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**A STUDY OF SURFACTANT EQUATIONS OF STATE AND TRANSPORT
DYNAMICS AT THE AIR/WATER INTERFACE**

by

RENNAN PAN

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

1996

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Abstract

A STUDY OF SURFACTANT EQUATIONS OF STATE AND TRANSPORT
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Adviser: Professor Charles Maldarelli

This dissertation studies the adsorption isotherm, surface equation of state and transport dynamics of water soluble nonionic surfactants at the air/water interface. A method which involves using the pendant bubble as a monolayer film balance is developed to directly measure the surface tension as a function of surface concentration. By using this method, both the equilibrium and dynamic surface tension/surface concentration data are measured, which effectively prove the commonly used assumption that the equilibrium and dynamic surface equations of state are equivalent. A molecular interaction model is developed for nonionic surfactants based on a molecular interaction approach, which includes: a kinetic rate equation, an adsorption isotherm and a surface equation of state. This model describes the equilibrium surface tensions and surface tension/surface concentration data better than the existing models. The four model parameters for a few polyethoxylated surfactants are obtained. The surfactant transport dynamics onto the air/water interface is studied for a model surfactant $C_{12}E_6$. Two new ideas to promote the kinetic effects in the transport dynamics have been proposed. One is for clean interface

adsorption, which states that the kinetic effect is increasing when the bulk concentration increases. The other is for overcrowded interface desorption, which says that the kinetic effect is increasing when the initial surface concentration increases. These ideas are proved theoretically and experimentally. By using these ideas, the kinetic rate constants and diffusion coefficient are measured for the model surfactant $C_{12}E_6$.

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Chapter 1

Introduction

1.1 Background

Surface active molecules (surfactants) are amphiphilic molecules which contain both polar (hydrophilic) and nonpolar (hydrophobic) chemical groups. When they are present in a system consisting of two fluid phases of different polarity (e.g. air/water or oil/water systems), surfactants adsorb preferentially at the interface between the two phases where they lower the surface or interfacial tension. Surfactants relocate at interfaces because they can configure themselves with the polar group in contact with the more polar phase, and the nonpolar group in contact with the more hydrophobic phase^[1,2].

Water soluble surfactants are surfactants with relatively small nonpolar groups which do not exclude the molecules from an aqueous environment. Surfactants dissolved in water are reservoirs for the supply of surfactant molecules to surfaces. For an aqueous surfactant solution in contact with air, there is an equilibrium between the surfactant in the aqueous phase and the surfactant on the water/air surface which is reached when the chemical potentials of the surfactant in the aqueous phase and on the surface are the same. The relationship between the bulk concentration and the amount of surfactant adsorbed on the surface at equilibrium is the equilibrium adsorption isotherm. The equilibrium surface equation of state relates the surface tension to the amount of surfactant adsorbed on the

surface at equilibrium. This equation of state can be obtained from the measurement of the surface tension as a function of the bulk concentration at equilibrium since the slope of the surface tension/bulk concentration curve is proportional to the surface concentration. The route to the equilibrium state is the dynamics of surfactant adsorption and desorption. Dynamic exchange is studied by measuring the dynamic surface tension. The equation of state which relates the surface tension to the surface concentration for nonequilibrium processes is the dynamic equation of state, and from this equation of state and dynamic tension data, the adsorption rate onto the surface can be inferred.

The transport of surfactant molecules between the bulk phase and the surface is divided into two steps: bulk diffusion and convection to a sublayer adjoining the surface, and a kinetic process involving adsorption and desorption from the sublayer to the surface. In bulk diffusion and convection, surfactant molecules transport between the bulk phase and the sublayer by diffusion and convection, which is described by the mass conservation equation. In kinetic adsorption and desorption, surfactant molecules exchange between the sublayer and the surface and is described by a kinetic rate equation. The diffusion coefficient and the kinetic rate constants are the transport parameters which control the dynamics of surfactant adsorption. Measurement of these parameters leads to a more complete understanding of the dynamic process of surfactant transport to a surface. Determination of dynamic equations of state allows for a more complete understanding of the surface tension changes accompanying the surfactant adsorption onto the surface.

Surfactants find many applications in interfacial industrial technologies because of their surface tension lowering ability. In practical applications, both the equilibrium and the dynamical surface tension behavior of surfactant solutions can be important, and in high speed interfacial processes, the dynamic surface tension behavior is the more important one. Examples include:

(i) The rapid water wetting of fabric for surface treatment, dyeing, or resin impregnation^[3,4,5,6]: An aqueous solution placed on the surface of a fabric penetrates into the fabric by capillary suction. Rapid wetting of the fabric is usually desired for the delivery of a resin or dye into the fiber matrix. Surfactant is often used to accelerate the wetting process. Surfactant adsorbing at the interface reduces the contact angle, causing the capillary pressure in the advancing liquid meniscus to decrease and thereby increasing the driving force for the impregnation flow. Bifurcation of the meniscus in the fabric matrix continually increases the interfacial area at the advancing front; this reduces the surface concentration at the front, requiring fast adsorption to maintain the rapid spreading. The importance of rapidly lowering the tension to increasing the rate of wetting is clearly demonstrated by Rosen and Hua^[3], who measured the wetting out time (WOT; the time necessary for a standard section of textile, placed on the surface of an aqueous solution, to drop by its own weight into the solution because of the water impregnation) as a function of the dynamic tension of various surfactants as measured one second from the interface creation by the maximum bubble pressure method. They have shown the increase in the wetting time with the dynamic tension at one second. However, equilibrium surface tensions do not correlate with the wetting out time.

(ii) Surfactant facilitated drop spreading^[7,8]: Herbicides are delivered to the leafy surfaces of plants by dissolution of the technical in an aqueous solution which is sprayed onto the foliage. The efficacy of a formulation depends on the amount of the technical retained on the leaf surface. Deposited aqueous drops of the formulation usually do not spread well because of the waxy coat on the leaf surface, and they therefore tend to slide off of or bounce from the leaf surface. Surfactant is used to facilitate drop spreading and enhance droplet retention by increasing the drop contact area. Surfactant adsorbing from solution reduces the contact angle which increases the spreading rate. Adsorption must be rapid because as the drop spreads, new interfacial area is created and the surface

concentration is depleted. The dynamic surface tension correlates well with the spray retention. Lower dynamic surface tension results in higher spray retention..

(iii) Sliding coating: In this process, flow velocities range from 0.35 to 2.03 m/s. The dynamical surface tension in fast time scales (10^{-3} to 1 s) affects significantly the stresses which control flow and film deformation^[9]. Dynamical surface tension affects the dynamical wettability in coatings and the "coatability window", i.e. the set of parameters which lead to quality coatings. Film retraction and "crawling" during coating can be avoided or minimized by low dynamic surface tensions in water-based coatings.

Other examples are found in enhanced oil recovery. Aqueous foams are often used to increase the sweep efficiency in carbon dioxide flooding processes, and dynamic tension controls the elasticity of the interface and thereby the stability of the foam^[10,11]. More examples can be found in food processing, particularly involving emulsions containing proteins, where the dynamic adsorption of the protein again controls the elasticity of the interface and the stability of the food emulsion.

1.2 Research Scope

The above examples illustrate clearly that surfactant transport at a surface and accompanying changes in tension play a crucial role in technological processes, and insight into transport and dynamic tension can lead to a better understanding of, and improvement in, these processes. Surfactant transport is characterized by the molecular diffusion coefficient and the kinetic rate constants. Dynamic tensions are characterized by dynamical equation of state which relates the time dependent surface tension to the surface concentration. This research seeks to measure kinetic rate constants, diffusion coefficients and surface equations of state. As we will discuss in the literature review (Chapter 2), our

knowledge of kinetic constants is limited. In addition, the usual approach in the literature is to assume the equilibrium equation of state is applicable to the dynamic processes as well. As we have mentioned, the equilibrium equation of state is obtained from the surface tensions as a function of the bulk concentrations at equilibrium. No direct measurements of dynamic equations of state have been made, and so this approach has not been validated.

This study is divided into three parts. In the first part, we develop a new technique to directly measure the dynamic equation of state. This method involves using a pendant bubble as a Langmuir trough to directly measure the surface tension as a function of the relative surface concentration. A pendant bubble is formed at the tip of an inverted needle immersed in a surfactant solution, and an equilibrium monolayer adsorbs onto the bubble interface. The surface area of the bubble is then contracted and/or expanded in a time period of 5-15 seconds. Experiments and numerical simulations show a negligible amount of surfactant exchange during the period of area change. The bubble is video imaged, and from digitization of the image the interface contour can be located. The contour is fitted to the Young-Laplace equation, from which the surface tension is obtained. By measuring the surface tension as a function of surface area, we obtain the tension as a function of surface concentration. A homologous series of polyethoxylated surfactants $C_{14}E_6$, $C_{14}E_4$, $C_{14}E_2$ are chosen as test surfactants to illustrate the method. These surfactants of the form $C_i E_j$, consist of a linear hydrocarbon chain ($CH_3-(CH_2)_{i-1}-$) and an ethoxylate ($-(O-CH_2CH_2)_j-OH$) as a polar group. We show that the dynamic equation of state so measured is equivalent to the equilibrium equation of state which agrees with equilibrium surface tension/bulk concentration measurements.

In the second part of the study, we use the surface tension/surface concentration data obtained from the first part of the study to illustrate that the existing adsorption isotherms are not satisfactory for the $C_i E_j$ surfactants. Then, we develop a new kinetic

scheme based on a molecular interaction approach, which leads to a new adsorption isotherm and surface equation of state. This molecular interaction model is verified by the surface tension/surface concentration data as well as equilibrium surface tensions.

In the last part of the study, we first examine the dynamic exchange process theoretically for both adsorption to an initially clean interface and desorption from an overcrowded interface. We develop criteria to distinguish under what conditions diffusion or kinetics determines the transport rate. We show that surfactant dynamics can shift from diffusional control, to mixed diffusive-kinetic control, and finally to kinetic control as the bulk concentration is increased for clean interface adsorption and as the initial surface concentration after compression is increased for desorption from an overcrowded interface. These criteria clarify the confusion of several literature investigations considering the controlling mechanism for surfactant adsorption, and can be used to choose experimental conditions that favor kinetic control in order to measure the kinetic rate constants.

We use these criteria to unequivocally measure the kinetic rate constants of a test surfactant $C_{12}E_6$ by using the pendant bubble apparatus. Two types of experiments are done, clean interface adsorption, and desorption reequilibration from an overcrowded surface. All dynamical experiments are undertaken using the pendant drop tensiometer, in which video imaging of a bubble at the tip of a capillary is used to measure surface tension. In clean interface adsorption, a bubble is created quickly through an inverted Teflon or stainless steel needle immersed in an aqueous surfactant solution. When the bubble is just formed, the amount of surfactant on the bubble surface is very small and can be regarded as zero. Surfactant transports from the bulk to the sublayer, and then kinetically adsorbs onto the surface until equilibrium is reached. As the process proceeds, the surface concentration increases because of adsorption and the surface tension decreases. The experiments are done at high concentrations so that the transport is mixed. Numerical

solution of the surfactant transport equations are obtained and compared to the dynamic tension data in order to determine the diffusion coefficient and kinetic rate constants. In desorption from an overcrowded surface, a bubble is formed at the tip of a Teflon needle immersed in an aqueous surfactant solution. After equilibrium is reached, the bubble is perturbed by a sudden contraction. The monolayer is compressed, and surfactant molecules desorb from the surface to the sublayer, and are transported from the sublayer to the bulk by diffusion until equilibrium is reached. Dynamical surface tensions are compared to numerical simulations to obtain the kinetic rate constants and diffusion coefficient. These experiments are done at high enough initial compressions to promote kinetic effects.

This dissertation is divided into six chapters. Chapter 2 details a literature review of previous studies of the dynamics of surfactants exchange, and the experimental methods used to study this process. We present the study of surfactant properties in Chapter 3, 4 and 5. Chapter 3 proves the existence of a dynamic surface equation of state and its equivalence to the equilibrium surface equation of state using the model polyethoxylated surfactants $C_{14}E_6$, $C_{14}E_4$ and $C_{14}E_2$. The new method to measure the surface equation of state is described in detail in this chapter. Chapter 4 describes the development of a new kinetic rate equation, adsorption isotherm, surface equation of state based on a molecular interaction approach, which are called the molecular interaction model. This molecular interaction model predicts the equilibrium properties well for the polyethoxylated surfactants $C_{14}E_6$, $C_{14}E_4$, $C_{14}E_2$, $C_{12}E_6$ and $C_{16}E_6$. The criteria for the controlling mechanism of surfactant adsorption is theoretically derived in Chapter 5. This chapter also details the experimental results for $C_{12}E_6$ and the interpretation which leads to the measurement of the kinetic rate constants. Chapter 6 summarizes this dissertation research and presents the conclusions.

Chapter 2

Literature Review

In this literature review, we begin in Section 2.1 by examining previous studies of surfactant equations of state and adsorption isotherms. In the following two sections (Section 2.2 and 2.3), we discuss the measurement of the surfactant kinetic rate constants and diffusion coefficients. These are obtained in experiments in which the dynamic surface tension is measured as surfactant adsorbs onto a clean surface or desorbs off from a compressed surface with an equilibrium monolayer. In Section 2.2 we review the methods for measuring these dynamic surface tensions, and in Section 2.3, we examine how the transport is modeled and the conclusions which have been reached on the transport parameters.

2.1 Equilibrium Adsorption Isotherms and Surface Equations of State

Obtaining a reliable surface equation of state is one of the keys to understanding surfactant adsorption dynamics. Unfortunately, not enough attention has been paid to this key point. The conventional method^[1,2,3,4] to find the equilibrium surface equation of state involves measuring the equilibrium surface tensions at different bulk concentrations. A kinetic scheme is then formulated, and by equating adsorption and desorption rates, an isotherm is obtained. This allows the Gibbs equation to be integrated to an explicit form, which is the relation between the equilibrium surface tension (γ_e) and the bulk concentration

(C_b). The adsorption isotherm and the Gibbs equation define the equilibrium surface equation of state. Comparison of the equilibrium equation of state with γ_e - C_b data allows for the determination of the equilibrium parameters of the adsorption isotherm.

The most commonly used adsorption isotherm is the Langmuir isotherm^[2,5]. In this adsorption isotherm, four assumptions are made^[6]: (i) The adsorption layer is a monolayer; (2) There is no interaction among the adsorbed molecules; (3) The surface is homogeneous; and (4) The equilibrium state is an equilibrium of adsorption and desorption. The Langmuir isotherm is found to model γ_e - $\ln C_b$ curve well in many surfactant systems^[2,5,7,8]. If molecular interactions among the surfactant molecules on the surface are strong for a surfactant system, particularly cohesive interactions among the hydrocarbon chains, then the Langmuir isotherm is not adequate. In these cases, the Frumkin isotherm is better to employ^[9,10,11]. The Frumkin isotherm is also based on the Langmuir formalism, but the molecular interactions of the surfactant molecules on the surface are taken into account in the activation energies of adsorption and desorption. More equilibrium approaches, including the Henry isotherm, Volmer surface equation of state, van der Waals surface equation of state^[12], generalized Frumkin isotherm and phase transition model^[11], are also used in the literature. By matching the theoretical γ_e - $\ln C_b$ curve to the experimental data, the best fitted equilibrium parameters and hence the equation of state can be found.

The common problem of the equilibrium approaches arises from the experimental limitations. Because of the difficulty in locating the slope on the γ_e - $\ln C_b$ curve to find surface concentrations by the Gibbs equation, remarkably different equilibrium parameters for the same surfactant system have been reported by different models^[11,13], which fit the γ_e - $\ln C_0$ experimental data equally well, and by different authors^[1,14]. More questions could be raised about the difference between the prepared concentration (C_0) and the real

bulk concentration (C_b) in the equilibrium surface tension measurements, because depletion of surfactant onto interfaces is important at low concentrations. Further, Lucassen^[15] found that the dynamical surface properties are much more sensitive to the surface equation of state than the equilibrium surface tensions. These facts reflect that fitting $\gamma_e - \ln C_0$ data is not a sensitive method to find the true equilibrium parameters. The possible solution is to directly measure the relationship between the surface tension and the surface concentration.

The direct measurement of the surface concentration was first done by McBain^[16], who used a microtome method. Salley^[17] and Dixon^[18] developed a method to directly measure the surface concentration by making use of radiolabeled atoms. These methods are very difficult to undertake, so they are not widely used by researchers. Recently, some new optical methods such as Fourier Transform spectroscopic measurements at an interface have been introduced to determine the surface concentration directly^[19,20,24]. More attempts have been made to measure the surface concentration by transferring surfactant monolayers to a solid substrate^[21]. These methods could possibly provide the direct measurement of surface concentration in the future, but they are still under development. So, a simple direct method to measure the surface concentration is warranted and as yet not available.

Another important issue involving studying surfactant adsorption dynamics is the validity of the commonly made assumption that the relationship between the dynamical surface tension and the dynamical surface concentration is the same as that at equilibrium. Loglio^[22] and Forham^[23] examined this question theoretically, but gave no experimental evidence. Therefore, two key issues need to be resolved about surface equations of state before studying surfactant adsorption dynamics. One is to find a simple method to directly measure the relationship between the surface tension and the surface concentration. The

other is to prove the assumption that the dynamical and equilibrium surface equations of state are equivalent.

2.2 Methods for the Measurement of Dynamic Surface Tension

Many methods for measuring dynamic surface tension have been reported in the literature^[14,24]. These are mainly of four types: (i) force methods: Wilhelmy plate and Du Nouy ring; (ii) the pendant drop or bubble method; (iii) pressure methods: maximum bubble pressure method and growing drop method; (iv) other methods.

Wilhelmy plate and Du Nouy ring methods have been used to measure equilibrium surface tensions^[25,26,27], and some authors^[28] have used these methods to measure dynamical surface tensions. In these methods, the force required to pull the ring or plate placed in a surface by surface tension is measured very accurately, and from this force the surface tension can be calculated. Because of the uncertainty of the contact angle (for plate) or correction (for ring), there can be a large error in the surface tension^[29]. In the measurements of dynamical surface tensions, the time from creating a fresh surface, to taking the first measurement, which is called the dead time, is usually bigger than one minute. So, they are not adequate to measure short time scale dynamics.

In the pendant drop or bubble method, a pendant bubble or drop is formed at the tip of a needle and the shape of the drop or bubble is measured. The theoretical shape is described completely by the Young-Laplace equation^[30,31]. By matching the theoretical shape generated by the Young-Laplace equation to the experimental drop or bubble shape, one can calculate the surface tension. In the last few years, this method has been developed to achieve high accuracy by using video image digitization and computers^[32,33]. Both dynamical and equilibrium surface tensions can be measured

with high accuracy. The dead time is reported of 2 to 4 seconds^[33]. The only important problem is the non-axisymmetric attachment of the bubble or drop to the tip of the needle.

The maximum bubble pressure method has been widely used to measure the dynamical surface tensions of surfactant solutions^[34,35,36]. This method involves measuring the maximum pressure to inflate a bubble in a liquid from a capillary. The assumption is made that the bubble reaches a hemisphere at the maximum pressure, then the radius of the bubble is equal to the radius of the capillary. By the Young-Laplace equation, the surface tension can be calculated easily. The maximum bubble pressure method is able to measure the dynamical surface tensions at short time scales. Fainerman^[37] reported the dynamical surface tension measured by this method in a time scale of 1 ms. The major problem in the use of this method to study adsorption dynamics is the difficulty in the formulation of mass transport, as convection is important and the bubble surface area is changing dramatically. The other problem is that the dynamical surface tensions are obtained from different bubbles.

The growing drop method is a newly developed method to measure the dynamical surface tension over a wide range of time scales^[38,39]. In this method, a drop grows from a capillary tip into a second immiscible phase or air. The pressure difference across the drop interface is measured by a pressure transducer connected to the capillary. The shape of the drop is imaged by a video camera and the drop radius is calculated by the image. The surface tension is again calculated by the Young-Laplace equation. The advantage of this method is that it captures the actual dynamic tension history of an interface, rather than the tensions at discrete interval times as with the maximum bubble pressure method. Recently Zhang^[40] improved this method by the use of an ultra-high-speed video camera, and the time scale for taking measurements is refined to 1/6 to 1 ms, which is the shortest time scale reported in the literature.

The oscillating jet method is also able to determine the dynamical surface tensions on a milliseconds scale^[41,42], which makes it attractive to study fast surfactant adsorption dynamics. In this method, the solution is ejected through a small elliptical orifice under constant pressure, and stationary waves are produced on the surface. These waves oscillate about their equilibrium circular form, with the restoring force being the surface tension. By measuring the wavelength, one uses the Bohr equation^[43] to calculate the surface tension. This method measures the dynamical surface tensions at discrete interval times, and the mass transport in this method is difficult to model. Details about this method are reviewed by Defay and Petre^[44].

The drop volume and weight techniques^[45,46] are frequently used methods to determine surface and interfacial tensions of surfactant solutions. The advantages are that only small amounts of solutions are required for measurement, and the measurement is highly reproducible. In this method, the volume or weight of a hanging drop detached from the tip of a needle is measured. From the force balance which includes the surface tension and the gravity forces, the surface tension is calculated. This method also measures the dynamic surface tensions at discrete time interval. The time scales of this method range from 0.04 s to minutes.

In the oscillating bubble method^[47,48], a cap of a bubble with definite size is produced at the tip of a capillary submerged in a surfactant solution, and the bubble is oscillated. If the capillary is small enough and the bubble caps are smaller than a hemisphere, the shape of the oscillating bubble does not deviate from the radial mode of oscillation. This allows for a straightforward description of the flow field. The phase shift between the pressure and radial oscillations is measured at various known forcing frequencies, and one can study the surfactant adsorption dynamics.

Another type of dynamic surface tension measurement involves imposing surface area changes, either in a Langmuir trough^[49] or in a reverse funnel^[50]. The surface tension is measured by a Wilhelmy plate. This method measures re-establishment of equilibrium after imposing a surface area change, and is useful to study the surfactant adsorption dynamics.

Some other methods, including the capillary rise method^[51], inclined plate technique^[52], free falling film method^[53], capillary wave method^[24], and Longitudinal wave method^[54] are also used to measure surface tensions by investigators. Different methods validate each other and give a complete picture in the area of the surface tension measurements.

2.3 Surfactant Adsorption Dynamics

The measurement of surfactant transport parameters involves experimentally measuring the dynamical surface tensions by the methods discussed in Section 2.2, and then theoretically modeling the surfactant transport by mass conservation equations, provided that the equation of state is known. The comparison of theoretical results with the experimental data gives the diffusion coefficient and kinetic rate constants.

The surfactant transport between the pre-micelle bulk and the surface is a two-step process: bulk diffusion and convection to a sublayer, kinetic adsorption and desorption between the sublayer and the surface. When a static method is used to measure dynamical surface tensions, where convection can be neglected, then Fick's law alone is sufficient to model the surfactant transport between the sublayer and the bulk. If the kinetic exchange between the sublayer and the surface is infinitely fast, then the diffusion-controlled

adsorption mechanism applies. For one dimensional diffusion-controlled adsorption to a planar surface, the Ward and Tordai equation^[55] is the rigorous solution to the mass transport equation. Lin^[33] extended Ward and Tordai's equation to a spherical geometry. By these equations, one can obtain numerical solutions of the surfactant transport. If the diffusion is much faster than the kinetic process, then the surfactant dynamics is kinetically controlled. The Langmuir formalism^[56,57,58] is usually used to model the adsorption and desorption. In the cases in which the kinetic process and the diffusion are of the same rate, a mixed diffusive and kinetic control formulation has to be employed to model the surfactant transport. One can solve the kinetic rate equation and the diffusion equation simultaneously to obtain a numerical solution, which is found in the literature^[13,59]. If the dynamic surface tensions are measured in which the convection is important, then one has to solve the mass transfer equation with convection. These approaches are also reported in the literature^[38,60,61].

Once the theoretical dynamic surface tension is obtained, fitting to the experimental data can be done. Most studies conclude that the diffusion-controlled mechanism appears to describe most surfactant systems well, and the diffusion coefficients are measured. Some important examples are as follows. Luccassen and Giles^[62] studied the polyethoxy surfactants $C_{12}E_3$, $C_{12}E_6$ and $C_{14}E_6$ at the air/water interface using the longitudinal wave technique. They observed that diffusion alone can explain the dynamic tensions. The absence of a kinetic barrier for another polyethoxy surfactant (Triton-100) was also found by Lin^[33] using the pendant drop technique at air/water interface. Similar results were found by Van Hunsell^[46] using the drop weight technique at the air/water and oil/water interfaces and the surfactants Triton-100 and Brij-58, and Van Hunsell^[63] using the imposed area change technique and Brij-58 at the air/water and oil/water interfaces. Miller, Loglio and their coworkers^[28,22,64] demonstrated that diffusion alone successfully explains the dynamical tensions obtained by using the drop weight and the imposed area

change technique at the air/water interface for the dimethyl phosphine oxides C₁₀DMPO, C₁₂DMPO and C₁₄DMPO and the diethyl phosphine oxides C₈DEPO, C₁₀DEPO and C₁₂DEPO. Defay^[42], Fainerman^[56], Joos^[7] and Lunkennheimer^[65] studied the higher chain alcohols, octanol, nonanol and decanol using the oscillating jet method, and did not demonstrate any evidence of a kinetic barrier either. More examples could be found in literature^[14,24,66].

The only kinetic rate constants which have been measured are those for the short chain alcohols and diols. Fainerman and Lylyk^[56] used the maximum bubble pressure method to study the adsorption of a series of n-alcohols, and were able to measure the kinetic rate constants for C₃ (propanol) through C₇ (heptanol). These results were confirmed by Joos and Serrien^[7] using the oscillating jet technique. Bleys and Joos^[3] also demonstrated with the oscillating jet technique the presence of a kinetic barrier in the adsorption of bifunctional alcohols (1,8 octanediol, 1,9 nonanediol and 1,10 decanediol) and acids. Recently Lin^[13] studied the n-decanol/water system using the pendant drop technique, and found the mixed diffusive and kinetic control adsorption mechanism in his system.

The presence of a kinetic effect is essential for measuring the kinetic rate constants. As most surfactant systems are claimed to follow the diffusion control mechanism, the kinetic rate constants have not been measured, and even the magnitude of the kinetic constants has not been established, despite their importance to the applications. Therefore, more efforts are needed to understand the equilibrium and dynamical adsorption characteristics of surfactant.

2.4 Summary

As we can see from the above review, kinetic rate constants are not well established, because of poor understanding of the surface equation of state, lack of criteria to distinguish the adsorption mechanisms and experimental limitations. The aim of this dissertation study is to understand both the equilibrium and dynamic surface equation of state better by developing a new method to directly measure the relationship between the surface tension and the surface concentration, to develop a new kinetic scheme based on the molecular interaction approach which also leads to a new surface equation of state, to establish criteria for the adsorption mechanism and clarify the confusion in the adsorption mechanisms, to measure the kinetic rate constants of surfactants.

Chapter 3

Study of Nonequilibrium Surfactant Equations of State By Using the Pendant Bubble as a Monolayer Film Balance

In this chapter we use a pendant bubble tensiometer acting as a Langmuir Trough to study surface equations of state for water soluble surfactants. We form a pendant bubble at the tip of an inverted Teflon needle immersed in a surfactant solution and allow surfactant molecules to adsorb onto the bubble surface. We then shrink and/or expand the bubble to compress and/or dilate the surfactant monolayer. Experiments are so arranged that a negligible amount of surfactant is exchanged on the bubble surface during the expansion and shrinkage. We calculate surface tensions and bubble surface areas by video imaging the pendant bubble, and digitizing the image to locate the interface contour, and then fitting the contour to the Young-Laplace equation. Without any models or assumptions, the change in surface tension with change in surface concentration can be directly measured. Experimental data on the change of surface tensions with surface areas are reported for the polyethoxylated surfactants C₁₄E₆, C₁₄E₄ and C₁₄E₂. These data are used to demonstrate that the instantaneous surface tension is a unique function of the surface concentration, and that this dynamic surface equation of state is in agreement with the equilibrium surface equation of state.

3.1 Introduction

When surfactant adsorbs from an aqueous solution onto an air/water interface, the adsorption proceeds until an equilibrium is reached between the amount of surfactant adsorbed on the surface (which is characterized by the surface concentration (Γ_0)) and the bulk concentration (C_b). The relationship between Γ_0 and C_b defines the equilibrium adsorption isotherm, and many models (Langmuir, Frumkin, van der Waals and Volmer) have been used to describe this equilibrium adsorption isotherm^[1,2,3,4]. It is a relatively simple matter to measure the equilibrium surface tension γ_e as a function of the bulk concentration. Then from the Gibbs equation^[5]

$$d\gamma_e = -RT\Gamma_0 d\ln C_b \quad (3-1)$$

it is clear that from the slope of the γ_e - $\ln C_b$ curve, the adsorption isotherm can be directly measured. This direct calculation is very inaccurate because of inaccuracy in the computation of the slope from the experimental data. An alternative method, which is the usual one pursued, is to substitute an analytical form for the adsorption isotherm into the Gibbs equation and then integrate the equation to obtain the equilibrium tension as a function of the bulk concentration $\gamma_e(C_b)$ and the constants of the adsorption model^[3,6,7]. The constants are then obtained by fitting the integrated equation to the data. With the constants known, the $\gamma_e(C_b)$ relation, in conjunction with the adsorption isotherm $\Gamma_0(C_b)$, defines the equation of state $\gamma_e(\Gamma_0)$. In practice this procedure works fairly well as long as the adsorption isotherm model is complete enough to include the all effects which may be different for different surfactants. For example, if interchain cohesion is important then isotherms which include van der Waals interaction (the van der Waals and Frumkin model) should be used. With the proper interactions included, the $\gamma_e(C_b)$ expressions quite accurately fit the equilibrium data. Thus at equilibrium, there is a unique relation between the surface tension and the bulk concentration. However, it should be noted that the

parameter fits are not very sensitive to the $\gamma_e(C_b)$ curve, and consequently the adsorption isotherm parameters are not known to great accuracy by this method.

If the interface is out of equilibrium, as for example when adsorption to an initially clean interface is proceeding, or an inhomogeneous state has developed in which surfactant is being convected along the surface, then how the surface tension relates to the instantaneous surface concentration is not as clear as in the equilibrium case. Two major questions arise. Firstly there is the question of whether the surface tension is an instantaneous function of the instantaneous surface concentration. Monolayer film balance studies of aqueous insoluble surfactants consistently show hysteresis loops^[8,9,10] as the surface pressure is measured as a function of the surfactant surface concentration (or area per molecule) for different rates of area expansion or compression. Only in the limit of infinitely slow expansions do these measurements lie on one curve^[11]. The hysteresis is usually attributed to molecular rearrangements of the surfactant, particularly the hydrophobe moiety, as the surface area is changed. The second question concerns whether the dynamic surface equation of state (DSES) - if it exists - is equivalent to the equilibrium surface equation of state (ESES) $\gamma_e(\Gamma_0)$ which is defined and measured as described above.

Past studies have all assumed that for bulk soluble surfactants that the nonequilibrium surface tension is a function solely of the instantaneous surface concentration, and that this dependence is given by the equilibrium relation $\gamma_e(\Gamma_0)$. This assumption has been used in all the hydrodynamic modeling of Marangoni forces due to surface concentration gradients. It is also the key assumption in computing the variation in surface concentration with time from the measurement of dynamic surface tension.

The underlying basis for the above assumption that the surface tension is an instantaneous function of the surface concentration, and that this relation is given by the equilibrium equation of state is that the bulk soluble surfactants rearrange quickly on the surface with changes in their surface density, so that there is a unique, rapidly achieved conformation for each surface density. The reason why this may be correct for bulk soluble surfactants is that the hydrophobic chain is usually short compared to insoluble surfactants and is therefore not capable of complex time consuming rearrangements.

The aim of this study is to demonstrate directly that for a series of polyethoxylated surfactants, C₁₄E₆, C₁₄E₄ and C₁₄E₂, the surface tension is a unique function of the instantaneous surface concentration, and that this equation of state is the same as the equilibrium equation of state.

To measure the dynamic equation of state, we use the pendant bubble tensiometer to do monolayer film balances. We form a bubble at the tip of a needle immersed in a surfactant solution and allow surfactant molecules to adsorb onto the bubble surface. We then compress and/or dilate the surfactant monolayer on the bubble surface by shrinking and/or expanding the bubble. As we will explain, experiments are arranged so that there is negligible surfactant loss or gain in the process of shrinking or expanding. We video image the pendant bubble and digitize the image to locate the interface contour, and then we fit the contour to the Young-Laplace equation to calculate the surface tension and surface area. Without any models or assumptions, the surface equation of state, both dynamic and equilibrium, can be studied from the surfactant film balance.

3.2 Experimental

Materials and Instruments

We use the polyethoxylated surfactants $C_{14}E_6(C_{14}H_{29}(OC_2H_4)_6OH)$, $C_{14}E_4(C_{14}H_{29}(OC_2H_4)_4OH)$ and $C_{14}E_2(C_{14}H_{29}(OC_2H_4)_2OH)$ in this study. All surfactants are obtained from Nikko Chemical Company (Japan). They are stored in a dark desiccator under nitrogen, and are used without further modification. Ethyl alcohol is obtained from Quantum Chemical Co. Aqueous solutions are prepared freshly for each experiment using clean water from a Milli-Q water purification system. Surface tensions are measured by a pendant bubble tensiometer.

Method

We apply the idea of the Langmuir Trough^[12] to the pendant bubble tensiometer to study water soluble surfactants. We compress and/or dilate a surfactant monolayer on a surface, and measure the surface tensions and the surface areas at the same time. If the amount of surfactant on the surface doesn't vary appreciably during each experiment, then the relationship between the surface tension and the surface concentration can be measured. An aqueous surfactant solution is placed in an optically transparent quartz cell, which is mounted in a thermostatted chamber. The temperature is controlled at $23 \pm 0.2^\circ\text{C}$ for all experiments. We first form a bubble at the tip of an inverted needle that is immersed in a surfactant solution. After equilibrium is reached, we start to shrink and/or expand the bubble over a period time of 5.0-15.0 seconds. The change of the bubble surface areas during shrinking and expanding is normally over 50%. Bubbles in this process are video imaged by a CCD camera and digitized and saved in a computer. The captured images are analyzed using Image Analyst software to locate the interface locus. The surface tension and bubble surface area are calculated by fitting the data to the Young-Laplace equation. A diagram of the apparatus is given in Figure 3-1.

The key to the success of these experiments is to keep the amount of surfactant on the bubble surface unchanged so that the surface area changes of the bubble reflects the change of the surface concentration of surfactant. To ensure that the exchange of surfactant between the surface and the bulk is small, we use low bulk concentrations to extend either adsorption or desorption time scales. Surfactants are so chosen that equilibrium surface tensions can be less than 40.0×10^{-3} N/m at some of these low bulk concentrations. The needle in this study is also specially designed. A 20 gauge stainless steel needle is inserted into a small piece of 1/16 inch Teflon tube, and the bubble is actually formed at the tip of Teflon tube. When we use such a needle and the bubble is expanded and contracted, surfactant on the bubble surface will not be transferred to the Teflon needle surface but will stay on the bubble surface. The surface concentration is always less than the maximum surface concentration during the process. Special care is taken to make sure that the monolayer is not overcompressed by not allowing the surface tension after shrinking to be lower than 35.0×10^{-3} N/m, which is above the surface tension at the critical micelle concentration of the surfactants used.

3.3 Results and Discussion

Validation of the Method

Rigorously when a bubble is being shrunk or expanded, the static Young-Laplace equation is not adequate to describe the shape of the moving bubble. Macleod^[13] and Zhang^[14] used the growing drop technique to measure dynamic surface tension and found that the growing drop shape is still the static Young-Laplace shape. Wong^[15] used the Boundary Integral technique to solve the hydrodynamics of shrinking and expanding pendant bubbles and found that the moving bubble shape differs significantly from the static Young-Laplace shape only at high capillary number ($Ca = \mu U / \gamma$, where μ is the

viscosity of liquid, U is a characteristic velocity and γ is the surface tension), but it is virtually the static Young-Laplace shape at low capillary number. In our bubble shrinking and expanding experiments the highest velocity at the apex of pendant bubbles is about 1.0×10^{-4} m/s. The viscosity of the surfactant-water solution is approximately 1.0×10^{-3} N·s/m² and the surface tensions are no lower than 35.0×10^{-3} N/m. The capillary number is therefore never greater than 1×10^{-5} . We would therefore expect that the shape of shrinking and expanding bubbles differs only slightly from the static Young-Laplace equation, and that the fit of a moving bubble shape to the static Young-Laplace equation would still yield accurate surface tension. To prove this hypothesis, we shrank and expanded bubbles in pure water. Figure 3-2 shows the surface tension(γ) result by fitting the shape of moving bubbles in pure water to the static Young-Laplace equation. The surface area(A) change of the bubble is also shown in Figure 3-2. From the surface tension data in Figure 3-2, we can see almost all the data points are within $72.3 \pm 0.3 \times 10^{-3}$ N/m, in excellent agreement with the literature value^[16]. These results prove that fitting shrinking and expanding bubble shapes to the Young-Laplace equation gives accurate surface tensions. However, there are still some points out of the $72.3 \pm 0.3 \times 10^{-3}$ N/m range, which happened when the area of the bubble was small.

As we shrink a bubble to a small surface area, the radius of curvature at the apex(R_0) will decrease, so the Bond number ($B_0 = \Delta\rho g R_0^2 / \gamma$, where $\Delta\rho$ is the density difference between two fluids, g is the gravitational constant and γ is the surface tension) is small. At low Bond number, the shape of bubble is close to spherical and fitting it to the Young-Laplace equation generates a large error. To show that the large surface tension error in Figure 3-2 is due to the fitting procedure, we shrank and expanded bubbles in a 30%(v) ethyl alcohol and 70%(v) water mixture, which has a low surface tension. The results are shown in Figure 3-3. From Figure 3-3, we can see that the surface tensions are within $34.7 \pm 0.3 \times 10^{-3}$ N/m, as Bond numbers are big in this low surface tension case even

though the bubble is small. The surface tensions are in excellent agreement with the literature data again^[17]. In the experiments to be described below in surfactant solutions, as we shrink and/or expand a bubble, the surface concentration of surfactant goes inversely with the bubble size, so the surface tension decreases as bubble size decreases. This keeps the Bond number large to assure an accurate fit. Therefore, fitting shrinking and expanding bubble shape to the Young-Laplace equation is adequate to measure surface tension in surfactant-water solutions.

Proof of the Balance of the Surfactant Monolayer on Pendant Bubbles

As we mentioned in Section 3.2, the key to the success of the experiments is to assure the conservation of surfactant on the pendant bubbles during the shrinking and expanding processes. For a shrinking or expanding bubble, the rate of change of surfactant on the surface can be expressed as equation (3-2),

$$\frac{d(A(t)\Gamma(t))}{dt} = A(t)N(t) \quad (3-2)$$

where $A(t)$ is the surface area of the bubble, $\Gamma(t)$ is the surface concentration and $N(t)$ is the surfactant flux onto the bubble surface. Then the maximum possible change of amount of surfactant on surface at time t can be estimated by,

$$\Delta(A(t)\Gamma(t)) = A_{\max} \int_0^t N(t)dt \quad (3-3)$$

where $A_{\max}$ is the largest surface area during the bubble shrinking and/or expanding process. The maximum possible surfactant flux ($\int_0^t N(t)dt$) can be estimated by assuming purely diffusion control. If there is a kinetic effect, the surfactant flux will be less. The maximum diffusive flux is that when the sublayer concentration is always equal to zero for

bubble expansion, and when the bulk concentration is assumed to be zero for bubble shrinkage. Therefore, the accumulated flux is

$$\int_0^t N(t)dt = 2C_b \sqrt{\frac{Dt}{\pi}} \quad (3-4)$$

where C_b is the bulk concentration for bubble expansion, and the sublayer concentration for bubble shrinkage, D is the diffusion coefficient and t is time. $\int_0^t N(t)dt$ is the flux due to surfactant transport from the bulk for bubble expansion, and to the bulk for bubble shrinkage. For bubble expanding experiments in $0.44 \times 10^{-3} \text{ kg/m}^3$ $C_{14}E_6$ solution, $C_b = 9.2 \times 10^{-4} \text{ mol/m}^3$. Assuming an equilibrium surface concentration of $\Gamma_0 = 3.0 \times 10^{-6} \text{ mol/m}^2$ and $D = 6.0 \times 10^{-10} \text{ m}^2/\text{s}$, then we have $\int_0^t N(t)dt / \Gamma_0 = 0.033$ at $t = 15 \text{ sec}$, which is the maximum possible extra amount of surfactant on the surface due to adsorption. In other words, the $\Gamma(t) / \Gamma_0$ will possibly have a maximum absolute error of 0.033 if the transport of surfactant from the bulk onto the surface is neglected, which will not appreciably affect the surface tension. For bubble shrinking experiments, if we don't allow the surface tension after shrinkage to be lower than the equilibrium surface tension at $0.44 \times 10^{-3} \text{ kg/m}^3$ $C_{14}E_6$ solution. Then, the highest possible sublayer concentration is less than $0.44 \times 10^{-3} \text{ kg/m}^3$. The estimation for bubble expansion is then also true for the bubble shrinkage. The effective diffusion coefficient will be bigger as we generate convective flux in bubble shrinking and expanding. If the effective diffusion coefficient is doubled, we will have $\int_0^t N(t)dt / \Gamma_0 = 0.047$ at $t = 15 \text{ sec}$, the exchange is still not significant.

Macleod^[13] and Zhang^[14] studied the growing drop experiments and found that surfactant did transport to the drop surface significantly while the drop was growing. This could be explained by the high concentrations they used. In these growing drop experiments, the concentrations used were 50 times higher than the concentrations we are

using, $\int_0^t N(t)dt/\Gamma_0$ would be 0.30 even at $t=0.1$ Section. Thus, using low concentrations is one of the keys to assure a negligible amount of surfactant change during bubble shrinking and expansion experiments.

Recently we have measured the kinetic rate constants for $C_{12}E_6$ using a static pendant bubble adsorption and desorption (see Chapter 5). Assuming that $C_{14}E_6$, $C_{14}E_4$ and $C_{14}E_2$ have the same magnitude of adsorption and desorption rate constants as $C_{12}E_6$, we can estimate the maximum possible change of amount of surfactant on the bubble surface assuming purely kinetic control. For an expanding bubble, the rate of change of surfactant on the surface could be expressed as equation (3-1). For purely kinetic control adsorption^[18],

$$N(t) = \beta C_s - \alpha \Gamma(t) \quad (3-5)$$

where β is the general adsorption rate constant, C_s is the sublayer concentration, α is the general desorption rate constant. For the estimation of the maximum possible change of surfactant, we use

$$N(t) = \beta C_b \quad (3-6)$$

For bubble expanding experiments, we choose the highest bulk concentration in our experiments, $C_b = 1.0 \times 10^{-3} \text{ mol/m}^3$. Assuming an equilibrium surface concentration $\Gamma_0 = 3.0 \times 10^{-6} \text{ mol/m}^2$ and $\beta = 1.0 \times 10^{-5} \text{ m/s}$, then we have $\int_0^t N(t)dt/\Gamma_0 = 0.05$ at $t = 15 \text{ sec}$, which is the maximum possible extra amount of surfactant on the surface due to adsorption. From the calculation, the change of surfactant on bubble surface is very small again.

Similar estimations can be done for the bubble shrinking process, and the result is the same.

To confirm these theoretical estimations, we undertake the following experiments. We form a pendant bubble in a surfactant solution and allow surfactant molecules to adsorb onto the bubble surface to reach equilibrium. We then expand or shrink the bubble with different rates. Figure 3-4 shows the results of surface tension changes with relative bubble surface area ($A/A(\gamma=50 \times 10^{-3} \text{ N/m})$) in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution at different expansion rates. As these bubbles before expansion are not in exactly the same size, we set up a reference bubble surface area to compare the data, which is the bubble surface area when the surface tension is $50 \times 10^{-3} \text{ N/m}$. The expansion rate is described by dA/dt . The surface area changes for all experiments are about $20 \times 10^{-6} \text{ m}^2$. While the bubble is being expanded, the surface area of the bubble increases. So the surface concentration of surfactant decreases, and this results in an increase of surface tension. From Figure 3-4, we clearly see that all the data lie on the same curve at the high expansion rates. As dA/dt decreases below $0.1269 \text{ mm}^2/\text{s}$, the data points start to separate from that curve because of adsorption of surfactant. When $dA/dt=0.1269 \text{ mm}^2/\text{s}$, the expansion takes about 150 seconds. Therefore, the change of surfactant on the bubble surface is negligible if the expansion experiment takes less than 15 seconds in a concentration of $0.44 \times 10^{-3} \text{ kg/m}^3$ or less for C_{14}E_6 solution. Figure 3-5 shows the results of surface tension changes with relative bubble surface area ($A/A(\gamma=40 \times 10^{-3} \text{ N/m})$) in $0.42 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution at different expansion rates. We see the experimental data agree well with the theoretical estimation for the bubble expansion.

Evidence is also given for the bubble shrinkage when we shrink bubbles with different rates. Figure 3-6 shows the results at different shrinking rates in a $0.066 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution. The two experiments are started from same surface area and the

two bubbles start from same surface tension. The first experiment is done at a higher shrinking rate. The surface area reaches the lowest in about 0.6 second. The second experiment is done at a lower shrinking rate. The surface area reaches the same as the lowest value in experiment one in about 2.7 seconds, which is typical time for our bubble shrinking experiment. From the , we can see they have same surface tension when they reach same surface area, which also proves that the bubble surface doesn't lose surfactant during shrinking, and again agrees with the theoretical estimation.

Aveyard^[11] used different rates of compression in the Langmuir trough to study the polyethoxylated surfactants C₁₂E₁ and C₁₂E₂, and found that no surfactant was lost in compression over a period time of 2-4 min. He concluded that it was because the surfactants are sufficiently insoluble in water. Bubble shrinking on the pendant bubble tensiometer is virtually using the same idea as monolayer compressing in the Langmuir trough, except that the former one has two advantages: one is that surface tension measurement is more accurate; the other is that surface area change could be done much more quickly. These advantages are other keys which make it possible to measure accurate (γ - Γ) relationships for water soluble surfactants. We have shown above that no surfactant was lost or added in bubble shrinking and expanding. The results agree well with Aveyard's results, because of the short time period we did the experiments.

Reversible Surface Tension/Surface Area Results

Having validated the method, we now describe our shrinking and expanding bubble experiments. A concentration is chosen at which the equilibrium surface tension is above 60×10^{-3} N/m. We form a bubble in the solution. After equilibrium is reached, we start to shrink the bubble and expand it back to over its original size. Figure 3-7 shows the results of surface tension changes with bubble surface area(A) for 0.044×10^{-3} kg/m³ C₁₄E₆

solution. While the bubble is being shrunk, the surface area of the bubble decreases. So the surface concentration of surfactant increases, and this results in a decrease of surface tension. The inverse is true when the bubble is being expanded. From Figure 3-7, we can clearly see that the γ -A data in expansion falls exactly along the same line as that in shrinkage. The reversibility of surface tension/surface area in shrinkage and expansion provides strong evidence that no hysteresis exists in the process as the surface tension comes back to the equilibrium value when the surface area is back to the original area. Thus the surface tension is an instantaneous function of the surface concentration. This also supports the argument that the bubble surface doesn't lose or gain surfactant over the time period of 15 seconds at such a low bulk concentrations. Figure 3-8 and Figure 3-9 are shrinking and expanding bubble results for $0.0349 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_4 solution and $0.0084 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solutions respectively. The data points from shrinking and expanding lie on the same curve again for both surfactants. Figure 3-10 shows the bubble expanding and shrinking then re-expanding results of surface tension change with bubble surface area(A) in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution. We also see the results are reversible. When we start to shrink and expand bubbles from non-equilibrium situations, the surface tension/surface area data are also reversible.

Comparison of Different Bubble Results

The reversibility of the surface tension in evidence from the above experiments for a single bubble indicates that no hysteresis exists in the shrinking and expanding process. More evidence is obtained when we investigate γ -A (surface tension-bubble surface area) curves for different bubbles. We form a bubble in a surfactant solution with a lower bulk concentration and shrink it to a smaller size. The γ -A data are calculated. Then we choose a higher bulk concentration at which the equilibrium surface tension is the same as one of the lower surface tensions from the above shrinking experiment and, form a bubble with

the same size. When equilibrium is reached, whose γ -A point will lie on the γ -A curve from the above shrinking experiment, we expand the bubble. Figure 3-11 shows the comparison between these two specially-designed experiments of bubble shrinking in $0.044 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution and expanding in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution. The two sets of data points lie on same curve. The environments (particularly the sublayer concentrations and the bulk concentrations) of the two bubbles are totally different. If we combine these results with the reversible single bubble shrinking and expanding results, they show conclusively that the surface tension is an instantaneous function of the surface concentration and the amount of surfactant on the bubble surface is conserved during bubble shrinking and/or expanding processes. This also proves that no surfactant goes onto the needle surface. Figure 3-12 shows the comparison between bubble shrinking and expanding experiments in $0.0084 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution and $0.42 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution. The results are the same.

From the above experiments and the theoretical verification, we can conclude no surfactant has been lost or added to the bubble surface in these experiments, because of low bulk concentrations, short period of time and specially designed needle. Therefore, $\Gamma(t) \cdot A(t)$ (where $\Gamma(t)$ is the surface concentration and $A(t)$ is the bubble surface area at time t) is a constant for each bubble in these experiments. By measuring the surface area change we know the change of surface concentration of surfactant. If we start to shrink or expand a bubble from the equilibrium, we can study the equilibrium equation of state. If we start to shrink or expand bubble from non-equilibrium situation, we can study the dynamic equation of state. The transient surface tension during shrinking or expanding is also dynamic which makes experimental data collection easier.

The another important point is that no hysteresis exists in the process and the surface tension is an instantaneous function of the surface concentration. Therefore, a

dynamic surface equation of state does exist. In other words, the dynamic surface tension is a unique function of the instantaneous surface concentration.

Proof of Identity Between ESES and DSES

As $\Gamma(t) \cdot A(t)$ is a constant for each bubble in the shrinking and/or expanding experiments, we can study surface equation of state easily. We shrink and/or expand bubbles from equilibrium and non-equilibrium, from different concentrations and from different bubble sizes, and measure the γ - A data which reflects the γ - Γ relation. As we don't know the absolute surface concentration of surfactant, we set up a reference surface concentration, which is the instantaneous surface concentration when the dynamic surface tension in expansion is $65 \times 10^{-3} \text{ N/m}$. We shrink and/or expand bubbles through this surface tension, and calculate the ratio of bubble surface areas $A(65 \times 10^{-3} \text{ N/m})/A(t)$, which is also $\Gamma(t)/\Gamma(65 \times 10^{-3} \text{ N/m})$ as $\Gamma(t) \cdot A(t)$ is a constant. Figure 3-13, Figure 3-14 and Figure 3-15 show the results for $C_{14}E_6$, $C_{14}E_4$ and $C_{14}E_2$, respectively. From these data points, we can see the reproducibility of our experiments are excellent. From Figure 3-13, we can see all the data points fall on the same curve for $C_{14}E_6$. As there are a few equilibrium data points, which means that the dependence of equilibrium surface tension on equilibrium surface concentration is this curve. There are also a number of dynamic points, which tells us that the relationship between the dynamic surface tension and the dynamic surface concentration is the same curve. Therefore we conclude that the dynamic surface equation of state for $C_{14}E_6$ is the same as equilibrium surface equation of state. For $C_{14}E_4$ and $C_{14}E_2$ we can obtain the same conclusion from Figure 3-14 and Figure 3-15.

3.4 Conclusion

A new monolayer balance method is developed to study surface equation of state for water soluble surfactants. This method has been shown to be easy to use, accurate and highly reproducible. In this study we effectively proved the equivalence of the dynamic surface equation of state and the equilibrium dynamic surface equation of state for polyethoxylated surfactants $C_{14}E_6$, $C_{14}E_4$ and $C_{14}E_2$ by using this method. The hysteresis of surface surfactant rearrangement in dynamical situations is not measurable for these surfactants. The dynamic surface tension is a function of the instantaneous surface concentration. Therefore, we can interpret dynamic surface tensions using equation of state obtained from equilibrium measurement to find intrinsic constants of materials.

The conventional method to find the equilibrium surface equation of state is to measure equilibrium surface tensions at different bulk concentrations. Using the Gibbs equation, one obtains surface concentration by $\Gamma_0 = -1/RT(d\gamma_e/d\ln C_b)$. However, it is very difficult to locate the slope on $\gamma_e - \ln C_b$ curve. For highly surface active materials, we will have significant surface pressure at very low concentrations. Because of the depletion of surfactant on surface, it is very hard to know the bulk concentration, which makes measured $\gamma_e - \ln C_0$ curve deviate from actual $\gamma_e - \ln C_b$ curve. Using the method we developed here, one is directly measuring the relationship of the surface tension and the surface concentration, and doesn't need to know the bulk concentration. Thus this method will be more accurate for the measurement of surfactant equations of state.

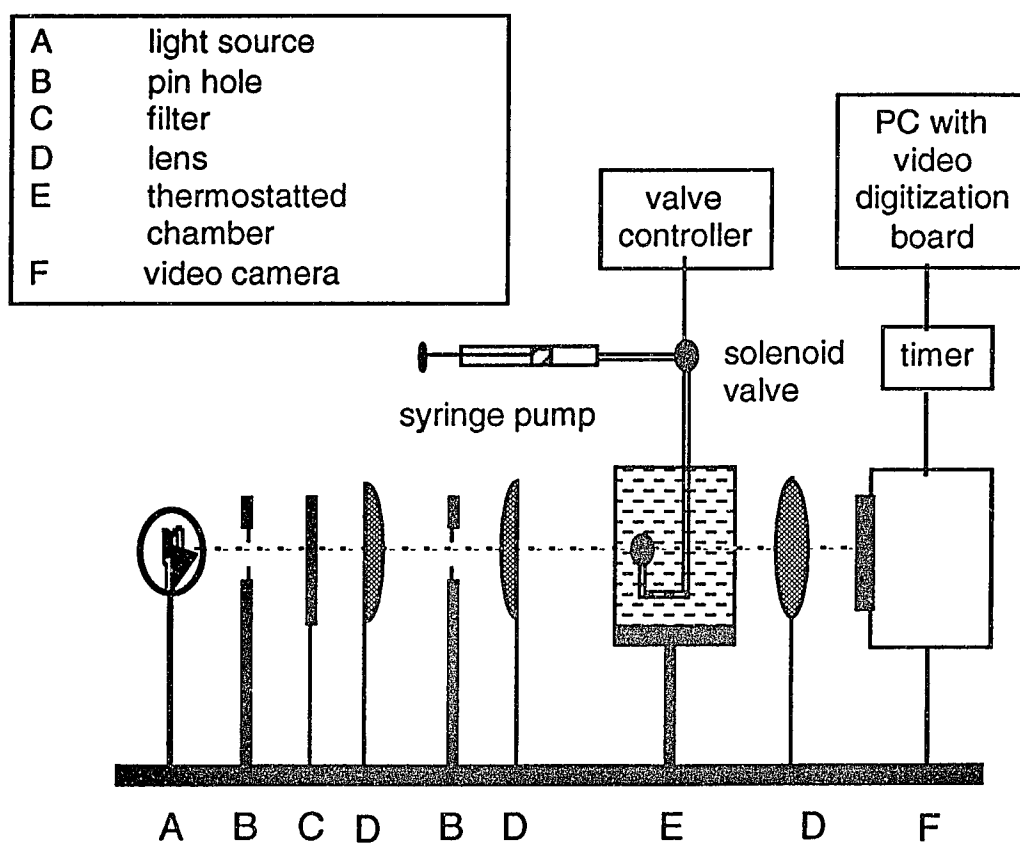


Figure 3-1 The pendant bubble tensiometer apparatus and video-image digitization equipment.

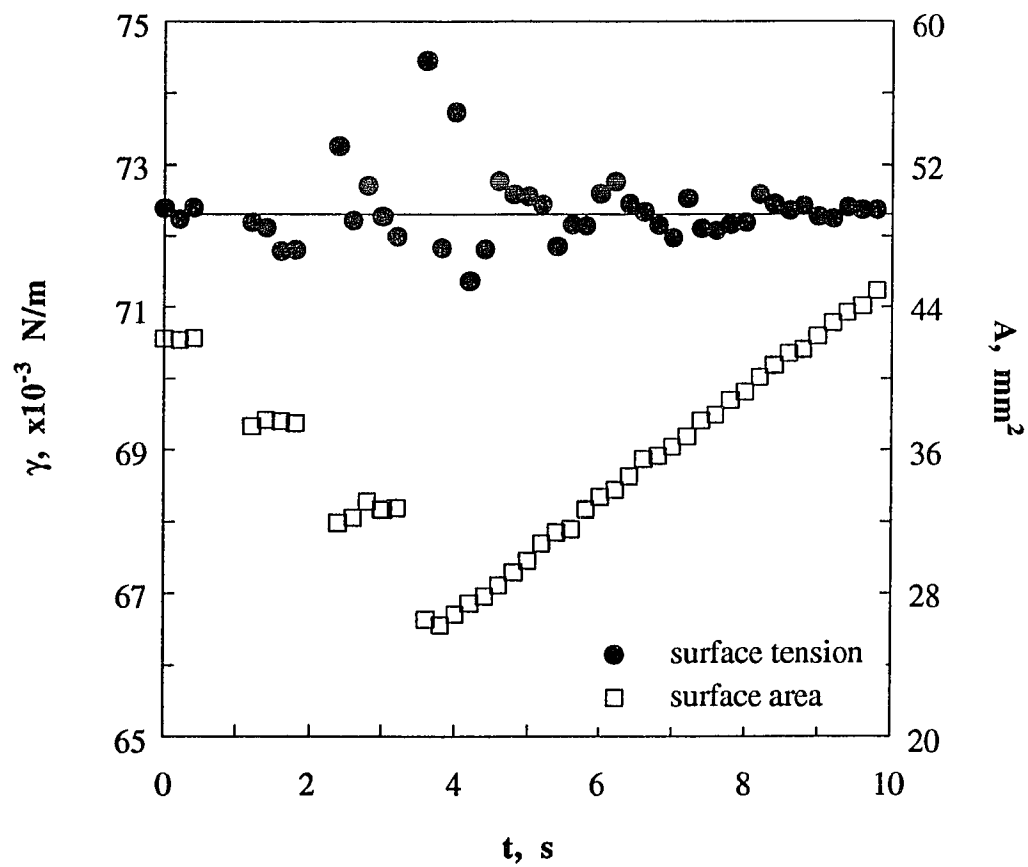


Figure 3-2 Surface tension and surface area of a pendant bubble shrinking and expanding in pure water.

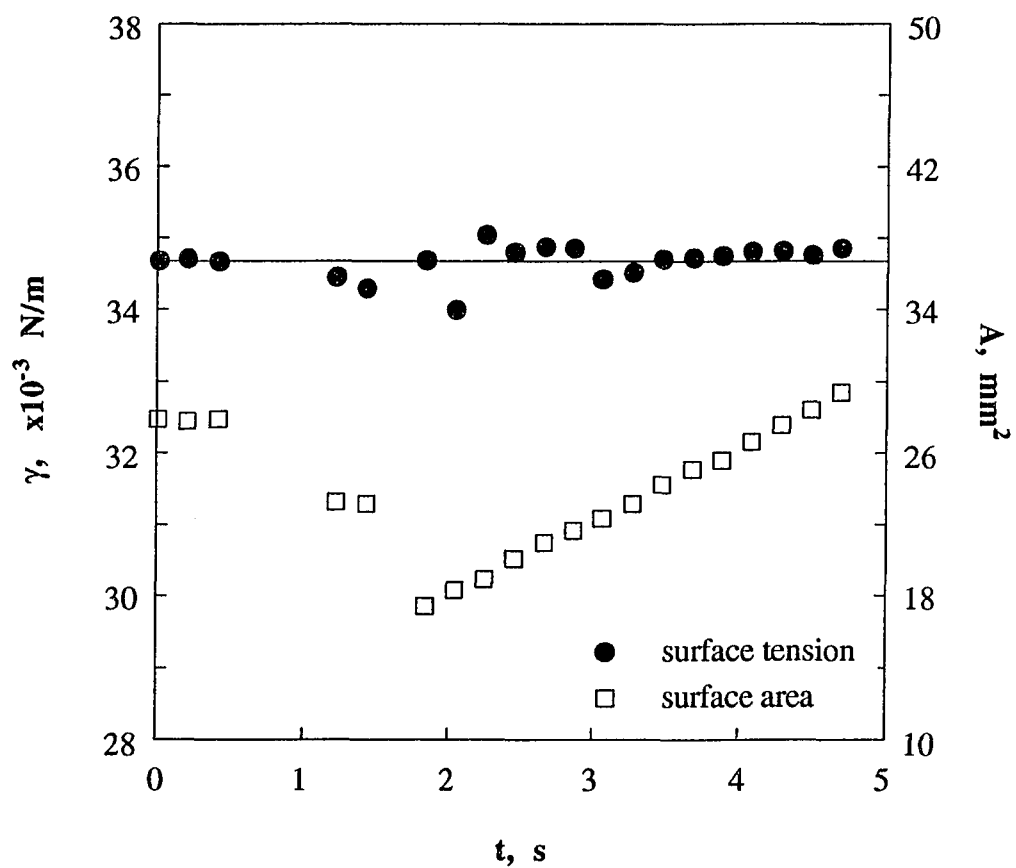


Figure 3-3 Surface tension and surface area of a pendant bubble shrinking and expanding in 30%(v) ethyl alcohol and 70%(v) water solution.

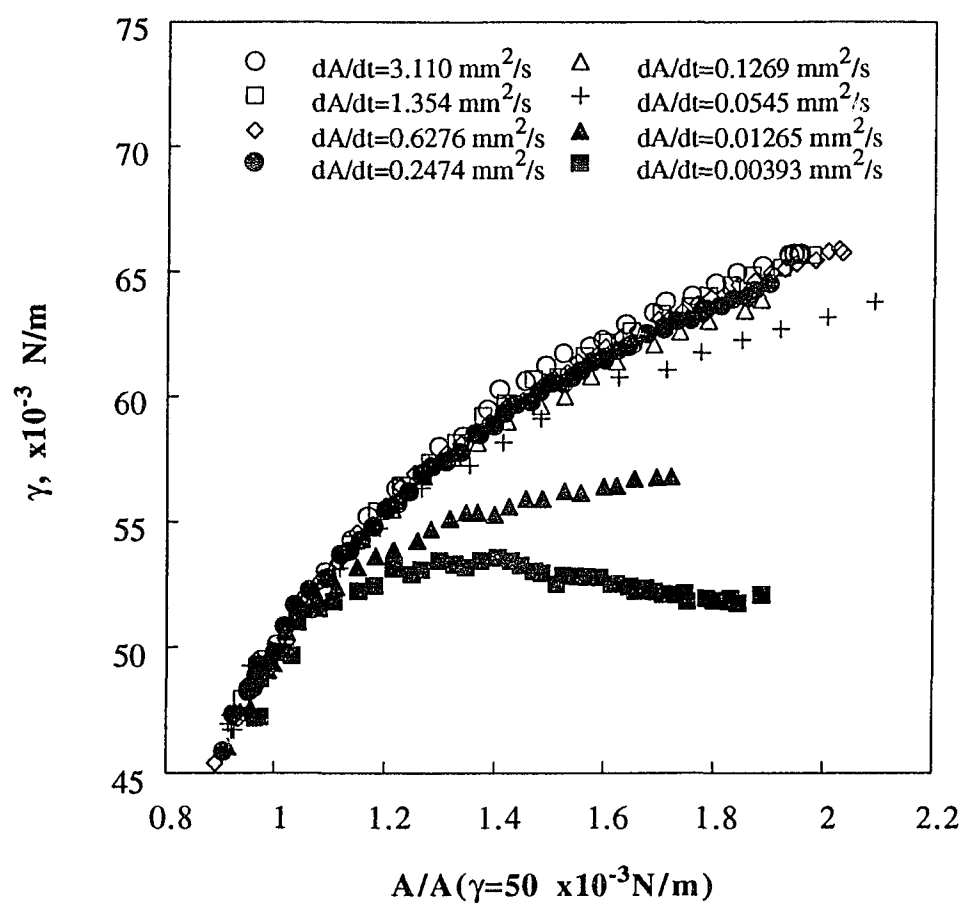


Figure3-4 The change of surface tension with relative surface area of pendant bubbles expanding in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution at different rates.

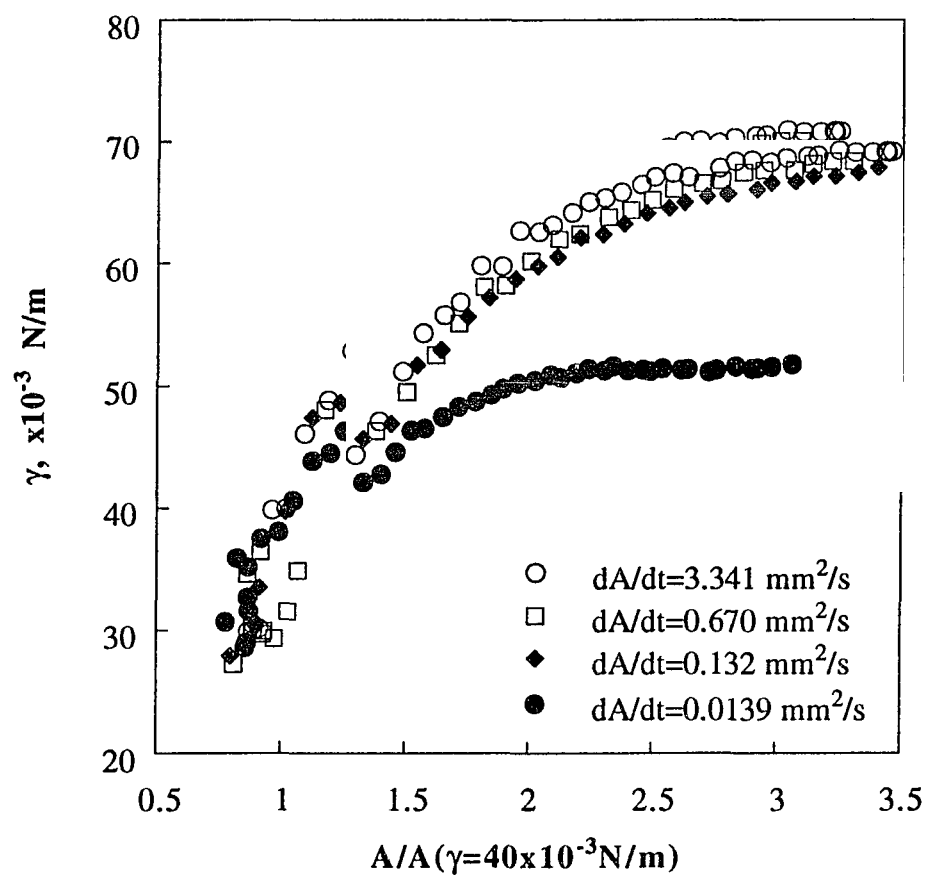


Figure 3-5 The change of surface tension with relative surface area of pendant bubbles expanding in $0.42 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution at different rates.

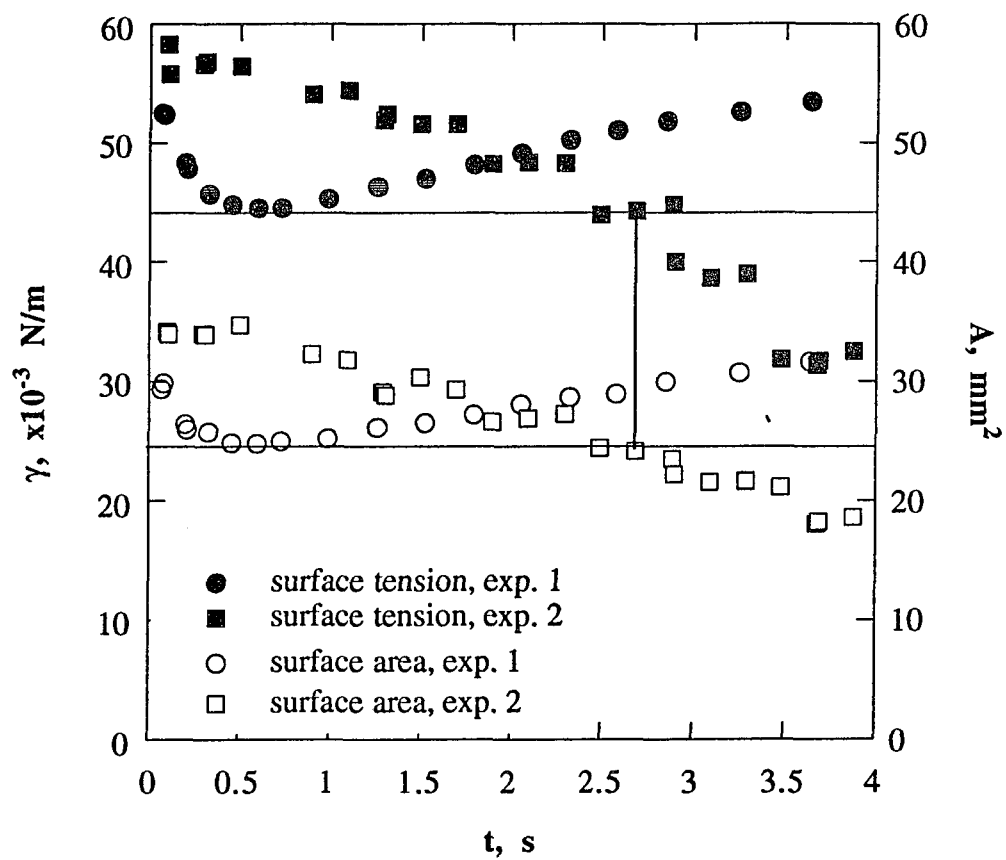


Figure 3-6 The comparison of surface tension and surface area relations of fast and slow shrinking pendant bubbles in $0.066 \times 10^{-3} \text{ kg/m}^3 \text{ C}_{14}\text{E}_6$ solution.

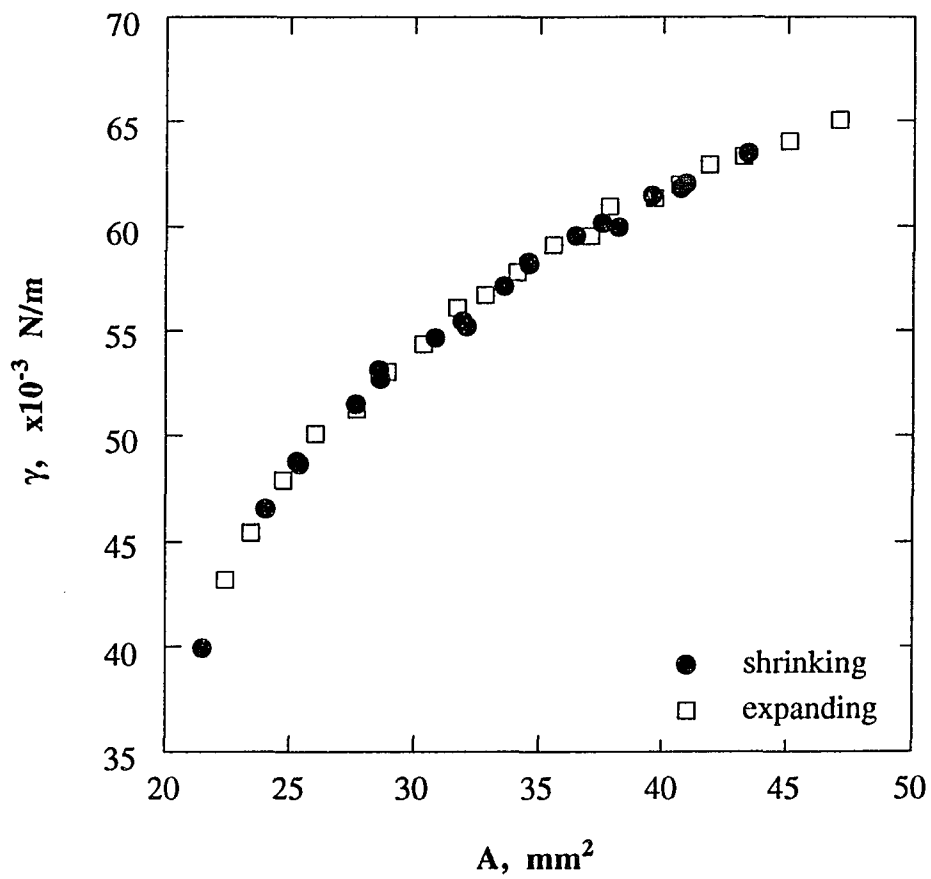


Figure 3-7 The change of surface tension with surface area of a pendant bubble shrinking and expanding in $0.044 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution.

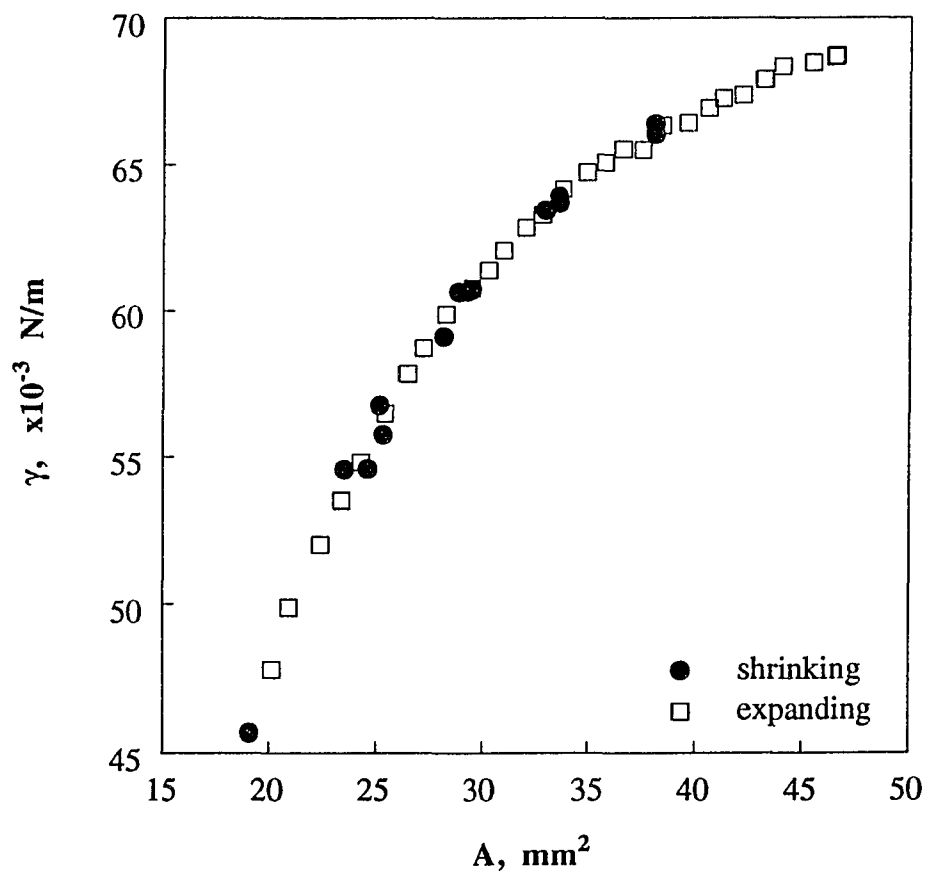


Figure 3-8 The change of surface tension with surface area of a pendant bubble shrinking and expanding in $0.0349 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_4 solution.

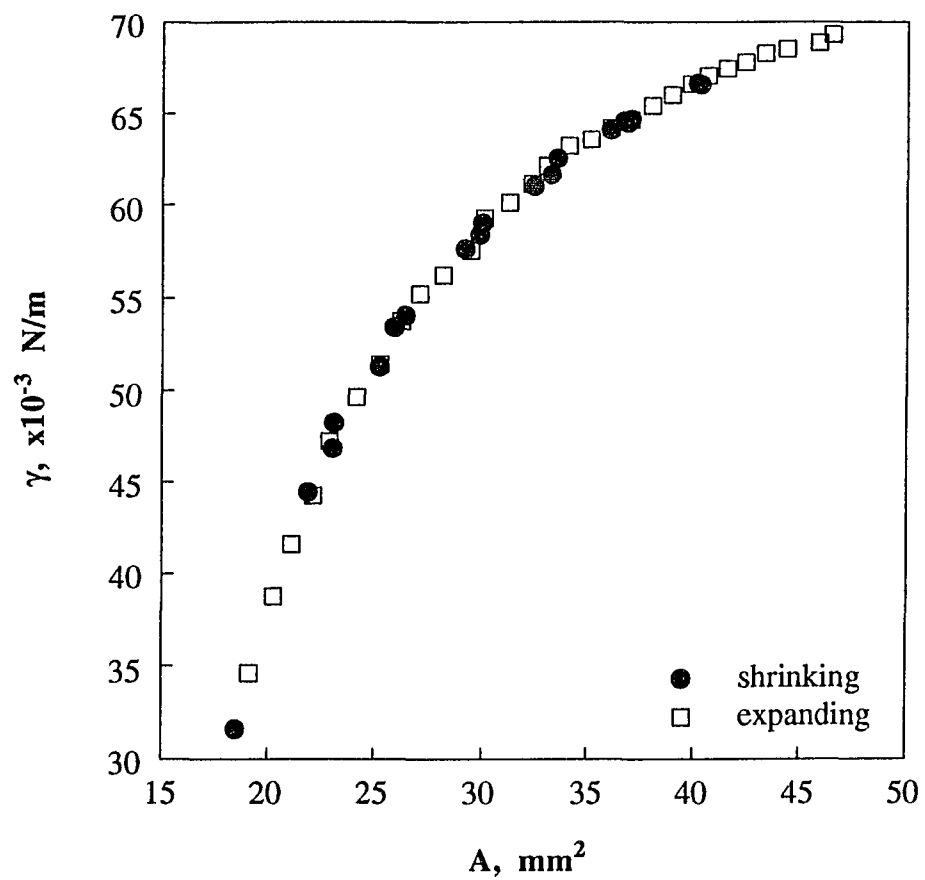


Figure 3-9 The change of surface tension with surface area of a pendant bubble shrinking and expanding in $0.0084 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution.

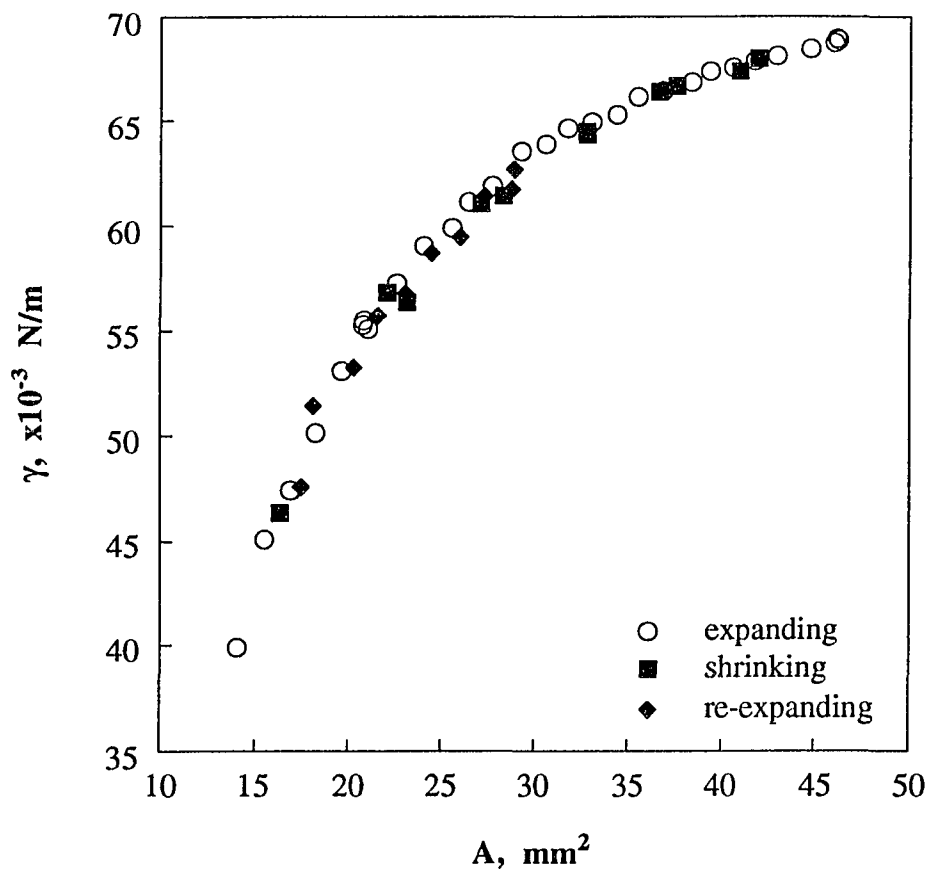


Figure 3-10 The change of surface tension with surface area of a pendant bubble expanding and shrinking then re-expanding in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution.

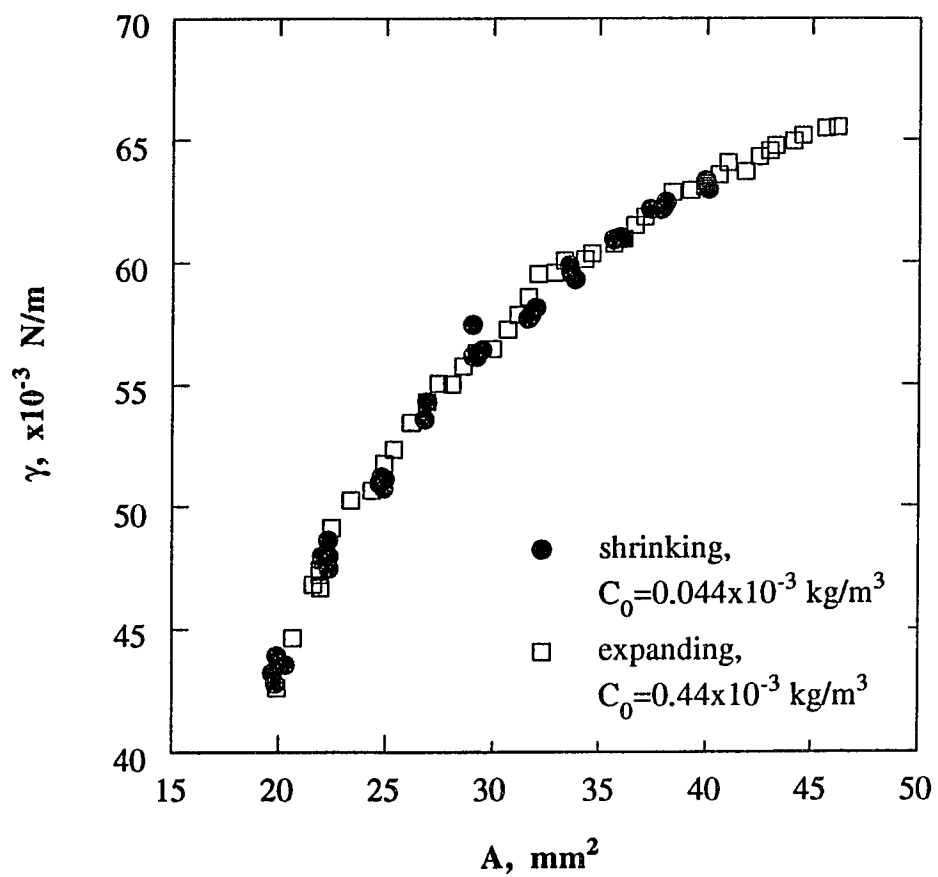


Figure 3-11 The comparison of surface tension and surface area relations of pendant bubbles shrinking in $0.044 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution and expanding in $0.44 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_6 solution.

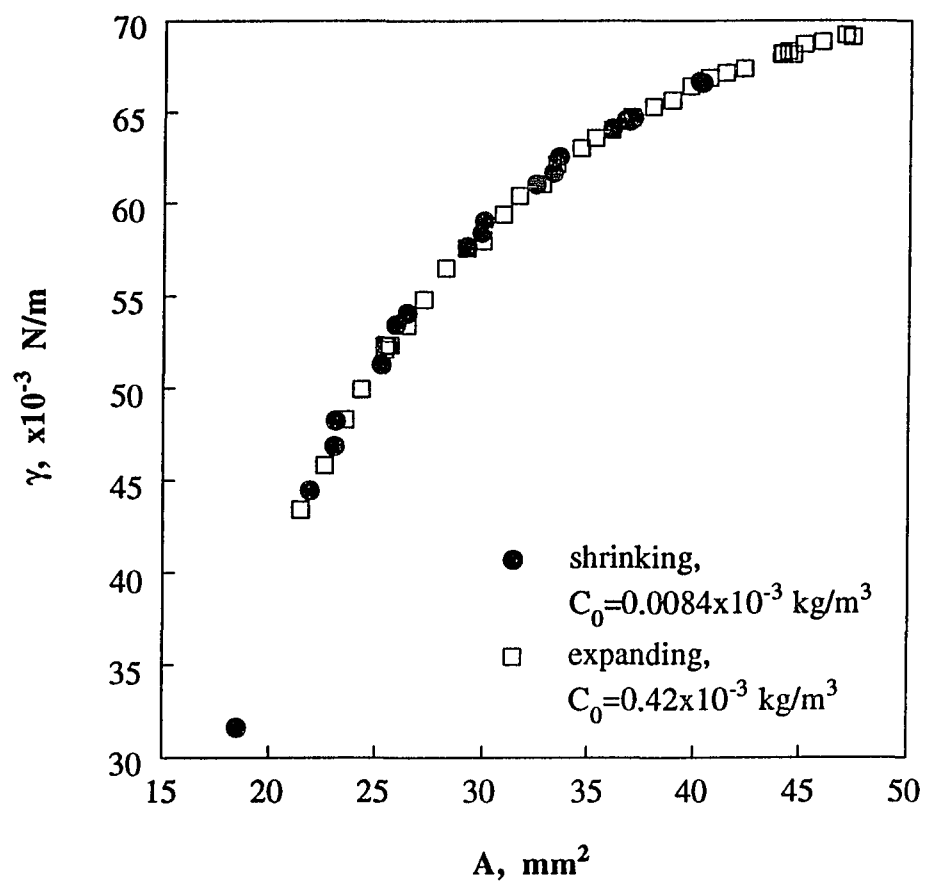


Figure 3-12 The comparison of surface tension and surface area relations of pendant bubbles shrinking in $0.0084 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution and expanding in $0.42 \times 10^{-3} \text{ kg/m}^3$ C_{14}E_2 solution.

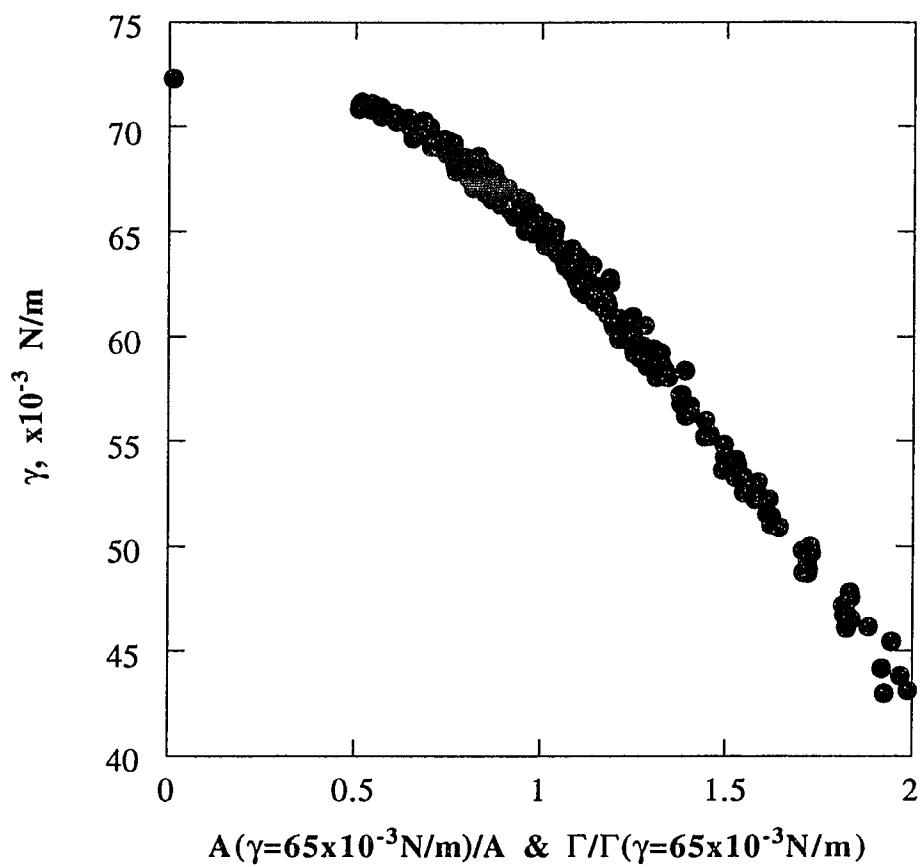


Figure 3-13 Relationship between surface tension and relative surface concentration for $C_{14}E_6$.

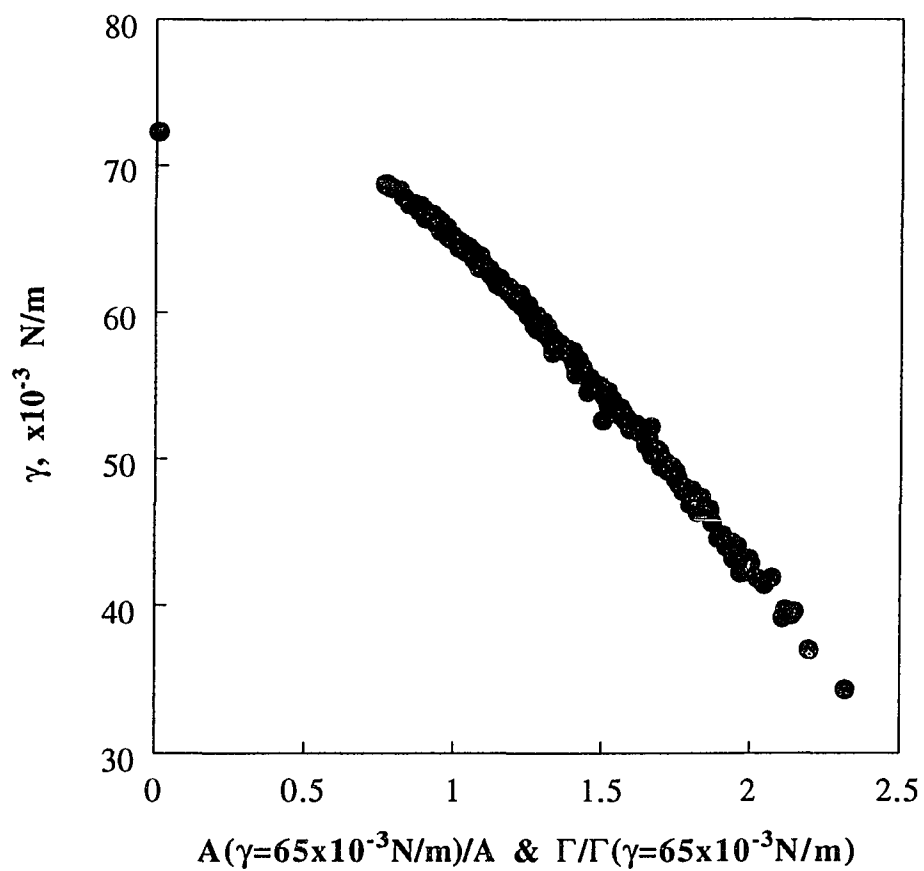


Figure 3-14 Relationship between surface tension and relative surface concentration for $C_{14}E_4$.

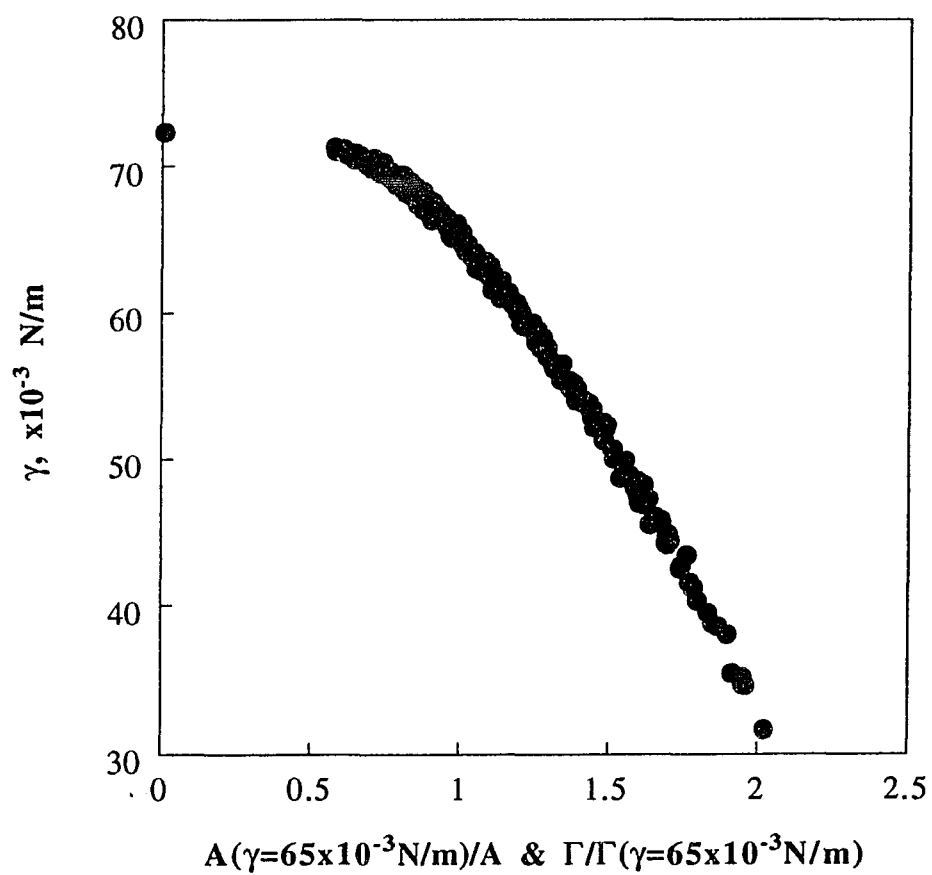


Figure 3-15 Relationship between surface tension and relative surface concentration for $C_{14}E_2$.

Chapter 4

Surfactant Equations of State on a Molecular Interaction Approach

4.1 Introduction

When surfactant molecules adsorb from an aqueous solution onto an air/water interface, the adsorption proceeds until an equilibrium is reached at which the chemical potentials of the surfactant at the interface and in the bulk are equal. The chemical potential of surfactant molecules at the interface can be described as a function of the surfactant surface concentration (Γ_0) (or the surface excess), which is the amount of surfactant at the interface per unit area. On the other hand, the bulk concentration (C_b) represents the chemical potential of surfactant in the bulk solution. The relationship between the bulk concentration and surface concentration at a constant temperature is the equilibrium adsorption isotherm. Adsorption of surfactant molecules at the air/water interface lowers the surface tension (γ). The relationship between the surface tension and surface concentration is the surface equation of state. The equilibrium adsorption isotherm and surface equation of state are the equilibrium characteristics of a surfactant.

A classical equation which relates the surface tension, surface concentration and bulk concentration is the Gibbs equation^[1],

$$d\gamma_e = -RT\Gamma_0 d\ln C_b \quad (4-1)$$

which is valid for equilibrium systems. From the Gibbs equation, we can obtain the equilibrium surface concentrations by measuring the equilibrium surface tensions at different bulk concentrations,

$$\Gamma_0 = -\frac{1}{RT} \frac{d\gamma_e}{d\ln C_b} \quad (4-2)$$

Then, the relationships among the surface tension, surface concentration and bulk concentration can be obtained. The commonly used method to find the adsorption isotherm and surface equation of state includes three steps^[2,3,4,5] (sometimes four steps, starting from a kinetic rate scheme): (i) to assume an analytical form of the adsorption isotherm with some unknown parameters; (ii) to substitute the adsorption isotherm into the Gibbs equation and integrate the equation to obtain a surface equation of state and an expression for the surface tension/bulk concentration relationship; (iii) to fit the surface tension/bulk concentration expression to the experimentally measured data to find the unknown parameters. With the parameters known, the adsorption isotherm and surface equation of state are established.

Numerous studies^[3,6,7,8,9,10] have been done so to find the surfactant equilibrium properties. The simplest adsorption isotherm is the Henry's isotherm^[11]:

$$\Gamma_0 = k_H C_b \quad (4-3)$$

where k_H is the equilibrium parameter, which has dimension of length. The corresponding surface equation of state is:

$$\gamma_e = \gamma_c - RT\Gamma_0 \quad (4-4)$$

The Henry's isotherm can be derived theoretically assuming the surface and bulk activity coefficients are all unity. This assumption is reasonable when the surface concentration and bulk concentration are low. Hence, the Henry isotherm is valid only at low surface and bulk concentrations. However, the Henry's isotherm is of great importance because it provides the limit when the surface concentration goes to zero.

The most commonly used adsorption isotherm is the Langmuir isotherm^[3,6,7,8]:

$$\frac{\Gamma_0}{\Gamma_\infty} = \frac{C_b}{C_b + a} \quad (4-5)$$

where Γ_∞ is the maximum surface concentration, and a is the Langmuir equilibrium adsorption constant, which is a measure of the surfactant activity. The corresponding surface equation of state is:

$$\gamma_e = \gamma_c + \Gamma_\infty RT \ln \left(1 - \frac{\Gamma_0}{\Gamma_\infty} \right) \quad (4-6)$$

The Langmuir isotherm can be derived via kinetic arguments or molecular thermodynamic arguments for ideal non-localized adsorption^[11]. The major assumption for this isotherm is that there is no interaction among surfactant molecules on the interface^[12]. The Langmuir isotherm is simplified to the Henry isotherm if $C_b \ll a$.

If the surfactant molecules interaction is significant, one may want to use the Frumkin isotherm^[9,10,13]:

$$C_b = \frac{a \frac{\Gamma_0}{\Gamma_\infty} \exp\left(K \frac{\Gamma_0}{\Gamma_\infty}\right)}{1 - \frac{\Gamma_0}{\Gamma_\infty}} \quad (4-7)$$

where Γ_∞ is the maximum surface concentration, a is the Frumkin equilibrium adsorption constant, and K is the Frumkin constant which is a measure of the surfactant molecular interaction. The surface equation of state derived from the Frumkin isotherm is:

$$\gamma_e = \gamma_c + \Gamma_\infty RT \left(\ln \left(1 - \frac{\Gamma_0}{\Gamma_\infty} \right) - \frac{K}{2} \left(\frac{\Gamma_0}{\Gamma_\infty} \right)^2 \right) \quad (4-8)$$

The Frumkin isotherm reduces to the Langmuir isotherm if $K=0$, which means no molecular interaction on the interface. More complicated isotherms include the general Frumkin isotherm^[14] and the phase transition isotherm^[13], which have been used for some special surfactants. For water insoluble surfactants, the Volmer surface equation of state^[11] and van der Waals surface equation of state^[11] are also used in the literature.

However, a major problem exists by using this procedure to find the equilibrium properties for water soluble surfactants. For these surfactants, the γ_e - $\ln C_b$ measurement is the only experimental data to verify the adsorption isotherm and surface equation of state. Because of the difficulty in locating the slope on the γ_e - $\ln C_b$ curve to find surface concentrations by the Gibbs equation, remarkably different surface tension/surface concentration relationships for the same surfactant system have been reported by using different models^[13,14], which fit the γ_e - $\ln C_b$ experimental data equally well, and by different authors^[2,15]. Figures 4-1 and 4-2 show how the surface tension/surface concentration relationship could vary dramatically even though the γ_e - $\ln C_b$ curve is almost

identical. So, in order to obtain accurate equilibrium parameters, experimental measurements other than the $\gamma_e\text{-ln}C_b$ measurement are needed.

In Chapter 3, we described the study using the pendant bubble as a monolayer film balance and directly measured the surface tension/surface concentration relationships. Also, by using this method we successfully verified the equivalence of equilibrium and dynamic surface equations of state. This Chapter aims to use the surface tension/surface concentration data to test the commonly used Langmuir and Frumkin isotherms. We show that the Langmuir and Frumkin isotherm are not satisfactory with these $C_i E_j$ surfactants. Then, a new kinetic scheme which takes into account the surfactant molecular interactions on the interface is developed. Consequently, a new adsorption isotherm and a surface equation of state are derived, which defines the molecular interaction model. This molecular interaction model is verified by both the $\gamma_e\text{-ln}C_b$ and surface tension/surface concentration data.

4.2 Development of the Molecular Interaction Model

We adopt the Arrhenius rate formulation for the adsorption and desorption of surfactant at an interface^[16],

$$\frac{d\Gamma}{dt} = \beta'_0 \exp\left(-\frac{E_A}{RT}\right) C_s - \alpha_0 \exp\left(-\frac{E_D}{RT}\right) \Gamma \quad (4-9)$$

where Γ is the surface concentration, t is the time, β'_0 and α_0 are the kinetic rate constants for adsorption and desorption, C_s is the sublayer concentration, E_A and E_D are the activation energies for adsorption and desorption, R is the gas constant and T is the temperature. The activation energy for adsorption is the energy needed to make a hole in the surface for a surfactant molecule, which can be formulated as:

$$E_A = \pi A N_0 = \frac{\gamma_c - \gamma}{\Gamma} \quad (4-10)$$

where π is the surface pressure, A is the occupied area per molecule, N_0 is the Avogadro's number, γ_c is the clean water surface tension and γ is the surface tension. The activation energy for desorption is the energy needed to overcome the molecular interaction on the interface. The molecular interaction consists of an attractive force and a repulsive force,

$$E_D = E^{attractive} + E^{repulsive} \quad (4-11)$$

The attractive force comes from the Van der Waals interaction. If the surface concentration is low, the separation among the surfactant molecules on the interface is much bigger than the surfactant molecular size. Then the van der Waals interaction energy is of the form $W \propto 1/d^5$ [17] or $W \propto \Gamma^{5/2}$, where W is the van der Waals interaction energy and d is the molecular separation. If the surface concentration is high, the separation among the surfactant molecules on the interface is in the same order of or smaller than the surfactant molecular size. In this case the van der Waals attraction energy is of the form $W \propto 1/d^{3/2}$ [17] or $W \propto \left(\sqrt{\Gamma}/(\sqrt{\Gamma_\infty} - \sqrt{\Gamma})\right)^{3/2}$. For the sake of simplicity, we use the following form to formulate the van der Waals interaction,

$$\frac{E^{attractive}}{RT} = \frac{E^{van\cdot der\cdot Waals}}{RT} = b_1 \Gamma \quad (4-12)$$

where b_1 is a constant which characterizes the van der Waals interaction.

For nonionic surfactants, the repulsive force is the hydration force, which has been measured to follow the exponential function[17],

$$\frac{E^{repulsive}}{RT} = \frac{E^{hydration}}{RT} = b_2'' \exp(b_3' d) \quad (4-13)$$

where b_2'' and b_3' are constants characterizing the hydration force. The molecular separation d can be approximated by $(1/\sqrt{\Gamma N_0} - 1/\sqrt{\Gamma_\infty N_0})$. Let $b_3 = b_3'/\sqrt{N_0}$, the hydration force is reformulated as,

$$\frac{E^{hydration}}{RT} = b_2' \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) \quad (4-14)$$

where b_2' is a constant which is determined by both the hydration force and maximum surface concentration, and b_3 is a constant which characterizes the hydration force decay length. From equations (4-12) and (4-14), the activation energy for desorption can be expressed as,

$$\frac{E_D}{RT} = b_1 \Gamma + b_2' \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) \quad (4-15)$$

By substituting equations (4-10) and (4-15) into equation (4-9), we obtain a kinetic equation for adsorption and desorption,

$$\frac{d\Gamma}{dt} = \beta_0 C_s \exp\left(-\frac{\gamma_c - \gamma}{\Gamma RT}\right) - \alpha_0 \exp\left(-b_1 \Gamma - b_2' \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \quad (4-16)$$

At equilibrium, $d\Gamma/dt=0$ and $C_s=C_b$. Then the adsorption isotherm can be obtained,

$$C_b = \frac{\alpha_0}{\beta_0} \Gamma_0 \exp\left(-b_1 \Gamma_0 - b_2' \exp\left(\frac{b_3}{\sqrt{\Gamma_0}}\right) + \frac{\gamma_c - \gamma}{\Gamma_0 RT}\right) \quad (4-17)$$

If we substitute equation (4-17) into the Gibbs equation, after rearrangement, the surface equation of state is obtained,

$$\gamma = \gamma_c - \left(1 + b_1 \Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) \right) \Gamma R T \quad (4-18)$$

where b_1 is a constant which characterizes the Van der Waals force, b_2 is a constant which is determined by both the hydration force and maximum surface concentration, and b_3 is a constant which characterizes the hydration force decay length. As the dynamic and equilibrium surface equations of state are equivalent, we don't need the subscripts for surface tension and surface concentration in equation (4-18). The kinetic equation can be rewritten as,

$$\frac{d\Gamma}{dt} = \beta_0 C_s \exp\left(-b_1 \Gamma - \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) - \alpha_0 \exp\left(b_1 \Gamma - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \quad (4-19)$$

and the adsorption isotherm is,

$$C_b = \frac{\alpha_0}{\beta_0} \exp\left(2b_1 \Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \quad (4-20)$$

If we define an equilibrium adsorption constant a : $a = \alpha_0/\beta_0$, then equation (4-20) can be rewritten as,

$$C_b = a \exp\left(2b_1 \Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \quad (4-21)$$

Equations (4-18), (4-19), (4-21) define the molecular interaction model. From equation (4-21), if the surface concentration is very low, then the molecular interaction model reduces to the Henry isotherm.

4.3 Determination of the Surface Concentration

By using the pendant bubble as a monolayer film balance, we have obtained the surface tension/relative surface concentration data. In order to find the absolute surface concentration, two methods are proposed. The first method involves measuring the equilibrium surface tensions. By the Gibbs equation, we can obtain the surface concentration. This method works well at high bulk concentrations, as depletion of surfactant onto the air/water interface during the measurements is relatively small. So, we can directly take the slope of $\gamma_e - \ln C_0$ curve at high concentrations to obtain an absolute surface concentration as the bulk surfactant concentration is virtually the same as the prepared concentration. In practice, we model the surface tension/relative surface concentration curve by an empirical equation, which is of the form,

$$\gamma = \gamma_c - q_1 \ln \left(1 + \frac{\exp(q_3 x) - 1}{q_2} \right) \quad (4-22)$$

where q_1 , q_2 and q_3 are empirical coefficients, $x = \Gamma/\Gamma(\gamma = 65 \text{ mN/m})$, which is the relative surface concentration. We use a TK-Solver to do the fitting. Figure 4-3 shows the empirical fit of the surface tension/relative surface concentration curve of C_{12}E_6 . The best fitted empirical coefficients are: $q_1 = 3.221 \times 10^{-3} \text{ N/m}$; $q_2 = 30.19$; $q_3 = 5.617$. Then we change equation (4-22) to an explicit form of Γ ,

$$\Gamma = \frac{\Gamma(\gamma = 65 \text{ mN/m})}{q_3} \ln \left(1 + q_2 \left(\exp \left(\frac{\gamma_c - \gamma}{q_1} \right) - 1 \right) \right) \quad (4-23)$$

and substitute equation (4-23) into the Gibbs equation to obtain an expression for the surface tension/bulk concentration relationship,

$$d\gamma_e = -\frac{\Gamma(\gamma = 65mN / m)}{q_3} \ln \left(1 + q_2 \left(1 - \exp \left(\frac{\gamma_e - \gamma}{q_1} \right) \right) \right) RT d \ln C_b \quad (4-24)$$

With the $\Gamma(\gamma = 65mN / m)$ and a pair of γ_e/C_b known, we can numerically integrate equation (4-24) to generate a γ_e - $\ln C_b$ curve. We fit the numerical solution of equation (4-24) to the experimentally measured γ_e - $\ln C_0$ curve. The difference of C_0 and C_b is corrected by the following equation, assuming the depletion of surfactant is only on the air/water interface,

$$C_0 = C_b + \frac{A_{air/water}}{V_{solution}} \Gamma \quad (4-25)$$

where $A_{air/water}$ is the surface area of air/water interface, $V_{solution}$ is the volume of surfactant solution, both in the equilibrium surface tension measurement. The ratio $A_{air/water}/V_{solution}$ is 25.0 m^{-1} in our experimental condition. Then the $\Gamma(\gamma = 65mN / m)$ can be obtained. Figure 4-4 shows the fit of γ_e - $\ln C_0$ curve for the surfactant $C_{12}E_6$. We find $\Gamma(\gamma = 65mN / m) = 1.157 \times 10^{-6} \text{ mol/m}^2$ for the surfactant $C_{12}E_6$. We also find from Figure 4-3 and Figure 4-4 that the two different measurements agree very well.

The second method involves using a Langmuir trough as a film balance. In this method, we treat the surfactants as water insoluble surfactants. We dissolve a preweighed surfactant in chloroform then spread a known amount of surfactant solution on the air/water surface in a Langmuir trough. After the chloroform is fully evaporated, a surfactant

monolayer is formed on the air/water surface. Then we compress the surfactant monolayer and record the surface pressure and surface area. A surface pressure/surface area curve can be generated. From this curve, we can calculate the surface concentration. Realistically, as we are dealing with water soluble surfactants, this method could fail. However, when the surface pressure is low, the sublayer concentration is also low assuming a diffusion limited surfactant desorption, then the diffusion flux away from the surface during compression is small. Hence, we can have a negligible amount of surfactant loss at low surface pressure. Therefore, an accurate surface tension/surface area curve can be obtained at low surface pressure. This method works very well for the surfactants with low C.M.C.s. We used this method to find that $\Gamma(\gamma = 65 \text{ mN/m}) = 1.37 \times 10^{-6} \text{ mol/m}^2$ for C_{16}E_6 ; $\Gamma(\gamma = 65 \text{ mN/m}) = 1.27 \times 10^{-6} \text{ mol/m}^2$ for C_{14}E_6 ; $\Gamma(\gamma = 65 \text{ mN/m}) = 1.81 \times 10^{-6} \text{ mol/m}^2$ for C_{14}E_4 ; $\Gamma(\gamma = 65 \text{ mN/m}) = 2.69 \times 10^{-6} \text{ mol/m}^2$ for C_{14}E_2 . Figures 4-5, 4-6, 4-7, 4-8 show the comparisons between the pendant bubble data and Langmuir trough data for C_{16}E_6 , C_{14}E_6 , C_{14}E_4 and C_{14}E_2 , respectively. From Figure 4-5, we can see that two data sets from totally different measurements are identical. This is because C_{16}E_6 has a very low C.M.C., which is $1.0 \times 10^{-3} \text{ mol/m}^3$ [2]. So, the sublayer concentration is always low which assures a low diffusion flux away from the interface. For C_{14}E_4 and C_{14}E_2 , the two data curves are the same at low surface pressure as we expected. For C_{14}E_6 , the two data curves don't agree well because of the surfactant loss during compression in the Langmuir trough experiment.

4.4 Determination of the Molecular Interaction Model Parameters

We use a TK-Solver to fit the molecular interaction surface equation of state to the surface tension/surface concentration curve. Figures 4-9, 4-10, 4-11 show the fits of the surface tension/surface concentration data for C_{14}E_2 , C_{14}E_4 and C_{14}E_6 . We can see the agreements between the model and experimental data are excellent. With the surface

equation of state known, we fit the molecular interaction model to the γ_e - $\ln C_0$ curve to determine the equilibrium adsorption constant a . Figure 4-12 shows the fit of γ_e - $\ln C_0$ curve for $C_{14}E_6$, from which we find the equilibrium adsorption constant $a=2.7 \text{ m}^{-1}$. Table 4-1 summarizes the best fitted parameters for this series. The equilibrium adsorption constants for $C_{14}E_4$ and $C_{14}E_2$ are estimated from the solubility limits and equilibrium surface tensions at these limits.

We apply the same procedure for another homologous series $C_{16}E_6$, $C_{14}E_6$ and $C_{12}E_6$, and obtain the molecular interaction parameters for this series. Table 4-2 lists the best fitted parameters for this series. The equilibrium adsorption constant for $C_{16}E_6$ is estimated from the C.M.C. value and equilibrium surface tension at C.M.C.

4.5. Discussion and Conclusions

The Molecular Interaction Model Evaluation

The conventional method to find the surface equation of state is to assume an adsorption isotherm then fit the model to the equilibrium surface tensions. If we use this conventional approach and apply the existing Langmuir and Frumkin isotherms to the surfactant $C_{14}E_6$, we can obtain the corresponding equilibrium properties. Figure 4-13 shows the fits by using the Langmuir and Frumkin isotherms. Again, we used equation (4-25) to calculate the prepared surfactant concentration with the $A_{air/water}/V_{solution}$ ratio of 25.0 m^{-1} . Showing on the x-axis in Figure 4-13 is the prepared surfactant concentration. We can see both the Langmuir and Frumkin models fit the γ_e - $\ln C_0$ curve nicely. The fitted parameters are: for the Langmuir model, $\Gamma_\infty=2.4 \times 10^{-6} \text{ mol/m}^2$, $a=4.0 \times 10^{-6} \text{ kg/m}^3$; and for the Frumkin model, $\Gamma_\infty=3.32 \times 10^{-6} \text{ mol/m}^2$, $a=8.43 \times 10^{-7} \text{ kg/m}^3$, $K=7.12$.

However, if we apply the Langmuir and Frumkin surface equations of state to predict the surface tension/surface concentration data, the results are not satisfactory. Figure 4-14 shows the Langmuir and Frumkin surface equations of state as well as the measured surface tension/surface concentration data for the surfactant $C_{14}E_6$. Obviously, the Langmuir model does not fit the surface tension/surface concentration data. The Frumkin model fits the data better, but it does not have the right shape of the measured surface tension/surface concentration curve. From Figure 4-11 and Figure 4-12, we can see that the molecular interaction model fits both the $\gamma_e - \ln C_0$ and surface tension/surface concentration data nicely. To this point, we conclude that the molecular interaction model is a better model.

The important issue has been shown again that the $\gamma_e - \ln C_0$ curve is not sensitive to surface equations of state. Figure 4-11 and Figure 4-14 showed a big variation of the surface equations of state. But when we use these models to fit the $\gamma_e - \ln C_0$ data, all of them fit the data nicely. On the other hand, if we fit the $\gamma_e - \ln C_0$ data to find an equation of state, we will also have big variations of the surface equation of state. Therefore, simply fitting the equilibrium surface tensions can not generate an accurate surface equation of state.

The other important issue is shown in Figures 4-9, 4-10 and 4-11. We see that the molecular interaction model curve is monotonic for $C_{14}E_4$ and $C_{14}E_6$. However, for the $C_{14}E_2$ surfactant, we see the molecular interaction model curve oscillates at surface tension close to the surface tension of pure water. This could signal phase transition. Pollard^[17] et al studied the two dimensional phase transition, and have observed a phase transition in low surface pressure for the $C_{14}E_1$ surfactant. So, if a phase transition exists at low surface pressure for the $C_{14}E_2$ surfactant, the model could be able to predict it.

From the Langmuir model, Frumkin model to molecular interaction model, the number of model parameter increases from two to four. This could be the reason why the fit is getting better along the models. However, since the two and three parameters models are not able to accurately describe the relationships among γ , C_b and Γ , a model with more parameters is appropriate.

The Physical Meaning of Model Parameters

As the molecular interaction model is derived from a surfactant molecular interaction approach, each parameter has its own physical meaning. First, b_1 is the constant which characterizes the van der Waals interaction. From Table 4-1 and 4-2, we see that b_1 is negative, which means the interaction is attractive. As the van der Waals interaction is assumed from hydrophobic tail-tail interaction, the surfactants with a same size of hydrophobic tail should have an approximately same b_1 . From Table 4-1, we can see this argument is true for the $C_{14}E_2$, $C_{14}E_4$ and $C_{14}E_6$ series. For different sizes of hydrophobic tail, the b_1 values should be different. From Table 4-2, we see b_1 is different for $C_{16}E_6$, $C_{14}E_6$ and $C_{12}E_6$ series. When the hydrophobic tail is bigger, the absolute b_1 value is bigger, which means the van der Waals interaction is increasing. These results agree very well with the van der Waals interaction theory. The other issue concerning the van der Waals interaction is the magnitude of the force. Since we simplified the van der Waals interaction in the model development, we can not compare the b_1 value with other measurements. Further, a two-dimensional Hamaker constant is not available. However, estimation of the van der Waals energy is still possible. If we take a surface concentration of 3.0×10^{-6} mol/m², in which case the surfactant molecules are closely packed on the interface, and b_1 of -1.354×10^{-6} m²/mol, then the van der Waals energy calculated by equation (4-12) is -10.02×10^3 J/mol, which agrees with the magnitude of van der Waals interaction energy^[18].

Secondly, b_3 is the constant which characterizes the decay length of hydration force. From Table 4-1 and 4-2, we see that each b_3 is negative, which agrees that the interaction is decaying along the increase of molecular separation. From equation (4-13), the characteristic decay length is $-1/b_3'$, which equals to $-1/(b_3\sqrt{N_0})$. With b_3 known from the model, we can calculate the characteristic decay length. The decay lengths thus calculated for $C_{14}E_2$, $C_{14}E_4$, $C_{14}E_6$ are 1.87×10^{-10} , 2.35×10^{-10} , 2.80×10^{-10} m, respectively. The decay lengths agree with the results obtained from other measurements^[18]. We see from this series that the decay length increases as the hydrophilic head is getting bigger. This result agrees that the hydration force is originated from the hydrophilic head-head interaction. Further, the decay lengths for, $C_{14}E_6$, $C_{12}E_6$ are 2.80×10^{-10} , 2.80×10^{-10} , 2.86×10^{-10} m. They are about the same as these surfactants have a same size of hydrophilic group.

Thirdly, the physical meaning of b_2 is mixed, which consists of both the hydration force and maximum surface concentration effects. However, one point is clear that the hydration force is repulsive as b_2 is positive. From Table 4-1, b_2 value decreases along the $C_{14}E_2$, $C_{14}E_4$, $C_{14}E_6$ series. This could be the effect of maximum surface concentration. We can see from Figures 4-9, 4-10, 4-11 how the maximum surface concentration changes. From Table 4-2, the b_2 value is approximately the same for the $C_{16}E_6$, $C_{14}E_6$, $C_{12}E_6$ series.

Finally, the equilibrium adsorption constant is a measure of the surface activity of a surfactant. Small a means high surface activity. As we expected, the equilibrium adsorption constant obtained reflects the surface activity well for the $C_{16}E_6$, $C_{14}E_6$, $C_{12}E_6$ series. From Table 4-2, we see that the a value increases as the size of hydrophobic tail decreases. It is a surprise for the $C_{14}E_2$, $C_{14}E_4$ and $C_{14}E_6$ series as we expected the

surfactant with a smaller hydrophilic head should be more surface active. Just from Table 4-1, we see the opposite trend. However, the actual surface activity is measured by $a \exp\left(2b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right)$ from the adsorption isotherm. We find that $a \exp\left(2b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right)$ is actually smaller for C₁₄E₂ and C₁₄E₄ when the surface concentration is high enough to significantly lower the surface tension.

The molecular interaction model is derived from an molecular interaction approach. It describes both the surface tension/surface concentration data and equilibrium surface tensions well. Each model parameter has its own physical meaning. However, this model has total four parameters. Further, in this approach, we fit one surface tension/surface concentration curve to obtain three parameters, which may lead to an arbitrary fitting. If we can use other methods to find the van der Waals parameter and hydration force decay length, then we can reduce the model parameters to two. By doing this, we would vigorously fit the model to the surface tension/surface concentration data to obtain b_2 , and to fit the model to the equilibrium surface tensions to obtain a .

Table 4-1

The best fitted molecular interaction model parameters for C₁₄E₂, C₁₄E₄ and C₁₄E₆

surfactant	C ₁₄ E ₂	C ₁₄ E ₄	C ₁₄ E ₆
b ₁ , x10 ⁶ m ² /mol	-1.4	-1.3	-1.4
b ₂ , mol ^{1/2} /m	0.42	0.25	0.21
b ₃ , x10 ⁻³ mol ^{1/2} /m	-6.9	-5.5	-4.6
$a = \alpha_0/\beta_0$, m ⁻¹	220*	46*	2.7

* estimated value

Table 4-2

The best fitted molecular interaction model parameters for C₁₆E₆, C₁₄E₆ and C₁₂E₆

surfactant	C ₁₆ E ₆	C ₁₄ E ₆	C ₁₂ E ₆
b ₁ , x10 ⁶ m ² /mol	-1.5	-1.4	-1.2
b ₂ , mol ^{1/2} /m	0.18	0.21	0.19
b ₃ , x10 ⁻³ mol ^{1/2} /m	-4.6	-4.6	-4.5
$a = \alpha_0/\beta_0$, m ⁻¹	1.4*	2.7	27

* estimated value

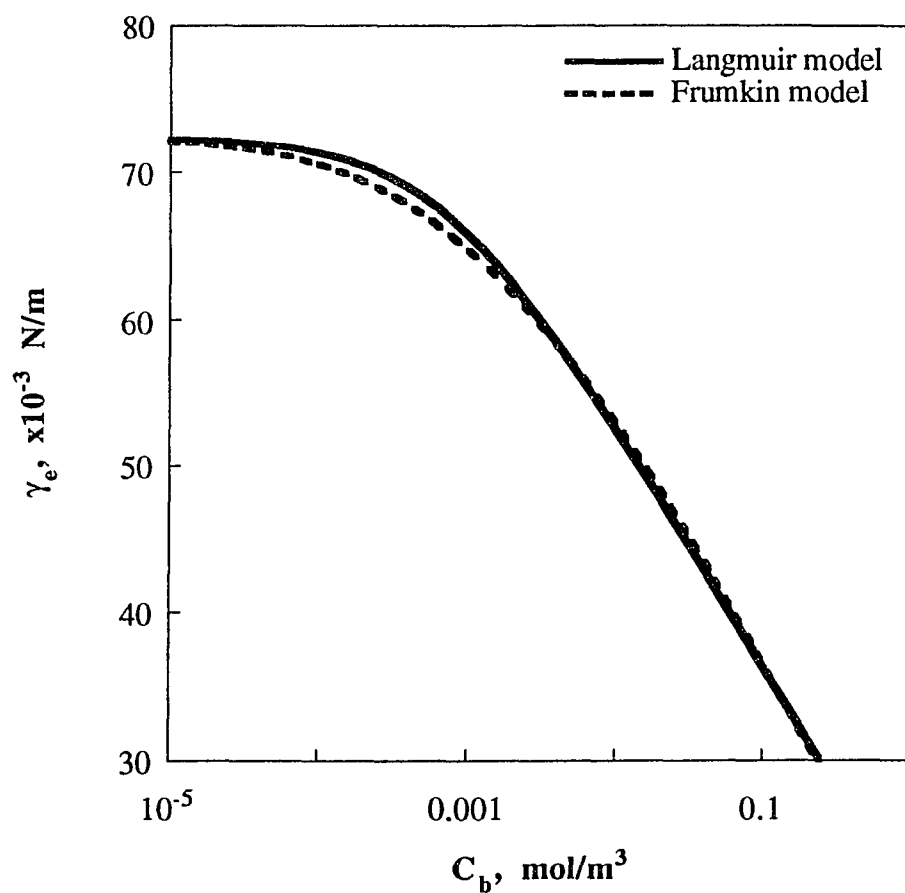


Figure 4-1 Equilibrium surface tensions for air/Triton X-100 aqueous solutions. Data were generated by using Langmuir model with parameters $\Gamma_{\infty}=2.91 \times 10^{-6}$ mol/m² and $a=6.62 \times 10^{-4}$ mol/m³, and using Frumkin model with parameters $\Gamma_{\infty}=2.91 \times 10^{-6}$ mol/m², $a=6.62 \times 10^{-4}$ mol/m³ and $K=2.52$. (From AIChE J., 36(1990)1785-1795).

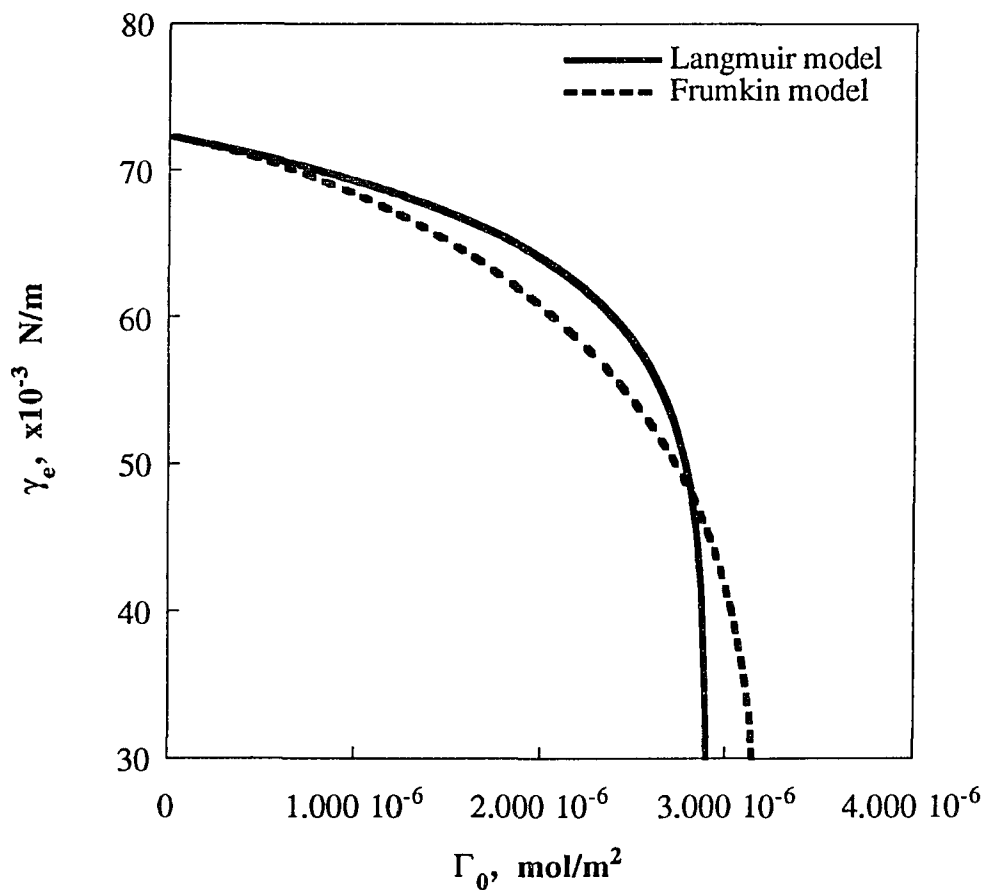


Figure 4-2 Equilibrium surface tensions vs. surface concentrations for air/Triton X-100 aqueous solutions. Data were generated by using Langmuir model with parameters $\Gamma_\infty = 2.91 \times 10^{-6} \text{ mol/m}^2$, and using Frumkin model with parameters $\Gamma_\infty = 2.91 \times 10^{-6} \text{ mol/m}^2$ and $K = 2.52$. (From AIChE J., **36**(1990)1785-1795).

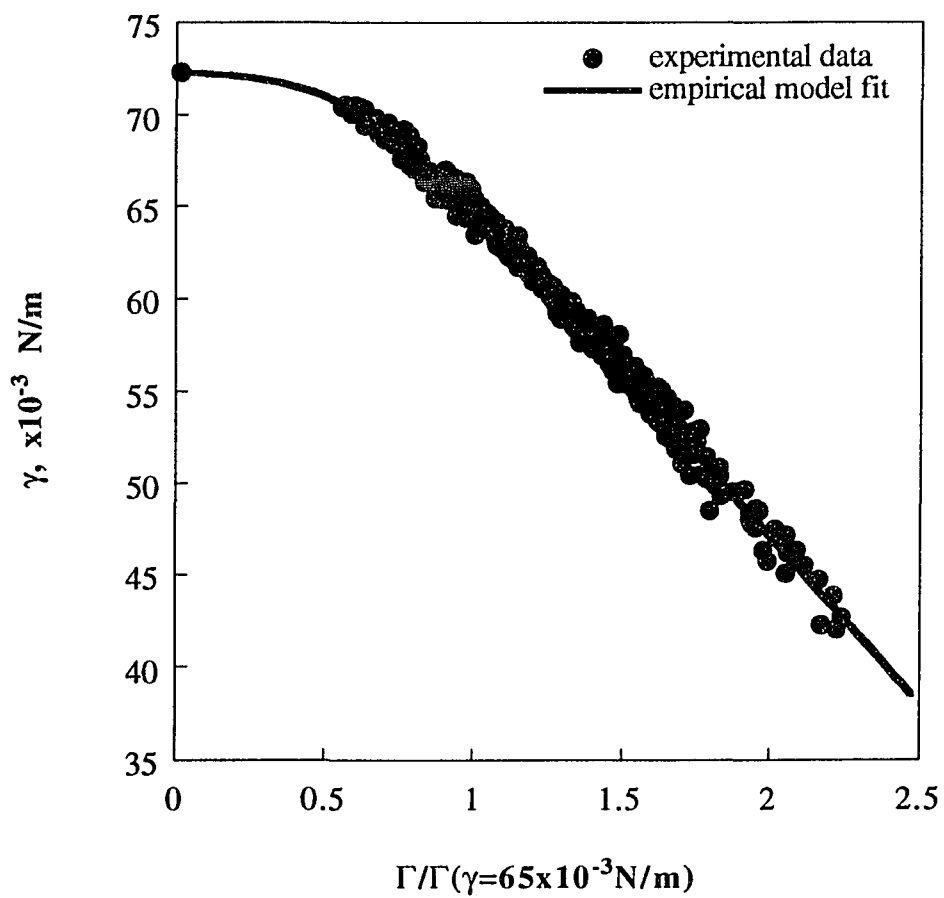


Figure 4-3 Empirical fit of the surface tension/relative surface concentration curve for C_{12}E_6 . (Fitted to the equation (4-22) with empirical coefficients $q_1 = 3.221 \times 10^{-3} \text{ N/m}$; $q_2 = 30.19$; $q_3 = 5.617$)

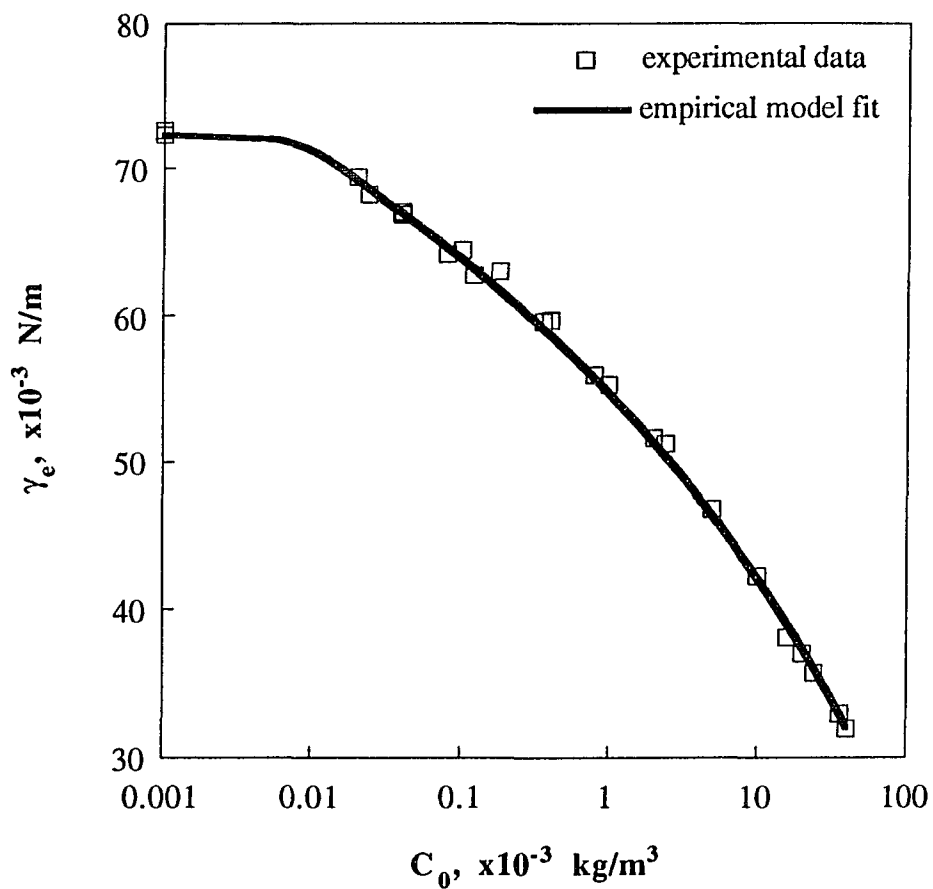


Figure 4-4 Empirical fit of the equilibrium surface tensions for $C_{12}E_6$. (Fitted to the equation (4-24) with $\Gamma(\gamma = 65 \text{ mN/m}) = 1.157 \times 10^{-6} \text{ mol/m}^2$ and $\gamma_e = 32 \times 10^{-3} \text{ N/m}$ at $C_b = 40.0 \times 10^{-3} \text{ kg/m}^3$.)

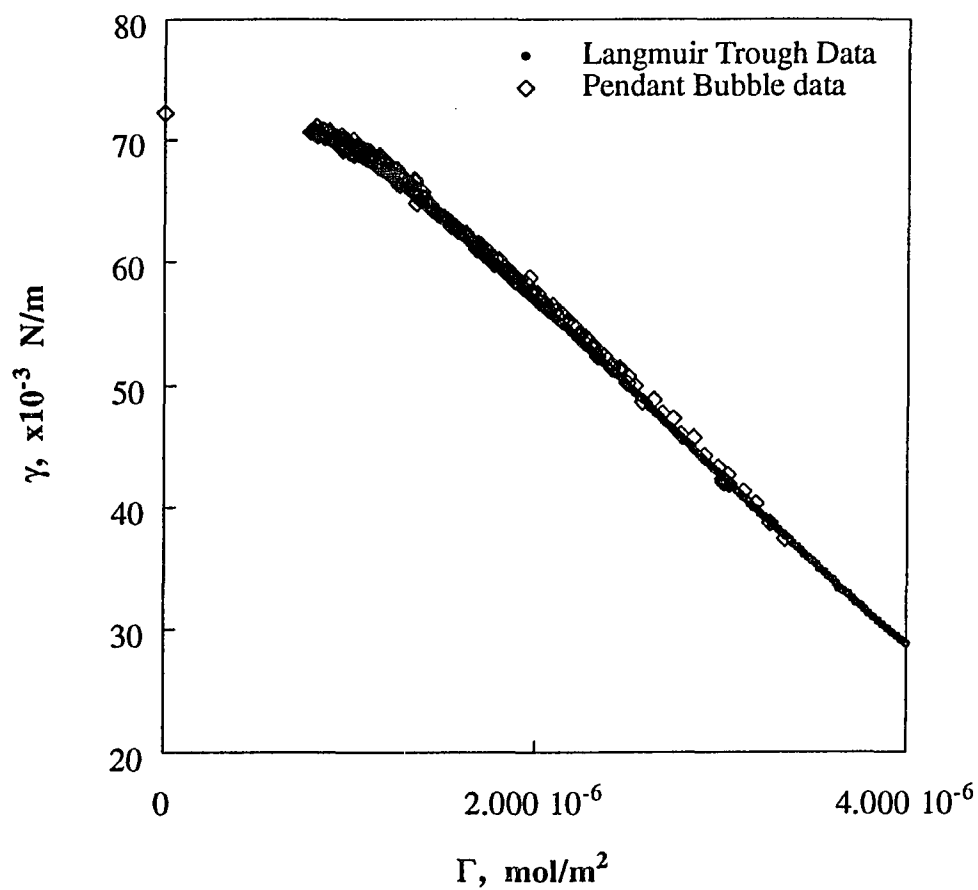


Figure 4-5 Comparison of the monolayer film balance data from the pendant bubble and Langmuir trough for C_{16}E_6 .

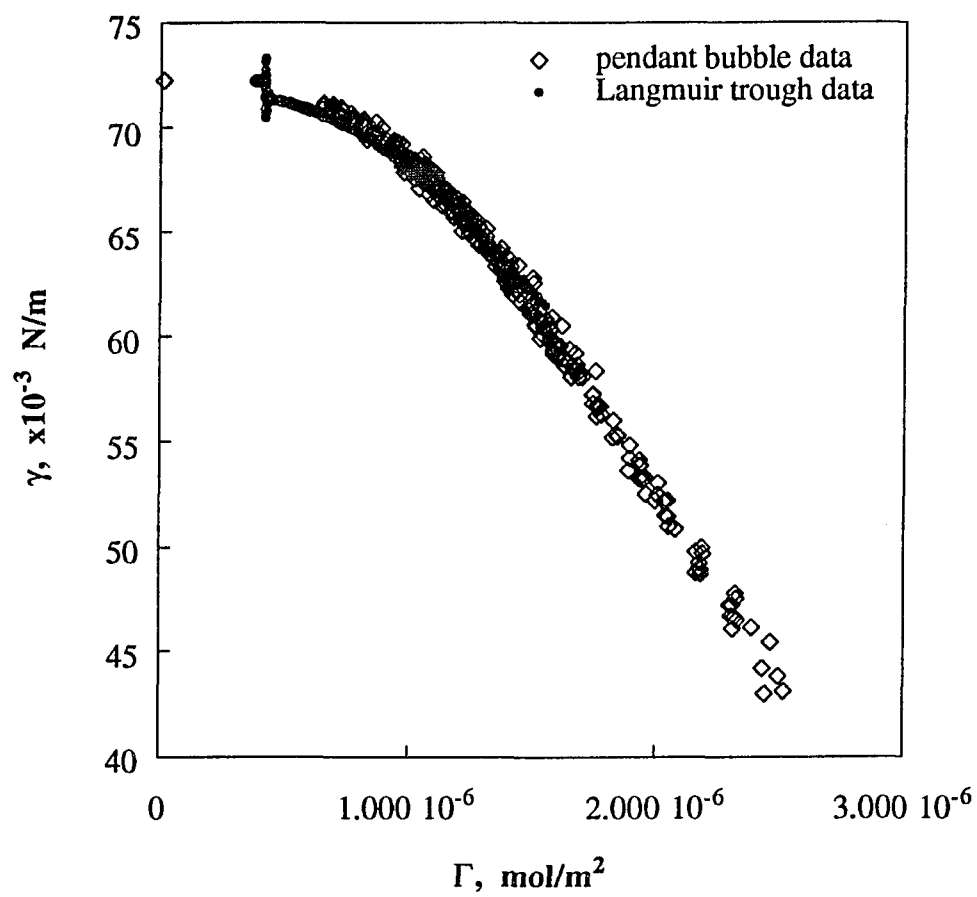


Figure 4-6 Comparison of the monolayer film balance data from the pendant bubble and Langmuir trough for C_{14}E_6 .

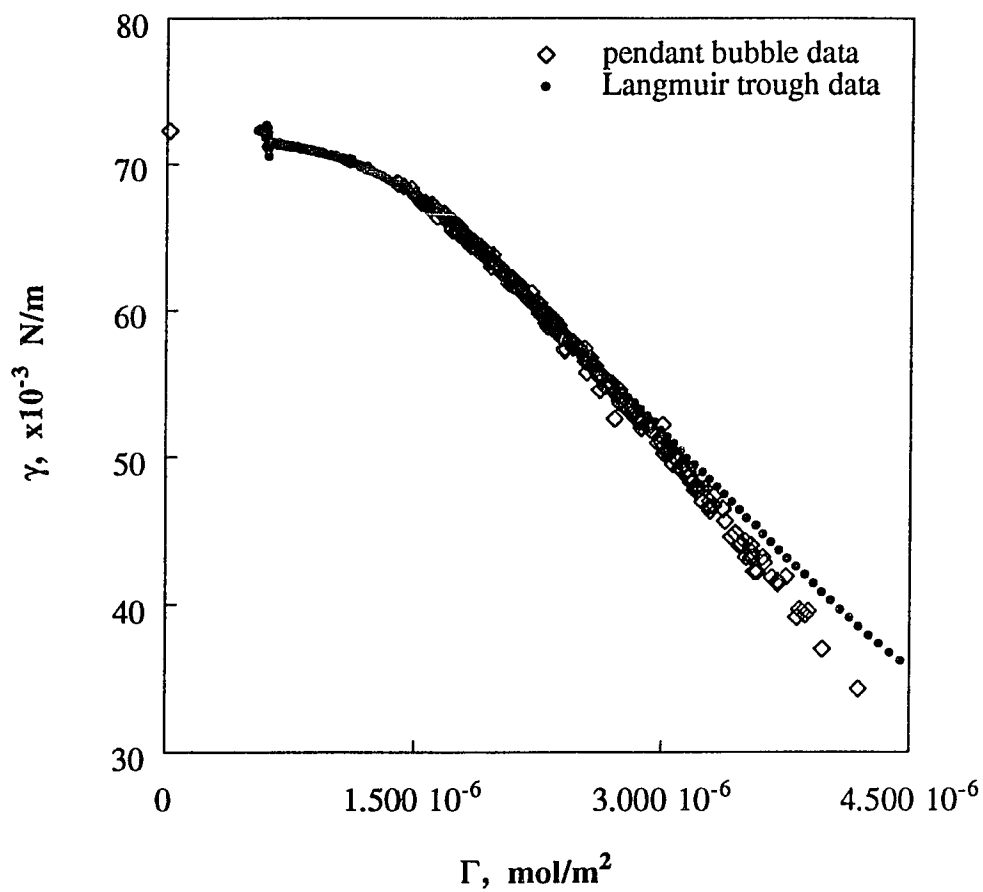


Figure 4-7 Comparison of the monolayer film balance data from the pendant bubble and Langmuir trough for C_{14}E_4 .

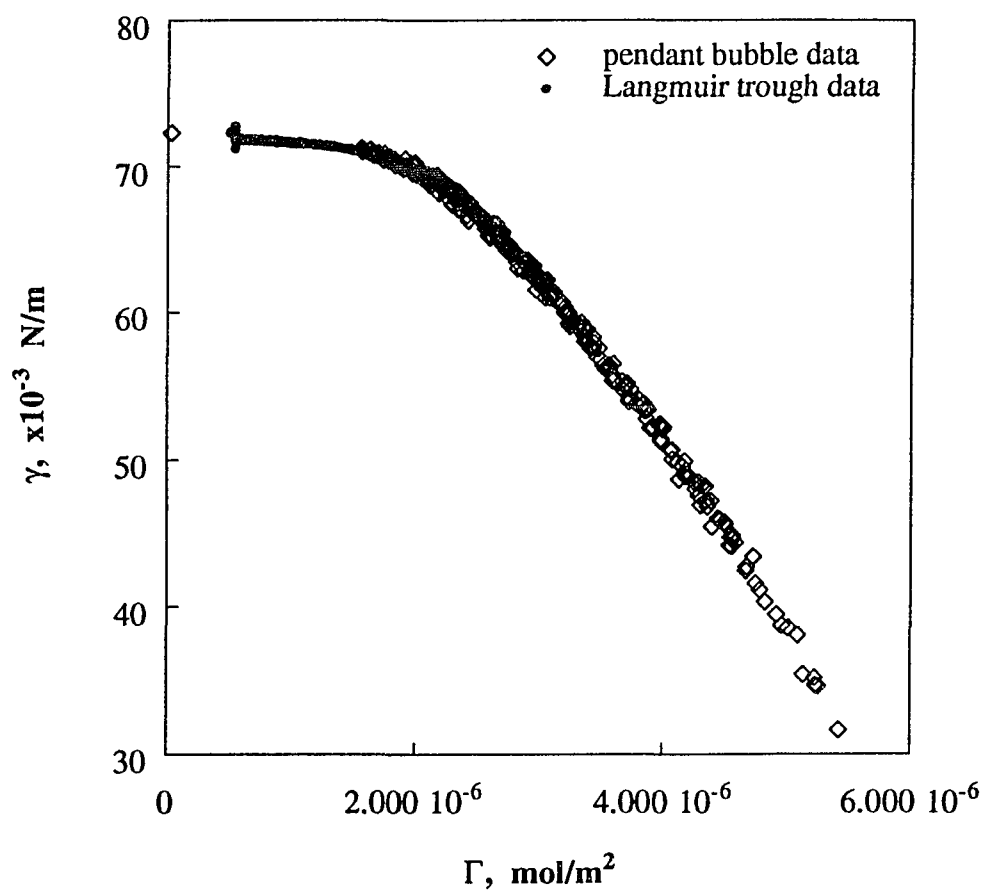


Figure 4-8 Comparison of the monolayer film balance data from the pendant bubble and Langmuir trough for C_{14}E_2 .

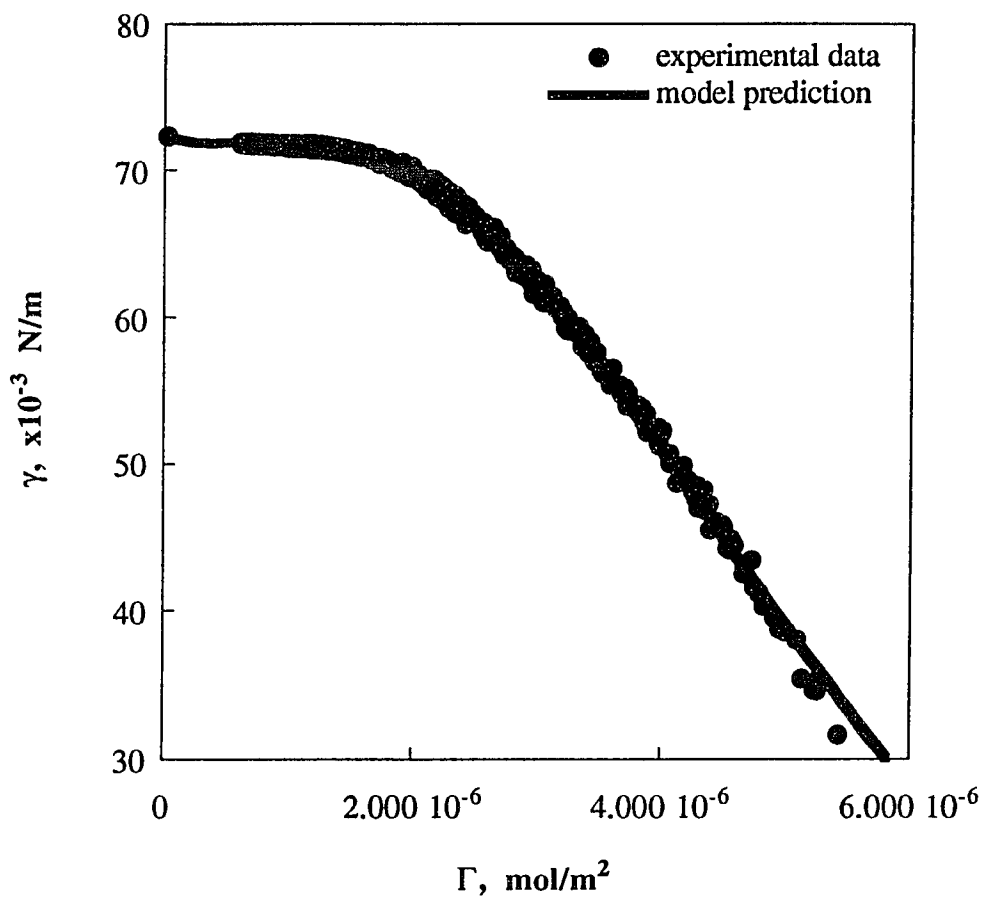


Figure 4-9 The molecular interaction surface equation of state fits for C_{14}E_2 with the best fitted parameters $b_1 = -1.4 \times 10^6 \text{ m}^2/\text{mol}$, $b_2 = 0.42 \text{ mol}^{1/2}/\text{m}$, $b_3 = -6.9 \times 10^{-3} \text{ mol}^{1/2}/\text{m}$.

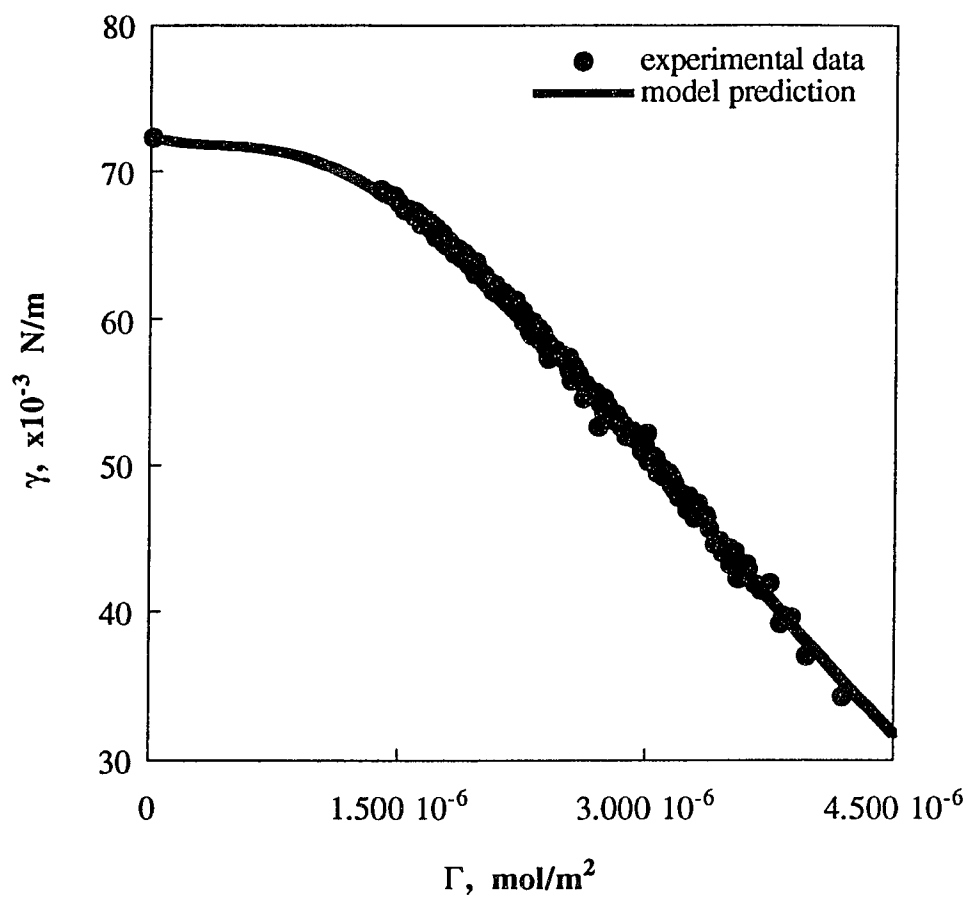


Figure 4-10 The molecular interaction surface equation of state fits for C_{14}E_4 with the best fitted parameters $b_1 = -1.3 \times 10^6 \text{ m}^2/\text{mol}$, $b_2 = 0.25 \text{ mol}^{1/2}/\text{m}$, $b_3 = -5.5 \times 10^{-3} \text{ mol}^{1/2}/\text{m}$.

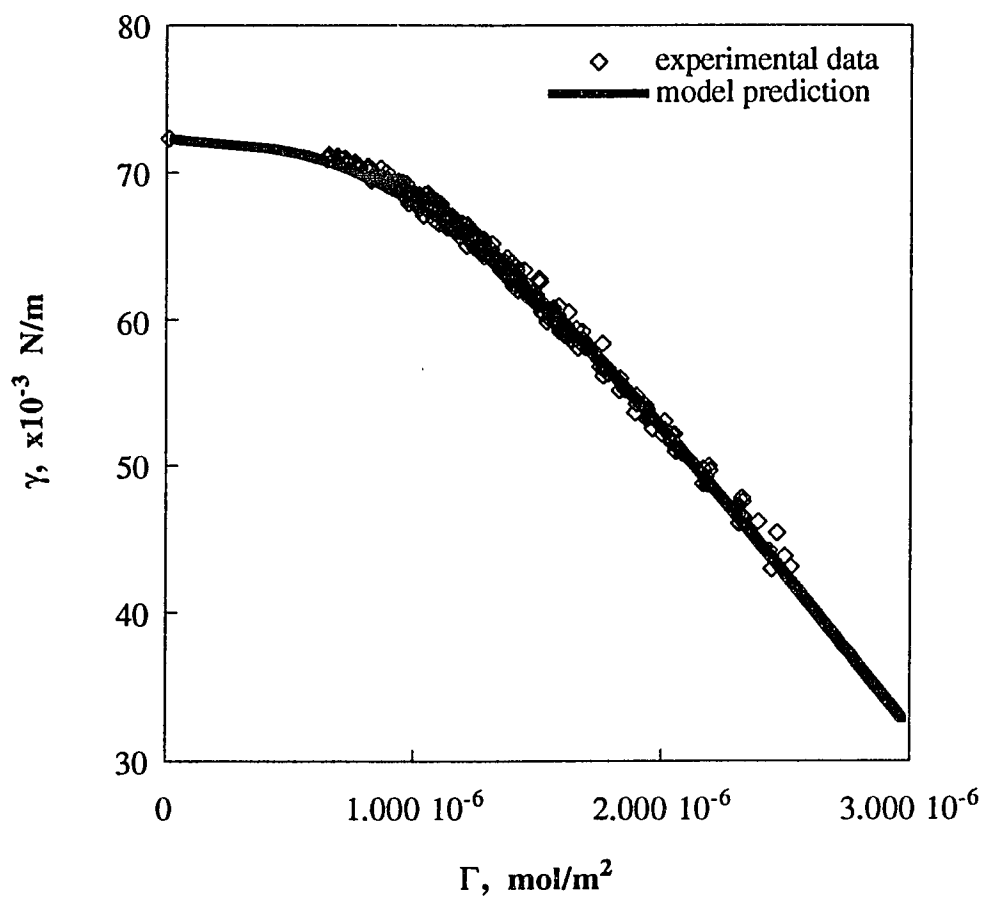


Figure 4-11 The molecular interaction surface equation of state fits for $C_{14}E_6$ with the best fitted parameters $b_1 = -1.4 \times 10^6 \text{ m}^2/\text{mol}$, $b_2 = 0.21 \text{ mol}^{1/2}/\text{m}$, $b_3 = -4.6 \times 10^{-3} \text{ mol}^{1/2}/\text{m}$.

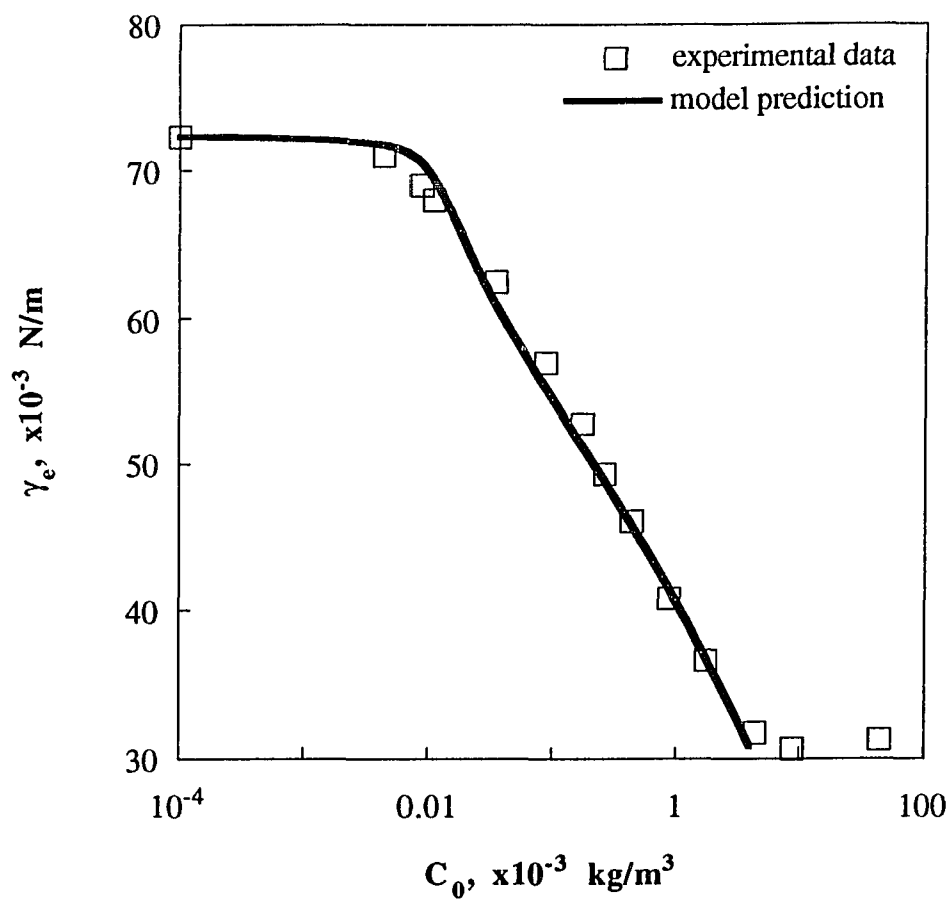


Figure 4-12 The molecular interaction model fits to the equilibrium surface tensions for aqueous $C_{14}E_6$ solutions with the best fitted parameter $a=2.7 \text{ m}^{-1}$.

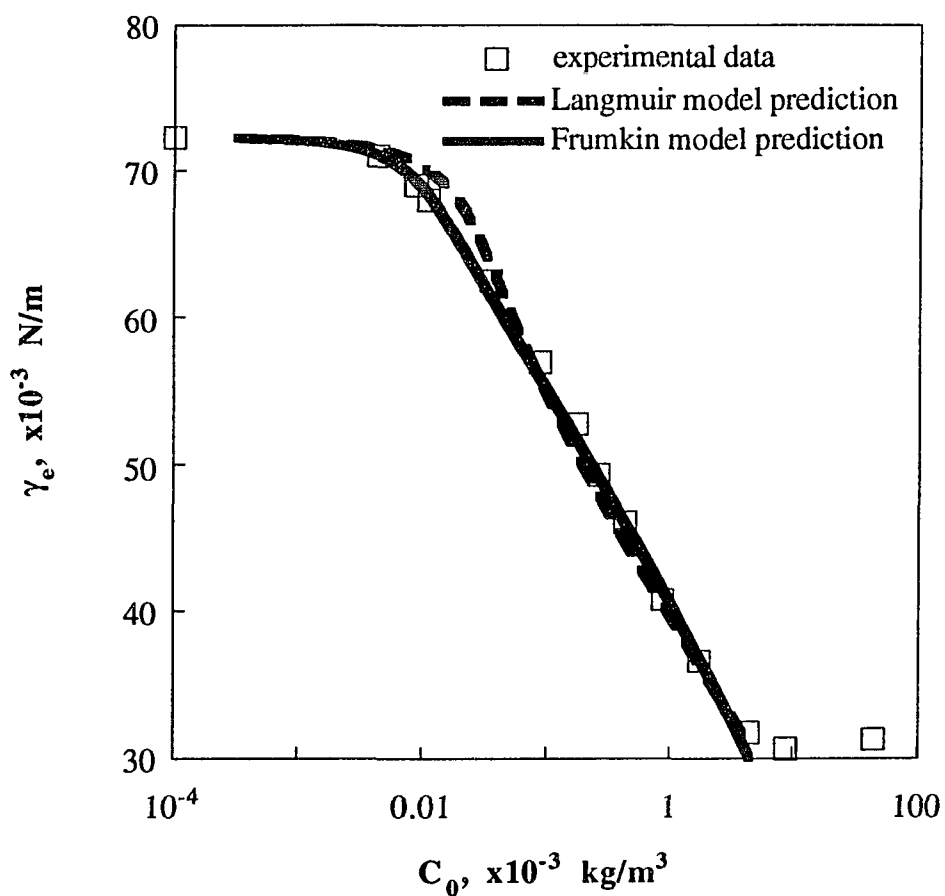


Figure 4-13 The Langmuir and Frumkin models fit to the equilibrium surface tensions of aqueous $C_{14}E_6$ solutions. (The best fitted parameters are: $\Gamma_\infty=2.4 \times 10^{-6}$ mol/m², $a=4.0 \times 10^{-6}$ kg/m³ for the Langmuir model; and $\Gamma_\infty=3.32 \times 10^{-6}$ mol/m², $a=8.43 \times 10^{-7}$ kg/m³, $K=7.12$ for the Frumkin model.)

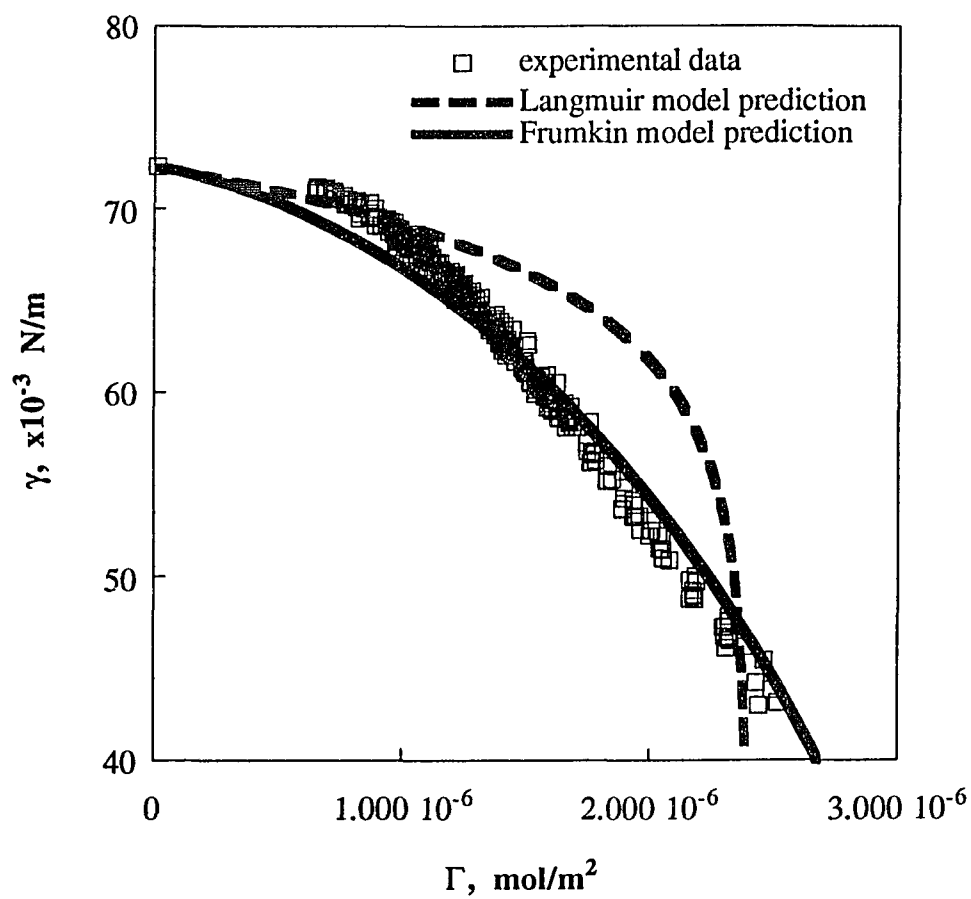


Figure 4-14 The Langmuir and Frumkin surface equations of state fit to the surface tension/surface concentration data for C_{14}E_6 .

Chapter 5

Conditions for Promoting Kinetic Control During Surfactant Adsorption to Clean Surfaces and Desorption from Compressed Equilibrium Monolayers, and Their Use in Measuring Kinetic Parameters by the Pendant Bubble Method

5.1 Introduction

The rate of exchange of surfactant molecules between a fluid interface and the surrounding bulk phases is determined by the kinetic flux between the surface and the bulk sublayers next to the surface, and the diffusive flux between these sublayers and the regions of the bulk phases extending away from the surface. The process of kinetic adsorption and desorption at an interface is usually described using an Arrhenius rate formulation; for exchange between one sublayer and the surface, the rate expression is of the form^[1]:

$$\frac{d\Gamma}{dt} = \beta_0 \exp\left(-\frac{E_A}{RT}\right) C_s - \alpha_0 \exp\left(-\frac{E_D}{RT}\right) \Gamma \quad (5-1)$$

where Γ is the surface concentration, C_s is the sublayer concentration, α_0 and β_0 are kinetic rate constants for desorption and adsorption, respectively, E_A/RT and E_D/RT are, respectively, the activation energies for adsorption and desorption divided by the thermal energy, RT . The activation energies can depend on the surface concentration Γ ; this

dependence describes cohesive or repulsive interactions among the molecules on the surface monolayer. We note in equation (5-1) that when diffusion is fast, the sublayer concentration is equal to the far field bulk concentration C_b , and the surface concentration on the surface is controlled solely by kinetics. For Langmuir kinetics, the activation energy for desorption is independent of the surface concentration, and the activation energy for adsorption is expressed by the equation: $e^{-E_A/RT} = e^{-E_A^0/RT}(\Gamma_\infty - \Gamma)$, where Γ_∞ is the maximum surface concentration, E_A^0 is independent of the surface concentration. Then equation (5-1) can be integrated to determine $\Gamma(t)$ for an initial surface concentration $\Gamma(0)$:

$$\frac{\Gamma(t) - \Gamma(0)}{\Gamma_0 - \Gamma(0)} = 1 - \exp(-(\alpha + C_b\beta)t) \quad (5-2)$$

where $\beta = \beta_0 \exp(-E_A^0/RT)$, $\alpha = \alpha_0 \exp(-E_D^0/RT)$, and Γ_0 is the surface concentration at equilibrium (obtained by setting the net exchange equal to zero in equation (5-1)). Thus the kinetic time scale for Langmuir kinetics is $\tau_{\text{kinetic}} = (\alpha + \beta C_b)^{-1}$, and we use this expression to generally characterize kinetic rates.

Past studies have used two types of experiments to measure the surfactant diffusion coefficients and kinetic rate constants (for reviews, see references[2,3,4,5]). These are:

(i) *Clean Interface Adsorption*: A fresh interface is created in a surfactant solution, and the relaxation in surface tension is measured as surfactant molecules adsorb from solution onto a static interface (the Wilhelmy plate or ring method and the pendant bubble technique) or a continuously deforming or flowing interface (oscillating jet, inclined plane, maximum bubble pressure, growing drop, and drop weight methods).

(ii) *Re-equilibration*: An equilibrium monolayer is perturbed either with small amplitude periodic oscillations (Langmuir trough and oscillating bubble methods) or large amplitude area changes (elastic ring or float on the air/water surface of a Langmuir trough,

a reversed funnel, pulsating bubble and shrinking or expanding pendant bubble techniques), and the tension oscillation or relaxation as the interface re-equilibrates is measured.

For clean interface adsorption and re-equilibration, by modeling the kinetic exchange with equation (5-1), and the bulk diffusive and convective transport with the convective-diffusion equation, $\Gamma(t)$ can be predicted as a function of the surfactant transport parameters. From the equilibrium adsorption equation ($\Gamma_0(C_b)$) and the Gibbs-Duhem equation for the surface or interfacial tension ($d\gamma_e = -RT\Gamma_0 d\ln C_b$), an equation of state relating the surface tension γ_e to the surface concentration can be obtained ($\gamma_e(\Gamma_0)$). From the equation of state the model prediction of the tension relaxation can be computed, and from a comparison of the model with the experimental results, ideally, the kinetic constants and the diffusion coefficient can be inferred. Equilibrium measurements of the tension as a function of the bulk concentration as well as direct measurements of the surface tension/surface concentration data, when fitted to the equation of state, provide inter-relationships between the kinetic constants, and these facilitate the determination of the kinetic constants from the dynamic tension data. For example for Langmuir kinetics, the equation of state is $\gamma_e - \gamma_c = RT\Gamma_\infty \ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) = -RT\Gamma_\infty \ln\left(1 + \frac{\beta C_b}{\alpha}\right)$, and fitting this curve to equilibrium data provides the ratio α/β .

In the above experiments, the interpretation of the surface tension relaxations begins by assuming that kinetic exchange is very fast, and that the transport is diffusion controlled over the time scales (or frequencies) of the experiment. With this assumption, an apparent diffusion coefficient is calculated. It is difficult to measure separately the diffusion coefficient of surfactant monomers by independent methods such as light scattering because the monomer concentration is usually very low. The apparent value is therefore usually

compared to a value obtained from the Stokes-Einstein equation (assuming some value for the hydrodynamic radius based on molecular considerations); If the apparent value is in reasonable agreement with the Stokes-Einstein value then no further interpretation of the experiment is done, the apparent value is considered as the diffusion coefficient, and the kinetic constants remain unresolved. If the calculated apparent diffusion coefficient differs greatly from the Stokes-Einstein expectation, then the transport process is either modeled as kinetically controlled, and comparison with data yields the kinetic parameters, or as mixed, and kinetic constants and diffusion coefficients are derived from a fit of the data. (An excellent discussion of this approach is presented in the review article of Chang and Francis^[5].)

Most investigations using the above techniques have concluded that surfactant transport in the dynamic tension relaxation is diffusion controlled, and have computed diffusion coefficients. Marked kinetic effects have only been observed in clean interface adsorption for bolaform surfactants with two hydroxyl (1,2 and 1,8 through 1,11 diols) or carboxylic acid groups (1,6 through 1,10 diacids) (Bleys and Joos^[6] and Joos et al.^[7], octanols of linear hydrocarbon chain with the hydroxyl at intermediate 2 through 4 positions in the chain (Bleys and Joos^[6]), and short and intermediate chain soluble n-alcohols (n=3-7) (Fainerman and Lylyk^[8], Joos and Serrien^[9], Chang and Franses^[10] and Tsionopoulos et al.^[11]). For re-equilibration experiments, the only surfactants which have demonstrated kinetic effects are again a bolaform surfactant, 1,9 diol (Panaiotov et al.^[12] and Joos et al.^[13]), n-octanol (Chang and Francis^[10]) and n-decanol (Lin, Lu and Hwang^[14]). From the clean interface adsorption and re-equilibration experiments, the values determined for α are uniformly of the order of 10^2 sec^{-1} , and values for β follow from the equilibrium ratio. Presumably, the slow kinetic exchange of the bifunctional diols, diacids and 2,3,4 octanols arises because the exchange of a surfactant with two separated polar groups or a polar group in an intermediate position in a linear hydrocarbon

chain is a slow process. This point of view is supported by the fact that as the intervening chain length increases for the diols and diacids, kinetic effects are no longer present and the process becomes diffusion controlled^[6]. Kinetic effects in the exchange of n-octanol and n-decanol from equilibrium monolayers are probably due to strong cohesive interactions between the hydrocarbon chains of these surfactants, facilitated by their slender architecture which allows them to pack lengthwise closely together: This cohesion reduces the desorption kinetic rate by increasing the activation energy for desorption, E_D (see equation (5-1)). As described by Lin et al.^[14], this reduction in the desorption rate is more effective when the surface density is larger, and is the reason why adsorption onto a clean interface of n-decanol can be observed to be diffusion limited, while re-equilibration or oscillation of an equilibrium layer is mixed. The kinetic control observed with the lower chain alcohols represents an effect due to larger bulk concentration. This effect is part of the ideas we will present in this paper, and we will discuss it shortly below.

Aside from the n- and branched alcohol and bifunctional diacid and diol studies, no other kinetic measurements exist. The reason usually given as to why kinetic effects are not manifest is that kinetic exchange timescale τ_{kinetic} is too short. In both clean interface adsorption and re-equilibration, the kinetic step precedes and initiates the bulk diffusive process, i.e. surfactant first kinetically adsorbs onto a clean interface, reducing the sublayer concentration which drives the diffusion towards the surface, or desorbs off of the overcrowded interface, increasing the sublayer concentration which drives the diffusion away from the surface. Consequently the time dependent change in surface concentration of surfactant is controlled by kinetics for short times and diffusion for longer times. If the kinetic exchange is too fast, then measurements only capture the diffusion limited regime.

The above argument, however, is not all that convincing. The diffusion coefficient is not precisely known but should not be a function of concentration. In this paper, we

introduce two new approaches for increasing the effect of kinetics relative to diffusion during surfactant transport in the experimental methods in an effort to provide methods to unambiguously measure the kinetic constants. The first approach is applicable to the experiments involving clean interface adsorption. We have already noted that for both clean interface adsorption and re-equilibration, early times are dominated by kinetics and later times by diffusion. In this paper, we will show that as the bulk concentration increases (but remains less than the critical micelle concentration so that micellar kinetics and transport do not become involved), the early interval in time over which kinetic control is effective is extended. The second method pertains to re-equilibration. We demonstrate that by increasing the initial surface compression, and hence the surface concentration above the equilibrium coverage, the interval during which kinetics is controlling is extended at the expense of diffusion.

The underlying reasons for why the kinetic control period is extended for both these cases can be seen by examining the transport at a planar interface bounded by a single semi-infinite phase in the absence of convective flow. The Ward and Tordai expression^[15], representing an integration of the unsteady bulk diffusion equation for this case, relates the surface concentration $\Gamma(t)$ to the sublayer concentration $C_s(t)$:

$$\Gamma(t) - \Gamma(0) = 2C_b \left(\frac{Dt}{\pi} \right)^{1/2} - 2 \left(\frac{D}{\pi} \right)^{1/2} \int_0^t C_s(t - \tau) d\sqrt{\tau} \quad (5-3)$$

where D is the bulk diffusion coefficient, C_b is the bulk concentration far from the interface and $\Gamma(0)$ is the initial surface concentration (which is equal to zero for clean interface adsorption, and is prescribed as some value in re-equilibration). Simultaneous numerical solution of equations (5-1) and (5-3) provides $\Gamma(t)$. However, analytic solutions in the form of a power series in $t^{1/2}$ can also be obtained. The first few terms in these solutions for $\Gamma(t)$ describe the behavior for early times, and clarify the contributing roles of bulk

concentration and the initial overcrowding to the shifting from purely kinetic control at the very earliest times to diffusive-kinetic transport at later times. The three term expansion is given below for the Langmuir kinetics:

$$\frac{\Gamma(t) - \Gamma(0)}{\Gamma_0 - \Gamma(0)} = \beta C_b t - \Phi (\beta C_b t)^{3/2} + (\Phi^2 - 1) (\beta C_b t)^2 \quad (5-4)$$

where $\Phi = \left(1 - \frac{\Gamma(0)}{\Gamma_\infty}\right) \left(\frac{\Gamma_\infty^2 \beta}{C_b D}\right)^{1/2}$. Since the leading order t term is kinetic, the above equation clearly shows that at the earliest times the process is kinetically controlled, as we have already remarked. Diffusive contributions, described by the parameter begin at order $t^{3/2}$ and contribute to order t^2 and all higher orders, and the appearance of this parameter at these orders signals the shifting from purely kinetic to mixed control. Diffusive effects become postponed when Φ is reduced in magnitude, as when the bulk concentration is increased or, for a re-equilibration, the initial overcrowding is increased. We therefore see from equation (5-4) why increasing the bulk concentration or the overcrowding extends the early time kinetic control to later times.

The aims of this Chapter are twofold. The first is to construct complete numerical solutions of equations (5-1) and (5-3) for all time in order to verify our postulates that in clean interface adsorption kinetic effects become emphasized when the bulk concentration increases, and that in re-equilibration, kinetic effects extend to longer times as the initial compression increases. We present these solutions in Section 5.2. The second objective is to demonstrate experimentally that by either increasing the bulk concentration or the initial compression, and promoting kinetic control, kinetic constants can be measured. The experimental part is given in Section 5.3. We study the adsorption of the polyethoxylated surfactant $C_{12}E_6$ at the air/water interface using the pendant bubble technique. The technique is based on the analysis of the shape of pendant bubbles formed and tethered to

the tip of a needle placed in the surfactant solution. We use the technique for both clean interface adsorption and re-equilibration studies. For clean interface adsorption, a pendant bubble is formed quickly (<1 second) by the injection of gas through a needle immersed in the surfactant solution. Surfactant adsorbs onto the freshly formed interface, reducing the tension of the bubble surface and elongating the bubble. Digitized video images of the bubble elongation are captured sequentially in time; for each digitized image, the locus of points comprising the bubble interface is constructed, and the surface tension of the bubble interface at that time is computed by matching the bubble profile to theoretical pendant shapes obtained by solving the Young-Laplace equation. Thus from the sequence of images, a surface tension relaxation can be constructed. Re-equilibration experiments are undertaken by first allowing a bubble to form an equilibrium monolayer on its surface, and then quickly reducing the bubble area (<0.5 sec). Video capture of the bubble shape as the surfactant re-equilibrates provides the surface tension re-equilibration. For both clean interface adsorption and re-equilibration, bubble shapes are captured only after the bubble is created, or the jump change in area is completed, so that convective effects are not important in the surfactant mass transfer. The technique was developed by Neumann and coworkers, and has been used in clean interface adsorption studies of Triton X-100, *n*-decanol and SDS at the air/water interface, and SDS at the oil/water interface, and re-equilibration investigations of proteins and *n*-decanol, both at the air/water interface [16,17,18,19,20,21]. In our study of $C_{12}E_6$, clean interface adsorption experiments are done at increasingly higher bulk concentrations, and re-equilibration experiments are done at increasingly larger initial compressions. We develop solutions of the kinetic-diffusion equations and compare to the experimental dynamic tensions. Comparisons at increasing concentrations (for clean interface adsorption) or larger initial crowding (for re-equilibration), show the progressive effect of kinetics, and we calculate from this shifting in control of the transport the kinetic rate constants for $C_{12}E_6$.

5.2 Numerical Solutions for Diffusive-Kinetic Surfactant Transport

Model Formulation

The pendant bubble is assumed to be a sphere of radius R_0 immersed in an infinite surfactant solution with farfield concentration C_b . The surfactant transport during clean interface adsorption and re-equilibration is assumed to be spherically symmetric. The effect of the pendant shape on the transport is negligible. Simulations indicate that, for the typical 1 mm sized bubbles used in pendant bubble experiments, the calculated surface concentration profiles in time for clean interface adsorption in a spherical geometry differs very little (less than about 20 percent for the cases studied) from the profiles computed assuming planar transport^[19]. As may be expected, this difference only arises for sufficiently long times for which gradients in the bulk become of order of the bubble radius. Since the spherical effect is not all that significant, the fact that the actual shape is pendant should not make an appreciable difference.

As mentioned in the Introduction, in order to avoid incorporation of convective effects, we only describe the surfactant transport during the time after the bubble has been created (for clean interface adsorption) or compressed (for re-equilibration). This point in time is referenced as $t=0$. For clean interface adsorption, we assume that at $t=0$, the surface concentration ($\Gamma(t)$) is equal to zero, and the bulk concentration ($C(r,t)$) is uniformly C_b . For re-equilibration following compression, we assume the surface concentration at $t=0$ is $\Gamma(0)$, and the bulk concentration is uniformly C_b . The compressed initial density is obtained from the measured surface tension immediately after the compression, and the surfactant equation of state relating the tension to the surface concentration. We therefore do not describe the surfactant transport in the short time period during which the bubble is created, and surfactant adsorbs to the growing surface,

or compressed and surfactant desorbs off of the surface. For clean interface adsorption we assume that during this time, the rapid area expansion dilutes the effect of adsorption, and we therefore expect that at the point at which the bubble becomes stationary, the interface is nearly clean. Our surface tension relaxation measurements at $t=0$, as given in Section 5.3, are indeed very close to the value for a clean surface, supporting this approach. For re-equilibration, we assume that a negligible amount of surfactant desorbs off of the surface during the rapid compression. In Chapter 3, we verified that the amount on the surface after the compression is within a few percent of the equilibrium amount on the surface before the bubble volume was reduced.

We apply the molecular interaction model developed in Chapter 4 for the surfactant $C_{12}E_6$. In the molecular interaction model, the adsorption isotherm is of the form:

$$C_b = a \exp \left(2b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp \left(\frac{b_3}{\sqrt{\Gamma}} \right) - \frac{2b_2}{b_3} \exp \left(\frac{b_3}{\sqrt{\Gamma}} \right) \right) \Gamma \quad (5-5)$$

where a is the equilibrium adsorption constant, b_1 is a constant which characterizes the van der Waals force, b_2 is a constant which is determined by both the hydration force and maximum surface concentration, and b_3 is a constant which characterizes the hydration force decay length. The equation of state for this equilibrium adsorption is:

$$\gamma = \gamma_c - \left(1 + b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp \left(\frac{b_3}{\sqrt{\Gamma}} \right) \right) \Gamma RT \quad (5-6)$$

where γ_c is the tension of the clean surface. And the kinetic rate equation is:

$$\frac{d\Gamma}{dt} = \beta_0 \exp \left(-b_1\Gamma - \frac{b_2}{\sqrt{\Gamma}} \exp \left(\frac{b_3}{\sqrt{\Gamma}} \right) \right) C_s - \alpha_0 \exp \left(b_1\Gamma - \frac{2b_2}{b_3} \exp \left(\frac{b_3}{\sqrt{\Gamma}} \right) \right) \Gamma$$

(5-7)

Nondimensionalizing the surface concentration by the equilibrium surface concentration at C.M.C. Γ_{CMC} ($\theta = \Gamma / \Gamma_{CMC}$), the sublayer concentration by the concentration scale $a\Gamma_{CMC}$ ($C_s^* = C_s / a\Gamma_{CMC}$), and time by the scale for bulk diffusion $1/Da^2$ ($\tau = tDa^2$) the nondimensional form of the kinetic equation is:

$$\frac{d\theta}{d\tau} = k_a \left(\frac{C_s^* \exp\left(-b_1\Gamma_{CMC}\theta - \frac{b_2}{\sqrt{\Gamma_{CMC}\theta}} \exp\left(\frac{b_3}{\sqrt{\Gamma_{CMC}\theta}}\right)\right)}{-\theta \exp\left(b_1\Gamma_{CMC}\theta - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma_{CMC}\theta}}\right)\right)} \right) \quad (5-8)$$

where k_a is the ratio of the bulk diffusion timescale ($1/Da^2$) to the kinetic scale for desorption α_0^{-1} : $k_a = \alpha_0 / Da^2 = \beta_0 / (Da)$. Note that the diffusion timescale selected to nondimensionalize time is independent of the bulk concentration; we make this choice in order that the same nondimensional time for simulations at different bulk concentrations represents the same dimensional point in time, and the relaxations can easily be compared to one another.

In order to solve equation (5-8), the sublayer concentration must be known. This concentration is obtained by solving for the unsteady diffusive transport in the bulk. A general integral solution to the unsteady diffusion equation for spherically symmetric diffusion to a sphere subject to the two boundary conditions that the bulk concentration far from the sphere is equal to C_b , and that the diffusive flux equals the rate of accumulation of surfactant at the bubble surface, and the two initial conditions that the bulk concentration is initially uniform, and the surface concentration is initially $\Gamma(0)$ is:

$$\begin{aligned} \theta(\tau) - \theta(0) = & 2 \frac{C_b}{a\Gamma_{CMC}} \left(\frac{\tau}{\pi} \right)^{1/2} - 2 \left(\frac{1}{\pi} \right)^{1/2} \int_0^\tau C_s^*(\tau - \tau') d\sqrt{\tau'} \\ & - \frac{1}{aR_0} \left(\frac{C_b}{a\Gamma_{CMC}} \tau - \int_0^\tau C_s^*(\tau - \tau') d\tau' \right) \end{aligned} \quad (5-9)$$

where aR_0 is the ratio of the bubble radius to the characteristic adsorption depth ($1/a$, the depth underneath the surface of a solution with concentration $a\Gamma_{CMC}$ that has the same amount of surfactant per unit area as the C.M.C. surface concentration Γ_{CMC}). The part of equation (5-9) in brackets multiplying this term accounts for the effect of the spherical interface on the transport; the bracketed term is zero for planar transport.

Numerical solutions of equation (5-9) and (5-8) have been obtained in several studies by discretizing the convolution integral[22,23,24,25,26,27]. Here we use an alternate approach in which the Laplace transformation of equation (5-9) is used to express the sublayer concentration as a convolution integral of the change in the surface concentration with time:

$$\begin{aligned} C_s^*(\tau) = & \frac{C_b}{a\Gamma_{CMC}} - \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\tau}} \frac{d\theta}{d\tau'} d\sqrt{\tau - \tau'} \\ & + \frac{1}{aR_0} \int_0^\tau \frac{d\theta}{d\tau'} \exp\left(-\frac{\tau - \tau'}{b^2}\right) \text{erfc}\left(\frac{1}{b}\sqrt{\tau - \tau'}\right) d\tau' \end{aligned} \quad (5-10)$$

where $\text{erfc}(x)$ denotes the complimentary error function. Note that the last term in equation (5-10) describes the effect of the spherical geometry, and tends to zero when the bubble radius becomes infinite ($R_0 \rightarrow \infty$). We use the following procedure to obtain numerical solutions of equation (5-8) and (5-10). For clean interface adsorption, for short surface ages ($t \rightarrow 0$), the surface coverage is small ($\theta \ll 1$), the kinetics is linear ($\frac{d\theta}{dt} = k_a(C_s^* - \theta)$), and an analytical solution of equations (5-8) and (5-9) can be

developed. For re-equilibration, equation (5-8) can be linearized around the initial conditions, and an analytical solution valid for short times can once again be developed. We choose a small time step $\Delta\tau$, and use the short time analytical solutions to compute the adsorption at the first few (n-1) time steps $\theta(t_i)$ ($\tau_i = i \Delta\tau$). For the next (nth) step, we use the following iterative method: (i) Use the n-2 and n-1 values for C_s^* and θ solutions to obtain an extrapolated value for $C_s^*(\tau_n)$ and $\theta(\tau_n)$; (ii) Use equation (5-8) to compute $\frac{d\theta}{d\tau}|_n$, the derivative at step n, from the values for $C_s^*(\tau_n)$ and $\theta(\tau_n)$ obtained in (i). From the value of the derivative at step n, obtain a corrected estimate of $\theta(\tau_n)$; (iii) Use equation (5-10) to obtain a corrected value for $C_s^*(\tau_n)$ by integrating the convolution integral using the trapezoid rule; (iv) Compare the corrected values with the extrapolated estimate of (i); repeat steps (ii) and (iii) to generate further corrected values and repeat until a prescribed tolerance is obtained between two iterations; (v) Compute the surface tension at time τ_n from equation (5-6). We define a nondimensional surface tension g by the relation:

$$\gamma^* = \frac{\gamma(\tau) - \gamma_e}{\gamma_c - \gamma_e} \quad (5-11)$$

where γ_e is the equilibrium tension for the equilibrium coverage Γ_0 as given by equation (5-5) and (5-6) for the bulk concentration C_b . The value of aR_0 for all simulations is equal to 0.03; this is the value that will correspond to our experimental conditions in Section 5.3. We choose the diffusion coefficient $D=5.7 \times 10^{-10}$ m²/s in all the simulations. In addition all simulations are for $b_1=-1.218 \times 10^6$ m²/mol, $b_2=0.1887$ mol^{1/2}/m, $b_3=-4.500 \times 10^{-3}$ mol^{1/2}/m, $a=26.67$ m⁻¹ and $\Gamma_{CMC}=3.0 \times 10^{-6}$ mol/m²; these are the values fitted for C₁₂E₆ from the equilibrium surface tension measurements and surface tension/surface concentration data.

Numerical Results

We first present the results for clean interface adsorption. In this case, we replace Γ_∞ by Γ_{CMC} , and $\beta\Gamma_{CMC}$ by β_0 , then $\Phi^2 = \left(\frac{\Gamma_{CMC}\beta_0}{C_b D} \right) = \frac{k_a}{\frac{C_b}{a\Gamma_{CMC}}}$, which is also the

ratio of the diffusional timescale to the kinetic time scale. We plot in Figure 5-1 - Figure 5-3 the nondimensional dynamic tension γ^* as a function of the nondimensional time τ . In each figure, the value of $C_b/a\Gamma_{CMC}$ is held fixed, and relaxations are given for the same three values of k_a , 92.09, 920.9 and 9209, and for diffusion limited exchange ($k_a \rightarrow \infty$). Three values of $C_b/a\Gamma_{CMC}$ are used: 9.209 (Figure 5-1), 92.09 (Figure 5-2) and 920.9 (Figure 5-3). These figures therefore correspond to a one hundred fold increase in the bulk concentration. Since k_a and t are independent of C_b , the relaxations for the same k_a presented in Figure 5-1 to 5-3 may be interpreted physically as relaxations for increasing bulk concentration and fixed kinetic parameters. We note that the range of $C_b/a\Gamma_{CMC}$ selected ($9.209 < C_b/a\Gamma_{CMC} < 920.9$) brackets the concentration range used in our clean interface adsorption experiments to be described in Section 4.3. The values of k_a used are chosen so that the parameter Φ^2 which represents the relative importance of kinetics to bulk diffusion has values in powers of ten in the range $10^{-1} - 10^3$.

Consider first the diffusion limited curves on each of these figures; these profiles show that as the bulk concentration increases, the diffusion limited relaxation becomes more rapid. The reason for this behavior is that when kinetics is very rapid, the sublayer concentration rapidly drops to zero after the clean surface is created, and the driving force for the bulk diffusion is simply proportional to the bulk concentration. The larger this concentration, the faster is the transport of surfactant from the bulk and the more rapid is the tension relaxation.

Consider next the relaxations for finite kinetics. If we focus on any one of the

three figures, changes in k_a for fixed $C_b/a\Gamma_{CMC}$ may be interpreted physically as an increase in the kinetic constants α_0 and β_0 , with their ratio a held fixed (so that the time scale does not change). As the kinetic parameters increase, the kinetic exchange accelerates, and the surface tension relaxations approach the diffusion limited curve. The key feature of Figure 5-1 to Figure 5-3 is how the relaxation profiles for a fixed k_a , relative to the diffusion limited profile, changes with increasing concentration. Clearly as $C_b/a\Gamma_{CMC}$ increases, the finite kinetic curve for a fixed k_a moves away from the diffusion limited curve, verifying the fact that, as the bulk concentration increases, kinetic effects control a larger part of the relaxation. We also note that the parameter Φ^2 describes very well the shifting of the finite kinetic relaxation curves away from the diffusion limited curves. For the same value of Φ^2 , the finite kinetic relaxations are shifted in the same proportion from the diffusion limited curves, irrespective of the individual values of $C_b/a\Gamma_{CMC}$ and k_a . A reasonable separation begins for Φ^2 smaller than 100.

Another important point can be obtained by combining Figure 5-1 to 5-3 with Figure 5-4. From Figure 5-1 we see the relaxation for finite kinetics is practically the same as the relaxation for diffusion control when $\Phi^2 = 1000$. If $\Phi^2 > 1000$, then k_a is even bigger for a fixed $C_b/a\Gamma_{CMC}$. Hence the relaxation for finite kinetics will be closer to the relaxation of the diffusion control. From Figure 5-4, we see the relaxation for mixed diffusive-kinetic control is practically the same as the relaxation for the kinetic control when $\Phi^2 = 0.1$. If $\Phi^2 < 0.1$, then k_a is even smaller for a fixed $C_b/a\Gamma_{CMC}$. Hence the relaxation for mixed control will be closer to the relaxation of the kinetic control. Therefore, Φ^2 is a criterion for distinguishing surfactant dynamic mechanisms in clean interface adsorption. If $\left(\frac{\Gamma_{CMC}\beta_0}{C_b D}\right) > 1000$, the adsorption mechanism is diffusion controlled, if $\left(\frac{\Gamma_{CMC}\beta_0}{C_b D}\right) < 0.1$ the adsorption is kinetically controlled and if $0.1 < \left(\frac{\Gamma_{CMC}\beta_0}{C_b D}\right) < 1000$, the adsorption is mixed diffusive-kinetic control.

We next discuss re-equilibration results. In the series of Figure 5-5 to 5-7, we fix the bulk concentration ($C_b/a\Gamma_{CMC}=9.209$), and the kinetic exchange ($k_a=9209.$), and we increase the initial surface compression: $\theta^i = 0.6$ (Figure 5-5), 0.8 (Figure 5-6) and 0.98 (Figure 5-7). In each of the figures we plot alongside the finite kinetic curves, the diffusion limited profiles. We note first from this set of figures that as the surface concentration after the compression increases, the diffusion limited tension relaxations accelerate. This behavior follows from the fact that when kinetic exchange is infinitely fast, the sublayer and the surface are in quasi-equilibrium. Thus the initial sublayer concentration immediately after the compression is the value in equilibrium with the surface concentration θ^i , as given by equation (5-5). The larger θ^i , the greater the sublayer concentration. As this initial sublayer concentration is the driving force for bulk diffusion away from the surface, the greater θ^i and therefore the initial sublayer concentration, the more rapid the surface tension re-equilibrates. If we compare the finite kinetic curves in each of the figures, we see that for the same value of the kinetic constant ($k_a = 9209.$), as the initial surface compression increases, the tension relaxations shift away from the diffusion limited curves. The parameter Φ^2 appropriately scales the increasing importance of kinetics as θ^i increases; $\Phi^2 = 160$ for Figure 5-5, 40 for Figure 5-6 and 0.40 for Figure 5-7. As Φ^2 decreases, the finite kinetic curves shift away from the diffusion limited relaxations. The results of Figure 5-5 to 5-7 verify that as the surface compression increases, kinetic effects exert a greater influence on the re-equilibration in surface tension following the area perturbation.

5.3 Clean Interface Adsorption and Re-equilibration Experiments

Materials and Methods

The surfactant $C_{12}E_6$, obtained from Nikko Chemical Company, Ltd. (Japan), is stored in the dark under nitrogen, and is used without further modification. Aqueous solutions are prepared freshly for each experiment using clean water from a Milli-Q water purification system. Equilibrium surface tension measurements as a function of bulk concentration are made using a Wilhelmy plate apparatus (Kruss K12 tensiometer) with a sandblasted platinum plate, and by the pendant bubble method as described below. For the Wilhelmy plate measurements, the surfactant solutions are thermostatted at 23 ± 0.5 °C in a 150 cm³ glass dish having a cross sectional area of 35 cm². Surface tensions are recorded in interval of 10-30 min, depending on concentration. Equilibrium is assumed to be achieved when there is no significant change in surface tension in the last five measurements; at the very low concentrations the equilibration lasted 24 hrs. The surface tension of pure water we obtained using this Wilhelmy plate technique is 72.9 mN/m.

Our measurement of equilibrium and dynamic tensions by the static pendant bubble method uses the arrangement given in Figure 5-8 and follows that of Lin et al.^[19]. White light is generated from a tungsten bulb, and its intensity is reduced by over 50% by passage through a gray filter and a pin hole. Only light which is focused by the first plano-convex lens passes through the second pin hole. The second plano-convex lens recollimates the light before an optically transparent quartz cell (2.5x4x4 cm) containing the surfactant solutions. The cell is mounted in a chamber such that three of the six sides are thermostatted (23 ± 0.5 °C). The two optical faces are not thermostatted because they must be both optically unimpeded and perpendicular to the parallel light. The remaining face is open to atmosphere. A bubble is formed at the tip of a 1/16 inch Teflon tube which is mounted in an inverted, stainless steel, hollow, 20 gauge capillary placed in the surfactant solution by pushing air through the capillary using a syringe pump. A valve placed between the pump and the capillary is closed to stop the bubble growth; typically the bubble is allowed to grow to a diameter of 2 or 3 mm, and the valve is closed. To form a bubble

requires only less than one second. For re-equilibration, a pendant bubble is created and an equilibrium monolayer is allowed to form on the bubble interface. The connection between the syringe pump and the valve is removed so that one port of the valve is exposed to atmosphere. The valve is opened after the equilibrium monolayer is formed, and this causes the bubble volume to shrink because the pressure in the bubble is larger than atmospheric. The valve is then closed, and the jump change in the pendant bubble interfacial area is complete. The jump is usually completed in a few tenths of a second. Area compression ratios (final area to initial area) used are between 0.5 and 0.8.

Parallel light passing over the bubble creates a silhouette of the pendant bubble which is imaged onto a CCD array video camera (Sony XC-77) using an objective lens. The video image is digitized directly by a Scion LG-3 frame capture board operating in a Macintosh II-FX. Image capture is accomplished using Image 1.54 software (N.I.H.) saving as many as 30 images per second (the video rate) to the system RAM of the computer. A timer (FOR.A, Japan), records the time directly on the video frames allowing the captured frames to be accurately sequenced in time. Location of the bubble profile coordinates is accomplished by using Image Analyst software (8.0, Automatix). Distances on the video image are calibrated using a tungsten sphere of precisely known diameter (1.5876 mm). Laplace equations describing the bubble shape are numerically integrated, and their solutions fitted to the edge profile obtained by image digitization by adjusting the surface tension as in reference.^[19] The surface tension of pure water using this technique is 72.3 mN/m. For bubbles created in surfactant solutions, the dynamic tension is measured until equilibrium is reached.

Using each method, equilibrium surface tensions are measured for concentrations in the range $0.02 - 40 \times 10^{-3} \text{ kg/m}^3$ (the upper limit being the determined CMC). The concentrations at the low end of this range are very low, and depletion of the bulk by

adsorption of surfactant onto the glass/water and air/water interfaces of the Wilhelmy apparatus dish and the quartz cell of the pendant bubble apparatus becomes a concern. Adsorption of ethoxylated alcohols at the glass/solution interface is not expected for $C_{12}E_6$ at concentrations much less than the CMC.[28,29,30]. Experiments where a given solution is repeatedly exposed to the glass dish of the Wilhelmy plate apparatus, the surface tension measured using the Wilhelmy plate, the solution removed and replaced with fresh solution indicated no depletion because the surface tension of each cycle remained fixed. Adsorption of surfactant at the air/water interface may also deplete the bulk. To this end, surface tensions of a $0.16 \times 10^{-3} \text{ kg/m}^3$ concentrated solution are measured using the Wilhelmy plate apparatus in a glass vessel filled to different heights such that the volume of solution varied at constant water/air surface area. The results show that surface tension decreases as volume increases, indicating significant adsorption and requiring, for both methods, correcting the bulk concentration for the amount adsorbed on the air/water interfaces.

Results for Equilibrium Surface Tensions as a Function of Bulk Concentration and the Surface Equation of State

The equilibrium surface tension is plotted as a function of prepared bulk concentration in Figure 5-9. The surface tension/surface concentration data are plotted in Figure 5-10. Showing on both figures is a (least squares) fit of the data using the Langmuir, Frumkin and Molecular interaction isotherm. The fitted parameters are, for the Langmuir isotherm, $\Gamma_{\infty} = 2.42 \times 10^{-6} \text{ mol/m}^2$ and $a = 0.0512 \times 10^{-3} \text{ kg/m}^3$; for the Frumkin isotherm, $\Gamma_{\infty} = 3.48 \times 10^{-6} \text{ mol/m}^2$, $a = 0.0157 \times 10^{-3} \text{ kg/m}^3$ and $K = 6.652$; and for Molecular interaction model, $b_1 = -1.2 \times 10^6 \text{ m}^2/\text{mol}$, $b_2 = 0.19 \text{ mol}^{1/2}/\text{m}$, $b_3 = -4.5 \times 10^{-3} \text{ mol}^{1/2}/\text{m}$, $a = 27 \text{ m}^{-1}$. We emphasize that the abscissa in Figure 5-9 is the prepared bulk concentration (C_{app} or C_0), which is corrected by $C_0 = C_b + \frac{A_{\text{air/water}}}{V_{\text{solution}}} \Gamma_0$, where $A_{\text{air/water}}$

and V_{solution} are, respectively, the air/water area and solution volume. For the Langmuir and Frumkin isotherms, the correction is done in the least squares fitting routine with the real bulk concentration to be used for C_b in equation (5-2) given by $C_b = C_0 - \frac{A_{\text{air/water}}}{V_{\text{solution}}} \Gamma_0$.

The equilibrium data is in excellent agreement with that of Lucassen and Giles^[31]. From Figure 5-9 we note the critical micelle concentration is equal to approximately 40×10^{-3} kg/m³, and this is in excellent agreement with values reported elsewhere^[32,33]. Just from Figure 5-9, we see all the three model fits to the equilibrium surface tension are reasonably good. However, from Figure 5-10, we can see the molecular interaction model is the best fit for the data. Therefore, we use the molecular interaction equation of state in our transport modeling.

Dynamic Tension Results and Calculation of Diffusion Coefficient and Kinetic Constants

Figures 5-11 to 5-15 show dynamic surface tension relaxations for adsorption onto clean interfaces at five different bulk concentrations (0.614×10^{-3} , 1.228×10^{-3} , 2.456×10^{-3} , 6.4×10^{-3} and 12.28×10^{-3} kg/m³). The time $t=0$ in these relaxations represents the point in time at which the bubble growth is terminated and the valve is closed. Each symbol on the figures represents a separate experiment. We see the reproducibility of the experiments is very good. In each of these figures, we show alongside the data diffusion limited relaxations (solid line) which have been fitted to the data (*separately for each concentration*) by adjusting the diffusion coefficient. The diffusion coefficients so obtained are not the same (5.2×10^{-10} , 4.5×10^{-10} , 4.0×10^{-10} , 2.8×10^{-10} and 2.2×10^{-10} m²/s for the five concentrations, in order of increasing concentration). We also plot on Figures 5-11 and 5-15 the surface tension relaxation curve with different diffusion coefficients, which shows the fit is sensitive to the diffusion coefficient. At these low bulk concentrations, the

diffusion coefficient should not depend on bulk concentration. Furthermore, the highest concentration is less than one-third the CMC, so we do not expect premicellar aggregate formation and their transport to affect the results. The fact that the calculated D is dependent on concentration, and that the computed diffusion coefficients decreases with concentration (implying the relaxations are slowing down) suggests the influence of kinetic barriers as we might expect from our clean interface adsorption theoretical results of Figures 5-1 to 5-3.

The re-equilibration in tension due to compression of pendant bubbles with established equilibrium monolayers is shown in Figure 5-16 with bulk concentration of $0.18 \times 10^{-3} \text{ kg/m}^3$. The bulk concentration used for re-equilibration is lower than those used for clean interface adsorption. The reason is that the surface concentrations are low at low bulk concentrations, and the monolayers are therefore not overcompressed beyond the C.M.C. surface concentration when the pendant bubble interface is contracted. The time $t=0$ represents the moment when the valve is reclosed, and the jump reduction in area is complete. In Figure 5-16, two different initial compressions (final area A_f divided by initial area A_i) are used, 0.77 and 0.65. With the initial compression ratio of 0.65, Figure 5-16 shows the experimental data of the re-equilibration of two pendant bubbles. The graph shows an excellent reproducibility in the re-equilibration experiments.

For the re-equilibrations in Figure 5-16, we also construct diffusion limited fits, and obtain a diffusion coefficient which best fits each of the two compressions. We find, as with the clean interface adsorption experiments of Figures 5-11 to 5-15, that the best fitting diffusion coefficient changes with the compression at fixed bulk concentration, and that the diffusion coefficient decreases as the initial compression increases ($4.5 \times 10^{-10} \text{ m}^2/\text{s}$ for compression ratio 0.77 and $3.0 \times 10^{-10} \text{ m}^2/\text{s}$ for a compression ratio of 0.65), indicating kinetic effects are slowing down the process. This behavior agrees with the theoretical

simulations for re-equilibration.

We fit simultaneously all five clean interface adsorption relaxations and the five re-equilibration experiments to a single diffusion coefficient D and kinetic parameter β_0 ; the results are shown as the theoretical lines in Figure 5-17 to Figure 5-21 for the clean interface adsorption experiments, and in Figures 5-22 and 5-23 for the re-equilibration relaxations. The fitting procedures are referred to Appendix I. The established value for D is $5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and β_0 is $7.0 \times 10^{-5} \text{ m/section}$. We note that satisfactory agreements at all concentrations and compressions are achieved. With D and β_0 , the Φ^2 for the clean surface adsorptions are 270.0, 135.0, 67.5, 27.0, 13.5 for the five concentrations from the lowest to the highest respectively. From the Φ^2 criterion for clean interface adsorption, all these cases should be mixed diffusive-kinetic control, which is confirmed by the experiments.

5.4 Discussion and Conclusions

In the literature, the adsorption of C_{12}E_6 has been studied by Bendure^[34] using the maximum bubble pressure method and Lucassen and Giles^[31] using an oscillatory, small amplitude perturbation technique. We consider Bendure's investigations first. Bendure interpreted his maximum bubble pressure data according to a diffusion limited model which did not account for convection of surfactant in the liquid sublayer adjoining the expanding bubble interface, or for the area expansion of the surface. Joos and Rillaerts^[35] developed a more complete diffusion limited theory which accounted for these effects, and we therefore use their model to discuss Bendure's data. In Joos and Rillaerts' model, the sublayer concentration C_s is taken to be zero, and diffusion gradients are assumed to penetrate to a depth which is much less than the bubble radius. With these assumptions they show that

$$\Gamma(t) = 2C_0 \sqrt{\frac{3Dt}{7\pi}} \quad (5-12)$$

Because of the zero sublayer concentration and small penetration depth assumptions, equation (5-12) is only valid for short times. The usual application of this equation to maximum bubble pressure dynamic surface tension data is to use the equation of state (equation 5-6) to compute the surface concentration, Γ , and then plot this surface concentration as a function of $t^{1/2}$. For short times, one anticipates (if the process is diffusion controlled) a linear regime, and from the slope of this linear regime the diffusion coefficient can be obtained. Joos and Rillaerts construct $\Gamma-t^{1/2}$ plots from Bendure's data for four concentrations (5.95, 8.5, 23.8 and 34.9 $\times 10^{-3}$ kg/m³, larger than our concentrations but still less than the CMC) and surface ages of 1-100 sec, and for each of these concentrations identify linear regions at early times consisting of a few points in the range of 1-20 section. From the slopes diffusion coefficients equal to 7.2, 8.4, 5.3 and 6.1 $\times 10^{-10}$ m²/s (in increasing concentration) are obtained. Joos and Rillaerts claim that since a linear regime has been identified, the adsorption is diffusion limited for the surface ages and range of concentrations studied. Comparing our results for C₁₂E₆ with those of Bendure we note first that our measured value for the diffusion coefficient (5.7 $\times 10^{-10}$ m²/s) falls in the range of those obtained by Bendure. Since the concentrations are high, according to the ideas advanced in this chapter, kinetic effects should have been discernible in Bendure's data. Kinetic effects may be one reason why the diffusion coefficient varies with concentration; as we have stated earlier, we do not expect a concentration dependence for D in the low range of surfactant concentrations used. More importantly, Joos and Rillaerts' model is probably too incomplete to be used to develop insight into whether kinetic effects are indeed playing a role in the maximum bubble pressure experiments. Since the model includes only diffusion, the sole way to discern a kinetic effect is to conclude that there is no clear evidence for an early time linear regime in the $\Gamma-t^{1/2}$ plots.

Examining the plots of their paper, one sees that for the two highest concentrations the linear regime is not clear, and for the lower concentrations it consists of at best a few points. Our approach of simulating the entire relaxation using a mixed formulation, and of comparing the whole numerical relaxation to the data is a more complete modeling of the process.

Lucassen and Giles' modeling is again diffusion limited, but more complete. These authors develop a relationship for the dependence of the oscillation in the surface tension $[\Delta\gamma e^{i\omega t}]$ on the area oscillation $[(\Delta A/A) e^{i\omega t}]$ where ω is the oscillation frequency. They find:

$$\begin{aligned}
 \Delta\gamma &= \varepsilon \frac{\Delta A}{A} \\
 |\varepsilon| &= \varepsilon_0 (1 + 2\zeta + 2\zeta^2)^{-1/2} \\
 \varepsilon_0 &= -\frac{d\Gamma_0}{d \ln \gamma_0} \\
 \tan \theta &= \frac{\zeta}{1 + \zeta} \\
 \zeta &= \sqrt{\frac{\omega_0}{\omega}} \\
 &= -\frac{dC_0}{d\Gamma_0} \sqrt{\frac{D}{2\omega}}
 \end{aligned} \tag{5-13}$$

where $\varepsilon (\varepsilon_0 e^{i\theta})$ is the complex dilatational modulus. Lucassen and Giles undertake experiments at different frequencies (0.01 - 1.0 radians/sec) and bulk concentrations ($0.5 - 40 \times 10^{-3} \text{ kg/m}^3$) and measure the absolute value of ε and the phase angle. By matching the data to the above model equations, values for the diffusion coefficient can be obtained. They find that D is not very sensitive to the concentration and is in the range of $2.5 - 4.0 \times 10^{-10} \text{ m}^2/\text{s}$, in reasonable agreement with our value. Lucassen and Giles present a sample fit of the data for the absolute value of the dilatational modulus which indicates that

the diffusion limited model agrees well with the data, and therefore they conclude that their experiments do not exhibit a kinetic effect. To reconcile the fact that our experiments exhibited a kinetic effect, consider first that when Lucassen and Giles fit their data, they do not use an equation of state as determined from equilibrium surface tension and other experiments, in order to specify ϵ_0 and the ratio $\frac{dC_0}{d\Gamma_0}$. Instead, they fit, for each concentration, the data for ϵ as a function of the frequency to two parameters, ϵ_0 and ω_0 , and then from the ratio of these parameters is calculated. This two parameter fitting approach may be one reason why the diffusion limited model fits the data so well; if they had attempted a one parameter fit for all concentrations and frequencies using just the diffusion coefficient and specifying ϵ_0 and from the equilibrium data (similar to what we have done) the agreement may not have been as good, and the possibility of kinetic effects could be investigated. The inclusion of kinetic effects in the small amplitude oscillation experiments of Lucassen and Giles is given by van den Tempel et al.[36]; they note that kinetic effects become important as the ratio $C_b \frac{\sqrt{D\omega}}{\alpha_0 \Gamma_\infty}$ must be larger than one. Using our values for the kinetic constant a_0 , it is easy to show that this parameter is larger than one for the frequencies and concentrations used in Lucassen and Giles experiments. Thus based on the results of our study, we do expect kinetic effects to manifest themselves in the small amplitude oscillation experiments.

The key point which has been overlooked in these studies is the surface equation of state. The equation of state that Bendure used in his study was the Langmuir isotherm. From our surface tension/surface concentration data, it is obvious that using the Langmuir model for $C_{12}E_6$ is oversimplified. The other equation of state which has been used is the Frumkin isotherm. The Frumkin model is a better model for $C_{12}E_6$, but it does not describe the surface tension/surface concentration curve very accurately. The inaccurate surface equation of state could be the reason why these studies have concluded a diffusion

limited adsorption for $C_{12}E_6$.

In the Introduction, we pointed out that kinetic constants have only been measured for the short chain *n*-alcohols and bifunctional diols. Bleys and Joos^[6] and Joos and Serrien^[9] tabulate values for β_0 for these surfactants, and they range over three orders of magnitude, from 3×10^{-6} m/s for the shortest chain alcohol (propanol) to 3×10^{-3} m/s for the longest chain diol (1,11 undecanediol). These authors note that the adsorption rate constant appears to increase with hydrocarbon chain length, and they find α_0 to be approximately constant (since a decreases with chain length) and equal to 10^2 s^{-1} . Our measured value for β_0 for $C_{12}E_6$, 7.0×10^{-5} m/s is within the range of values already measured for this parameter for the diols and alcohols. Since $\alpha_0 = a \cdot \beta_0$, we compute α_0 to be equal to $1.87 \times 10^{-3} \text{ s}^{-1}$, which is much smaller than the values for the desorption rate constant calculated for the short chain alcohols or diols. This result follows directly from the fact that the polyethoxylated surfactant is much more surface active than the diols and alcohols, and consequently its value for a is much smaller. These results imply that the more surface active surfactants, which are the more technologically important, may have desorption rate constants much smaller than anticipated from the alcohol and diol results.

In this Chapter, we have introduced two methods for measuring the kinetic rate constants for surfactant exchange which involves using high bulk concentrations to increase the rate of bulk diffusion relative to the kinetic rate for clean interface adsorption, and using increasingly larger initial compressions for re-equilibration, thereby causing the dynamic relaxations to be controlled by both diffusion and kinetics. The technique is ideally suited to strongly surface active materials. The only limitation is the fact that as the concentration is increased, strongly surface active materials will eventually reach their critical micelle concentrations, and surfactant will then be transported by both monomer and micelle. Micelle diffusion introduces an additional parameter, as well as the possibility that

micelle/monomer kinetic exchange can influence the transport.

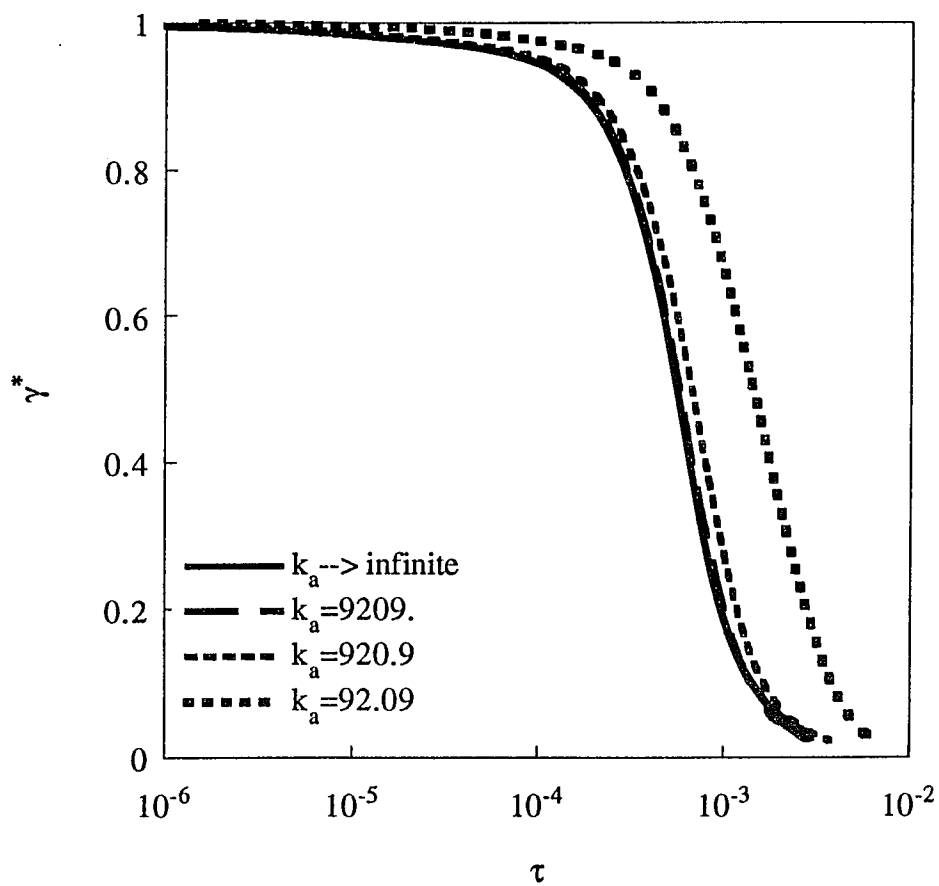


Figure 5-1 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in clean surface adsorption, $C_b/a\Gamma_{CMC} = 9.209$.

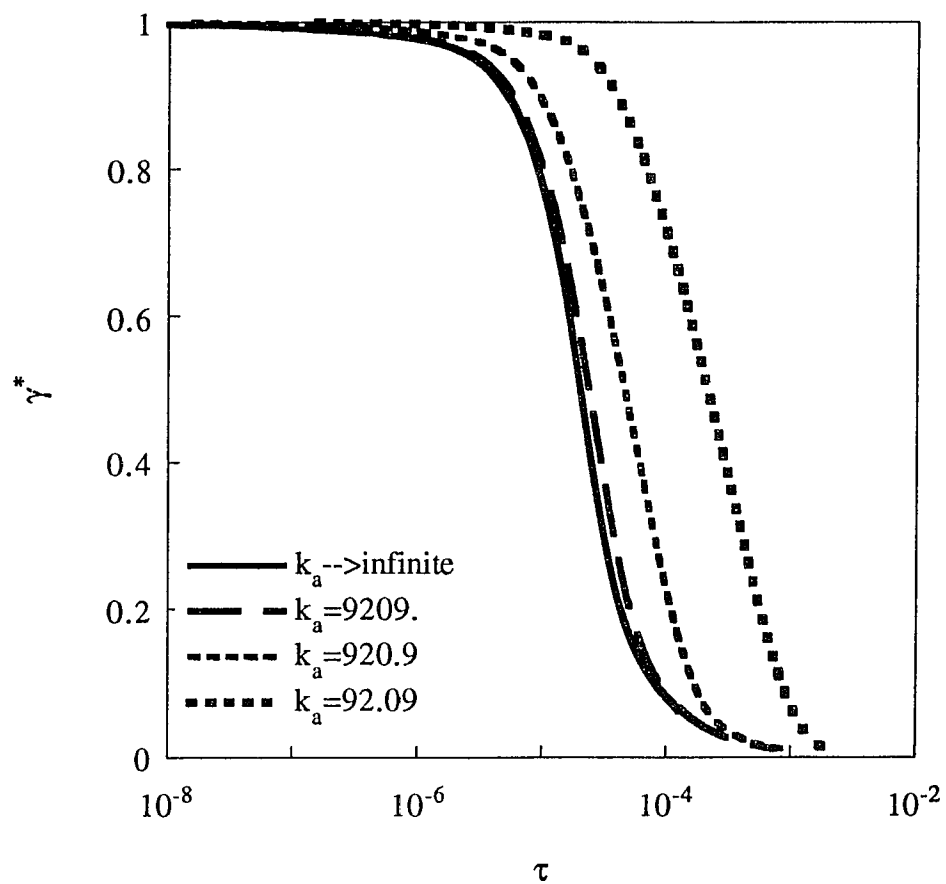


Figure 5-2 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in clean surface adsorption, $C_b/a\Gamma_{CMC} = 92.09$.

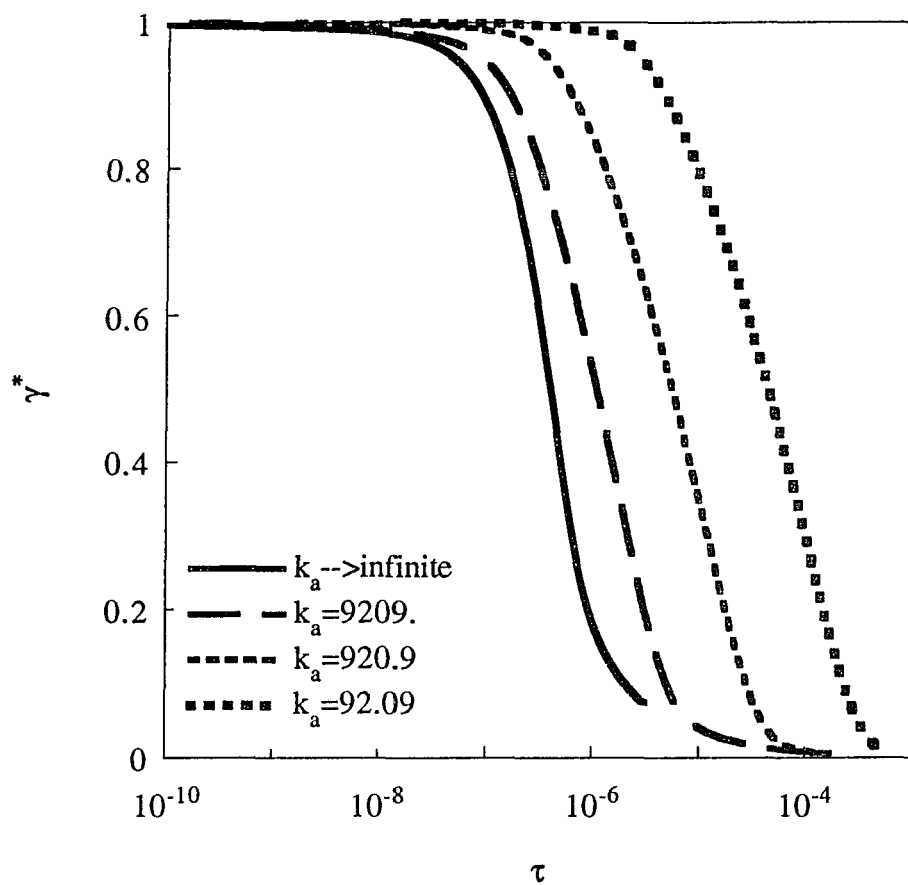


Figure 5-3 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in clean surface adsorption, $C_b/a\Gamma_{CMC}=920.9$.

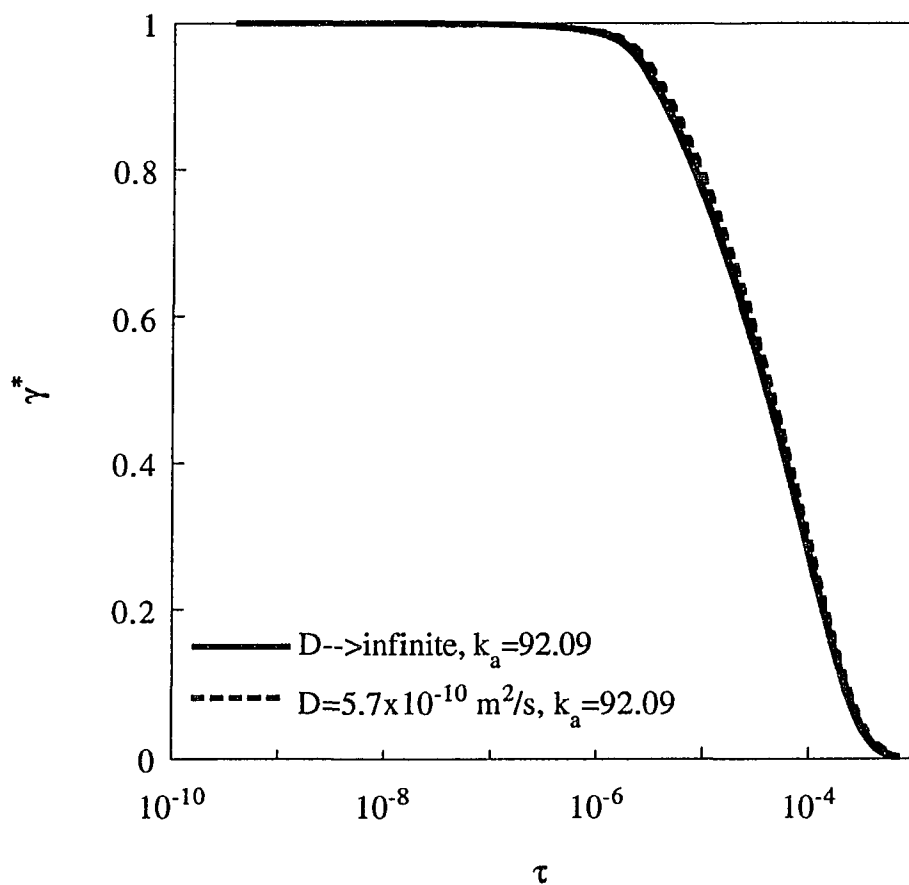


Figure 5-4 The comparison of the kinetic control ($D \rightarrow \infty$) and mixed diffusive kinetic control surface tension relaxations in clean surface adsorption, $C_b/a\Gamma_{CMC} = 920.9$.

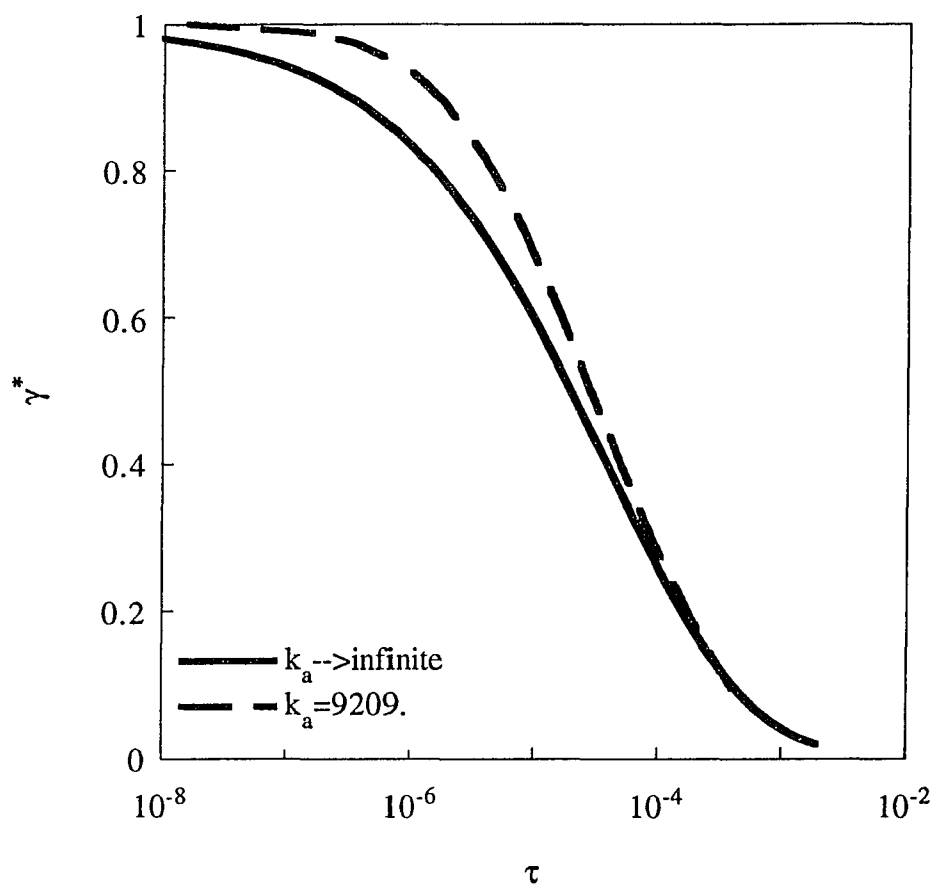


Figure 5-5 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in re-equilibration, $D=5.7 \times 10^{-10}$ m²/s, $C_b/a\Gamma_{CMC}=9.209$, $\theta^i=0.60$.

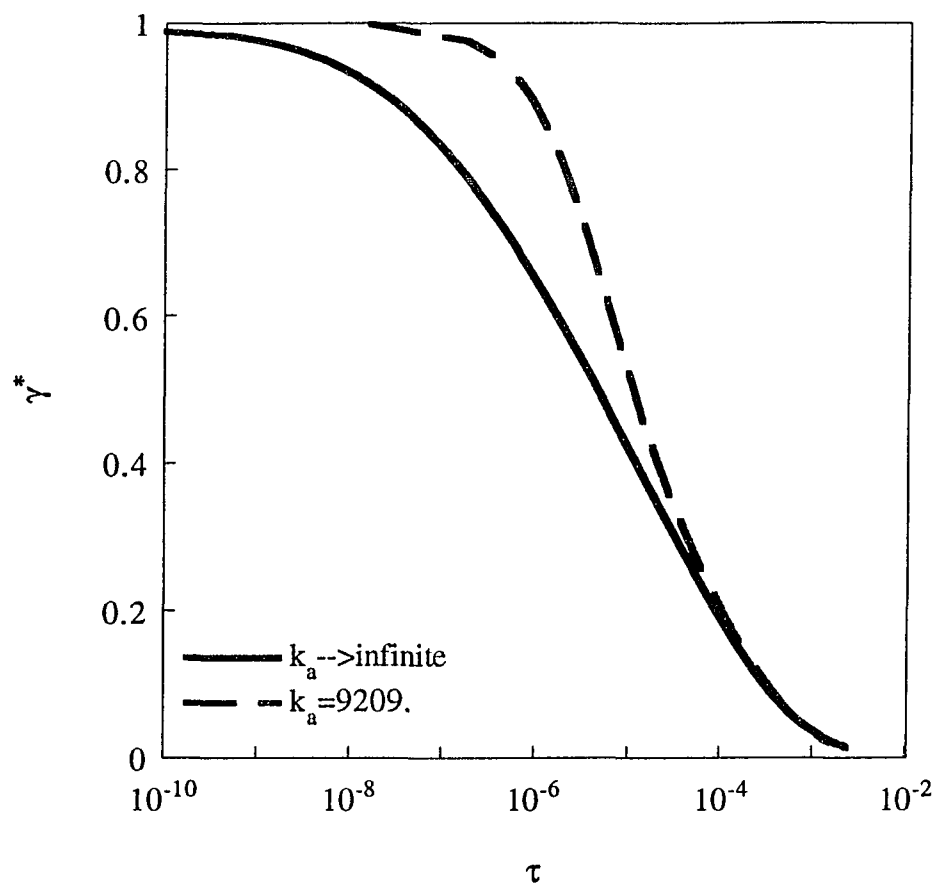


Figure 5-6 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in re-equilibration, $D=5.7 \times 10^{-10}$ m^2/s , $C_b/a\Gamma_{CMC}=9.209$, $\theta^i=0.80$.

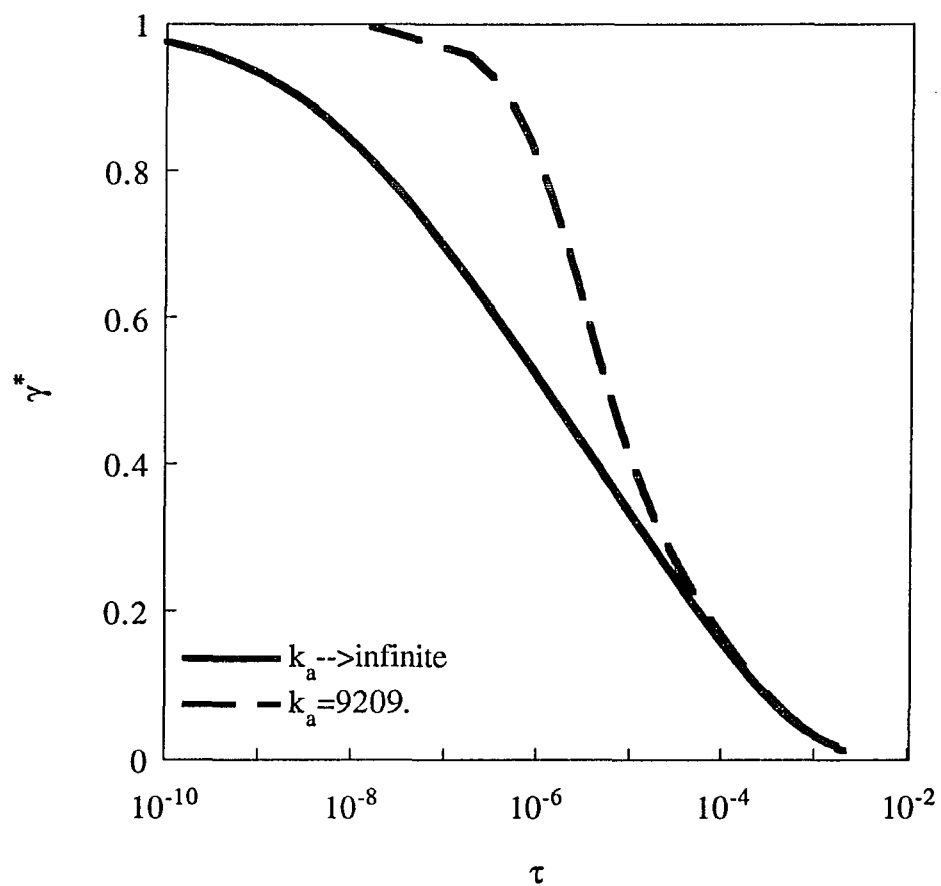


Figure 5-7 The comparison of the diffusive control ($k_a \rightarrow \infty$) and mixed diffusive-kinetic control surface tension relaxations in re-equilibration, $D=5.7 \times 10^{-10}$ m^2/s $C_b/a\Gamma_{CMC}=9.209$, $\theta^i=0.98$.

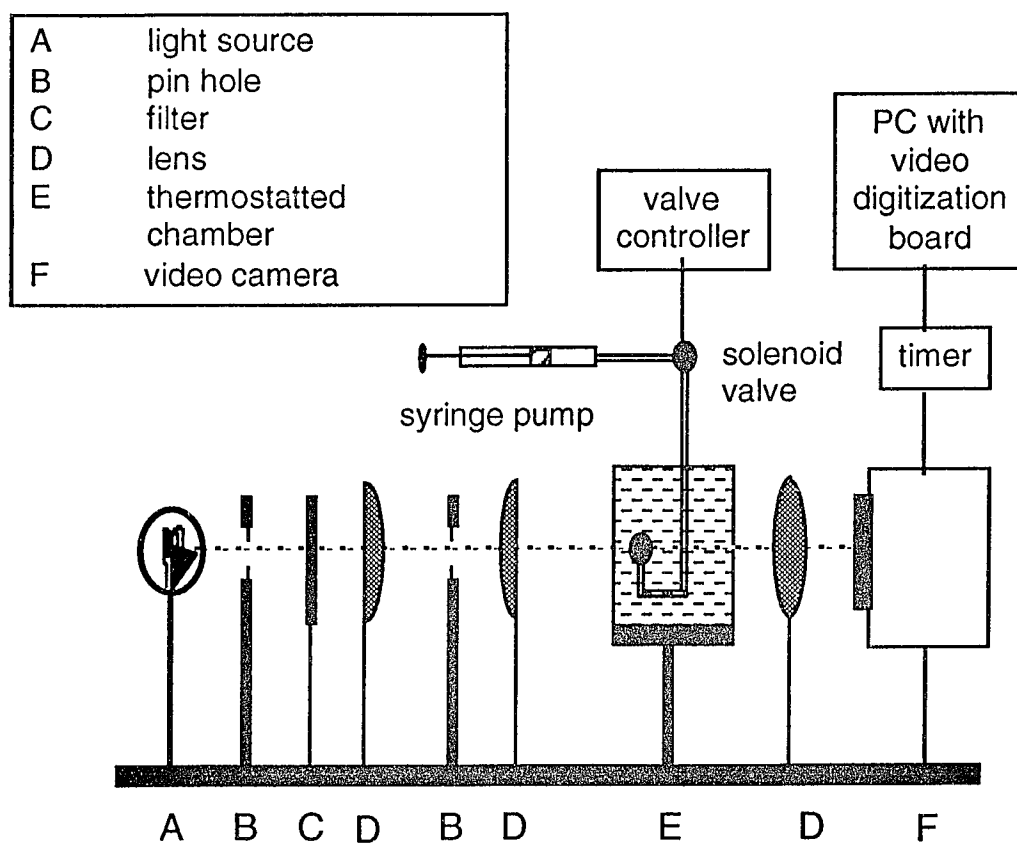


Figure 5-8 The pendant bubble tensiometer apparatus and video-image digitization equipment.

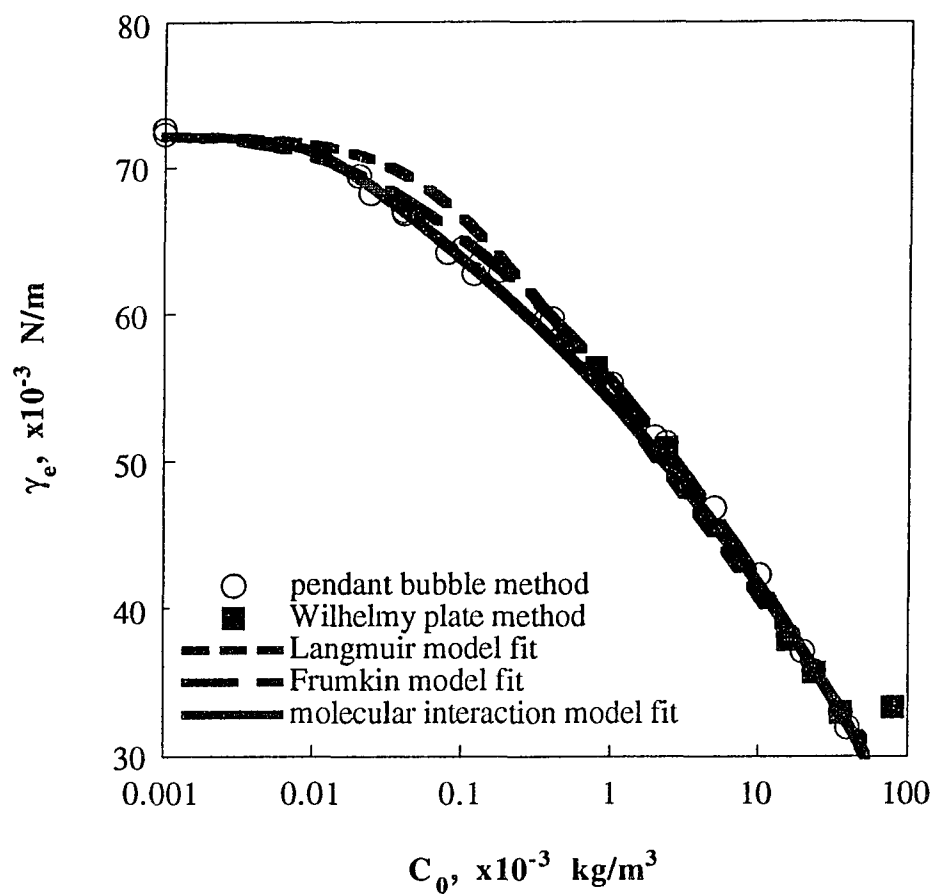


Figure 5-9 The equilibrium surface tensions for air/ C_{12}E_6 aqueous solutions and the Langmuir, Frumkin isotherm and molecular interaction model fitting.

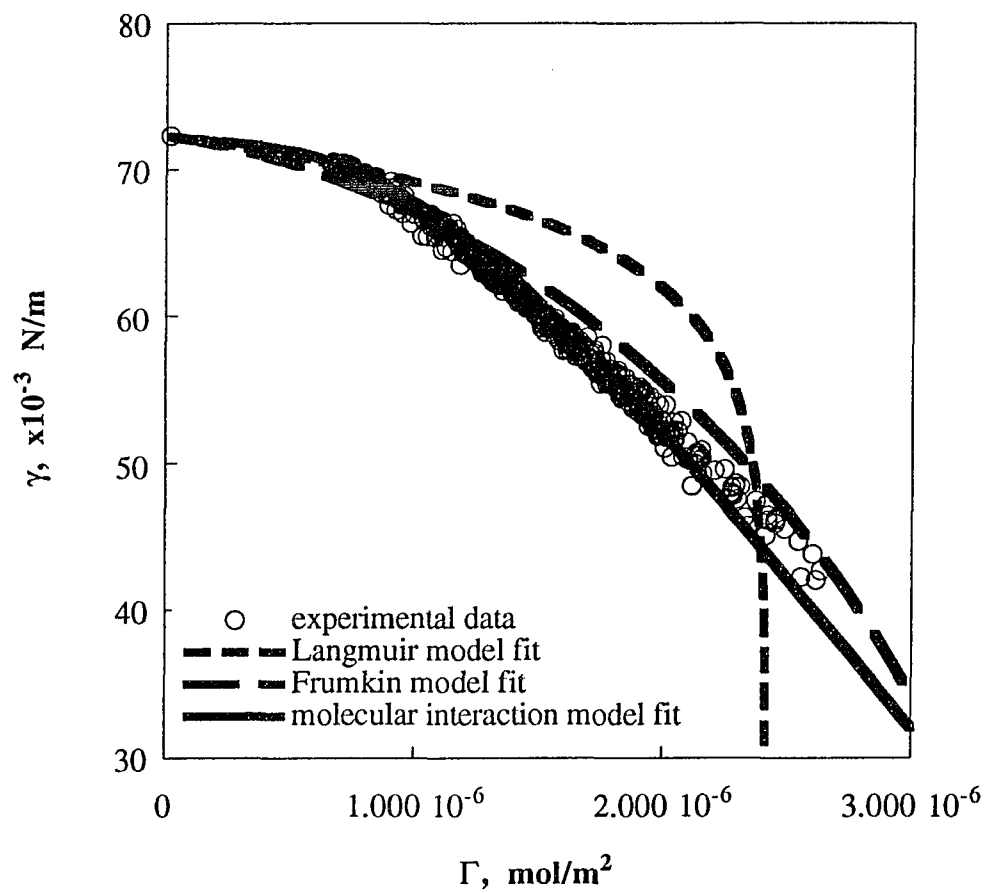


Figure 5-10 The surface tension/surface concentration data for air/ C_{12}E_6 aqueous solutions and the Langmuir, Frumkin and molecular interaction model fitting.

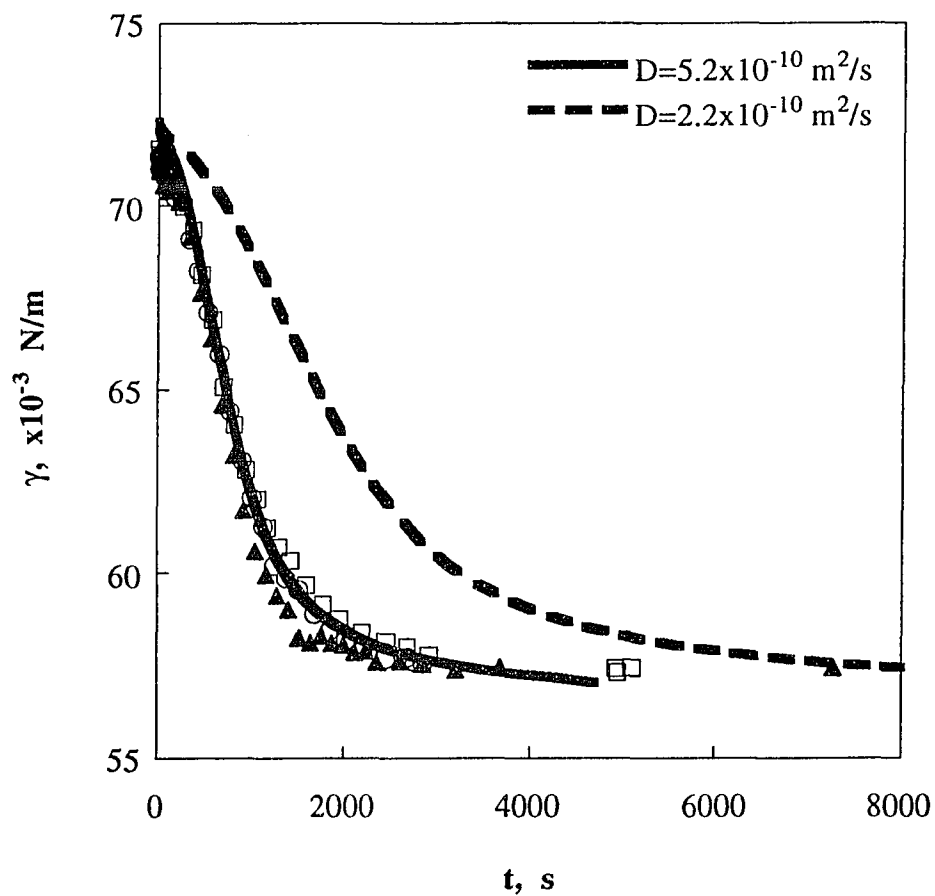


Figure 5-11 Dynamic surface tensions of clean surface adsorption in $0.614 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and purely diffusion controlled theoretical fits with $D=5.2 \times 10^{-10} \text{ m}^2/\text{s}$ and $D=2.2 \times 10^{-10} \text{ m}^2/\text{s}$.

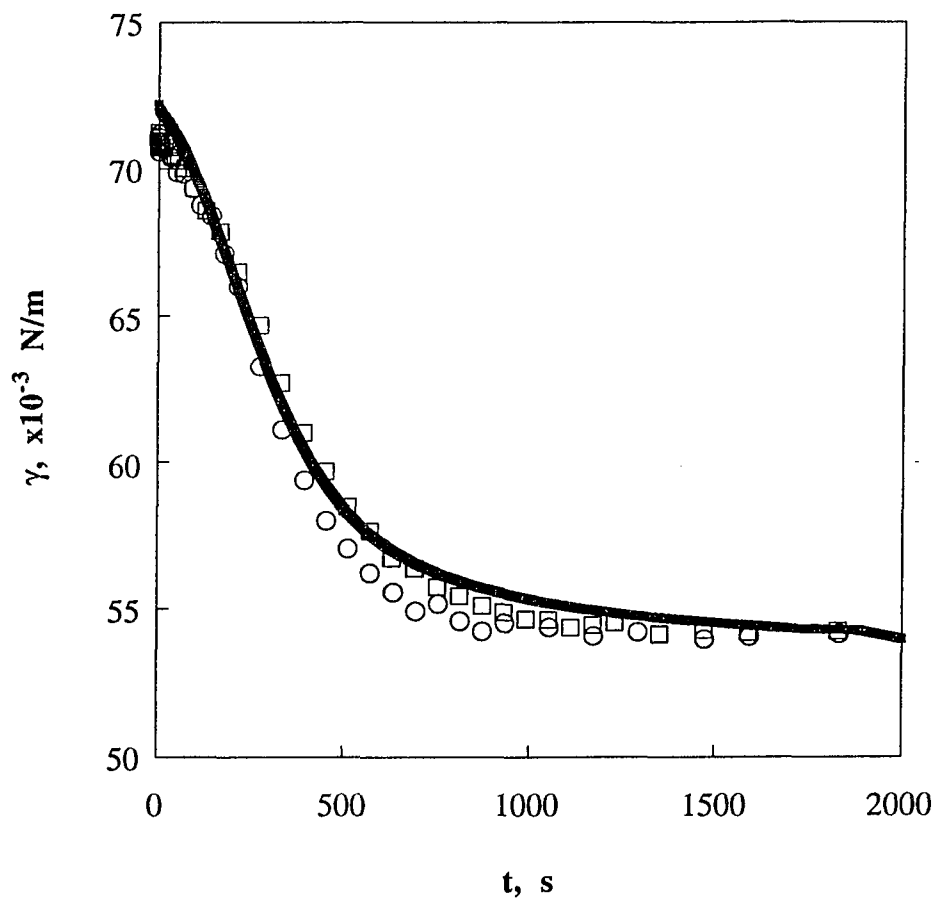


Figure 5-12 Dynamic surface tensions of clean surface adsorption in $1.228 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and purely diffusion controlled theoretical fit with $D=4.5 \times 10^{-10} \text{ m}^2/\text{s}$.

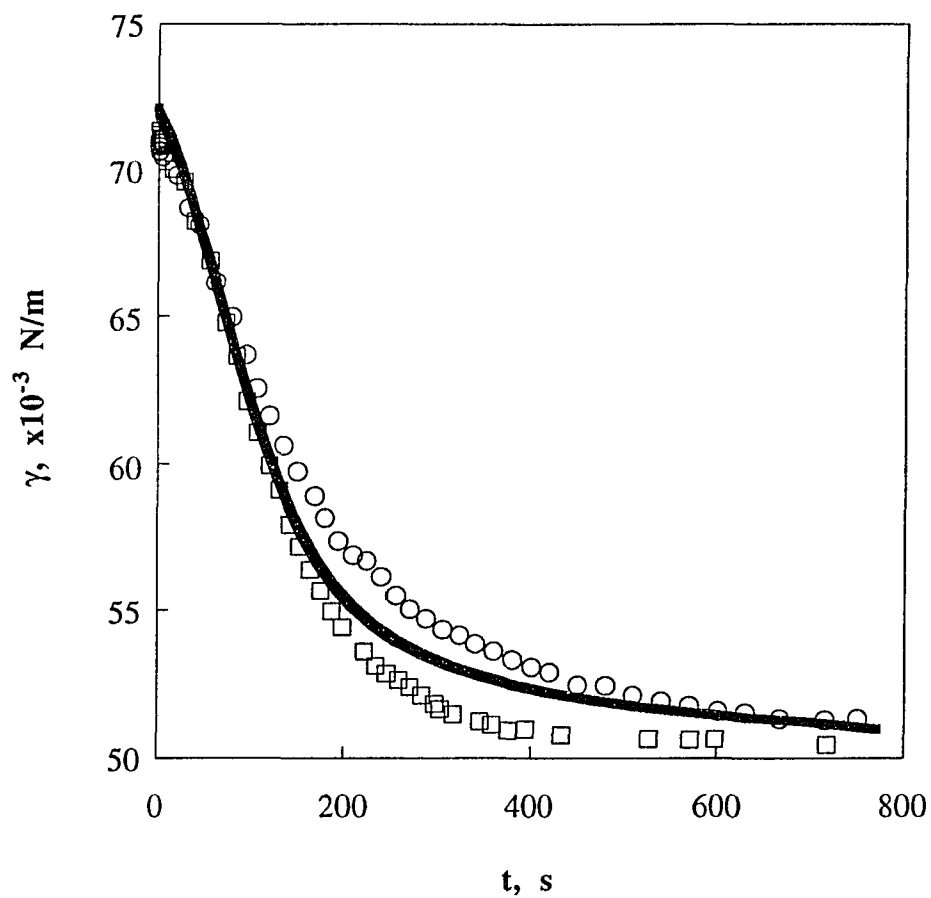


Figure 5-13 Dynamic surface tensions of clean surface adsorption in $2.456 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and purely diffusion controlled theoretical fit with $D=4.0 \times 10^{-10} \text{ m}^2/\text{s}$.

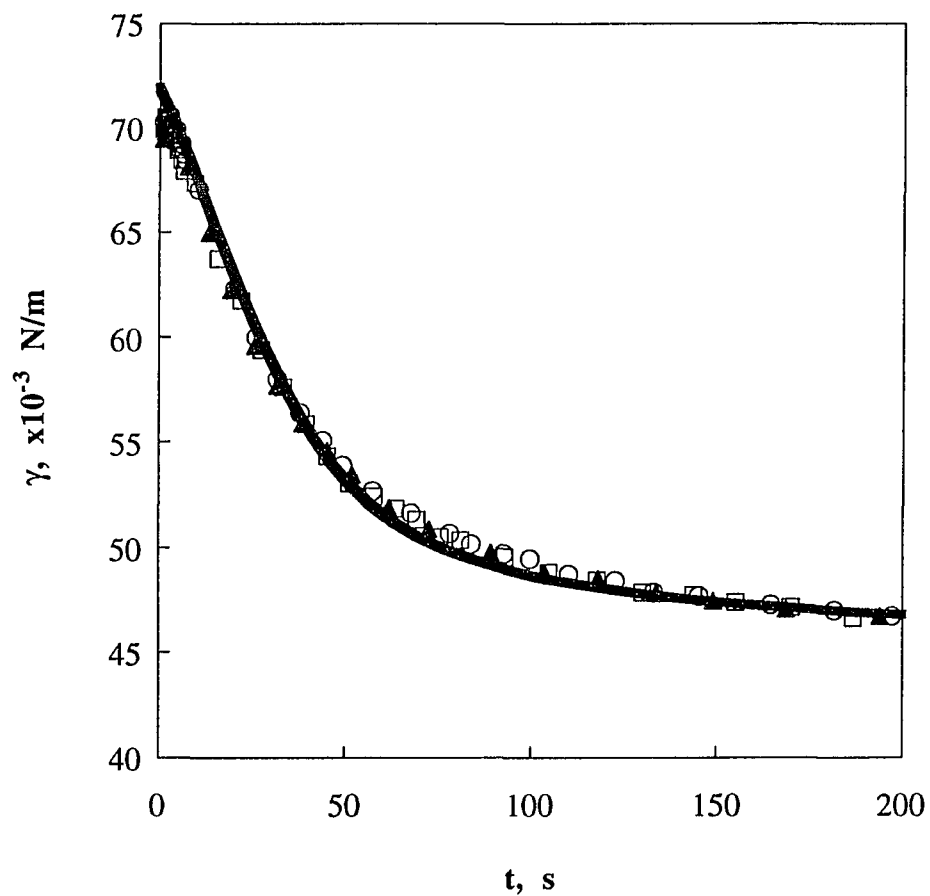


Figure 5-14 Dynamic surface tensions of clean surface adsorption in $6.14 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and purely diffusion controlled theoretical fit with $D=2.8 \times 10^{-10} \text{ m}^2/\text{s}$.

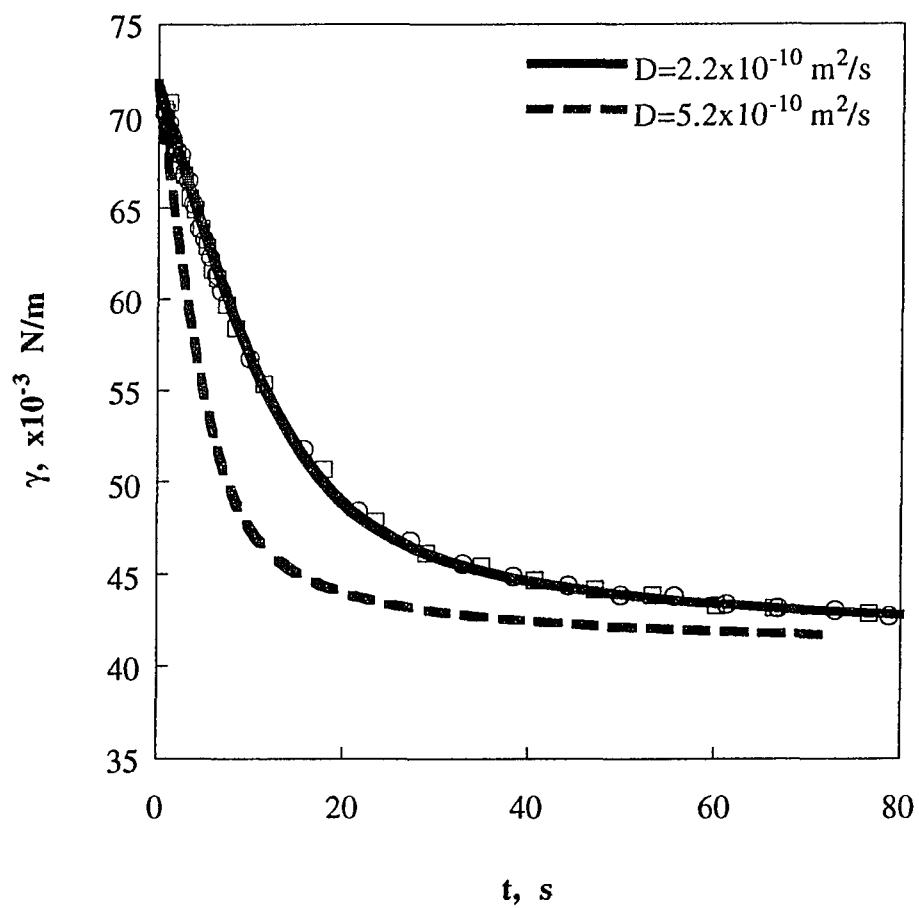


Figure 5-15 Dynamic surface tensions of clean surface adsorption in $12.28 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and purely diffusion controlled theoretical fits with $D = 2.2 \times 10^{-10} \text{ m}^2/\text{s}$ and $D = 5.2 \times 10^{-10} \text{ m}^2/\text{s}$.

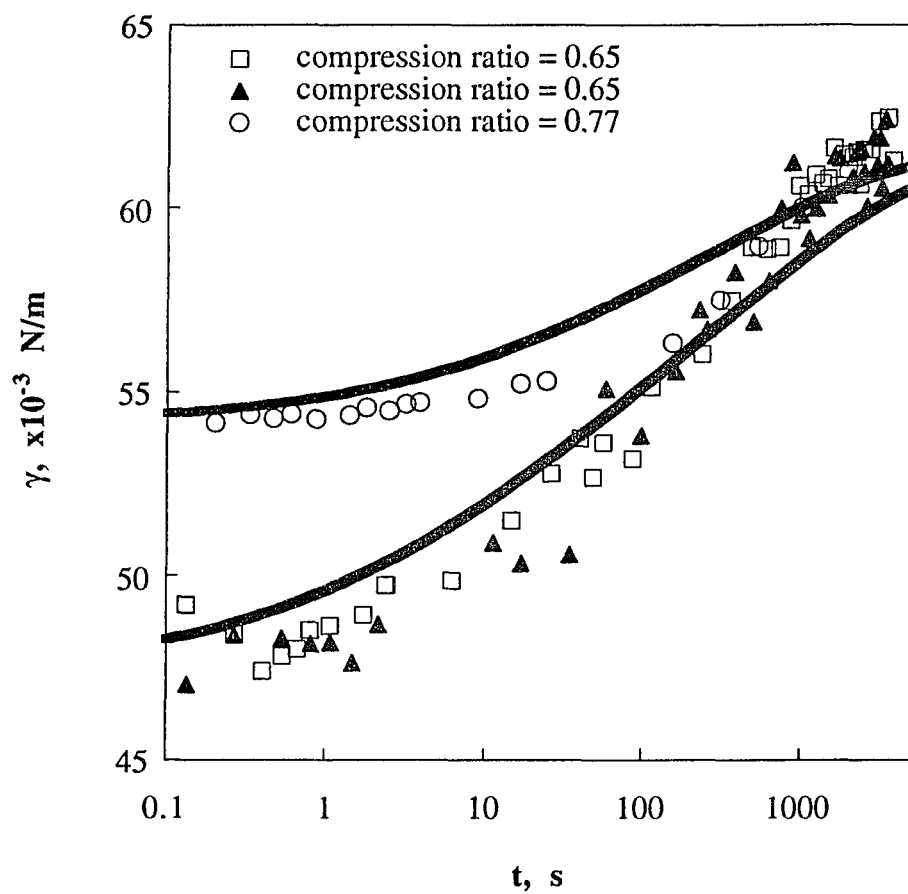


Figure 5-16 Dynamic surface tensions of re-equilibration in $0.18 \times 10^{-3} \text{ kg/m}^3 \text{ C}_{12}\text{E}_6$ aqueous solution and purely diffusion controlled theoretical fit with $D=4.5 \times 10^{-10} \text{ m}^2/\text{s}$ for compression ratio=0.77 and $D=3.0 \times 10^{-10} \text{ m}^2/\text{s}$ for compression ratio=0.65.

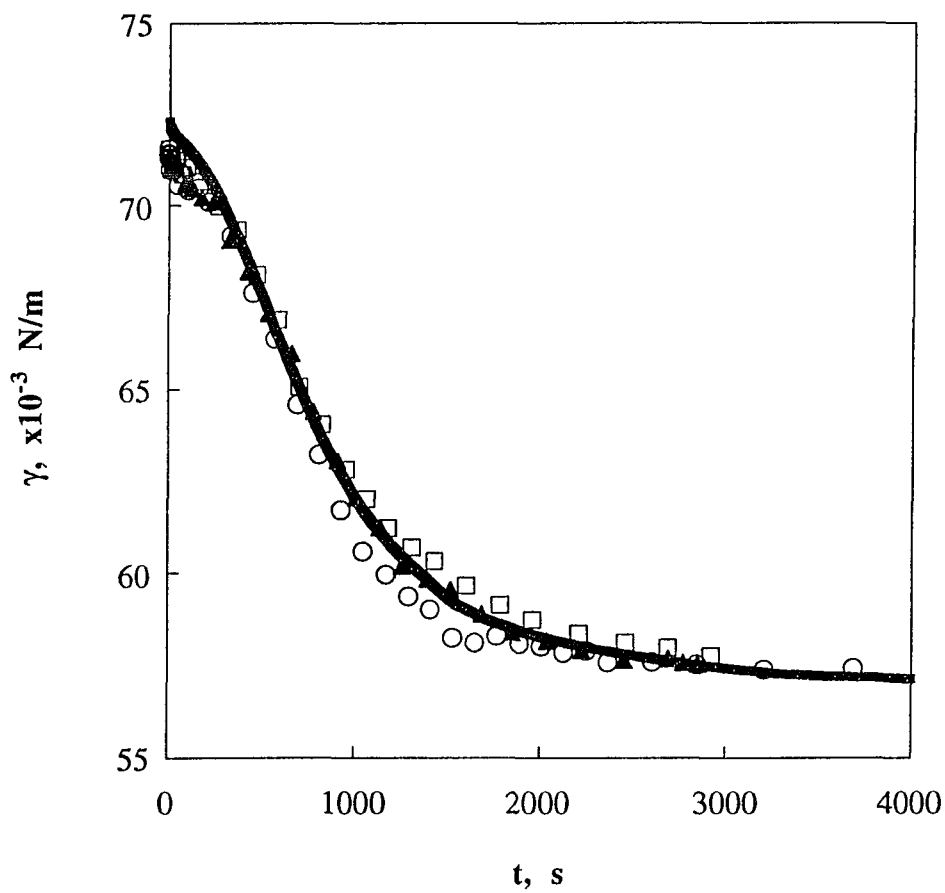


Figure 5-17 Dynamic surface tensions of clean surface adsorption in $0.614 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and mixed diffusive-kinetic control theoretical fit with $D=5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0=7.0 \times 10^{-5} \text{ m/s}$.

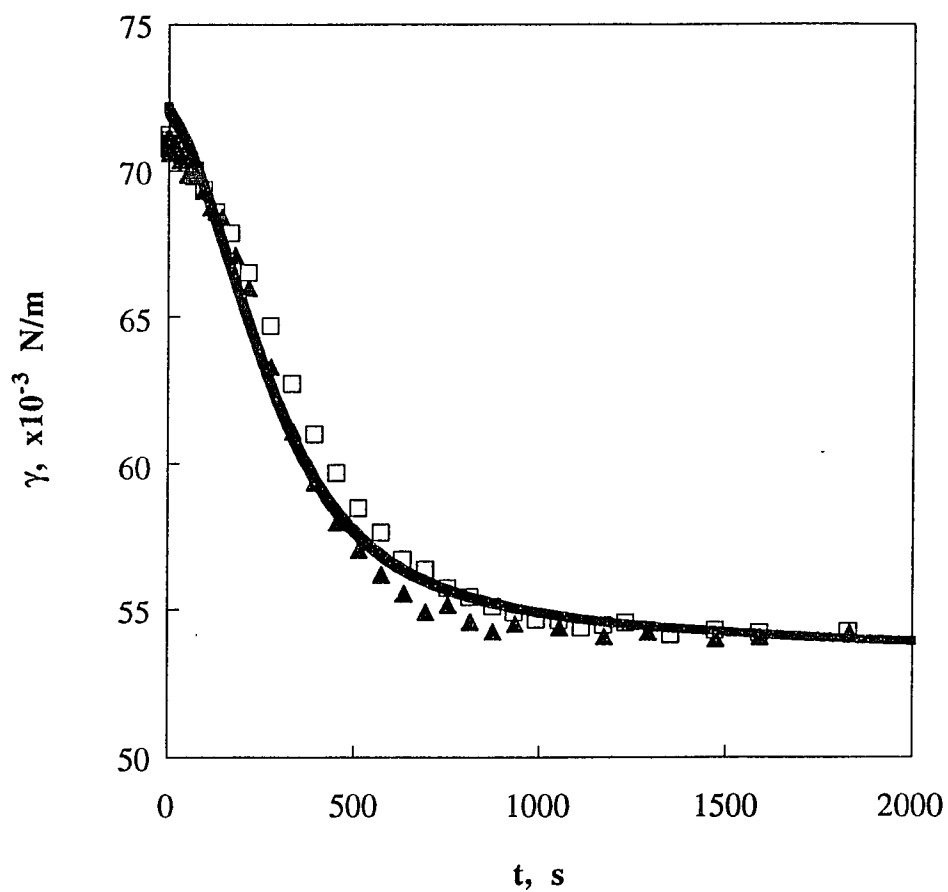


Figure 5-18 Dynamic surface tensions of clean surface adsorption in $1.228 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and mixed diffusive-kinetic control theoretical fit with $D=5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0=7.0 \times 10^{-5} \text{ m/s}$.

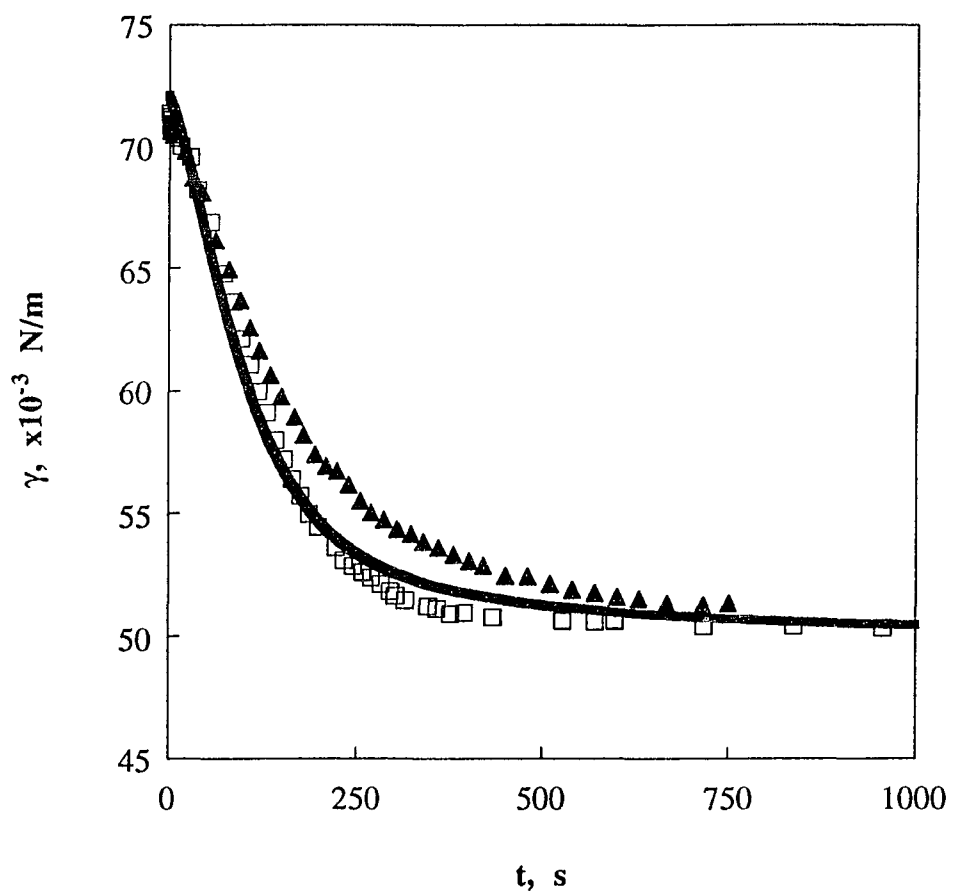


Figure 5-19 Dynamic surface tensions of clean surface adsorption in $2.456 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and mixed diffusive-kinetic control theoretical fit with $D=5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0=7.0 \times 10^{-5} \text{ m/s}$.

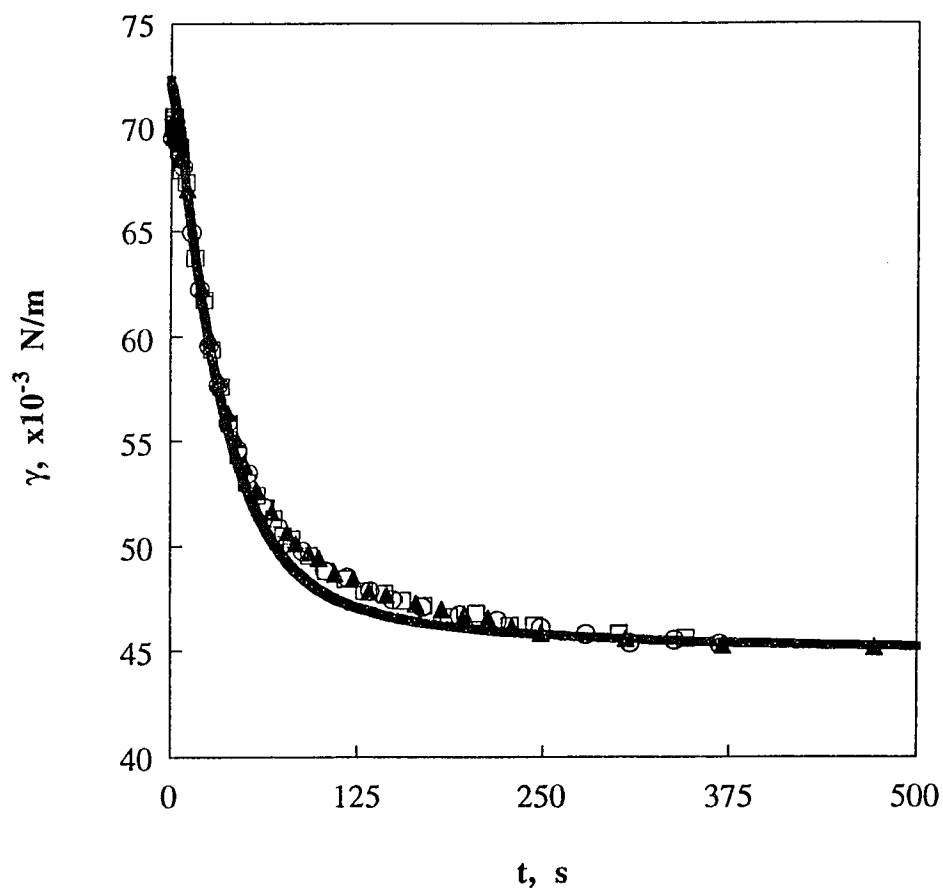


Figure 5-20 Dynamic surface tensions of clean surface adsorption in $6.14 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and mixed diffusive-kinetic control theoretical fit with $D=5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0=7.0 \times 10^{-5} \text{ m/s}$.

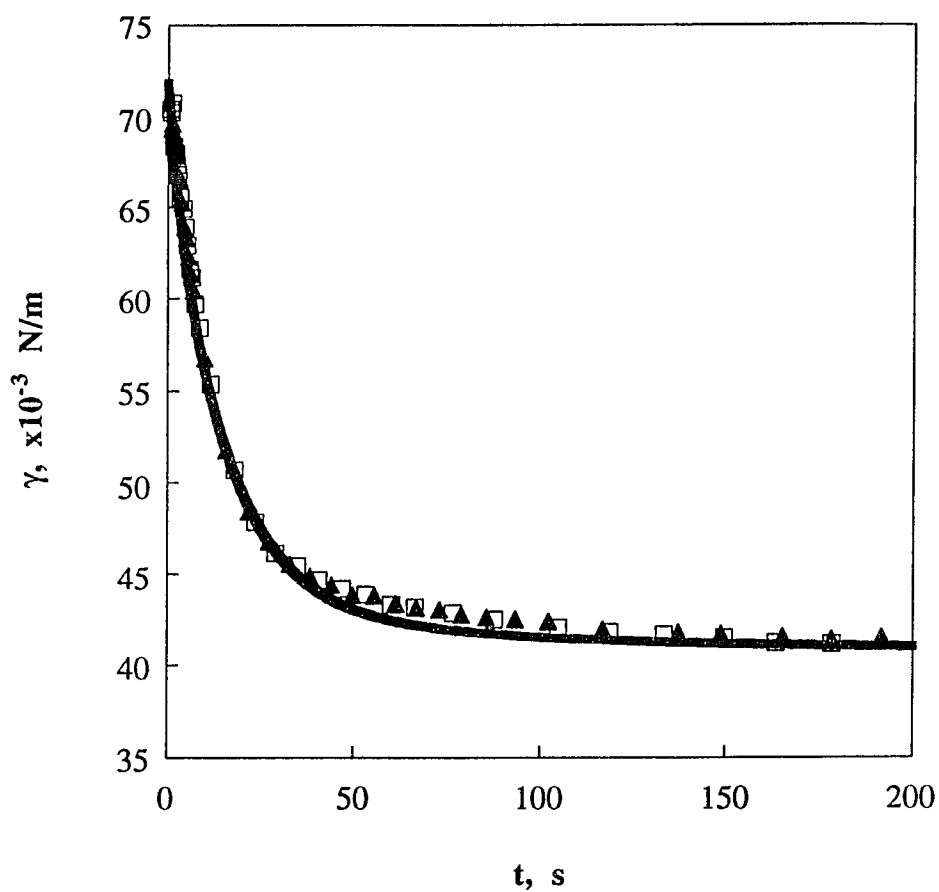


Figure 5-21 Dynamic surface tensions of clean surface adsorption in $12.28 \times 10^{-3} \text{ kg/m}^3$ C_{12}E_6 aqueous solution and mixed diffusive-kinetic control theoretical fit with $D=5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0=7.0 \times 10^{-5} \text{ m/s}$.

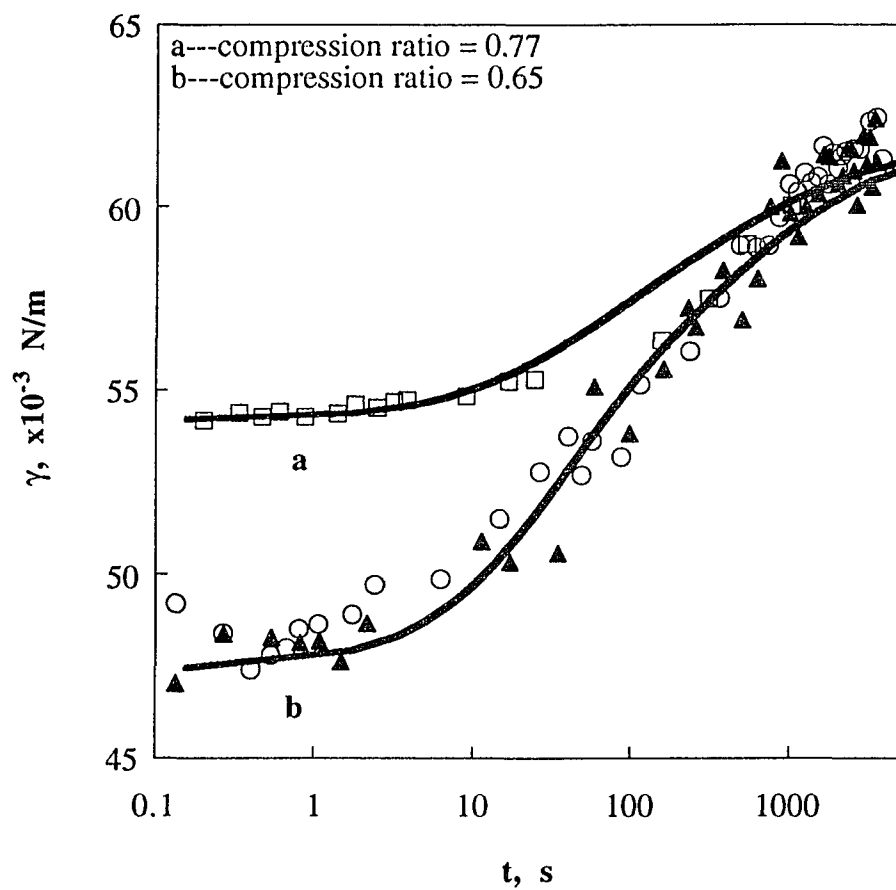


Figure 5-22 Dynamic surface tensions of re-equilibration in 0.18×10^{-3} kg/m³ C₁₂E₆ aqueous solution and mixed diffusive-kinetic control theoretical fit with $D = 5.7 \times 10^{-10}$ m²/s and $\beta_0 = 7.0 \times 10^{-5}$ m/s.

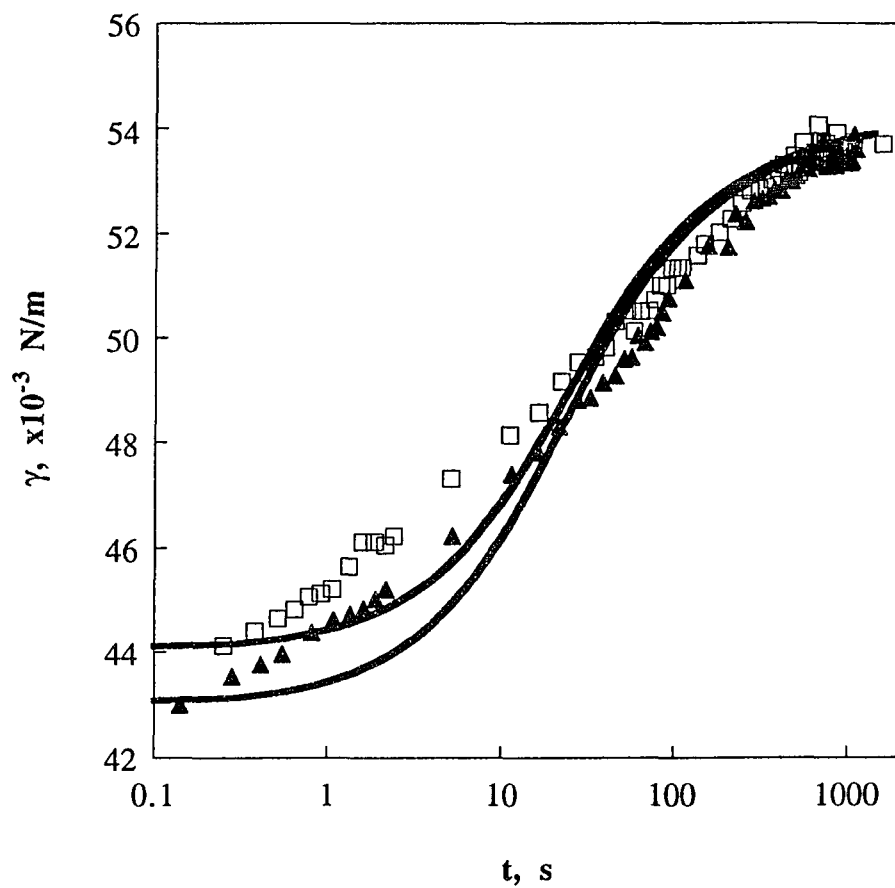


Figure 5-23 Dynamic surface tensions of re-equilibration in $1.0 \times 10^{-3} \text{ kg/m}^3 \text{ C}_{12}\text{E}_6$ aqueous solution and mixed diffusive-kinetic control theoretical fit with $D = 5.7 \times 10^{-10} \text{ m}^2/\text{s}$ and $\beta_0 = 7.0 \times 10^{-5} \text{ m/s}$.

Chapter 6

Conclusions

In this dissertation, the equilibrium and dynamic properties of a few water soluble polyethoxylated surfactants on the air/water interface have been studied experimentally and theoretically. Three major conclusions have been reached throughout this dissertation study: (i) The dynamic surface equation of state exists and is equivalent to the equilibrium surface equation of state; (ii) A new surface equation of state has been developed based on a molecular interaction approach; (iii) The adsorption and desorption rate constants have been measured for a model surfactant $C_{12}E_6$.

A method which involves using the pendant bubble as a monolayer film balance has been developed to directly measure the surface tension as a function of surface concentration, which defines the surface equation of state. This method has been shown easy to use, accurate and highly reproducible. We have taken the polyethoxylated surfactants as model nonionic surfactants and successfully proved that the dynamic and equilibrium surface equations of state are equivalent. The surface tension/surface concentration data from the direct measurement lead to a more complete understanding of the equilibrium properties of surfactants.

A molecular interaction model has been developed for nonionic surfactants based on a molecular interaction approach, which includes: a kinetic rate equation, an adsorption

isotherm and a surface equation of state. The adsorption isotherm and surface equation of state for a few polyethoxylated surfactants have been obtained through the equilibrium surface tension and surface tension/surface concentration measurements. Compared with the existing models, such as the Langmuir and Frumkin model, the molecular interaction model better describes the surface tension/surface concentration data. This model has four parameters, which is more than that of the Langmuir and Frumkin model. However, all the parameters have their physical meanings, which could be obtained from other measurements. A crucial point against the conventional method to find the equation of state has also been proved that simply fitting the equilibrium surface tension does not yield an accurate surface equation of state.

The surfactant transport dynamics onto the air/water interface has been studied for a model surfactant $C_{12}E_6$. Two new ideas to promote the kinetic effects in the transport dynamics have been proposed. One is for clean interface adsorption, which states that the kinetic effect is increasing when the bulk concentration increases. The other is for overcrowded interface desorption, which says that the kinetic effect is increasing when the initial surface concentration increases. These ideas have been proved theoretically and experimentally. By using these ideas, the kinetic rate constants and diffusion coefficient have been measured for the model surfactant $C_{12}E_6$.

Appendix I

Development of a Mixed Diffusive-Kinetic Control Fitting Program Using the Finite Element Method

In this appendix we develop a FORTRAN routine for optimizing the fitting of the diffusion coefficient and the kinetic rate constants to the dynamic tension data. In Section 5.2, we used the Laplace transform to solve the diffusion equation and obtained a solution in the form of convolution integral. We used this solution to develop the theoretical simulations. However, to fit the solutions to the dynamic surface tension data is easier by using the finite element method, as there are a number of existing subroutines. Optimization routines which fit dynamic data to model simulations usually require the model to be expressed as a series of ordinary differential equations in time of the form,

$$\frac{dy_i}{dt} = f(y_1, y_2, \dots, y_n, t, v_i) \quad i = 1, 2, \dots, n \quad (7-1)$$

Here v_i are the parameters that we want to determine values for so that the integrated solutions optimally match the data for $y_i(t)$.

To recast our transport equations in the form of equation (7-1), we use a finite difference formulation. Surfactant transport between one bulk and an interface is a two step process: bulk diffusion and convection, kinetic adsorption and desorption. If convection is not important, then we can simply use Fick's law to formulate bulk transport,

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (7-2)$$

The adsorption and desorption process can be described by a kinetic expression,

$$\frac{d\Gamma}{dt} = \beta_0 \exp\left(-b_1\Gamma - \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) C_s - \alpha_0 \exp\left(b_1\Gamma - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \quad (7-3)$$

Treating the pendant bubble as a sphere with transport only radially, the differential equation assumes:

$$\frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (7-4)$$

with B.C. and I.C.,

$$\begin{array}{ll} & C(r \rightarrow \infty, t) = C_b \\ \text{B.C.} & \frac{\partial \Gamma}{\partial t} = D \frac{\partial C}{\partial r} \Big|_{r=R_0} \\ & \Gamma(t=0) = \Gamma^i \\ \text{I.C.} & C(r, t=0) = C_b \end{array}$$

From Chapter 4, the surface equation of state is:

$$\gamma = \gamma_c - \left(1 + b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right) \right) \Gamma RT \quad (7-5)$$

then we can calculate the theoretical dynamical surface tension. The definitions in above equations are:

C ---surfactant bulk concentration

C_b ---farfield bulk concentration

C_s ---sublayer concentration

D ---diffusion coefficient

t ---time

Γ ---surface concentration

Γ_i ---initial surface concentration

β_0 ---adsorption rate constant

α_0 ---desorption rate constant

R ---gas constant

T ---temperature

R_0 ---radius of the bubble

γ ---surface tension

γ_c ---clean liquid surface tension

b_1, b_2, b_3 ---the molecular interaction model parameters

To recast the problem in finite difference form, we define $\rho=1/r$, then equation (7-4) is transferred to,

$$\frac{\partial C}{\partial t} = D\rho^4 \frac{\partial^2 C}{\partial \rho^2} \quad (7-6)$$

with B.C. and I.C.,

$$C(\rho = 0, t) = C_b$$

$$C(\rho < 1/R_0, t = 0) = C_b$$

$$\frac{d\Gamma(t)}{dt} = D \frac{\partial C}{\partial r} \Big|_{r=R_0} = - \frac{D}{R_0^2} \frac{\partial C}{\partial \rho} \Big|_{\rho=\frac{1}{R_0}}$$

If we discretize equation (7-6) in ρ , and use 4th order approximation for second derivative, and substitute into the boundary conditions, we obtain a sets of ODEs:

$$\left\{ \begin{array}{l} C(1) = C_b \\ \frac{dC(2)}{dt} = \frac{D(\Delta\rho)^2}{24} \begin{pmatrix} 20C(1) - 30C(2) - 8C(3) + 28C(4) \\ -12C(5) + 2C(6) \end{pmatrix} \\ \frac{dC(i)}{dt} = \frac{D(i-1)^4(\Delta\rho)^2}{24} \begin{pmatrix} -2\dot{C}(i-2) + 32C(i-1) - 60C(i) \\ +32C(i+1) - 2C(i+2) \end{pmatrix} \\ \frac{dC(n-1)}{dt} = \frac{D(n-2)^4(\Delta\rho)^2}{24} \begin{pmatrix} 20\dot{C}(n) - 30C(n-1) - 8C(n-2) + \\ 28C(n-3) - 12C(n-4) + 2C(n-5) \end{pmatrix} \\ \frac{dC(n)}{dt} = \frac{D(n-1)^4(\Delta\rho)^2}{24} \begin{pmatrix} -\frac{415}{3}C(n) + 192C(n-1) - 72C(n-2) \\ +\frac{64}{3}C(n-3) - 3C(n-4) - \\ 100\frac{R_0^2}{D} \begin{pmatrix} \beta_0 \exp\left(-b_1\Gamma - \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) C_s \\ -\alpha_0 \exp\left(b_1\Gamma - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \end{pmatrix} \Delta\rho \end{pmatrix} \\ \frac{d\Gamma}{dt} = \beta_0 \exp\left(-b_1\Gamma - \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) C_s - \alpha_0 \exp\left(b_1\Gamma - \frac{2b_2}{b_3} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma \\ \gamma = \gamma_c - \left(1 + b_1\Gamma + \frac{b_2}{\sqrt{\Gamma}} \exp\left(\frac{b_3}{\sqrt{\Gamma}}\right)\right) \Gamma RT \end{array} \right. \quad (7-7)$$

with I.C.: $C(i)=C_b$ @t=0
 $\Gamma=\Gamma^i$ @t=0

We use the integration package LSODE to solve this sets of ODEs and an algebraic equation to obtain theoretical dynamic surface tension. Figure 7-1 shows the solution

obtained from the finite element method compared with the solution obtained from convolution integral assuming the Frumkin adsorption isotherm. They agree each other exactly.

To do the optimization, we define an objective function:

$$\Psi(\beta_0, D) = \sum_{j=1}^{N_{data\ set}} \sum_{i=1}^{N_{data\ point}} \left(\gamma^{theoretical} \Big|_{t_i} - \gamma_i^{experimental} \right)^2 \quad (7-8)$$

Minimizing $\Psi(\beta_0, D)$ gives the best fitted β_0 and D . At the minimum of $\Psi(\beta_0, D)$,

$$\begin{cases} \frac{\partial \Psi}{\partial D} = 0 \\ \frac{\partial \Psi}{\partial \beta_0} = 0 \end{cases} \quad (7-9)$$

We apply the Newton-Raphson method directly to solve equation (7-9). The initial guess of diffusion coefficient and adsorption rate constant is obtained from the purely diffusional and kinetic model fit. Then, we use the following equation to do the iteration until a certain tolerance is reached,

$$\begin{pmatrix} D(n) \\ \beta_0(n) \end{pmatrix} = \begin{pmatrix} D(n-1) \\ \beta_0(n-1) \end{pmatrix} - \begin{pmatrix} \frac{\partial^2 \Psi}{\partial^2 D} & \frac{\partial^2 \Psi}{\partial D \partial \beta_0} \\ \frac{\partial^2 \Psi}{\partial \beta_0 \partial D} & \frac{\partial^2 \Psi}{\partial^2 \beta_0} \end{pmatrix}_{n-1}^{-1} \begin{pmatrix} \frac{\partial \Psi}{\partial D} \\ \frac{\partial \Psi}{\partial \beta_0} \end{pmatrix}_{n-1} \quad (7-10)$$

The first and the second derivatives in equation (7-10) are calculated numerically,

$$\left\{ \begin{aligned} \frac{\partial \psi}{\partial x} &= \frac{\psi(x + \Delta x) - \psi(x - \Delta x)}{2\Delta x} \\ \frac{\partial^2 \psi}{\partial x^2} &= \frac{\psi(x + \Delta x) - 2\psi(x) + \psi(x - \Delta x)}{\Delta x^2} \\ \frac{\partial^2 \psi}{\partial x \partial y} &= \frac{\psi(x + \Delta x, y + \Delta y) - \psi(x + \Delta x, y - \Delta y) - \psi(x - \Delta x, y + \Delta y) + \psi(x - \Delta x, y - \Delta y)}{4\Delta x \Delta y} \end{aligned} \right.$$

(7-11)

where x and y are D or β_0 . The following are the FORTRAN programs which implement the discussed fitting procedures.

The input.fit file is:

READ IN REQUIRED PARAMETERS

MOLECULAR WEIGHT WM

450.0D0

TEMPERATURE TTT (DEGREE CENTIGRADE)

23.5D0

EQUILIBRIUM CONSTANTS B1 B2 B3 A

-1.218D6

0.1887D0

-4.5D-3

12000.0D0

INITIAL GUESS OF THE ADSORPTION RATE CONSTANT BETA0

10.0D-5

INITIAL GUESS OF THE DIFFUSION COEFFICIENT D (M^2/S)

6.0D-10

SURFACE TENSION OF PURE WATER GC (mN/m)

72.3D0

AREA/VOLUME RATIO OF THE CONTAINER AV (M^{-1})

25.0D0

TIME STEP (EXPONENTIAL TERM)

0.1D0

TOLERANCE

0.005D0

NUMBER OF FITTING FILES

17

END OF INPUT

The source program is:

```

C    TWO PARAMETERS FITTING THE MIXED DIFFUSIONAL-KINETIC
C    CONTROL
C    SURFACTANT TRANSPORT TO THE DYNAMIC SURFACE TENSION TO
C    FIND THE C DIFFUSION COEFFICIENT AND KINETIC RATE CONSTANTS
C
C    PLEASE LOOK AT THE INPUT.FIT FILE FIRST
C
C    Declaration of variables
C
    DOUBLE PRECISION ATOL, RTOL, RWORK, T, TOUT, Y
    DOUBLE PRECISION WM, CP, C0, TT, TTT, B1, B2, B3, A, BETA0, D, B,
    DELTS
    DOUBLE PRECISION TE, GE, AE, SUMERR, DT, BT, DELTD, DELTB, D0,
*      BETA00, DCORR, BCORR, SUMER0, TSEX, TOLERE
    INTEGER I, IOPT, ISTATE, ITASK, ITOL, IWORK, LIW, LRW, MF, NEQ,
*      J1, J2, J, NFILE
    CHARACTER*80 CHAR1, CHAR2, CHAR3, CHAR4, CHAR5, CHAR6,
*      CHAR7, CHAR8, CHAR9, CHAR10, CHAR11, CHAR12, CHAR13
    PARAMETER (NEQ=50,R=8.314D0)
    DIMENSION ATOL(NEQ), IWORK(5*(20+NEQ)),
*      RWORK(5*(22+9*NEQ+NEQ**2)), Y(NEQ), TE(200), GE(200),
*      AE(200), DT(3), BT(3), SUMERR(3,3), SUMER0(3,3)
    COMMON WM, C0, TT, B1, B2, B3, A, BETA0, D, B, DELTS
    EXTERNAL FCN, JAC
C

```

C CONNECT UNIT 6 FOR OUTPUT TO THE SCREEN

C

OPEN(6,FILE='fit.d',STATUS='UNKNOWN')

C

C ENABLE DISPLAY OF ERROR MESSAGE ON UNIT 6

CALL XSETF(1)

CALL XSETUN(6)

C

C

C READ IN REQUIRED PARANETERS

C

OPEN (8, FILE='input.fit',STATUS='UNKNOWN')

READ (8,15) CHAR1

READ (8,15) CHAR2

READ (8,10) WM

READ (8,15) CHAR3

READ (8,10) TTT

READ (8,15) CHAR4

READ (8,10) B1

READ (8,10) B2

READ (8,10) B3

READ (8,10) A0

READ (8,15) CHAR5

READ (8,10) BETA00

READ (8,15) CHAR6

READ (8,10) D0

READ (8,15) CHAR7

```
      READ (8,10) GC
      READ (8,15) CHAR8
      READ (8,10) AV
      READ (8,15) CHAR9
      READ (8,10) TSEX
      READ (8,15) CHAR10
      READ (8,10) TOLERE
      READ (8,15) CHAR11
      READ (8,*) NFILE
10    FORMAT (D26.16)
15    FORMAT (A80)
C
C PRINT*, WM, TTT, A0
C PRINT*, B1, B2, B3
      PRINT*, D0, BETA00
C PRINT*, NFILE, TSEX, TOLERE
C
C INPUT OF REQUIRED PARAMETERS
C
C UNITS CONVERSION
C
C TEMPERATURE
      TT=TTT+273.15D0
C
C EQUILIBRIUM CONSTANTS
      A=A0/WM
C
```

C CALCULATING THE TRIAL MATRIX

C

```

1      DELTD=0.01*D0
      DELTB=0.01*BETA00
      DO 5 I=1,3
          DT(I)=D0+(I-2)*DELTD
          BT(I)=BETA00+(2-I)*DELTB
5      CONTINUE

```

C

```

      DO 6 J1=1,3
          DO 7 J2=1,3
              SUMER0(J1,J2)=0D0
7          CONTINUE

```

```

6      CONTINUE

```

C

C READ IN FITTING DATA FILES

C

```

      DO 999 III=1,NFILE
          IF (III.EQ.1) OPEN (8, FILE='1',STATUS='UNKNOWN')
          IF (III.EQ.2) OPEN (8, FILE='2',STATUS='UNKNOWN')
          IF (III.EQ.3) OPEN (8, FILE='3',STATUS='UNKNOWN')
          IF (III.EQ.4) OPEN (8, FILE='4',STATUS='UNKNOWN')
          IF (III.EQ.5) OPEN (8, FILE='5',STATUS='UNKNOWN')
          IF (III.EQ.6) OPEN (8, FILE='6',STATUS='UNKNOWN')
          IF (III.EQ.7) OPEN (8, FILE='7',STATUS='UNKNOWN')
          IF (III.EQ.8) OPEN (8, FILE='8',STATUS='UNKNOWN')
          IF (III.EQ.9) OPEN (8, FILE='9',STATUS='UNKNOWN')

```

```

      IF (III.EQ.10) OPEN (8, FILE='10',STATUS='UNKNOWN')
      IF (III.EQ.11) OPEN (8, FILE='11',STATUS='UNKNOWN')
      IF (III.EQ.12) OPEN (8, FILE='12',STATUS='UNKNOWN')
      IF (III.EQ.13) OPEN (8, FILE='13',STATUS='UNKNOWN')
      IF (III.EQ.14) OPEN (8, FILE='14',STATUS='UNKNOWN')
      IF (III.EQ.15) OPEN (8, FILE='15',STATUS='UNKNOWN')
      IF (III.EQ.16) OPEN (8, FILE='16',STATUS='UNKNOWN')
      IF (III.EQ.17) OPEN (8, FILE='17',STATUS='UNKNOWN')
      IF (III.EQ.18) OPEN (8, FILE='18',STATUS='UNKNOWN')
      IF (III.EQ.19) OPEN (8, FILE='19',STATUS='UNKNOWN')
      IF (III.EQ.20) OPEN (8, FILE='20',STATUS='UNKNOWN')

C
C
      READ (8,*) CP0, B, SCI

C
C      PRINT*,CP0, B, SCI
C
      CP=CP0/WM

C
C FINITE DIFFERENCE OF SPACE
C
      DELTS=1D0/B/(NEQ-2)

C
C READ IN EXPERIMENTAL DATA
C
      DO 40 I=1,200
20      READ (8,*,END=50) TE(I),GE(I),AE(I)

```

```

C          30    FORMAT (F8.3,F6.3,F11.6)
C          PRINT*,TE(I),GE(I),AE(I)
40    CONTINUE
50    NN=I-1
C
C FINDING THE REAL BULK CONCENTRATION
      SC0=.000001
11      FE=2*B1*SC0+(1/SQRT(SC0)-2/B3)*B2*EXP(B3/SQRT(SC0))
      *      +ALOG(SC0)-DLOG(CP-AV*SC0)+DLOG(A)
      DFE=2*B1+(1-B3/SQRT(SC0))/2*B2/SC0/SQRT(SC0)
      *      *EXP(B3/SQRT(SC0))+AV/(CP-AV*SC0)
      SC0=SC0-FE/DFE
      IF(ABS(FE/DFE/SC0).LT.0.001) GOTO 16
      GOTO 11
16      G0=GC-(1.+B1*SC0+B2/SQRT(SC0)*EXP(B3/SQRT(SC0)))
      *      *R*TT*SC0*1000!
      C0=(CP-AV*SC0)
C          PRINT*,SC0,G0,(CP-AV*SC0)*WM
C
C
      DO 900 J1=1,3
          BETA0=BT(J1)
          DO 910 J2=1,3
              D=DT(J2)
C
C
C INITIALIZATION OF LSODE CALL LIST PARAMETERS
C

```

```

      DO 100 I=1,NEQ-1
          Y(I)=C0
100   CONTINUE
      Y(NEQ)=SCI*4D-6
C
      T=0D0
      TOUT=TE(1)
C
      ITOL=2
      RTOL=1D-4
      DO 110 I=1,NEQ-1
          ATOL(I)=1D-4*C0
110   CONTINUE
      ATOL(NEQ)=1D-4*4D-6
C
      ITASK=1
      ISTATE=1
      IOPT=0
C
      LRW=5*(22+9*NEQ+NEQ**2)
      LIW=5*(20+NEQ)
C
      MF=21
C
C SOLUTION AND OUTPUT OF THE RESULTS
C
      SUMERR(J1,J2)=0D0

```

```

C
DO 120 I=1,NN
    CALL LSODE(FCN,NEQ,Y,T,TOUT,ITOL,RTOL,ATOL,ITASK,
*           ISTATE,IOPT,RWORK,LRW,IWORK,LIW,JAC,MF)
    G=GC-(1+B1*Y(NEQ)+B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))
*           *Y(NEQ)*R*TT*1000D0
    SUMERR(J1,J2)=SUMERR(J1,J2)+(G-GE(I))**2
C    IF(ABS(G0-G).LT.2.0) GOTO 910
C    WRITE (6,60),T,G,GE(I)
C    60    FORMAT (F7.2,',',F5.2,',',F5.2)
    IF(ISTATE.LT.0) THEN
        WRITE (6,*) ISTATE
        STOP
    ENDIF
    TOUT=TE(I+1)
120 CONTINUE
C
910 CONTINUE
C
C    WRITE (6,61),SUMERR(J1,1),SUMERR(J1,2),SUMERR(J1,3)
C
C    61    FORMAT (F11.4,',',F11.4,',',F11.4)
900 CONTINUE
C
DO 503 J1=1,3
    DO 504 J2=1,3
        SUMER0(J1,J2)=SUMER0(J1,J2)+SUMERR(J1,J2)

```

504 CONTINUE

503 CONTINUE

999 CONTINUE

C

WRITE (6,*),SUMER0(1,1),SUMER0(1,2),SUMER0(1,3)

WRITE (6,*),SUMER0(2,1),SUMER0(2,2),SUMER0(2,3)

WRITE (6,*),SUMER0(3,1),SUMER0(3,2),SUMER0(3,3)

C

C WRITE (4,*),SUMER0(1,1),SUMER0(1,2),SUMER0(1,3)

C WRITE (4,*),SUMER0(2,1),SUMER0(2,2),SUMER0(2,3)

C WRITE (4,*),SUMER0(3,1),SUMER0(3,2),SUMER0(3,3)

C

C CALCULATING THE DERIVATIVES

PD=(SUMER0(2,3)-SUMER0(2,1))/(2*DELTD)

PB=(SUMER0(1,2)-SUMER0(3,2))/(2*DELTB)

PDD=(SUMER0(2,3)-2*SUMER0(2,2)+SUMER0(2,1))/DELTD**2

PBB=(SUMER0(1,2)-2*SUMER0(2,2)+SUMER0(3,2))/DELTB**2

PDB=(-SUMER0(1,1)+SUMER0(1,3)+SUMER0(3,1)-SUMER0(3,3))

* /(4*DELTD*DELTB)

PRINT*,PD,PB,PDD,PBB,PDB

DCORR=(PDB/PBB*PB-PD)/(PDD-PDB**2/PBB)

BCORR=(PDB/PDD*PD-PB)/(PBB-PDB**2/PDD)

D0=D0+DCORR/2

BETA00=BETA00+BCORR/2

PRINT*,D0,BETA00

IF(ABS(DCORR/D0).LT.0.01.AND.ABS(BCORR/BETA00).LT.0.01)

GOTO 920

```

                GOTO 1
920  PRINT*, D0, BETA00
      STOP
      END

C
C-----
C
C FCN defines the system of ODEs.
C
      SUBROUTINE FCN(NEQ,T,Y,F)
C
      DOUBLE PRECISION F,T,Y
      DOUBLE PRECISION WM,C0,TT,B1,B2,B3,A,BETA0,D,B,DELTS
      INTEGER NEQ
      DIMENSION F(NEQ),Y(NEQ)
      COMMON WM,C0,TT,B1,B2,B3,A,BETA0,D,B,DELTS
C
C  PRINT*,WM,B1,DELTS
C
      F(1)=0D0
      F(2)=D*DELTS**2/24*(20*Y(1)-30*Y(2)-8*Y(3)+28*Y(4)-12*Y(5)
*          +2*Y(6))
C
      DO 100 I=3, NEQ-3
          F(I)=D*(I-1)**4*DELTS**2/24*(-2*Y(I-2)+32*Y(I-1)
*          -60*Y(I)+32*Y(I+1)-2*Y(I+2))
100  CONTINUE

```

C

```

F(NEQ-2)=D*(NEQ-3)**4*DELTS**2/24*(20*Y(NEQ-1)
*      -30*Y(NEQ-2)-8*Y(NEQ-3)+28*Y(NEQ-4)-12*Y(NEQ-5)
*      +2*Y(NEQ-6))
F(NEQ-1)=D*(NEQ-2)**4*DELTS**2/24*(-415/3*Y(NEQ-1)
*      +192*Y(NEQ-2)-72*Y(NEQ-3)+64/3*Y(NEQ-4)-3*Y(NEQ-5)
*      -100*B**2/D*DELTS*(BETA0*EXP(-B1*Y(NEQ)
*      -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))*Y(NEQ-1)
*      -A*BETA0*EXP(B1*Y(NEQ)
*      -2*B2/B3*EXP(B3/SQRT(Y(NEQ))))*Y(NEQ)))
F(NEQ)=BETA0*EXP(-B1*Y(NEQ)
*      -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))*Y(NEQ-1)
*      -A*BETA0*EXP(B1*Y(NEQ)
*      -2*B2/B3*EXP(B3/SQRT(Y(NEQ))))*Y(NEQ)

```

C

RETURN

END

C-----

C JAC computes the Jacobian matrix

C

SUBROUTINE JAC(NEQ,T,Y,ML,MU,PD,NROWPD)

C

DOUBLE PRECISION PD,T,Y

DOUBLE PRECISION WM,C0,TT,B1,B2,B3,A,BETA0,D,B,DELTS

INTEGER ML,MU,NEQ,NROWPD

DIMENSION PD(NROWPD,NEQ),Y(NEQ)

COMMON WM,C0,TT,B1,B2,B3,A,BETA0,D,B,DELTS

C

C PRINT*,WM,B1,DELTS

C

DO 210 I=1, NEQ

PD(1,I)=0.0

210 CONTINUE

C

PD(2,1)=D*DELTS**2/24*20

PD(2,2)=D*DELTS**2/24*(-30)

PD(2,3)=D*DELTS**2/24*(-8)

PD(2,4)=D*DELTS**2/24*28

PD(2,5)=D*DELTS**2/24*(-12)

PD(2,6)=D*DELTS**2/24*2

C

DO 220 I=3,NEQ-3

PD(I, I-2)=D*(I-1)**4*DELTS**2/24*(-2)

PD(I, I-1)=D*(I-1)**4*DELTS**2/24*32

PD(I, I)=D*(I-1)**4*DELTS**2/24*(-60)

PD(I, I+1)=D*(I-1)**4*DELTS**2/24*32

PD(I, I+2)=D*(I-1)**4*DELTS**2/24*(-2)

220 CONTINUE

C

PD(NEQ-2,NEQ-6)=D*(NEQ-3)**4*DELTS**2/24*2

PD(NEQ-2,NEQ-5)=D*(NEQ-3)**4*DELTS**2/24*(-12)

PD(NEQ-2,NEQ-4)=D*(NEQ-3)**4*DELTS**2/24*28

PD(NEQ-2,NEQ-3)=D*(NEQ-3)**4*DELTS**2/24*(-8)

PD(NEQ-2,NEQ-2)=D*(NEQ-3)**4*DELTS**2/24*(-30)

$$PD(NEQ-2,NEQ-1)=D*(NEQ-3)**4*DELTS**2/24*20$$

C

$$PD(NEQ-1,NEQ-5)=D*(NEQ-2)**4*DELTS**2/24*(-3)$$

$$PD(NEQ-1,NEQ-4)=D*(NEQ-2)**4*DELTS**2/24*64/3$$

$$PD(NEQ-1,NEQ-3)=D*(NEQ-2)**4*DELTS**2/24*(-72)$$

$$PD(NEQ-1,NEQ-2)=D*(NEQ-2)**4*DELTS**2/24*192$$

$$PD(NEQ-1,NEQ-1)=D*(NEQ-2)**4*DELTS**2/24*(-415/3$$

$$* -100*B**2*DELTS/D*BETA0*EXP(-B1*Y(NEQ)$$

$$* -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))$$

$$PD(NEQ-1,NEQ)=-100*B**2*DELTS/D*(BETA0*Y(NEQ-1)*EXP(-$$

B1*Y(NEQ)

$$* -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))$$

$$* *(-B1-B2/2*Y(NEQ)**(-3/2)*EXP(B3/SQRT(Y(NEQ))))$$

$$* *(1+B3/SQRT(Y(NEQ)))-BETA0*A*EXP(B1*Y(NEQ)$$

$$* -2*B2/B3*EXP(B3/SQRT(Y(NEQ))))$$

$$* -BETA0*A*EXP(B1*Y(NEQ)$$

$$* -2*B2/B3*EXP(B3/SQRT(Y(NEQ)))*Y(NEQ)$$

$$* *(B1+B2*Y(NEQ)**(-3/2)*EXP(B3/SQRT(Y(NEQ))))$$

C

$$PD(NEQ,NEQ-1)=BETA0*EXP(-B1*Y(NEQ)$$

$$* -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))$$

$$PD(NEQ,NEQ)=BETA0*Y(NEQ-1)*EXP(-B1*Y(NEQ)$$

$$* -B2/SQRT(Y(NEQ))*EXP(B3/SQRT(Y(NEQ))))$$

$$* *(-B1-B2/2*Y(NEQ)**(-3/2)*EXP(B3/SQRT(Y(NEQ))))$$

$$* *(1+B3/SQRT(Y(NEQ)))-BETA0*A*EXP(B1*Y(NEQ)$$

$$* -2*B2/B3*EXP(B3/SQRT(Y(NEQ))))$$

$$* -BETA0*A*EXP(B1*Y(NEQ)$$

```
*      -2*B2/B3*EXP(B3/SQRT(Y(NEQ))))*Y(NEQ)
*      *(B1+B2*Y(NEQ)**(-3/2)*EXP(B3/SQRT(Y(NEQ))))
```

C

RETURN

END

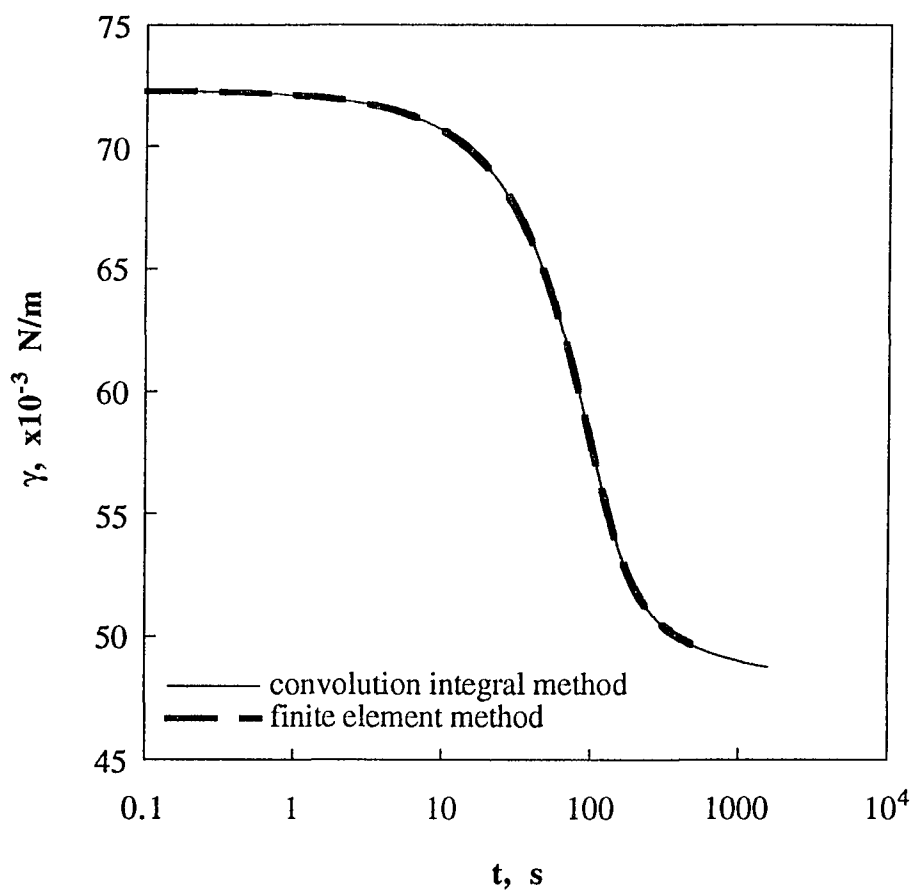


Figure 7-1 Theoretical dynamic surface tensions obtained from the finite element method and the convolution integral method for a Frumkin model with $C_b=0.00807 \text{ mol/m}^3$, $D=6.0 \times 10^{-10} \text{ m}^2/\text{s}$, $\beta=4.0 \text{ m}^3/(\text{mol s})$.

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