at $\sim 3600\text{ cm}^{-1}$. The first of these two peaks ($\sim 3200\text{ cm}^{-1}$) is attributed to the more structured and more hydrogen bonded water in close proximity of the hydrophobic surface ($7\text{-}10\text{\AA}$). The second peak ($\sim 3600\text{ cm}^{-1}$) is attributed to the presence of non-hydrogen bonded free OH groups, which point toward the hydrophobic surface, and are present in the water layer closest to the surface.

Figure 5.9A shows the FTIR-ATR of pure water in contact with the hydrophobic OTS monolayer. Note that the penetration or sampling depth of the IR beam for the setup in these experiments is a few hundreds of nanometers. This sampling depth is very large compared to the thickness of the structured water ($7\text{-}10\text{\AA}$) present near the surface. Therefore, the spectrum in Figure 9A represents the bulk water. This spectrum has a peak around 3400 cm^{-1} in the OH stretch region, which is in agreement with the voluminous data available for the spectra of bulk water^{173,213}.

The changes in the spectra on the adsorption of C_{12}E_4 and $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ adsorbed at their maximum packing (73 ± 4 and $49\pm 3\text{ \AA}^2/\text{molecule}$ respectively) are shown in Figures 5.8B and C, respectively. Note that the absorbance (in region $3000\text{-}3700\text{ cm}^{-1}$) for C_{12}E_4 and $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ in Figures 5.8 B and C is approximately 100 times less than that of the absorbance of water shown in Figure 5.8A. The reason behind this is that background spectrum for Figure 5.8B and C is the spectrum of water in contact with the OTS monolayer (spectrum in Figure 5.8A). Therefore, Figures 5.8 B and C show only the

changes in the spectra on the adsorption of the surfactants. In Figures 5.8 B and C, we observe a positive absorbance peaks in the CH stretching region ($\sim 2800\text{-}3000\text{ cm}^{-1}$) and negative absorbance in the OH stretch region ($3000\text{-}3700\text{ cm}^{-1}$). The negative peaks emerge because of the fact that the surfactant molecules, during the adsorption on the surface, replace water molecules, which are present near the surface. The negative absorbance peak for C_{12}E_4 and $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ is at $\sim 3275\text{ cm}^{-1}$, in comparison to $\sim 3400\text{ cm}^{-1}$ for the bulk water. This shows that the water molecules, replaced by the surfactant molecules near the hydrophobic surface, are more hydrogen bonded than the bulk water. The negative OH peak for $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ is larger than that of C_{12}E_4 , probably due to the denser packing of $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$. The thickness of the structured water region is $\sim 7\text{-}10\text{ \AA}$. Compared to this, the thickness of C_{12}E_4 on OTS monolayer is $\sim 16\text{-}20\text{ \AA}$ ¹⁴⁵. The thickness of $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ layer can be assumed to be in the same range, considering the length of fully stretched $\text{M}(\text{D}'\text{E}_4\text{OH})\text{M}$ molecule is $\sim 21\text{ \AA}$ (calculated using Chem3D® software). Considering this, it is possible that in addition to the removal of more structured water, some bulk like water molecules are also replaced by the adsorbing surfactant. This can explain why the negative absorbance peak is $\sim 3275\text{ cm}^{-1}$ rather than at $\sim 3200\text{ cm}^{-1}$, as shown for the structured water in the SFG spectra in Figure 5.8.

An important observation in these result is that no separate negative peak is observed at $\sim 3600\text{ cm}^{-1}$ corresponding to the free OH (Figure 5.8). The reason behind this is that number of water molecules, with free OH in the layer nearest to the surface, is expected to be much lower than the total number of structured and bulk water molecules displaced by the surfactants. Therefore, the peak at ~ 3600 is masked by the stronger peak at $\sim 3275\text{ cm}^{-1}$.

In efforts to observe the effect on the surfactants adsorption on the free OH stretch, we carried out adsorption experiments for $C_{12}E_8$ and $M(D'E_8OH)M$ at concentrations $\sim 1/30$ times the CAC. The spectra obtained over time are shown in Figures 5.11 and 5.12. For $C_{12}E_8$, (Figure 5.11), the evolutions of positive absorbance in CH stretch region and negative absorbance in the OH stretch region are observed. The spectra look similar to the spectrum of fully packed $C_{12}E_4$, as shown in Figure 5.10. However, there are some differences. The packing of the surfactants is much lower than the fully packed monolayer of $C_{12}E_4$ (Figure 5.10B). Also, the negative absorbance peak for the OH region is centered at $\sim 3200\text{cm}^{-1}$ in Figure 5.11, rather than at $\sim 3275\text{cm}^{-1}$ as observed in Figure 5.10B. This change in the negative OH peak can be described by the fact that at low surfactant density on the surface, most of the water molecules, replaced by the surfactants, are the structured water molecules, which have an IR peak ~ 3200 . As the surfactant's surface concentration rises, due to limited thickness of structured water compared to the length of the surfactant molecule, increasingly larger fraction of bulk water molecules are replaced from the surface to accommodate increasing surface concentration. Therefore, the negative OH peaks shifts from ~ 3200 (Figure 5.11) to ~ 3275 (Figure 5.10B) cm^{-1} . In Figure 5.11, at 123 minutes, a peak at $\sim 3600\text{ cm}^{-1}$ is also observed, indicating a slight increase in free OH. The reason behind this is not clear to the author.

The adsorption of the trisiloxane surfactants tells a different story. The spectra of $M(D'E_8OH)M$ adsorbed at low concentrations are shown in Figure 5.12. The evolution of the OH stretch band, on adsorption of $M(D'E_8OH)M$, is totally different from $C_{12}E_8$. Initially, there is a small negative band. Then, as the concentration increased, a positive

band starts to appear at 3200cm^{-1} , at the same time the negative band shift at $\sim 3550\text{cm}^{-1}$. This behavior is explained by the fact that the free OH, which are present in the water layer closest to the hydrophobic surface (Figure 5.8) are removed by the trisiloxane surfactant resulting in a negative peak at $\sim 3550\text{cm}^{-1}$. These water molecules (with free OH) are then pushed in structured water region or in bulk water, thereby gaining hydrogen bonds. The result is an equivalent increase in a positive peak at $\sim 3200\text{cm}^{-1}$. On further adsorption, more structured water is also removed from the surface, resulting in a strong negative peak at $\sim 3300\text{cm}^{-1}$, which masks the 3550cm^{-1} peak.

The comparison of the adsorption and alkyl poly-ethoxylate surfactants is illustrated in Figure 5.13. The trisiloxane surfactants, because of the peculiar "T" shape of their hydrophobic group, are effective in removing the free OH from the hydrophobic surface, in addition to the removal of the structured water. The trisiloxane group is very compact and rigid. There is no freedom to move around, as all seven methyl groups are rigidly attached to silicon atoms. As a result, the trisiloxane group acts like a thick disk, which sits flat on the surface, and very effectively removes the first layer of water, consisting of a large number of free OH groups dangling towards the surface. The maximum packing is equal to the area of the trisiloxane group, because of which it effectively removes almost all of the free OH from the surface. On the other hand, the hydrophobic part of the alkyl poly-ethoxylate surfactants is a long hydrocarbon chain, which is much more mobile, and free to move around. The configuration of the hydrocarbon chain is such that it is inclined at an angle of $\sim 35^\circ$ (Section 5.4.2) from the normal. Even at the maximum packing (which is much larger than the physical size of the hydrocarbon chain cross-section), the hydrocarbon chains are not able to effectively

remove the free OH from the surface. In addition hydrocarbon chains are still surrounded by water molecules.

An important point, which is observed in Table 5.1 is that trisiloxane surfactants pack to almost the same density on the hydrophobic solid-water and air-water interfaces. On the other hand the alkyl poly-ethoxylate surfactants pack on the hydrophobic solid-water interface to much lower density than on the air-water interface. The reason behind this difference in behavior of the alkyl poly-ethoxylate surfactants is that on the air-water interface hydrocarbon chain is able to come out of water, while on the hydrophobic surface it stays in water, and are surrounded by water molecules when adsorbed on the interface. On air-water interface, the hydrocarbon chains are able to come out of water, thereby getting rid of the structured water, which is present around them in bulk. As a result, the driving force for adsorption of alkyl poly-ethoxylate surfactants on air-water interface is much larger than on a hydrophobic solid water interface, which results in denser packing at the air-water interface.

The trisiloxane surfactants are much different from the alkyl poly-ethoxylate surfactants regarding their behavior on the air-water and solid-water interface. The trisiloxane surfactants, due to their "T" shaped, rigid, and compact hydrophobic group, effectively remove the free OH near the surface, in addition to the removal of the structured water. Also, due to the disc shape of the trisiloxane group, they can orient themselves as inverted "T" ($\perp$). In this manner, they can get rid of the structure water, which surrounds them in the bulk. Due to all these effects, the driving force of adsorption on the hydrophobic surface is much higher for the trisiloxane surfactants is much higher than the alkyl poly-ethoxylate surfactants. As a result, the trisiloxane pack much more

densely on the hydrophobic surface than the alkyl poly-ethoxylate surfactants. The fact that $M(D'E12OH)M$ packs more densely on hydrophobic solid water interface than air-water interface, suggests that the driving force of adsorption for trisiloxane surfactants is higher for the hydrophobic solid-water interfaces than the air-water interface.

These ideas can also be expressed as enhanced hydrophobic attraction between the trisiloxane hydrophobe and the hydrophobic or air-water surface, and also among the trisiloxane hydrophobe adsorbed on the surface. Ruckenstein⁴³ have speculated that the reason for the super-spreading behavior of the trisiloxane surfactants can be the short range hydrophobic attraction between the surfactant and the hydrophobic surface.

Due to the ability to effectively get rid of the structured water around them by adsorbing on the hydrophobic solid surface, the packing of the trisiloxane surfactants on the air-water and hydrophobic solid-water interfaces is same. As a result, the structure of the adsorbed monolayer is also expected to be the same (Figures 4.11 and 5.13). The higher driving force for adsorption, the trisiloxane surfactants are able to overcome some of the repulsion between the poly-ethoxylate chains. This explains the fact that the number of ethoxylate groups does not significantly affect the maximum packing of the trisiloxanes significantly (Table 5.1 and 4.3). On the other hand, the maximum packing of the alkyl poly-ethoxylate surfactants on the air-water interface is controlled by the repulsion among the poly-ethoxylate chains of the adsorbed surfactants. The driving force of adsorption for the alkyl poly-ethoxylate surfactants is not strong enough to overcome the repulsion between the poly-ethoxylate chains on the air-water interface. On the hydrophobic solid-water interface, the driving force for adsorption for the alkyl poly-ethoxylate surfactants seems to be even less, as suggested by much leaner packing than

air-water interface. This again is due to the fact that hydrocarbon chain are unable to come out of water on a hydrophobic-solid surface.

The interfacial surface energy contains both enthalpic and entropic contributions. Around a small hydrophobic solute, water molecules restructure around the solute, resulting in mainly entropic contribution to the free energy¹²⁴. However, on an extended highly hydrophobic surface, due to the presence of free non-hydrogen bonded water, there is a significant enthalpic contribution to the interfacial surface energy. The alkyl poly-ethoxylate surfactants, due to their long hydrocarbon chain hydrophobic group, are unable to remove the free OH. Also they are also unable to effectively get rid of the structured water around them. The trisiloxane surfactants remove the free OH from the surface and thereby reducing the enthalpic part of the surface energy. In addition, due to their "T" structure, to some extent, they are also able to get rid of the structured water present the trisiloxane hydrophobe. This reduces the entropic part of the interfacial tension. Therefore, the trisiloxane surfactants reduce the surface energy of a hydrophobic solid-water interface more than the alkyl poly-ethoxylate surfactants. As a result, they reduce the water contact angle on highly hydrophobic solid surfaces to almost zero and exhibit super-spreading behavior.

The hydrogen bonding of water in contact with hydrophobic surface can depend on the nature and hydrophobicity of the surface. Without any proof or references, the author speculates that on surfaces with lower hydrophobicity, it is possible that there may not be any free OH in the water layer next to the interface. As a result, the ability of the trisiloxane surfactants to remove these free OH, may not contribute to the driving force for adsorption. Consequently, it is possible that on a surface with lesser hydrophobicity,

the adsorption characteristics of the trisiloxane and poly-ethoxylate surfactants may be similar.

5.5 Conclusions

In this study, using ATR-IR technique, we have shown that the trisiloxane surfactants adsorb on the hydrophobic solid water surfaces to higher density than the alkyl poly-ethoxylate surfactants. The trisiloxane surfactants are able to remove the free OH present near the hydrophobic surfaces, and as a result reduce the hydrophobic solid water surface tension to lower values than the alkyl poly-ethoxylate surfactants. These effects are attributed to the peculiar "T" shaped, compact trisiloxane hydrophobic group. Using these results we explain the super-spreading characteristics of the trisiloxane surfactants which make them "super-spreaders"

In addition, we have shown for the first time (no prior studies are known to the author), how the hydrogen bonding structure of the interfacial water in contact with a hydrophobic surface is modified on adsorption of surfactants. The changes in the hydrogen bonding structure are also affected by the molecular structure of the surfactant.

	Hydrophobic solid-water interface		Air-water interface
	By ATR FTIR	Other techniques	
M(D'E ₄ OH)M	49±3*		53, Surface Tension @
M(D'E ₈ OH)M	49±3*	50, M(D'E _{7.5} OCH ₃)M Depletion technique Ⓔ	54, Surface Tension @
M(D'E ₁₂ OH)M	59±4*	-	69.2, Surface Tension @
C ₁₂ E ₄	73±4*	51, Neutron Reflectivity#	36, Surface Tension Δ 44, Neutron reflectivity †
C ₁₂ E ₈	75±4*	75, Neutron Reflectivity †	65, Surface Tension ‡ 62, Neutron reflectivity †
C ₁₂ E ₁₂		92, Neutron Reflectivity †	78, Neutron reflectivity †

References:

*: Present work; @: Present work, Chapter 4; #: Fragneto et al¹⁴⁵; †: Thritle et al¹⁴⁴; Δ:

Hsu et al⁶⁷; ‡: Lin et al⁶⁸; Ⓔ: Ananthapadmanabhan et al¹⁰

Note: All hydrophobic solids are silane SAMs, except the one used by

Ananthanpadmanabhan et al.

Table 5.1: Area per unit molecule of surfactants on hydrophobic solid-water and air-water interface (Å²/molecule) at CAC

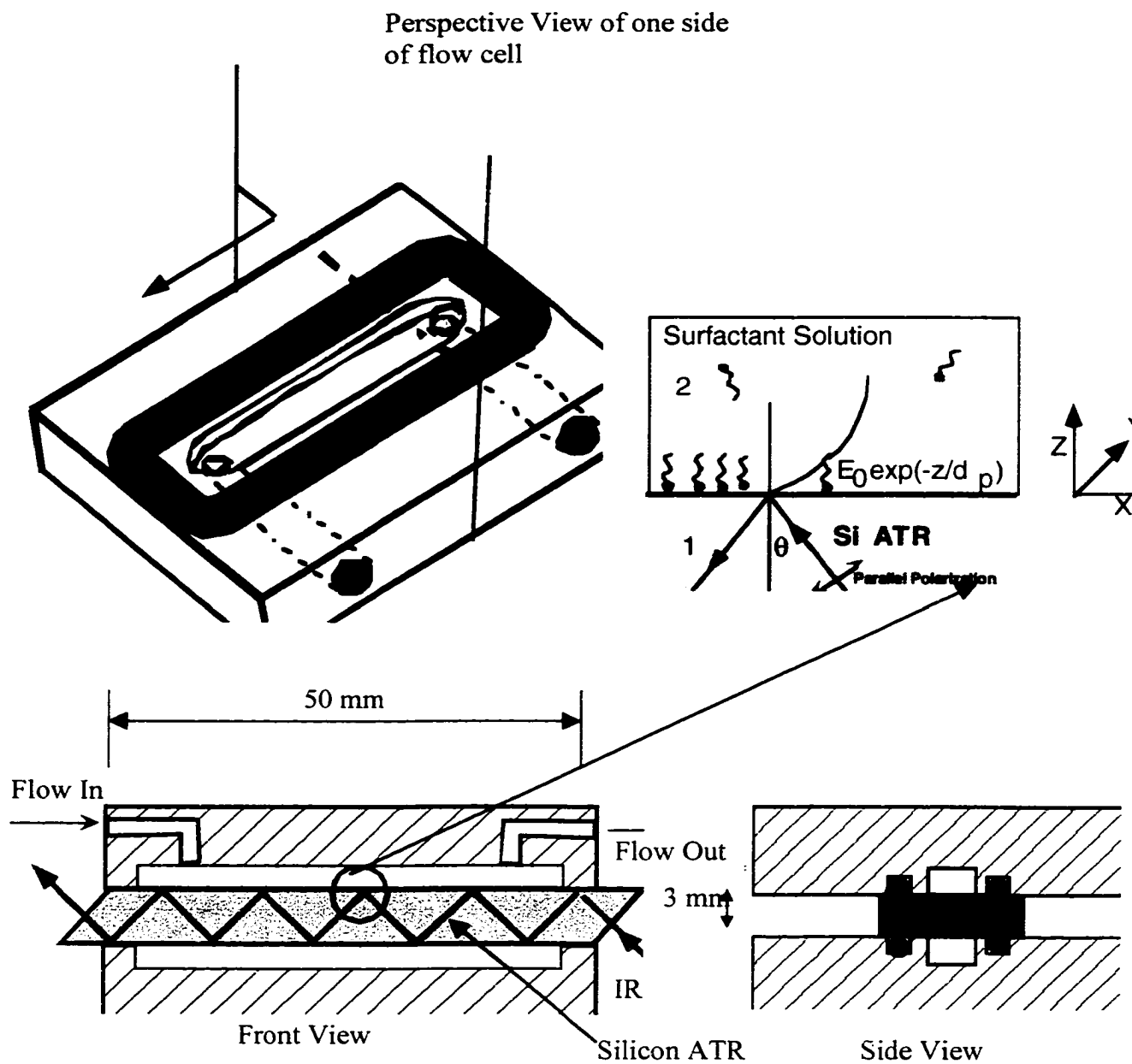


Figure 5.1: Description of ATR flow cell assembly

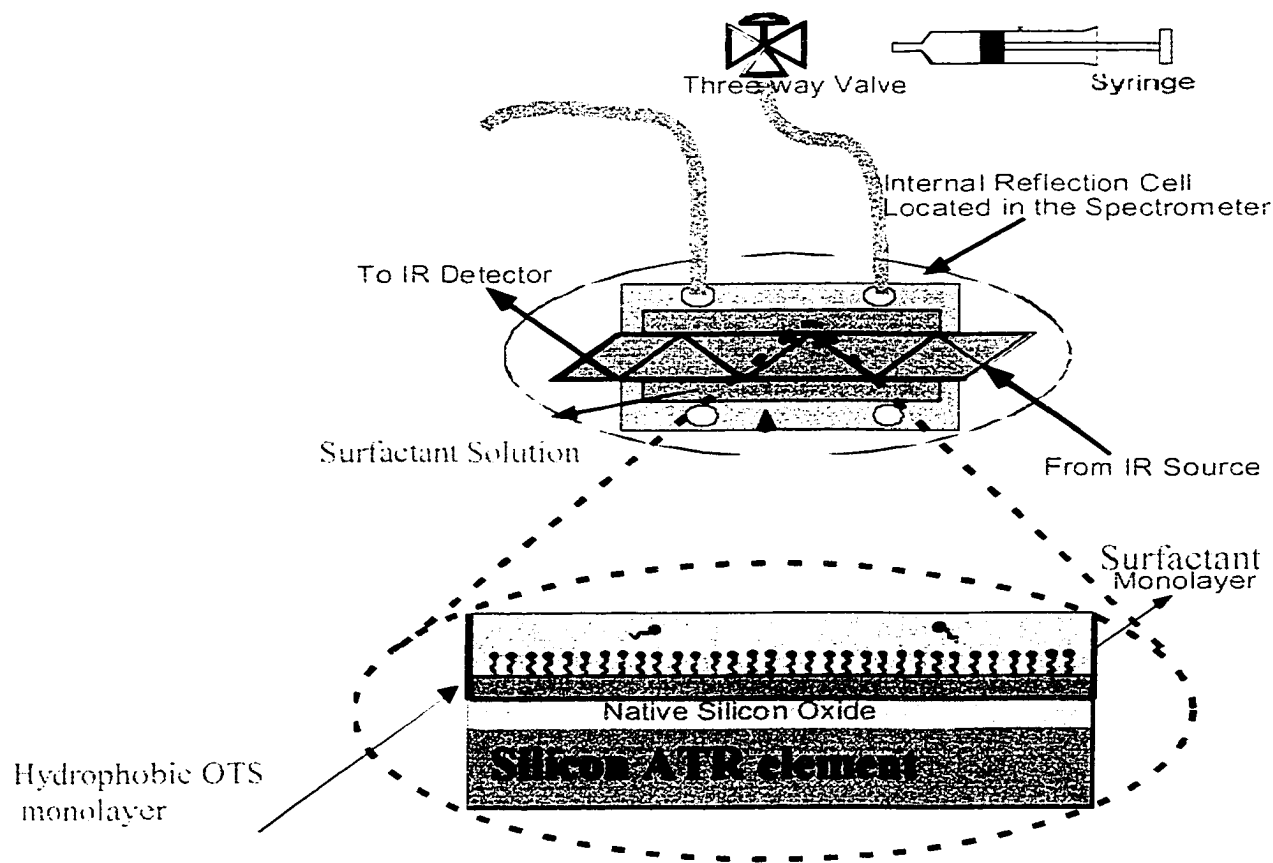


Figure 5.2: Illustration of ATR flow cell experiment

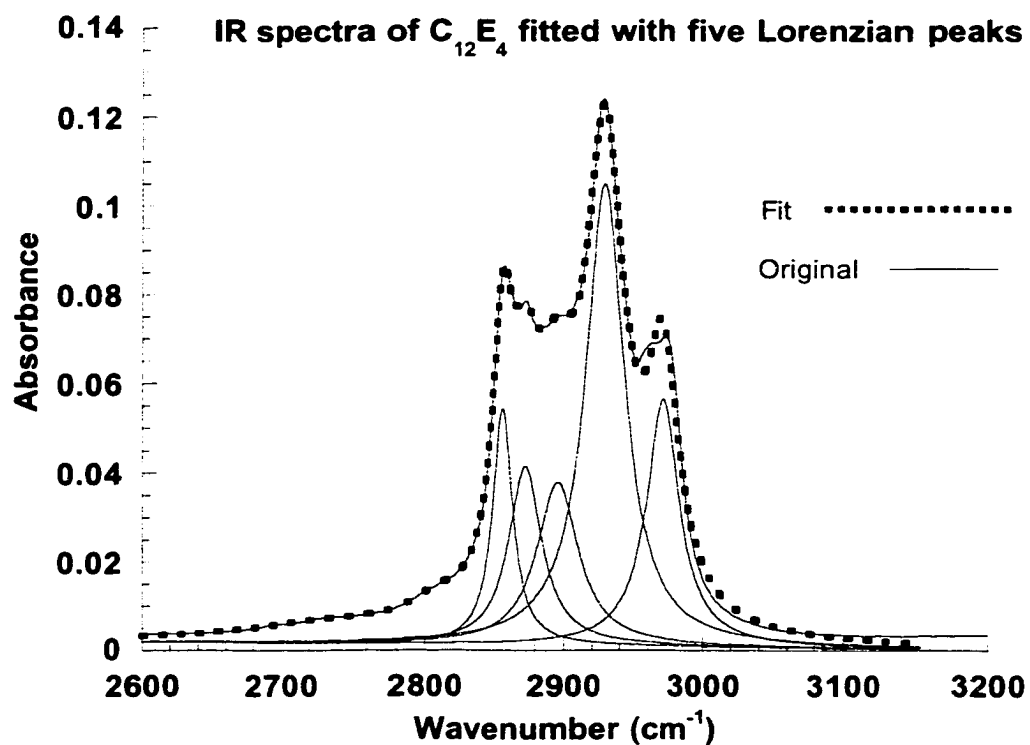


Figure 5.3: IR spectra of $C_{12}E_4$ in transmission mode, fitted with five Lorentzian peaks in the CH stretch region.

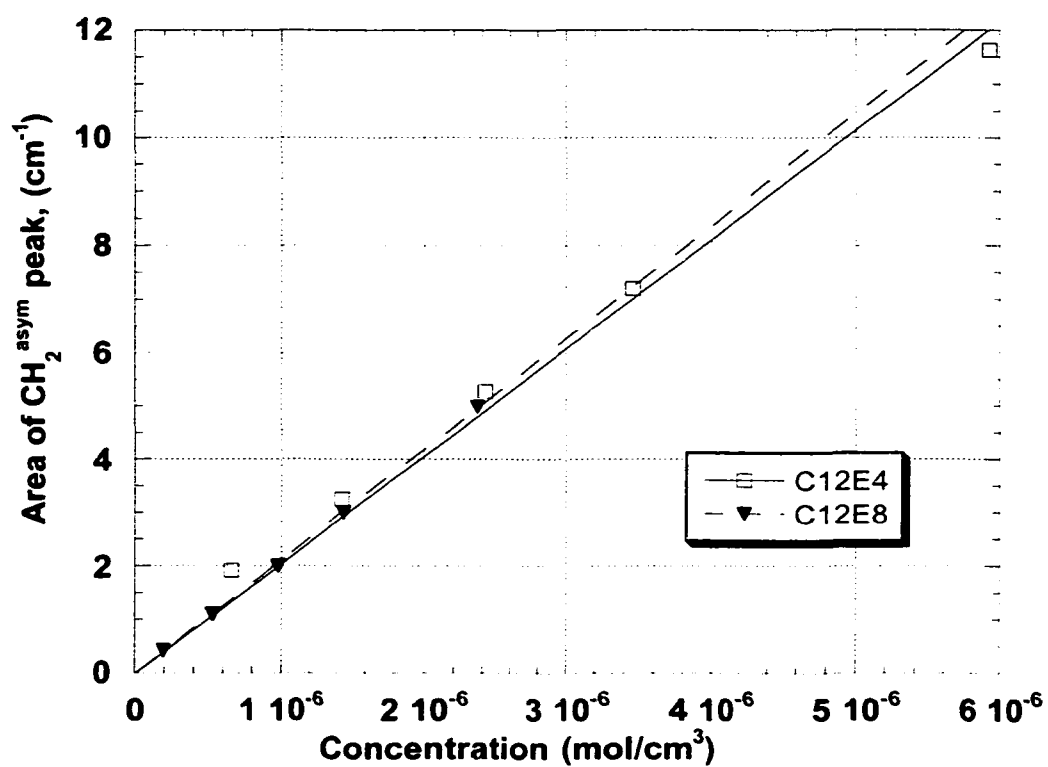


Figure 5.4: Calculation of integrated molar absorptivity (ϵ) of $\text{CH}_2^{\text{asym}}$ peak ($\sim 2925 \text{ cm}^{-1}$) for C_{12}E_4 and C_{12}E_8

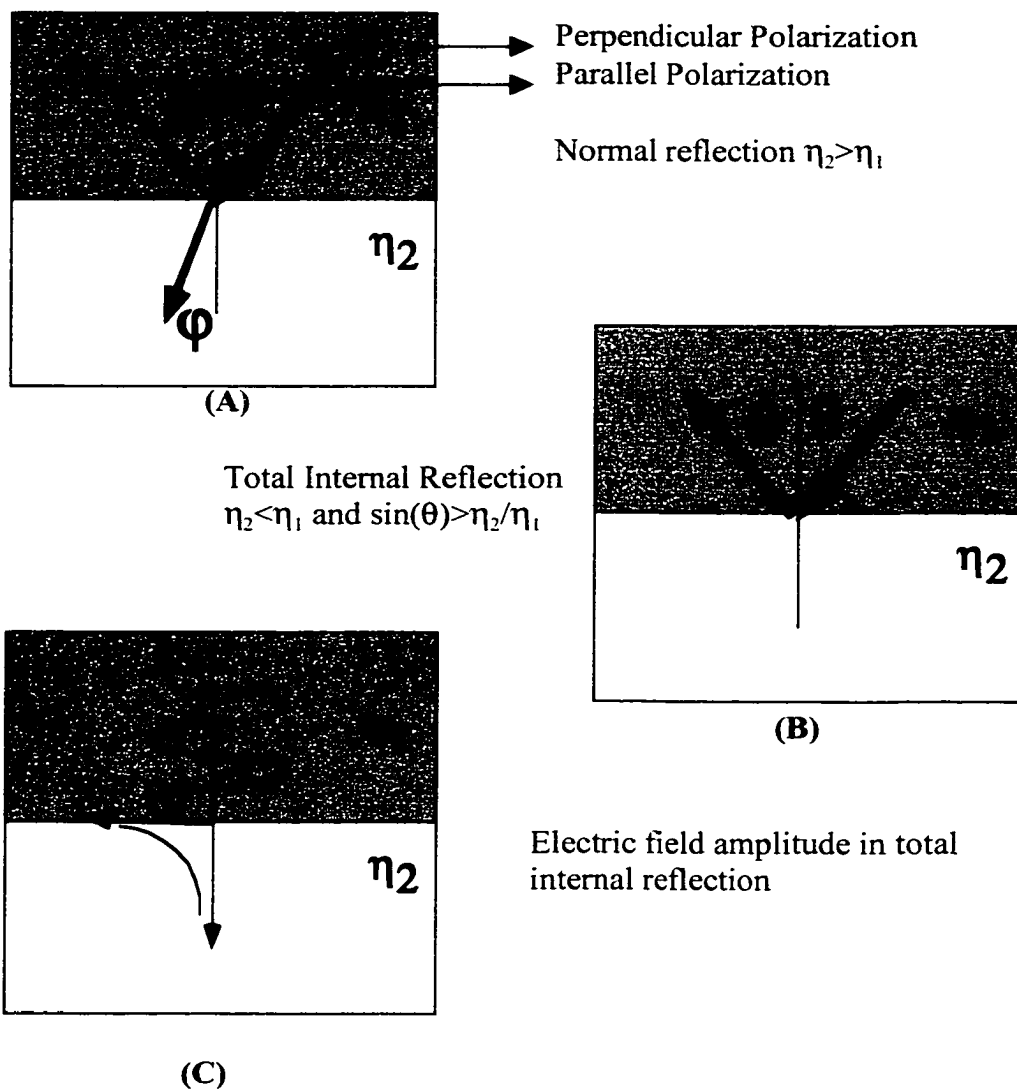


Figure 5.5: Normal and total internal reflection

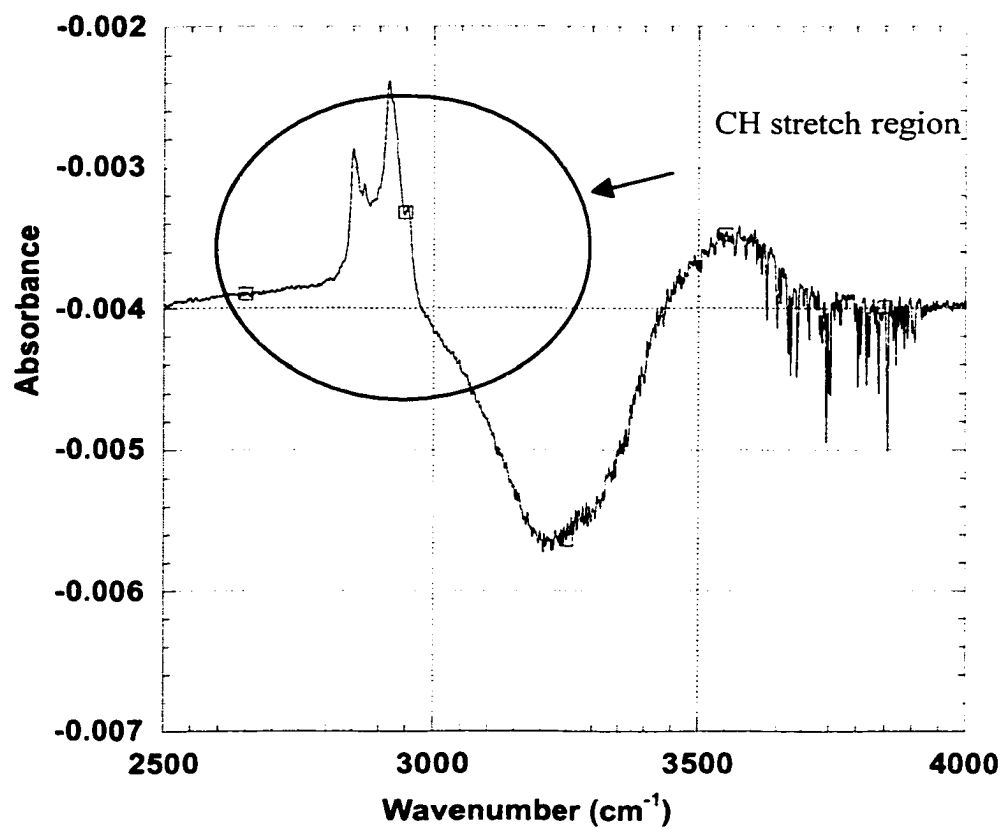


Figure 5.6: A spectrum of $C_{12}E_4$ adsorbed on OTS monolayer, deposited over Si ATR.

The background spectrum is water in contact with the OTS monolayer.

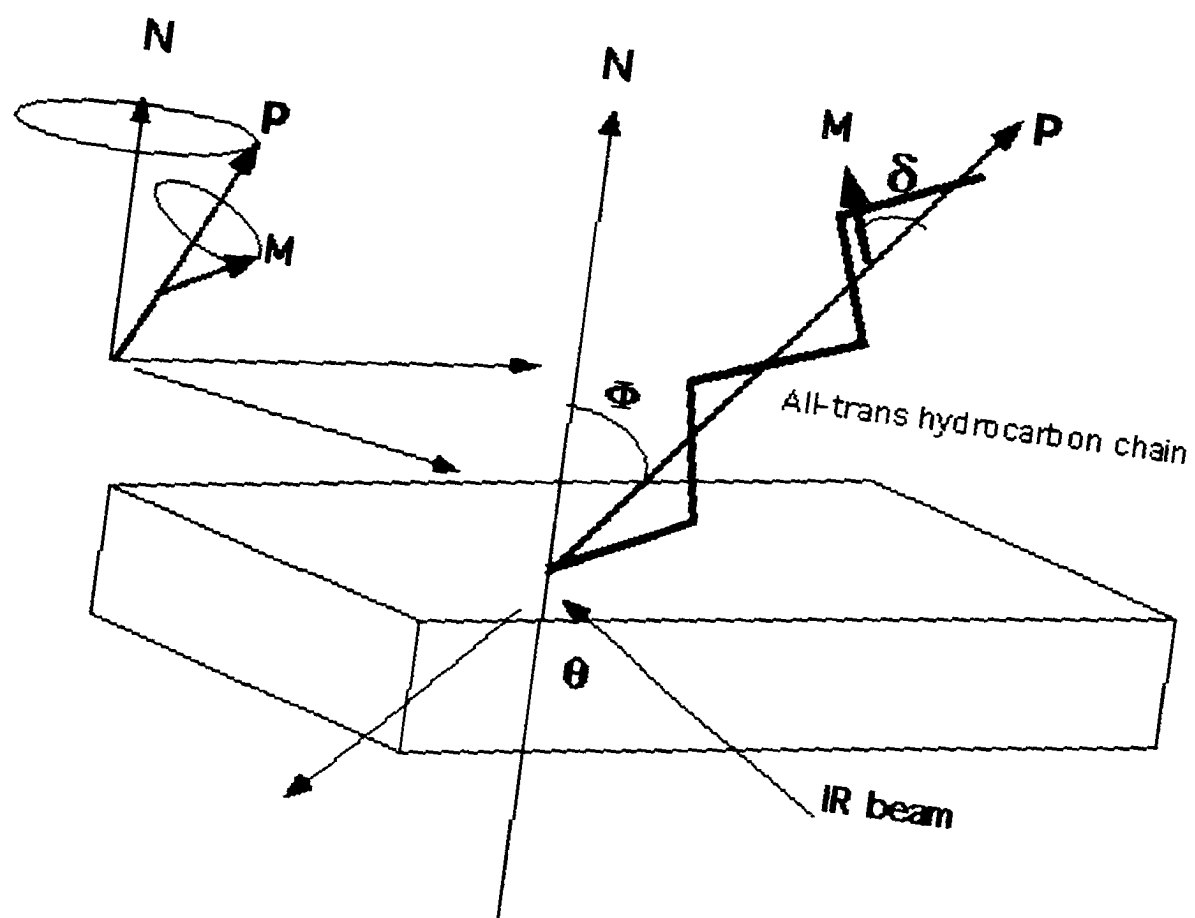
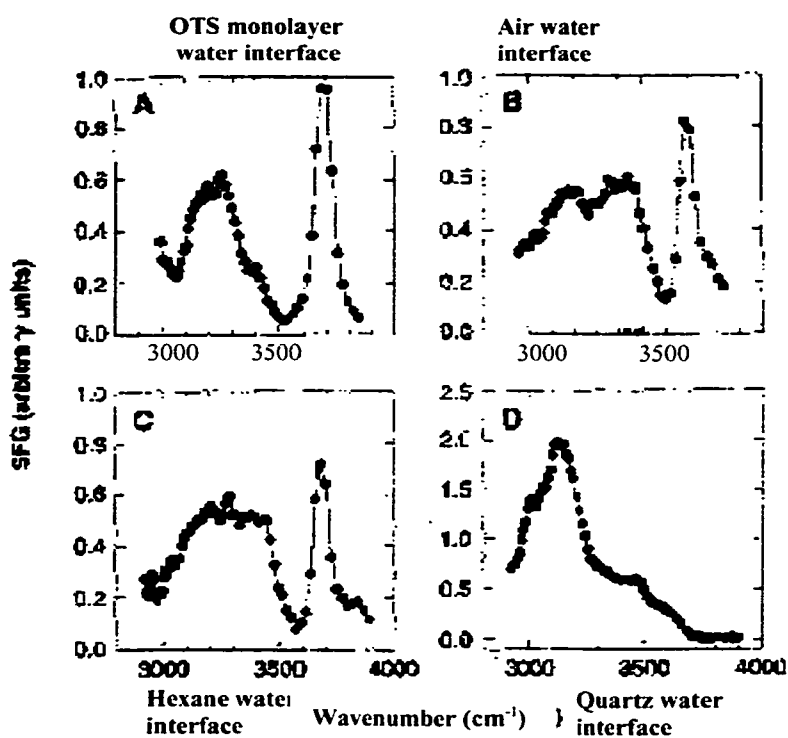


Figure 5.7: Calculation of dichroic ratio of a hydrocarbon chain normal to a surface



SFG spectra of interfaces obtained by Du et al

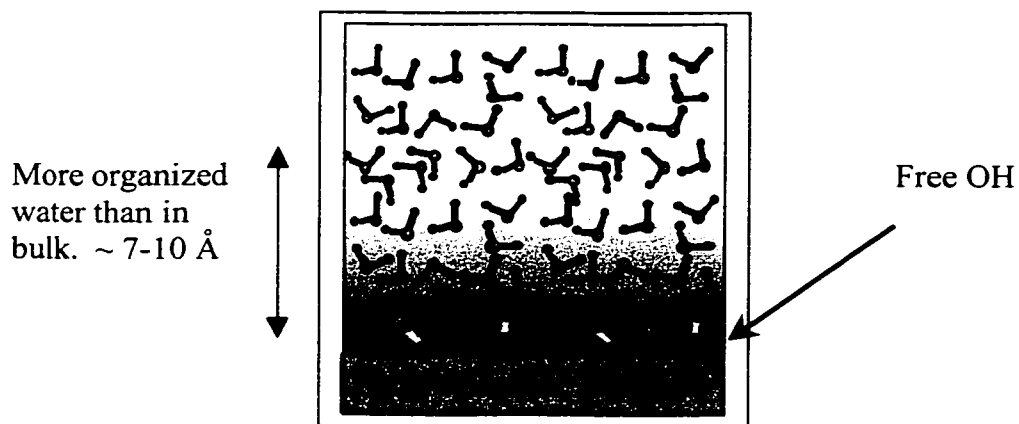


Figure 5.8: Description of the interfacial water structure suggested by Du et al.

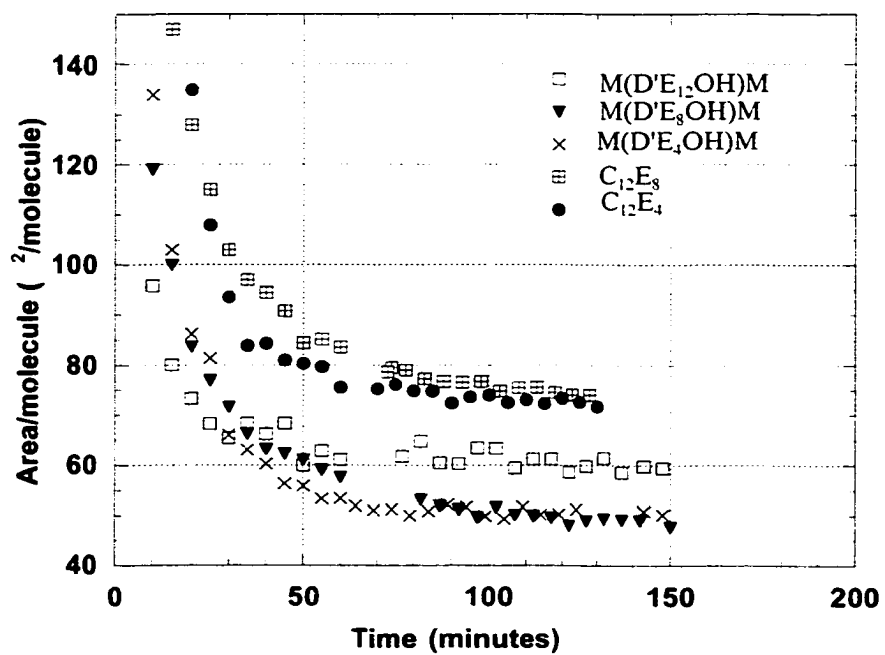


Figure 5.9: Adsorption of surfactants on the OTS monolayer at CAC

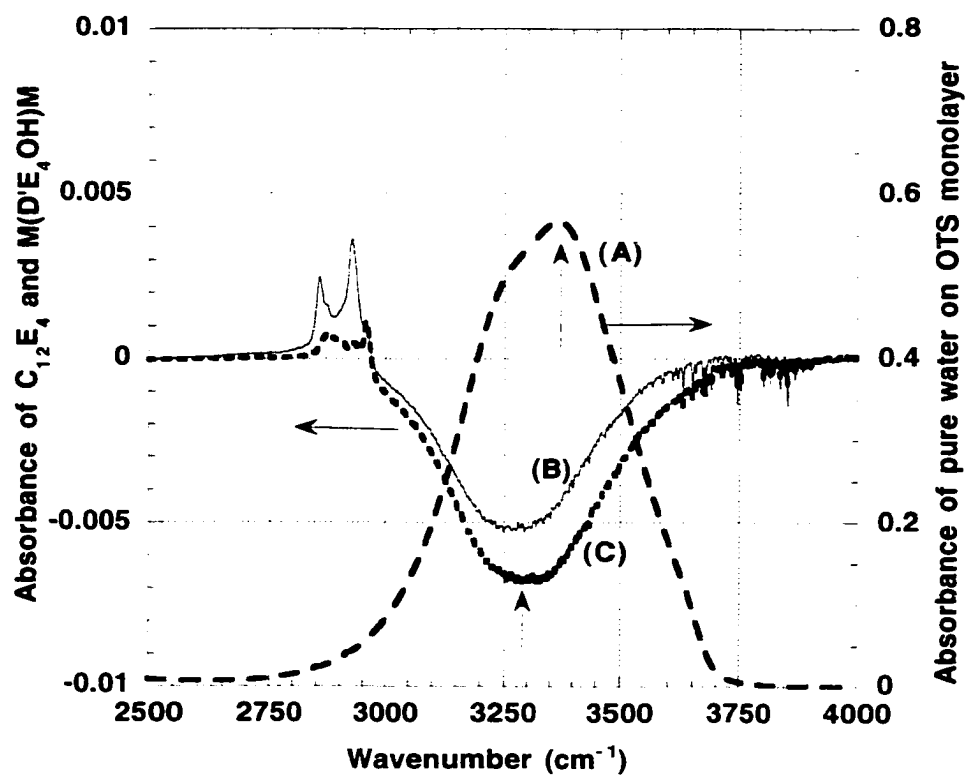


Figure 5.10: (A) FTIR-ATR spectrum of water on OTS monolayer. (B) and (C) changes in the spectra on adsorption of C₁₂E₄ and (M(D'E₄OH)M), respectively.

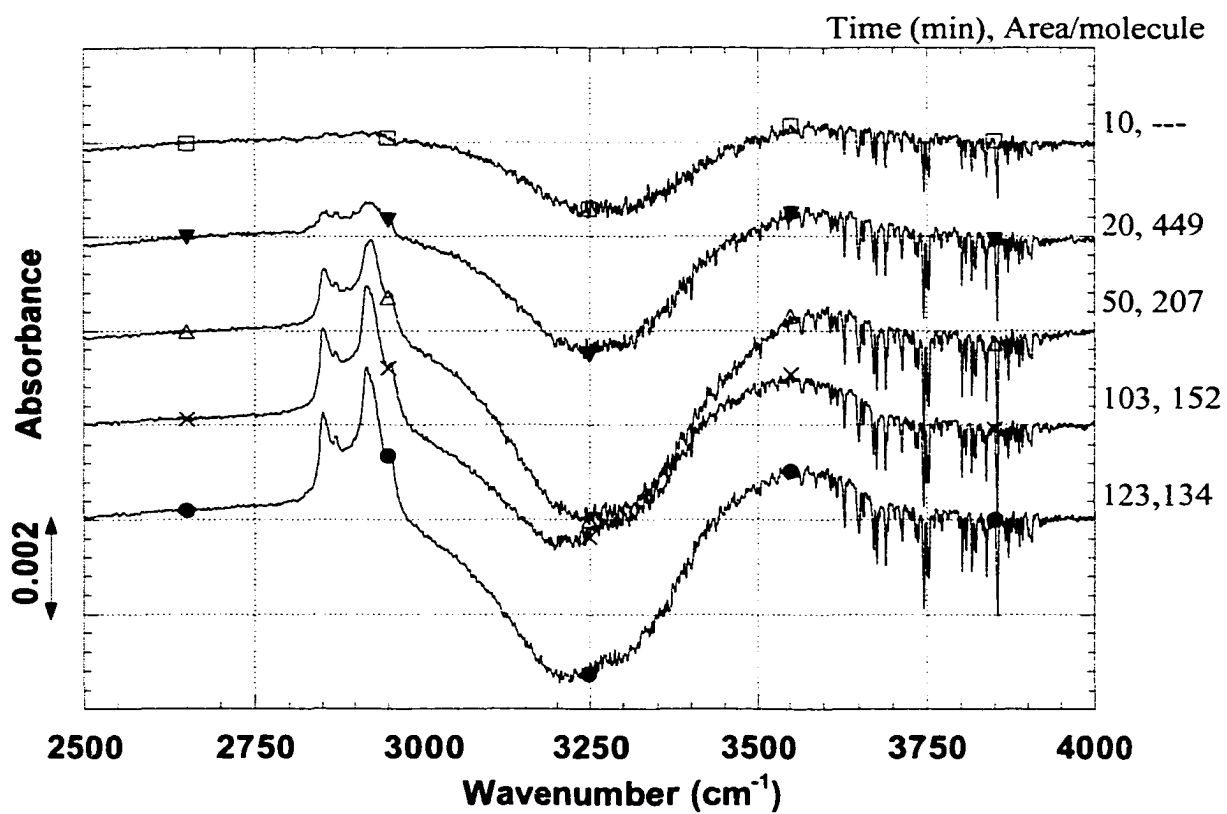


Figure 5.11: Changes in the spectra during adsorption of $C_{12}E_8$ from solution on to OTS monolayer. Concentration : CAC/30

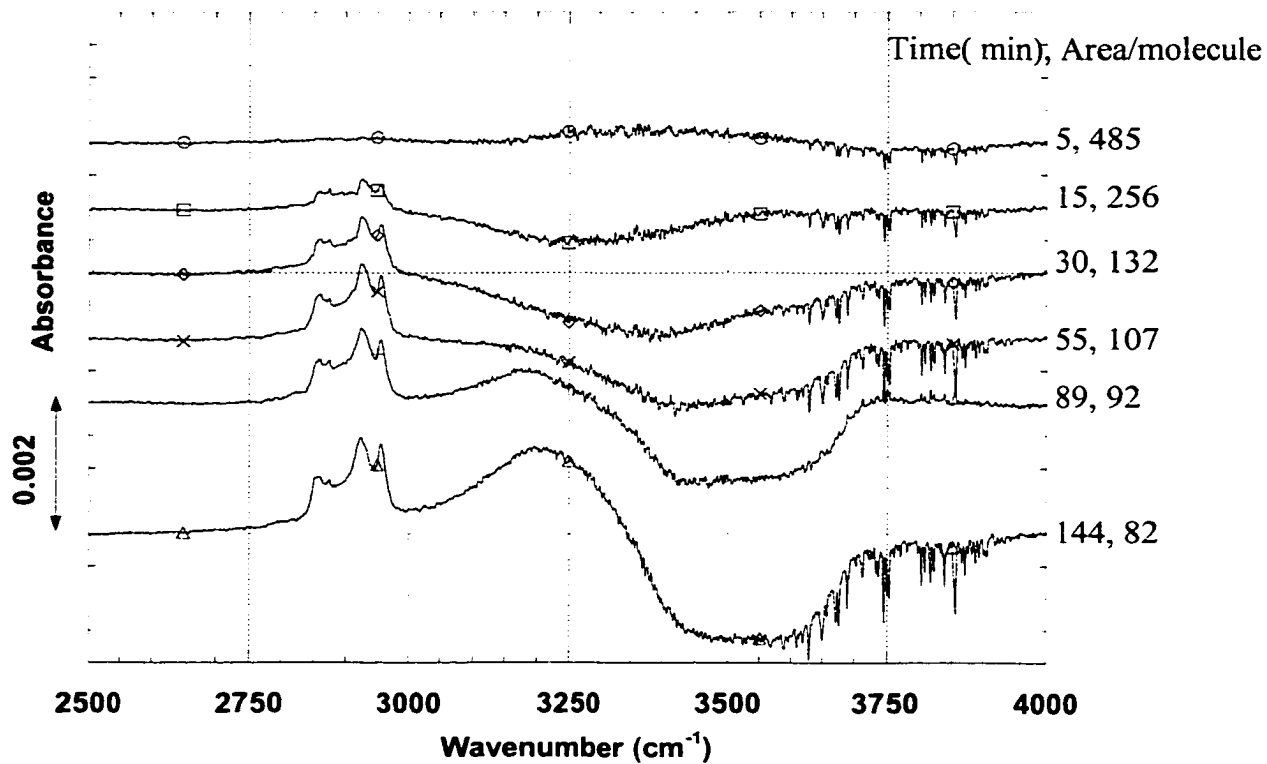


Figure 5.12: Changes in the spectra during adsorption of M(D'E₈OH)M from solution on to OTS monolayer. Concentration : CAC/30

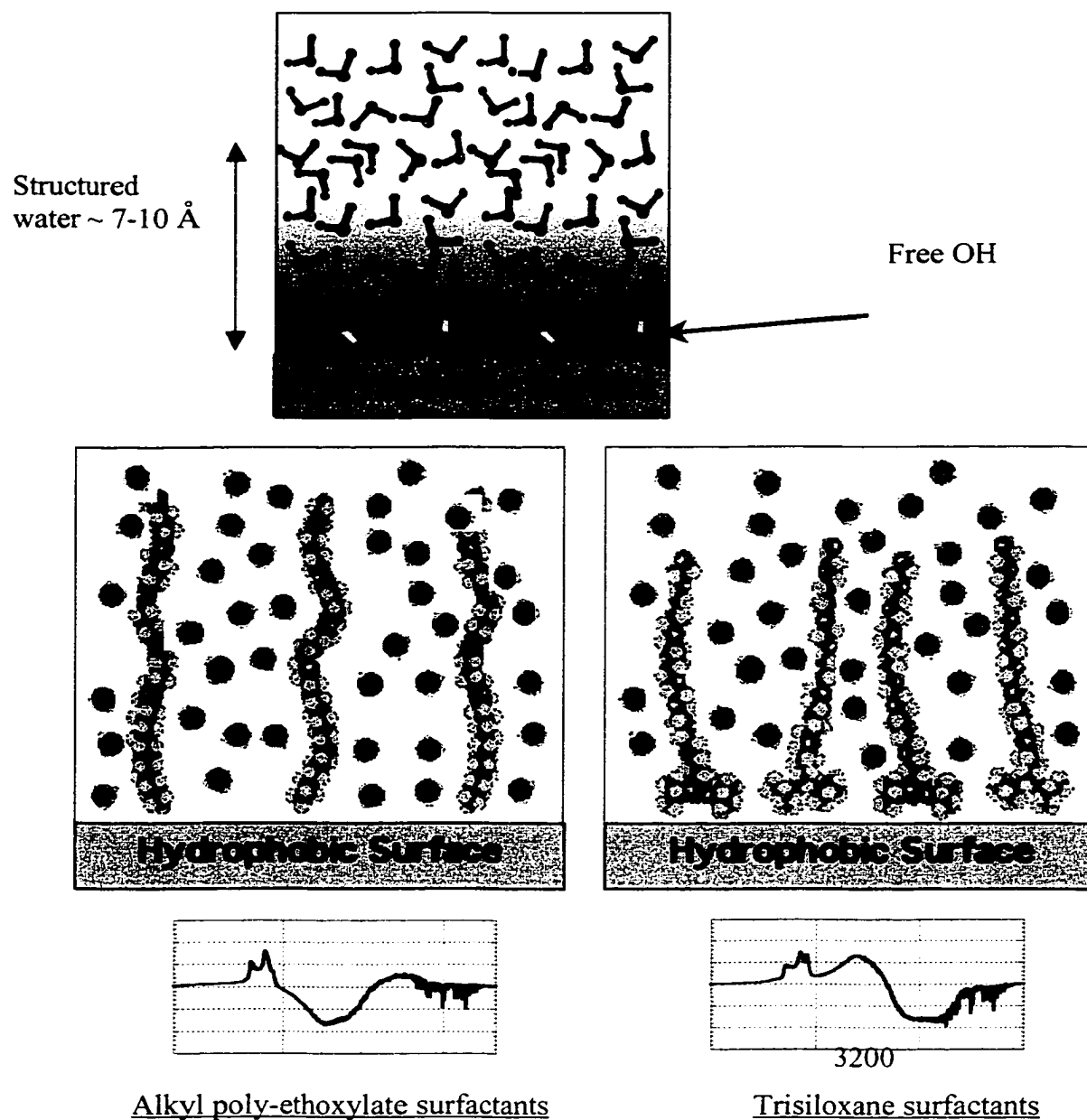


Figure 5.13: Structure of the adsorbed monolayers of trisiloxane and alkyl poly-ethoxylate surfactants.

Chapter 6:

Summary and Future work

6.1 Summary

The exceptional ability of the trisiloxane surfactants to enhance spreading of water on highly hydrophobic surfaces has been the focus of many studies. The reason behind their "super-spreading" ability is not yet clear. In this work, we explain the reason of their "super-spreading" ability by comparing their adsorption characteristics on air-water and hydrophobic solid-water surface with that of alkyl poly-ethoxylate surfactants ($C_{12}E_j$).

In the first part, we have developed model hydrophobic surfaces using self-assembled silane monolayers. These surfaces have been used for surfactants' adsorption experiments. Using Atomic Force Microscope as a tool to study the morphology of partial silane monolayers, we have developed mixed silane monolayers by sequential adsorption of different silanes. In these mixed monolayers, domains of one-chemical functionality are surrounded by other chemical functionality. The size and morphology of the domains can be controlled from nanometer to micrometer scale by controlling the deposition conditions.

The adsorption characteristics of trisiloxane surfactants on air-water interface have been studied by pendant bubble technique and compared with that of $C_{12}E_j$ surfactants. The adsorption of the trisiloxane and $C_{12}E_j$ surfactants on hydrophobic silane monolayers has been investigated using FTIR spectroscopy in attenuated total internal reflection mode. Due to the peculiar "T" structure of the hydrophobic groups, the

trisiloxane surfactants have larger driving force to adsorb on air-water interface. Consequently, they pack more densely than $C_{12}E_j$, and reduce the surface tension faster and to values lower than that of $C_{12}E_j$ surfactants.

On hydrophobic solid water interface, we have, for the first time, observed the changes induced in the hydrogen bonding of water near hydrophobic solids, as a result of surfactants' adsorption, and the effect of surfactant structure on the hydrogen bonding of the interfacial water. The trisiloxane surfactants reduces the hydrophobic-solid water surface energy to lower values because of their ability to remove free OH present near the hydrophobic surface. This is again attributed to their "T" structure. In conclusion, the super-spreading ability of the trisiloxane surfactants is due to their ability to reduce hydrophobic solid-water surface tension and air-water surface tension, which in turn is attributed to the structure of their hydrophobic group.

6.2 Future Work

The mixed silane monolayers can be used for a variety of applications as mentioned in Section 3.1 Formation of mixed monolayers, with wider variety of functional groups can be explored. This can be achieved by using different silanes. Some efforts could be also directed toward forming molecular scale homogeneous mixed monolayers containing silanes of different functionality. Domains of different chemical functionality can also be formed using optical mask on silane monolayers with photosensitive end groups. Another possible way (only a speculation) to change the morphology of the monolayers is to use a silane with a polar or charged group. By applying a strong electric field in a particular direction, the surface diffusion of the adsorbing molecules can be directed in some specific direction, which possibly can influence the fractal morphology of the partial monolayers.

Future work, directed towards the adsorption characteristics of the trisiloxane surfactants may be limited. However, numerical and hydrodynamic simulations can be carried out to study the effect of various adsorption parameters in drop impact and Marangoni flow driven spreading. With the adsorption characteristics of monomeric surfactants known, dynamic surface tension data above CAC can be used to study properties of various phases in bulk, such as, the comparative ability of a micellar or lamellar phase to supply the surfactant effectively onto the interface.

The kinetic adsorption characteristics of the surfactants on hydrophobic solids are still not available. More experiments can be carried out in a properly designed flow cell to evaluate these properties. The water restructuring effect is a matter of much larger

debate and consequences, not just in the surfactants, but also in other fields. Not much can be done by one person in this aspect.

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