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**A study of the effects of cohesive forces on the sorption kinetics
of surfactants by pendant drop digitization**

Lin, Shi-Yow, Ph.D.

City University of New York, 1991

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A STUDY OF THE EFFECTS OF COHESIVE FORCES ON THE SORPTION
KINETICS OF SURFACTANTS BY PENDANT DROP DIGITIZATION

by

SHI-YOW LIN

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.

1991

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

4/23/91
Date

Charles Maldarelli
Professor Charles Maldarelli
Chair of Examining Committee

4/24/91
Date

Gerard G. Lowen
Professor Gerard G. Lowen
Executive Officer

Dr. Kevin McKeigue

Dr. Herbert Weinstein

Dr. Gabriel Tardos

Dr. Peter Ganatos

Supervisory Committee

The City University of New York

Abstract

A STUDY OF THE EFFECTS OF COHESIVE FORCES ON THE SORPTION KINETICS OF SURFACTANTS BY PENDANT DROP DIGITIZATION

by

Shi-Yow Lin

Advisers: Professor Charles Maldarelli (Mentor)
Dr. Kevin McKeigue (Co-Mentor)

Surfactants are molecules with nonpolar and polar (or ionizable) chemical groups which adsorb preferentially onto a fluid interface where they lower the interfacial tension. When surfactant molecules with single, slender hydrocarbon chains and small polar groups adsorb onto a surface, strong van der Waals attractive forces can develop at sufficiently high surface concentrations. This cohesion arises because at high surface concentrations the adsorbed molecules are pushed out of the surface, and begin to stack lengthwise in loose bundles. This arrangement brings the hydrocarbon chains into close proximity to each other, and strong van der Waals attraction can develop.

The presence of cohesive forces affects the dependence of the equilibrium surface tension and surface concentration on the bulk concentration, and dynamic surface tensions and concentrations caused by nonequilibrium processes involving surfactant bulk-sublayer exchange. In this thesis, these effects are studied theoretically and experimentally. Experimentally, a pendant drop apparatus using video image digitization is developed to measure equilibrium and dynamic interfacial tensions. Theoretically, sorption kinetic models are constructed which incorporate the influence of cohesion through an activation energy approach.

The major results are: (i) cohesive effects give rise to a phase transition like region in which small increases in the bulk concentration cause very large increases in the surface coverage

accompanied with little change in the surface tension; (ii) for clean interface adsorption, an early induction period appears in the relaxation in surface tension because of the phase transition characteristic of the equilibrium surface tension; (iii) there are conditions for which the clean interface adsorption is diffusion controlled while the re-equilibration is controlled by both kinetic sorption and bulk diffusion. This leads to the possibility of measuring the diffusion coefficient by comparing measured relaxations for adsorption with the diffusion limited simulations, and then calculating kinetic constants by comparing theoretical and experimental re-equilibrations.

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CHAPTER 1

INTRODUCTION

Surface active molecules (surfactants) are chemical species which contain both polar and nonpolar groups, and which adsorb preferentially at fluid interfaces separating hydrophobic and hydrophilic bulk phases. Surfactant molecules adsorb at these interfaces because adsorption lowers the interface energy by allowing the separate juxtaposition and interaction of the nonpolar group of the molecule with the molecules of the hydrophobic phase, and the polar group with the molecules of the hydrophilic phase. Adsorbed surfactant molecules can also interact energetically with each other, and it is this aspect of surfactant adsorption that is studied in this thesis.

When a surface active molecule with a single, long, slender hydrocarbon chain and a small polar group adsorbs onto an interface with very little additional surfactant, the molecule is oriented with the polar group anchored to the hydrophilic phase. The long chain is moved by thermal energy, and its position fluctuates between configurations in which it lies along the interface to orientations in which it extends perpendicular to the interface and into the hydrophobic phase. This is a gaseous state of surface adsorption. As the surface concentration increases, however, steric interactions due to molecular crowding begin to limit the chain movement, and the hydrophobic chains are pushed together and out of the interface plane. Because the chains are long and slender and the polar groups are small, the molecules can pack lengthwise in loose bundles which extend

out into the hydrocarbon phase. This packing geometry promotes strong van der Waals attraction between the chains, and the cohesive energy allows the structure to remain intact over the dispersal effect of thermal energy.

When strong cohesive forces develop between molecules on the surface, the desorption rate off of the surface and the surface tension is affected. Surfactant molecules adsorb onto the interface because their energy when situated on the surface is less than that when positioned in the bulk phase. The rate of desorption is dependent on the size of this energy difference: The smaller the difference the larger the desorption rate. When strong intermolecular attractions develop between adsorbed chains on the surface, the energy of the adsorbed molecule is reduced further, and the desorption rate proportionately decreases. With regard to the effect on surface tension, when surfactant molecules adsorb onto an interface, they lower the interfacial tension of the surface by creating a surface pressure. At low surface coverage, this pressure increases linearly with surface concentration, and it is analogous to the pressure exerted in a three dimensional gas. At higher surface concentrations, cohesion reduces this pressure and a range of surface concentrations exists for which increasing the surface concentration does not cause a large increase in surface pressure. Eventually the coverage becomes large enough that the cohesion is outbalanced by steric repulsions, and the surface pressure then increases sharply with concentration.

This thesis examines how the effects of cohesion discussed above influence the equilibrium adsorption and surface tension, and dynamic adsorption and surface tensions caused by nonequilibrium processes involving exchange of surfactant between the surface and the adjoining bulk sublayer. The study is both experimental and theoretical. Theoretically, an activation energy approach is utilized to develop expressions for the kinetics of adsorption and desorption which include the influence of cohesive forces. These kinetic expressions

are then used to develop equilibrium adsorption isotherms, i.e. expressions for the surface concentration as a function of the bulk concentration, and surface tension equations of state which express the equilibrium surface tensions as a function of the surface concentration or bulk concentration. Next, two dynamic surface tension processes are considered theoretically. The first is adsorption onto a clean interface from a bulk solution initially of uniform surfactant concentration. In this process, referred to as clean interface adsorption, surfactant molecules from the sublayer underlying the interface adsorb onto the interface depleting the sublayer concentration. Surfactant material diffuses from the bulk to the sublayer, and the series processes of diffusion and kinetic adsorption continue until an equilibrium monolayer is formed. In the second process, a monolayer in equilibrium with a bulk of uniform surfactant concentration is perturbed by a sudden contraction of the interface. Surfactant desorbs off of the surface into the sublayer, and bulk diffusion subsequently carries the excess material out into the bulk. This process is referred to as re-equilibration. For both clean interface adsorption and re-equilibration, dynamic surface concentration and interfacial tension profiles are computed by numerical solution of the surfactant bulk diffusion and surface kinetic equations.

Experimentally, dynamic surface tensions for clean interface adsorption and re-equilibration are measured on the surface of a pendant drop by using video image digitization. First, dynamic surface tensions for clean interface adsorption are measured for a test surfactant, Triton X-100, for which cohesive effects are not important. The results are used to demonstrate the experimental procedure, and the methodology for comparing the theoretical dynamic profiles with the experimental results. Next, clean interface adsorption and re-equilibration dynamic surface tensions are measured for n-decanol, a surfactant for which cohesive forces do develop at

sufficiently high surface concentrations. The experimental dynamic surface tensions demonstrate the characteristics predicted by the numerical simulations, and experimental and theoretical results are compared to determine the diffusion coefficient and the sorption kinetic constants of the alcohol molecule.

The primary reasons for undertaking this study are twofold. The first is concerned with understanding the influence of adsorption of surfactant onto the interfaces of moving drops and bubbles. When a surfactant adsorbs onto the surface of a moving fluid particle, surface convection causes the surfactant to be swept to stagnation points on the particle surface where the flow converges. These points are termed converging stagnation points. Surfactant will begin to accumulate at these points if the rate of desorption is slow compared to the rate at which convection sweeps material to the converging point. Accumulation reduces the local interfacial tension creating surface pressures which oppose the fluid motion and thereby retard the interface velocity. Such decreases in surface mobility affect greatly the mobility of foam in rock pores in oil recovery, the rate of interphase mass transfer and coalescence of droplets in emulsions and air bubbles in foams, and the magnitude of thermocapillary migration velocities.

If the surfactant molecule which is adsorbing onto the particle can develop strong cohesive forces when concentrated, then the interface can be very readily immobilized. As mentioned above, cohesive effects lower the desorption rate. Thus as the surfactant is swept and concentrated at stagnation points on the surface, their desorption rate will be reduced considerably. If the reduction is large enough so that the desorption rate falls below the convective sweeping rate, large regions around the converging stagnation points of the particle surface can become immobilized. The results of this study provide both a framework for understanding cohesive energy enhanced immobilization, and for decanol, values for the kinetic

constants and interaction energies necessary to develop quantitative criterion for immobilization.

A second reason for undertaking this study is connected with the development of the pendant drop apparatus for the measurement of ultra-low interfacial tensions. The measurement of ultra-low interfacial tensions ($< 10^{-2}$ mN/m) is critical in many processes, as for example, in steam or foam drive oil recovery methods, where ultra-low tensions are required to reduce the capillary pressure necessary to drive fluids through rock pores. The accurate measurement of ultra-low tensions is difficult with conventional methods such as the Whilhelmy plate, DuNuoy ring or capillary rise techniques. The reason for this is that such ultra-low tensions are either too small to be measured by an electrobalance, or the capillary rise is too small to be measured by a goniometer or telegiometer. However, methods which directly measure interfacial deformation, and relate this to the surface tension through the Young-Laplace equation, become more accurate as the tension or the deformability decreases. Two particular deformation-measuring techniques are the spinning drop and the pendant drop methods. It is hoped that this study of the pendant drop technique in which the deformation is video-digitized for measurement may improve the accuracy of the pendant drop method, and thereby be of use in the measurement of ultra-low tensions.

This thesis is divided into five chapters. The first details a literature review of past studies of the sorption kinetics of surfactants and the measurement of dynamic surface tensions. The next chapter describes the pendant drop apparatus used to measure the dynamic surface tension, and presents some clean interface adsorption experimental and theoretical results for Triton X-100, a surfactant for which the effects of cohesive energies is not important. The study of cohesive effects begins in Chapter 3. In this chapter, an activation energy approach is used to formulate kinetic expressions for adsorption and desorption which incorporate cohesive effects.

These kinetic expressions are used to develop adsorption isotherms and equations of state. The expressions are also used to obtain surface tension relaxation profiles for clean interface adsorption assuming infinitely fast kinetics (diffusion control). The profiles indicate that cohesive forces, because they reduce the surface pressure, give rise to an early induction period where the tension changes very slowly. This chapter also presents relaxation data for decanol for clean surface adsorption, and demonstrates that the theoretical diffusion limited results can accurately describe the relaxation for a fitted value of the diffusion coefficient. In the next chapter (Chapter 4) the influence of cohesion on re-equilibration is discussed. This chapter develops the important result that for a certain range of kinetic constants and at high surface coverage, re-equilibration can be of mixed control, while clean interface adsorption can be diffusion limited. This result is used in the next chapter (Chapter 5), where re-equilibration curves are experimentally obtained for decanol and compared with theory to determine self consistent values for the kinetic constants. The final chapter (Chapter 6) summarizes the major findings and gives recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Surface active molecules: structures and properties

A surfactant is a "amphiphilic" compound which has a long chain hydrocarbon tail (nonpolar) and a short ionizable or polar group. Some simple polar groups are carboxylic acid (COOH), carboxylate ion (COO^-), alcohol (OH), sulfonate (SO_3^-) and amine (NH_3^+). Hydrocarbon chains may be straight or branched, saturated or unsaturated. Aromatic and naphthenic rings may also be present in the hydrocarbon region.¹

Water, a highly polar material, resists incorporation of nonpolar hydrocarbon chains into its structure. Polar materials, in contrast, have considerable solubility in water. When a surfactant molecule, which has a hydrocarbon chain and a polar group, is added to water, it seems clear that the most favorable configuration would be one where the hydrocarbon chain of each molecule is removed from the water but the polar group remains in the water. As shown in Figure 2-1, this ideal condition can be achieved if the molecules adsorb at the interface between the water and an adjacent fluid as a mono-molecular layer or "monolayer". When surfactants are added to water at low concentrations, they, highly enriched at the surface, reduce the surface tension dramatically and, in addition, possess aggregation or structure-forming capabilities.

Micellization is another important property of surfactants. It too is a consequence of the reluctance of water to incorporate hydrocarbon chains. At very low concentrations dissolved surfactant, like most other solutes, it exists as individual molecules. But, at a

particular concentration (critical micelle concentration) it becomes more favorable for the surfactant molecules to form aggregates called micelles. As shown in Figure 2-1. the polar group is in contact with water while the hydrocarbon chains form the interior of the micelle which may contain perhaps a hundred molecules and is approximately spherical in shape. At higher surfactant concentrations micelles may become a normal hexagonal phase or a lamellar phase. A general display of the various physical properties of a solution of a typical surfactant such as sodium dodecyl sulfate is shown in Figure 2-2.

2.2 Dynamic surface phenomena

Dynamic surface phenomena arise in systems containing interfaces not in equilibrium with the adjoining liquid phase(s). Examples are systems where eventually equilibrium is reached by transport of soluble surface active material from a solution and systems where insoluble surface active matter is present in a non-equilibrium state. Such non-equilibrium situations can be obtained either by the creation of fresh interface or by disturbing an existing equilibrium one. An example of the former method is seen when an air bubble or liquid drop is created in a medium containing a bulk soluble surfactant. In the latter method, starting from an equilibrium situation, the air bubble or liquid drop, whose interface is at equilibrium, is disturbed by shrinking or expanding its volume. In each case, one then observes how the interfacial tension changes with time under the influence of the forces trying to re-establish equilibrium. The process of re-equilibration can take anything from less than milliseconds to hours or even days, depending on which relaxation mechanisms are operative. Taking the process of adsorption at an expanded or freshly-created interface as an example, one can envision three possibilities:

- (i) diffusion of surfactant from deeper layers of the solution to the sub-surface layer immediately adjacent to the surface;

- (ii) the actual adsorption from this sublayer onto the surface, possibly retarded by an adsorption barrier;
- (iii) rearrangement of adsorbed surfactant into a state in which the surface exerts its equilibrium tension.

Existing theories consider at most two of these processes, ignoring either third³⁻¹² or the second.¹³

Rearrangements in the surface may consist of reorientation, complex formation, chemical reactions, phase transitions or formation of three-dimensional structure resembling liquid crystals. For single small molecules, reorientation is a very fast process, taking less than 10^{-3} sec. Such fast processes have no effect on the behavior of a system in practical applications: by far the larger part of both technological and biological processes occurs in a time scale of 10^{-1} sec or longer. These long time scales require co-operative processes occurring over large distances and involving either many small molecules or macromolecules.

At an expanded or freshly-created interface the amount of surface active material per unit area (Γ) is less than at equilibrium and the surface tension (γ) is correspondingly higher. During equilibration the only quantities measured are the surface tension as a function of time and the constant solution concentration far from the interface. From the results of these measurements one attempts to extract detailed information on the three steps making up the process of adsorption. In the simplest case the first step, i.e. diffusion is rate-determining, the other two steps requiring a time which is much shorter than the characteristic time of the measurement. This means that equilibrium between sub-surface concentration (C_s), adsorption (Γ) and surface tension (γ) is established instantaneously. The sub-surface concentration $C_s(t)$ can be predicted by solving the diffusion equation, and, if necessary, taking into account convection. The surface tension has the value which it would have for a solution of concentration C_s at equilibrium. The relation γ vs C_s can then be

extracted from the long time asymptotes of the surface tension relaxation or it can be measured in separate experiments under equilibrium conditions. A theoretical γ vs time curve can be obtained in this way and compared to the experimental one.

Obviously, the desorption process is the reverse of the adsorption process. It can be studied¹⁴⁻¹⁶ by following events at an interface where the adsorption is higher than at equilibrium, e.g. an interface that has been compressed, or one where surfactant has been accumulated by transport from another phase.

For a number of systems, agreement with diffusion has been found, validating the assumption of instantaneous equilibrium in the sub-surface and the surface.^{4,8-12,17} In such cases all time effects are due to transport from the bulk solution. In other cases, adsorption or desorption appears to proceed measurably slower than would be expected on the basis of diffusion alone.^{7,12,18,19} The most popular interpretation of such results postulates the presence of a barrier in (free) energy between the sub-surface and the surface, leading to a slow equilibration process. Using this terminology, it appears that adsorption barriers occur far less frequently than desorption barriers. Apparent adsorption barriers were observed only for dipolar molecules^{5,19} such as adipic acid, azelaic acid, and 1,8-octanediol and short chain alcohols (C_3 - C_6).^{12,18}

In principle it is possible to extract a rate constant for the subsurface-surface equilibration process from the measured surface tension vs time curves in cases where "barriers" are postulated. Translating the term "ad/de-sorption barrier" into operationally defined parameters requires the introduction of a model for the exchange process between subsurface and surface. The Langmuir isotherm^{6,12,18} is the most widely used. The Frumkin isotherm²⁰ is applied when the van der Waals forces between the adsorbed surface active molecules on the interface are not negligible.

2.3 Measurement of Dynamic Surface Tensions

The experimental measurement of surface tension relaxation due to surfactant adsorption, and the calculation of a diffusion coefficient or sorptive kinetic constants from these measurements, has been undertaken using many techniques. These are of three types: (i) methods involving hydrodynamic flow, (ii) static techniques involving no fluid convection and (iii) surface oscillation techniques. Methods involving flow are useful for studying adsorption processes which occur on time scales of the order of milliseconds to seconds, while static methods are more accurate on scales of the order of seconds to hours. Oscillation techniques can resolve time scales of the order of milliseconds to several minutes.

Some of the methods involving convection which have been used are: the oscillating jet technique,^{4,21-23} the maximum bubble pressure method,²⁴⁻²⁷ the free falling film²⁸ or inclined plate technique,²⁹ the drop volume or weight method,^{30,31} and the (reversed) funnel method.³² The convection in each of these techniques is different: For the oscillating jet, the fluid is issuing through an orifice, for the inclined plane method liquid is flowing with a free surface down a plane and for the maximum bubble pressure and drop volume methods the surfactant solution is expanding radially in the vicinity of the interface. In these methods, diffusion coefficients or kinetic constants are generally obtained by (i) identifying an exposure time t for which the surface has been in contact with the surfactant solution, (ii) measuring the surface tension for that time, and (iii) computing the adsorption theoretically by solving the surfactant mass transfer to the interface. In most cases, convection is ignored altogether, and the theoretical solutions used to compare with the data is the planar diffusion controlled result of Ward and Tordai³ (and only for short and long contact times). For the maximum bubble pressure and drop weight methods, however, theoretical equations have been constructed to account for the radial convection induced by the

drop growth.^{9,30,33} Theoretical solutions of these convection equations have been compared with short time experimental data to obtain diffusion coefficients.⁹

The static methods used for the measurement of the surface tension relaxation are the Whilhelmy plate and Du Nouy ring method,³⁴ the static drop volume method³⁵ and the pendant drop technique.^{36,37} These have the advantage that surfactant transfer in the bulk can be described accurately by diffusion alone. Relaxation data from the plate and ring methods,¹⁰ and the static drop volume technique¹¹ have been compared with the short time solution of Ward and Tordai in order to determine diffusion coefficients. Comparison with intermediate times was also undertaken¹⁰ approximately by regarding the intermediate time solution for the surface concentration as linear in $\log t$, and deducing the diffusion coefficient from the shift of the experimental data for the adsorption (plotted as $\log t$ and regarded as linear) from the theoretical curve.

The primary surface oscillation techniques are the longitudinal wave method of Lucassen³⁸⁻⁴¹ and the oscillating bubble technique.^{42,43} The longitudinal wave method, when undertaken using small lateral oscillations of the interface creating small deviations from equilibrium, has the advantage that a perturbational analytical solution can be developed for the oscillation of the surface tension as a function of the surfactant mass transfer and hydrodynamic motion. Using this method,³⁸⁻⁴⁰ diffusion controlled adsorption was demonstrated for decanoic acid and several surfactants of the ethylene oxide adduct type for a range of frequencies of 10^{-2} to 10 sec^{-1} .

The pendant drop technique used in this study is a static method. Once the surface is formed by this method, it is not subjected to any changes due to outside influence prior to or during the measurement. It should be noted that this method is independent of contact angle effects and permits an accurate study of changes in surface composition with time.

Young⁴⁴ and Laplace⁴⁵ developed the pendant drop method of inflection in 1805 by locating a horizontal plane at the level where the profile curve passed through a point of inflection and computing the volume of the drop from its profile⁴⁶. The most widely used pendant drop method is the one of a selected plane.^{46,47} In this method, the equatorial diameter (d_e) and the diameter (d_s) in a selected plane at a distance d_e from the apex to the drop are measured. Therefore the surface tension is evaluated^{48,49} from the Bashforth and Adams tables⁵⁴ which relate two drop shape functions H ($= -\beta d_e^2/b^2$) and S ($= d_e/d_s$). Misak⁵⁰ correlated $1/H$ as a function of S using five equations and made this calculation much easier.

Before the advent of video digitization, classical pendant drop tensiometry was not used to obtain surface tension relaxation profiles because sequential photography is cumbersome. Recent advances in video image digitization and microcomputer availability have opened the possibility of fast and accurate recording of the drop shape coordinates and their subsequent numerical analysis.^{36,37} With video digitization, sequential profiles in time can readily be obtained and stored. The optimal estimation techniques^{51,52} for fluid/fluid interfacial tension are also developed by getting a best match between the theoretical Laplacian curve and the physically observed one. Thus, pendant drop tensiometry enhanced by video image digitization becomes a powerful tool for the accurate measurement of the interfacial tension of fluid/fluid interface. Recently, this technique has also been applied to the measurement of ultra-low interfacial tension which is useful in tertiary oil recovery.⁵³

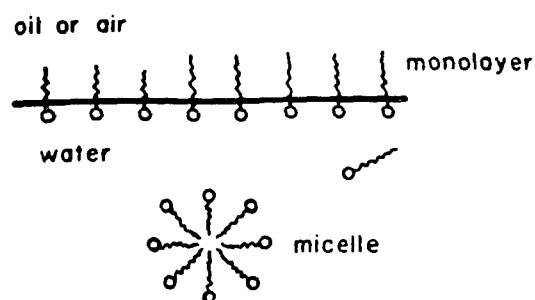


Figure 2-1. Idealized diagram showing surfactant behavior.

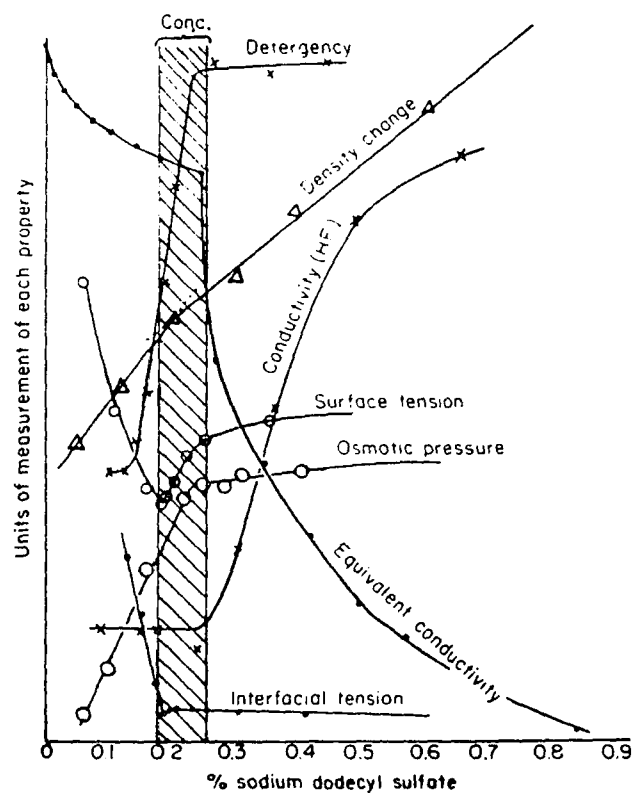


Figure 2-2. Properties of surfactants solutions - sodium dodecyl sulfate. (From Ref. 2)

CHAPTER 3

Diffusion Controlled Surfactant Adsorption Studied By Pendant Drop Digitization

3.1 Introduction

Pendant drop tensiometry, enhanced by video image digitization, has emerged as a very accurate method for measuring of the surface tension of fluid/fluid interfaces. In this method, video images of the silhouettes of pendant bubbles or drops are digitized to determine the interface loci. These loci are then compared with theoretical interfacial shapes generated by the solution of the Young-Laplace equation, and the surface tension, which determines the theoretical constructs, is then varied until an optimum is achieved between the theoretical shape and the experimental loci.^{51,52} Because this approach uses much more information about the drop shape, it is a much more accurate and reproducible method for measuring the surface tension than the classical selected plane technique of pendant drop tensiometry⁴⁶ that uses only the diameters of a photographed drop at two locations are used.

The aim of this chapter is to use pendant drop tensiometry enhanced by video image digitization to examine the unsteady adsorption of surface active molecules onto a fluid/fluid interface. When a fresh surface is created initially in a liquid medium containing surfactant molecules, surfactant in the sublayer adjacent to the surface kinetically adsorbs onto the interface. This depletes the concentration in the sublayer and gives rise in the liquid to a diffusive flux of surfactant toward the surface. Surface eventually

becomes saturated with surfactant; as this driving force for kinetic adsorption becomes zero, the bulk phase returns to a uniform concentration of surfactant. The adsorption of surfactant onto the interface lowers the interfacial tension, and therefore the coupled sorptive and diffusive process can be studied experimentally by measuring the interfacial tension relaxation.

The experimental measurement of surface tension relaxation due to surfactant adsorption and the calculation of diffusion coefficients or sorptive kinetic constants from these measurements have been undertaken using many techniques. These are of three types: (i) methods involving hydrodynamic flow, (ii) static techniques involving no fluid convection and (iii) surface oscillation techniques. Methods involving flow are useful for studying adsorption processes that occur on time scales of the order of milliseconds to seconds, while static methods are most accurate on scales of the order of seconds to hours. Oscillation techniques can resolve time scales of the order of milliseconds to several minutes.

Some of the methods involving convection used here are: oscillating jet technique,^{4,21,22} maximum bubble pressure method,^{12,24,25,27} free falling film²⁸ or inclined plate technique,⁸ drop volume or weight method,^{30,31} (reversed) funnel method.³² The convection differs in each of these techniques: For the oscillating jet, the fluid issues through an orifice, for the inclined plane method liquid flows with a free surface down a plane, and for the maximum bubble pressure and drop volume methods the surfactant solution expands radially in the vicinity of the interface. In these methods, diffusion coefficients or kinetic constants are generally obtained by: (i) identifying an exposure time t , for which the surface has been in contact with the surfactant solution; (ii) measuring the surface tension for that time; and (iii) computing the adsorption theoretically by solving the surfactant mass transfer to the interface. In most cases, convection is ignored altogether, and

theoretical solutions used to compare with the data are the planar diffusion controlled result of Ward and Tordai³ (and only for short and long contact times). For the maximum bubble pressure and drop weight methods, however, theoretical equations have been constructed to account for the radial convection induced by the drop growth.^{9,30,33} Theoretical solutions of these convection equations have been compared with short-time experimental data to obtain diffusion coefficients.⁹

The static methods used for the measurement of the surface tension relaxation are the Whilhelmy plate and Du Nouy ring method,³⁴ the static drop volume method³⁵ and the pendant drop technique.^{36,37} These have the advantage that surfactant transfer in the bulk can be described accurately by diffusion alone. Relaxation data from the plate and ring methods¹⁰ and the static drop volume technique¹¹ have been compared with the short-time solution of Ward and Tordai to determine diffusion coefficients. Intermediate times were comared¹⁰ approximately by regarding the intermediate time solution for the surface concentration as linear in $\log t$ and deducing the diffusion coefficient from the shift of the experimental data for the adsorption (plotted as $\log t$ and regarded as linear) from the theoretical curve.

Primary surface oscillation techniques are the longitudinal wave method of Lucassen³⁸⁻⁴¹ and the oscillating bubble technique.^{42,43} The longitudinal wave method, when undertaken using small lateral oscillations of the interface creating small deviations from equilibrium, has the advantage that a perturbative analytical solution can be developed for the oscillation of the surface tension as a function of the surfactant mass transfer and hydrodynamic motion. Using this method, diffusion controlled adsorption was demonstrated for decanoic acid and several surfactants of the ethylene oxide adduct type³⁸⁻⁴⁰ for a range of frequencies of 10^{-2} and 10 s^{-1} .

Before the advent of video digitization, classical pendant drop tensiometry was not used to obtain surface tension relaxation profiles

because sequential photography is cumbersome. With video digitization, however, sequential profiles in time can readily be obtained and stored. The goals of this chapter are twofold. The first is to demonstrate that by sequential digitization, video-enhanced pendant drop tensiometry can be used to accurately determine surface tension relaxation profiles. The second is to employ a diffusion controlled test surfactant system (Triton X-100 in water) and to show how relaxation profiles determined by this method can be used to evaluate the diffusion coefficient and to set lower bounds on the kinetic constants. In this regard, the coupled sorption and diffusion equations are solved numerically and compared with the experimental profiles for the entire length of the relaxation time. As will be shown, this allows for a more reliable and reproducible measure of the diffusion coefficient.

This chapter first details the experimental apparatus used for the video enhanced pendant drop tensiometry measurements and the algorithm from which the surface tension is computed. Next the theoretical framework for the surfactant mass transfer process and the numerical solution procedure are discussed. Subsequently, the experimental relaxation profiles are compared with the diffusion-limiting mass transfer solutions, which leads to the computation of the diffusion coefficient. Finally, the reasons for the discrepancy between the experimental and theoretical relaxation profiles are explained.

3.2 Experimental Measurement Technique

3.2.1 Apparatus

The equipment shown in Figure 1 is used to create a silhouette of a pendant drop, to video image the silhouette, and to digitize the image. The equipment consists of an image forming and recording system, a drop-forming system, and a video image profile digitizer.

The image forming and recording system consists of a light source (a halogen lamp with constant light intensity), a plano-convex lens system for producing a collimated beam, a quartz cell enclosed in a thermostatically controlled chamber, an objective lens (effective focal length 60 mm, $f/\#$ 7.1), and a solid-state video camera (CCD-71 series, Dage-MIT Inc.). The drop onto the active area of the camera is magnified approximately $\times 1.5$. The drop-forming system consists of a stainless steel inverted needle (ID=0.016 inch) which is connected to the normally closed port of a three-way miniature solenoid valve (Lee Co.) via 1/16" ID teflon tubing. The common port of the valve is connected by the same teflon tubing to a gas-tight Hamilton syringe placed in a syringe pump (Sage Instruments). The valve is controlled by the output signal of a D/A Data Translation card (DT2801) installed on a IBM-PC AT. The video image digitizer (DT 2861 Arithmetic Frame Grabber, Data Translation), also installed on the backplane of the AT, digitizes the picture into 480 lines $\times$ 512 pixels and assigns to each one a level of grey with eight bit resolution. Note that the maximum rate with which an image can be digitized is 1/30 of a second.

An edge detection routine was devised in the following way. An example of an original digitized image is shown in the inset of Figure 3-2. Figure 3-2 shows a change in the grey level from the black inside (0 level) to the bright outside (255 level) in a few pixels. This change is not a step increase from 0 to 255, but is continuous. The fact that it is not a step increase can in principle be attributed to the fact that the light is not exactly parallel and the refraction of light around the bubble. However, the calibration images of the stainless-steel ball (see below) also exhibited a similar grey level variation. Since refraction in this case is minimal, the grey level change in both the bubble and sphere cases may be attributed principally to the imperfection in the light source. It is probable that nonparallel rays are randomly distributed; such a distribution will create, around the true edge of the drop, a symmetric

distribution in the grey level. A close inspection of Figure 3-2 indicates that the variation is symmetric around 127.5, and therefore the true edge should be located by identifying the symmetry point. It also indicates that in the immediate vicinity of 127.5, the change is nearly linear. Therefore, the drop edge is obtained by first interpolating a straight line between the two points that bound the grey level 127.5. The edge is defined as the x or z position which, for the interpolated line, corresponds to an intensity of 127.5. Note that the location procedure is performed in the coordinate direction in which the normal to the surface has the larger component. Thus, near the apex the edge location is done along the z direction while near the sides of the drop it is done along the x direction.

The image forming system was calibrated by digitizing a stainless-steel sphere with a known diameter of $1.581 \text{ mm} \pm 1 \text{ }\mu\text{m}$. The coordinates of the digitized sphere were processed to calculate the average length between pixels along a row and along a column. The calibration procedure yielded values of 0.10096 pixel/ μm horizontally and 0.12817 pixel/ μm vertically. The origin of this asymmetry is in the positioning of the active picture elements on the pickup area of the CCD camera. The camera used (CCD-71 from Dage Instruments, Inc.) has a pickup area 8.8 mm (horizontal) and 6.6 mm (vertical), and 510 picture elements arranged horizontally and 492 vertically. Thus, the number of pixels per unit length is smaller in the horizontal direction.

3.2.2 Materials and Methods

The surfactant that was dissolved in the aqueous phase was Triton X-100, $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ($n=9-10$), obtained from Aldrich Chemical Co. and used without modification. The water, with which the aqueous solutions were made was purified via a Millipore water purification system, with the output water having a specific conductance of $0.056 \text{ }\mu\text{S/cm}$. The pendant drop phase is either air or

fluorocarbon oil (FC-43, Sigma Co.). Acetone (HPLC grade) used to verify the measurement was obtained from Fisher Scientific Co.

The experimental protocol was as follows: The quartz cell was initially filled with the aqueous solution, and the drop forming needle was positioned in the cell in the path of the collimated light beam. At this point, the solenoid valve was not energized. The syringe pump was turned on, and the fluid in the syringe (either air or fluorocarbon oil) was allowed to pass through the normally open port of the valve. Via input from the keyboard, the D/A card energized the valve and allowed the fluid to pass through the needle, thereby forming a bubble of air or a drop of oil. The valve was then closed (also by input from the keyboard) when the drop achieved a diameter of approximately 2 mm. The drop so created is one of constant mass, and the change in volume as the surface tension relaxes is only a few percent over a time period of a 2-3 h. The time required to create an air bubble of this size is ≈ 2 s, and that for the oil drop ≈ 4 s. Sequential digital images were then taken of the drop, first at intervals of approximately 1 s, and then later in intervals of the order of tens of seconds. All experiments were undertaken at $22.0 \pm 0.5^\circ\text{C}$. After the surface tension relaxation was complete, the images were processed to determine the drop edge coordinates.

3.2.3 Surface Tension Calculated From the Drop Profile

The classical Laplace equation relates the pressure drop across a curved interface

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \quad (1)$$

where γ is the boundary tension, R_1 and R_2 are the two principal radii of curvature of the surface, and ΔP is the pressure difference across the interface. For the pendant drop geometry, Eq. 1 can be recast as a set of three first-order differential equations for the spatial positions x and z and turning angle ϕ of the interface as a function

of the arc length s . Nondimensionalizing by the radius of curvature at the apex ($x'=x/R_0$, $z'=z/R_0$, and $s'=s/R_0$), the first-order equations have the following form:⁵²

$$\begin{aligned}\frac{d\phi}{ds'} &= 2 + Bz' - \frac{\sin\phi}{x'} \\ \frac{dx'}{ds'} &= \cos\phi \\ \frac{dz'}{ds'} &= \sin\phi\end{aligned}\quad (2)$$

where B defines the Bond number or capillary constant and is given by $\frac{\Delta\rho g R_0^2}{\gamma}$ and $\Delta\rho$ is the density difference between the fluids and g is the gravitational acceleration constant. The equations are subject to the boundary conditions $x'(0)=z'(0)=\phi(0)=0$. Equation 2 is integrated by using a fourth-order Runge-Kutta scheme initialized with the approximate solution $z' = \frac{-2}{B} [1 - J_0((-B)^{1/2}x)]$ which is valid near the apex⁵³ where $\phi \ll 1$. (Here $J_0(x)$ is the Bessel function of the first kind.)

The surface tension is computed from the data and the theoretical curve in the following way. An objective function E is defined as the sum of squares of the normal distance d_n between the measured points u_n and the calculated curve v obtained from the integration of Eq. 2 (i.e., $E = \sum_{n=1}^N [d_n(u_n, v)]^2$; N is the total number of experimental points). The objective function depends on four unknown variables, X_0 and Z_0 , the actual location of the apex, R_0 and B . To obtain the optimum congruence between the theoretical curve and the data points, the objective function is minimized with respect to the four parameters ($\frac{\partial E}{\partial q_i} = 0$, $i=1,2,3,4$). Minimization equations are solved by applying directly the Newton-Raphson method, and from the optimum values of R_0 and B the tension γ can be computed.

From the data sets, there are approximately 600 measured coordinates of the drop edge for each image, with $R_0 \approx 1$ mm. To obtain d_n for each point, first a theoretical curve consisting of 6000 points is generated, and then d_n is computed as the distance from the

experimental point to the closest of the discrete theoretical points. The Newton-Raphson procedure is arrived at in the following way: X_0 is initially guessed as the centroid of the 600 x location data points, and Z_0 as the average of the three lowest z coordinates. Initial guesses for R_0 and B are obtained by using the selected plane method for pendant drops.^{46,48} The equatorial diameter (d_e) and the diameter (d_s) in a selected plane at a distance d_e from the apex to the drop are obtained from the raw data. By integrating Eq. 2 for different values of B, graphs can be constructed of B, d_e/R_0 , and $B(d_e/R_0)^2$ ($=H$) as a function of d_s/d_e ($=S$). The Misak correlation⁵¹ correlates $1/H$ as a function of S. As S is known from the raw data, H and therefore γ can be obtained. A separate correlation is constructed of B as a function of S; with the knowledge of γ , an initial guess for R_0 can be obtained. Two to five iterations are necessary for the program to converge, and the standard deviation of the distance between a measured point and the calculated curve is about 0.1 pixel ($\approx 1 \mu\text{m}$). Error analysis and curve fitting of a typical run are shown in Figures 3a and 3b.

An estimate for the error involved in the measurement of the surface tension may be constructed as follows. The error in the location of the edge at each edge coordinate may be estimated to be 0.1 pixel since it is the standard deviation of the exact theory (Eq. 2) from the experimental data. A random number generator is used to create a set of random numbers with an average value of zero and a standard deviation of 0.1 pixel. The program that computes the surface tension as a function of the edge coordinates is run with a set of data, in which each edge coordinate of a sample run is perturbed by an element of the random number set. The assignment of the perturbation was done such that in the region surrounding the apex of the drop the z location is perturbed, while the x coordinate is perturbed for the remaining data points. The results for several random number sets

indicate a deviation from the computed value of γ for the unperturbed data set of less than ± 0.1 mN/m.

This measurement technique was verified by measuring the surface tension of air/water and air/acetone. The values of the surface tension obtained from this work as compared with that reported in the literature⁵⁵ are shown in Table 1. A conservative estimate for the reproducibility of these measurements is ± 0.1 mN/m, and as this is in agreement with the error estimate, a value of 0.1 mN/m may be assigned to the accuracy of the measurements reported here. With this bound, the values of γ measured for air/water and air/acetone agree with the literature values.

In unsteady experiments, the relaxation in the surface tension causes the bubble shape to elongate. This elongation is considerable: As an example consider a relaxation in surface tension from 70 to 49 mN/m; the edge data for such a relaxation shows that the location of the apex moves 21 pixels in the z direction. Note that this change is much larger than the 0.1 pixel standard deviation distance between the experimental points and the fitting curve.

3.3 Theoretical Framework

Discussed in this section are the theoretical framework describing the unsteady adsorption of surfactant onto a pendant drop interface and its effect on the interfacial tension. The pendant drop is treated as a spherical drop surrounded by an infinite medium containing a surfactant.^{56,57} The surfactant is assumed not to dissolve into the drop phase. Mass transfer to an initially clean drop surface is described by Fick's law,

$$D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}) = \frac{\partial C}{\partial t} \quad (r > b, t > 0) \quad (4)$$

(in which the diffusion is assumed to be spherically symmetric and convection effects are neglected) with boundary and initial conditions

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

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

$$\begin{aligned}\frac{d\Gamma(t)}{dt} &= D\left(\frac{\partial C}{\partial r}\right) & (r=b, t>0) \\ \Gamma(t) &= 0 & (t=0)\end{aligned}$$

Where r and t are the spherical radial coordinate and time, D denotes the diffusion coefficient, $C(r,t)$ the bulk concentration, $\Gamma(t)$ the surface concentration, b the drop radius, and C_0 the concentration far from the drop. By the Laplace transform, the solution to the above set of equations can easily be formulated in terms of the unknown subsurface concentration $C_s(t)=C(r=b,t)$:

$$\Gamma(t) = \frac{D}{b} [C_0 t - \int_0^t C_s(\tau) d\tau] + 2\left(\frac{D}{\pi}\right)^{1/2} [C_0 \sqrt{t} - \int_0^t C_s(t-\tau) d\sqrt{\tau}] \quad (5)$$

or in nondimensional form:

$$\Gamma'(t') = \frac{h}{b} [t' - \int_0^{t'} C'_s(\tau) d\tau] + \left(\frac{2}{\pi}\right) [\sqrt{t'} - \int_0^{t'} C'_s(t'-\tau) d\sqrt{\tau}]$$

where $\Gamma'=\Gamma/\Gamma_0$ (Γ_0 is the equilibrium surface concentration at the bulk concentration C_0), $C'_s=C_s/C_0$, $t'=\frac{t}{h^2/D}$ and $h=\Gamma_0/C_0$ is the adsorption depth.

Note that this result differs from the classical solution of Ward and Tordai³ for the unsteady diffusion toward an initially clean planar surface by the extra term $\frac{h}{b}[t' - \int_0^{t'} C'_s(\tau) d\tau]$, which accounts for the interface curvature. It will be shown later that this term plays an important role for long times.

To complete the solution for the surface concentration, the sorption kinetics must be specified. The model used here utilizes the Langmuir formalism in which on a liquid surface there is a finite number of adsorption sites, as for a solid surface. The adsorption rate is proportional to the concentration of surfactant C_s just below the surface and the fraction of surface area unoccupied, while the desorption rate is proportional to the fraction of the area covered by adsorbed surfactants. Thus

$$\frac{d\Gamma}{dt} = \beta \exp(-E_a/RT) C_s (\Gamma_\infty - \Gamma) - \alpha \exp(-E_d/RT) \Gamma \quad (6a)$$

where β , α , E_a , E_d are the preexponential factors and the energies of activation for adsorption and desorption, respectively, Γ_∞ is the

saturated surface concentration, T is the temperature and R the gas constant.

The activation energies for adsorption and desorption are assumed to depend on the surface coverage, and here a linear dependence is used.⁵⁸ Thus,

$$\begin{aligned} E_a &= E_a^0 + \nu_a \Gamma \\ E_d &= E_d^0 + \nu_d \Gamma \end{aligned} \quad (6b)$$

where E_a^0 , E_d^0 , ν_a and ν_d are constants. At equilibrium, the time rate of change of Γ vanishes and gives

$$\Gamma = \frac{\Gamma_\infty C_s}{a \exp(k\Gamma/\Gamma_\infty) + C_s} \quad (7)$$

where

$$a = \frac{\alpha \exp(-E_d^0/RT)}{\beta \exp(-E_a^0/RT)} = \bar{\alpha}/\bar{\beta} \quad \text{and} \quad k = (\nu_a - \nu_d)\Gamma_\infty/RT$$

Equation 7 is the Frumkin adsorption isotherm,²⁰ which relates the subsurface and surface concentrations. Equation 7 becomes the Langmuir adsorption isotherm when $\nu_a = \nu_d = k = 0$.

When the surfactant solution can be considered ideal, the Gibbs adsorption equation $dy = -\Gamma RT d \ln C$ and the equilibrium isotherm allow for the calculation of the surface tension explicitly in terms of Γ :

$$\begin{aligned} \gamma_0 - \gamma &= -\Gamma_\infty RT \left[\ln(1-y) - \frac{1}{2} ky^2 \right] \\ &= \Gamma_\infty RT \left[y + \frac{1}{2} (1+k)y^2 + \frac{1}{3} y^3 + \frac{1}{4} y^4 + \dots \right] \end{aligned} \quad (8)$$

where $y = \Gamma/\Gamma_\infty$, and γ_0 is the clean surface tension. Equation 8 is the Frumkin equation⁵⁹ with an extra $ky^2/2$ term on the right hand side representing the linear dependence of activation energies for adsorption and desorption on the surface coverage. Equation 8 of course is only strictly true at equilibrium. By fitting equilibrium data of the surface tension as a function of the bulk concentration using Eqs. 7 and 8, the equilibrium constants k and a , and the maximum coverage Γ_∞ can be obtained. It is also assumed here for the nonequilibrium relaxation process that Eq. 8 gives the unsteady surface tension $\gamma(t)$ as a function of the unsteady coverage $\Gamma(t)$ obtained from the solution of the transport equations (Eq. 5 and 6).

Equations 5 and 6 must be solved numerically. The technique used is similar to that used by Miller and Kretzschmar,⁶⁰ and is described as follows. First, the convolution integral of C_s in Eq. 5 is integrated by first partitioning the interval $(0,t)$ into intervals of size δ in time, and integrating separately each interval by assuming a linear relation in time for C_s .

$$\begin{aligned} \int_0^t C_s(t-\tau)/\sqrt{\tau} \, d\tau &= \sum_{i=0}^{n-1} \int_{i\delta}^{(i+1)\delta} \{ [C((n-i-1)\delta) - C((n-i)\delta)]\tau/\delta \\ &\quad + [(i+1)C((n-i)\delta) - iC((n-i-1)\delta)] \} / \sqrt{\tau} \, d\tau \\ &= \left[\frac{4}{3} C(n\delta) + \frac{2}{3} C((n-1)\delta) \right] \sqrt{\delta} \\ &\quad - \sum_{i=1}^{n-1} \frac{2}{3} [C((n-i)\delta) - C((n-i-1)\delta)] [(i+1)^{3/2} - i^{3/2}] \sqrt{\delta} \\ &\quad + \sum_{i=1}^{n-1} 2 [(i+1)C((n-i)\delta) - iC((n-i-1)\delta)] [(i+1)^{1/2} - i^{1/2}] \sqrt{\delta} \end{aligned} \quad (9)$$

After integration, Eq. 5 is of the form

$$C_s(t_n) = b_1 \Gamma(t_n) + b_2 \quad (10)$$

where $t_n = n\delta$.

The next step in the numerical procedure depends upon whether the sorption kinetics is finite or not. If the kinetics were infinite and the mass transfer is only diffusion controlled, then $\Gamma(t)$ were calculated by substituting C_s in Eq. 10 into Eq. 7. After that, the dynamic surface tensions were obtained from Eq. 8. If, however, sorption kinetics are finite, then the equation $C_s(t_n) = b_1 \Gamma(t_n) + b_2$ must be solved simultaneously with Eq. 6 to obtain $\Gamma(t_n)$, and finally $\gamma(t_n)$ from Eq. 8. Eq. 6 is solved by assuming $C_s(t)$ is constant in each time interval, and then, for that interval, integrating Eq. 6 numerically.

3.4 Results

Relaxations in the surface tension due to Triton X-100 adsorption were measured at the air/water interface. The data were recorded from one second up to a few hours. Figure 4 shows representative dynamic surface tension profiles (against air) of Triton X-100 aqueous solutions at six different bulk concentrations. The reproducibility of

these profiles is shown in Figure 5 together with the results of several pendant bubbles at three fixed concentrations. To demonstrate the applicability of the method to liquid/liquid interfaces, relaxation profiles at the fluorocarbon oil/water interface were obtained at two different concentrations of Triton X-100 solutions, Figure 6.

The equilibrium surface tensions for aqueous Triton X-100 solutions at the aqueous/air interface are extracted from the long time asymptotes in Figure 4, and are plotted as the symbols in Figure 7. The isotherm described by Eqs. 7 and 8 can be fitted to the data by varying the values of Γ_{∞} , a and k . The results are given as the solid line in Figure 7; the constants are $\Gamma_{\infty}=3.20 \times 10^{-10}$ mol/cm², $a=3.11 \times 10^{-10}$ mol/cm³, and $k=2.52$. From the figure, the CMC for Triton X-100 at the aqueous-air interface can be inferred to be approximately 2.3×10^{-7} mol/cm³.

It should be noted that by taking into account the fact the energies for adsorption and desorption depend on the surface coverage (Eq. 6b), a much better fit of the equilibrium data is achieved at the low concentrations than the $k=0$ von Szyszkowski's equation ($\gamma=\gamma_0 - RT\Gamma_{\infty} \ln(1+C/a)$). The von Szyszkowski's fit is given as the dotted line in Figure 7 with constants $\Gamma_{\infty}=2.91 \times 10^{-10}$ mol/cm² and $a=6.62 \times 10^{-10}$ mol/cm³. From the definition of k , a positive value may be interpreted in the following way: at increasing surface coverage, work is required to insert additional surfactant molecules onto the surface, and therefore the desorption rate increases relative to that of adsorption.

If the relaxation of Triton X-100 were assumed to be diffusion controlled, Figures 4 and 5 may be used to determine a diffusion coefficient for the surfactant molecule in the aqueous phase. A candidate profile for this determination must have certain characteristics. The first is that the relaxation should not be too fast. Since the time scale for the diffusional relaxation process is

of the rh^2/D , higher concentrations yield faster relaxations. From Figure 4 it is clear that the profiles of the highest two concentrations (i.e. 4.64×10^{-8} and 1.24×10^{-7} mol/cm³) fall off too rapidly for any accurate analysis. Second, the asymptote of the relaxation should differ substantially from the clean surface tension, so that errors in the measurements at particular times remain small in comparison to the overall change in the surface tension. Since this requires the bulk concentration not to be too small, the three middle bulk concentrations are used to determine the diffusion coefficient.

Theoretical diffusional relaxations, described previously, are given in Figure 5 for the three middle concentrations of Figure 4. To obtain these curves, the radius of the drop (b) was set equal to the curvature R_0 at the apex. In addition, these curves were obtained using a value of 2.6×10^{-6} cm²/s for the diffusion coefficient, a value which minimizes, for all these concentrations, the difference between the theoretical and the experimental profiles. To examine the sensitivity of this determination of D, Figure 8 graphs the standard deviation as a function of the diffusion coefficient for two pendant bubbles at each of the three bulk concentrations. From this study, the average value of D is 2.6×10^{-6} cm²/s, and the standard deviation is 0.14×10^{-6} cm²/s. A value of D of $2.6 \pm 0.3 \times 10^{-6}$ cm²/s (the accuracy being estimated by twice the standard deviation) compares favorably with the range of $1.9-2.3 \times 10^{-6}$ cm²/s obtained for a similar concentration range by Van hunsel et al.³¹ using the drop volume method.

Two important characteristics of these theoretical profiles and their relationships with the experimental data should be noted: First for the spherical model it could be argued that since the ratio of the adsorption depth to the drop radius is small for the three concentrations used for theoretical matching ($h/b = 0.36, 0.24$ and 0.16 for $C_0 = 9.89 \times 10^{-9}, 1.55 \times 10^{-8}$, and 2.32×10^{-8} mol/cm³, respectively), only the planar Ward and Tordai expression is

necessary. Figure 9 shows the ratio (r_s) of the spherical term ($\frac{h}{b}[t' - \int_0^{t'} C'_s(r) dr]$) to that of the entire expression for $\Gamma'(t)$ for diffusion controlled adsorption using a Langmuir isotherm. In the nondimensional formulation, two dimensionless parameters appear, $h/b = (\Gamma_0/C_0)/b$ and C_0/a ; in the curves of Figure 9, a , b and Γ_∞ are held constant, and C_0 is varied generating different values for h/b (and C_0/a). The curves indicate that for times much less than h^2/D ($t' \ll 1$), the planar result is sufficient even for relatively large h/b . More importantly, however, they indicate that no matter how small the value of h/b , there are long nondimensional times for which the spherical term becomes important. This reflects the physical fact that for long enough time, the diffusional flux to the interface lowers the bulk concentration far outside the adsorption depth, and the process is thereby affected by the bulk geometry. In the experimental relaxations which are fitted, h/b is of the order of 10^{-1} , and therefore the spherical term becomes important ($r_s > 0.1$) after one nondimensional unit or 10^2 s (since h^2/D is of the order of 10^2 s). Figure 5 shows that there are many data points after 10^2 s, and therefore the use of the planar result to fit these points would yield values of the diffusion coefficient which would be too large because the spherical term is positive. For example, using the planar result, the analogue of Figure 8 yields a value of $3.4 \pm 0.5 \times 10^{-6}$ cm²/s for the diffusion coefficient of the Triton X-100 molecule.

Second, the diffusion fits of Figure 5 concerns the possibility of estimating the kinetic constants. The model (Eqs. 6a and 6b), there are four constants: $\bar{\alpha}$, $\bar{\beta}$, ν_a and ν_d . However, the fitting of the equilibrium data gives a relationship between $\bar{\alpha}$ and $\bar{\beta}$, and ν_a and ν_d , thus leaving two kinetic constants as undetermined. To simplify the analysis, however, the dependence of activation energies on the surface coverage will be neglected, and the simplified Langmuir kinetics will be used. A Langmuir fit has already been shown for the

equilibrium data (Figure 7); using this type of kinetics to describe unsteady sorption coupled with bulk diffusion involves only one unknown kinetic constant. Detailed in Figure 10 are theoretical curves of the surface tension relaxation in dimensional time for the diffusion limited model, and for several finite values of β for $C_0 = 9.89 \times 10^{-9} \text{ mol/cm}^3$ and $D = 2.6 \times 10^{-6} \text{ cm}^2/\text{s}$. Also plotted on the figure are the data for that particular surfactant concentration. Comparing the finite β curves to the diffusion limited relaxation, it is clear that β is at least as large as $0(5 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, and a corresponding lower bound for $\bar{\alpha}$ ($= a\beta$) is of the order 10^{-1} s^{-1} .

3.5 Discussion and Concluding Remarks

The technique of pendant drop tensiometry enhanced by video imaging is an effective tool for studying unsteady adsorption of surfactant molecules onto both a liquid/gas and a liquid/liquid interface. In principle, the technique is applicable to the study of the adsorption process of any surface active molecule onto a fluid surface as long as the surface activity is strong enough to appreciably lower the surface tension and the bulk concentration is not too high to make a large diffusional flux completes the surface adsorption too quickly.

To obtain quantitative information about the relaxation, the equilibrium adsorption must first be fitted using an isotherm (i.e. $\gamma = f(C_0)$). This isotherm is then used later in the theoretical modeling to obtain the surface tension at a particular point in time in terms of the subsurface concentration at that time (i.e. $\gamma(t) = f(C_s(t))$). This is a particularly crucial step, since if the model fitting of the data were poor, then the value of γ which the model assigns to a particular C_s will be in error. Here a Langmuir formalism was used in which the activation energies for adsorption and desorption depend on the surface coverage (Eqs. 6-8). It was found that by including the dependence of the activation energies on Γ , a much better fit of the

equilibrium data at low concentrations was achieved. The value of k , which best fits the equilibrium data, is for the Triton X-100 molecule, positive and equal to 2.52. It should be noted that the use of this type of isotherm in which activation energies are surface concentration dependent is restricted to values of k larger than -4. For values of k less than this critical one, there exists a bulk concentration for which $\frac{\partial \Gamma}{\partial C}$ becomes infinite and a region for which $\frac{\partial \gamma}{\partial \Gamma}$ becomes positive.

The agreement achieved between the theoretical and experimental relaxations by varying the diffusion coefficient is, on the average, fairly good as reflected by the small values of the standard error at the optimum D (cf. Figure 8). A careful examination of the fits at various bulk concentrations reveals that the deviation between the theoretical and experimental curves increases with the bulk concentration (see also Figure. 8) and that this deviation occurs principally during the middle time interval. In this middle interval the relaxation in the experimental surface tension appears to decelerate. The reasons for this behavior are not completely clear, but it may be conjectured that the slow experimental relaxation during the middle interval is due to the fact that the population distribution of n (the number of ethoxy groups) of the Triton X-100 used is not extremely sharp (cf. a discussion of the molecular weight distribution of Triton X-100 by Rouviere et al.⁶¹ In this case, there is more than one adsorbing species; each species, though most likely having the same diffusion coefficient, has different surface activities because of differing numbers of ethoxy groups. Miller et al.⁶² has examined theoretically the unsteady adsorption of two surfactants with differing surface activity and equal diffusivities. He finds that decelerations and/or plateau behavior in the surface tension relaxation can occur at the middle time intervals, if the surface activities (as measured by the Langmuir-von Szyskowski constant a) differ by an order of magnitude or more.

The use of the data of the entire relaxation curve is important in obtaining the diffusion coefficient. As noted in the Introduction section, most studies use a simpler procedure in which only the short or long contact time experimental data are compared with theoretical constructs. Consider the exclusive use of the short contact time data. As is well known, as $t \rightarrow 0$, the diffusion controlled expression of Ward and Tordai indicates that Γ increases as $\sqrt{t}$:

$$\Gamma(t) \approx 2\left(\frac{D}{\pi}\right)^{1/2} C_0 \sqrt{t} \quad (t \rightarrow 0) \quad (11)$$

The usual approach is to first convert the surface tension relaxation data into a temporal profile of surface concentration by using the equilibrium isotherm, then plot the short time (concentration) values with $\sqrt{t}$, and finally by fitting a straight line through the data, obtain D from the slope using the above equation. If this data reduction were applied, for example, to the short time relaxation profiles of the bulk concentrations of 1.55×10^{-9} and 9.89×10^{-9} mol/cm³ (cf. Figure 4), the short time surface concentration data falls correctly on straight lines in $\sqrt{t}$, and the average diffusion coefficient is fairly close (2.9×10^{-6} cm²/s as opposed to 2.6×10^{-6} cm²/s), but the standard deviation is 0.7×10^{-6} cm²/s as opposed to 0.14×10^{-6} cm²/s. The larger standard deviation reflects the fact that the short time approach is not reproducible because fewer points are used and that the short time data are influenced greatly by variable initial conditions such as momentary convection and initial adsorption during the drop creation period. The short time method has another drawback: as the numerical solution of Eqs. 5 & 7 shows, the departure of the exact solution from the approximate one as given in Eq. 11 becomes larger than 5% when Γ/Γ_0 exceeds 0.1 for $C_0 = 1.55 \times 10^{-9}$ mol/cm³, and 0.4 for $C_0 = 9.89 \times 10^{-9}$ mol/cm³. As C_0 further increases, the cutoff value for Γ/Γ_0 for an error of less than 5% increases to approximately 0.8, but at these higher concentrations the adsorption proceeds too quickly to obtain enough data points corresponding to $\Gamma/\Gamma_0 < 0.8$. For example, in the data taken in this study, except for

the two lowest concentrations (1.55×10^{-9} and 9.89×10^{-9} mol/cm³), the relaxation proceeded too quickly to obtain enough data points which could be used with the short time approximation. Nevertheless, the use of the remaining of the relaxation profile at higher concentrations (1.55×10^{-8} and 2.32×10^{-8} mol/cm³) yielded more accurate values for the diffusion coefficient than the numerical solution for the entire relaxation.

Acknowledgment

This chapter has been published as a paper (Lin et al.⁶³) co-authored with Kevin McKeigue and Charles Maldarelli in AIChE J. The material contained herein is copyright The American Institute of Chemical Engineering Society, 1990.

Table 1
Verification of Measurement

	γ (mN/m)	
	This Study	Literature
Air/Water	72.5 ± 0.1	72.44
Air/Acetone	23.6 ± 0.1	23.45

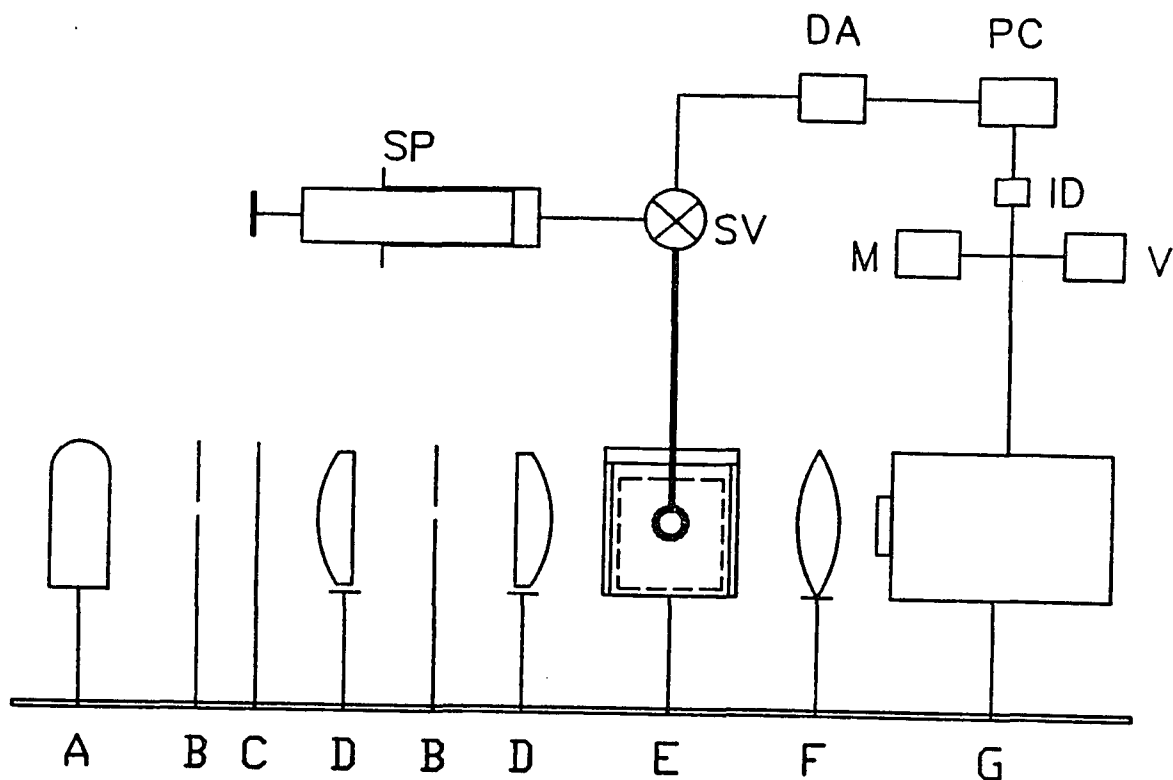


Figure 1. Schematic of the pendant drop tensiometry apparatus and the video image digitization equipment.

A: Light source. B: Pin hole. C: Filter.

D: Plano-convex lens. DA: D/A Data Translation card.

E: Thermostatic chamber, Quartz cell, and suspending needle.

F: Objective lens. G: Video camera. ID: Image digitizer.

M: Monitor. PC: IBM-PC AT. SP: Syringe and syringe pump.

SV: Solenoid valve. V: Video recorder.

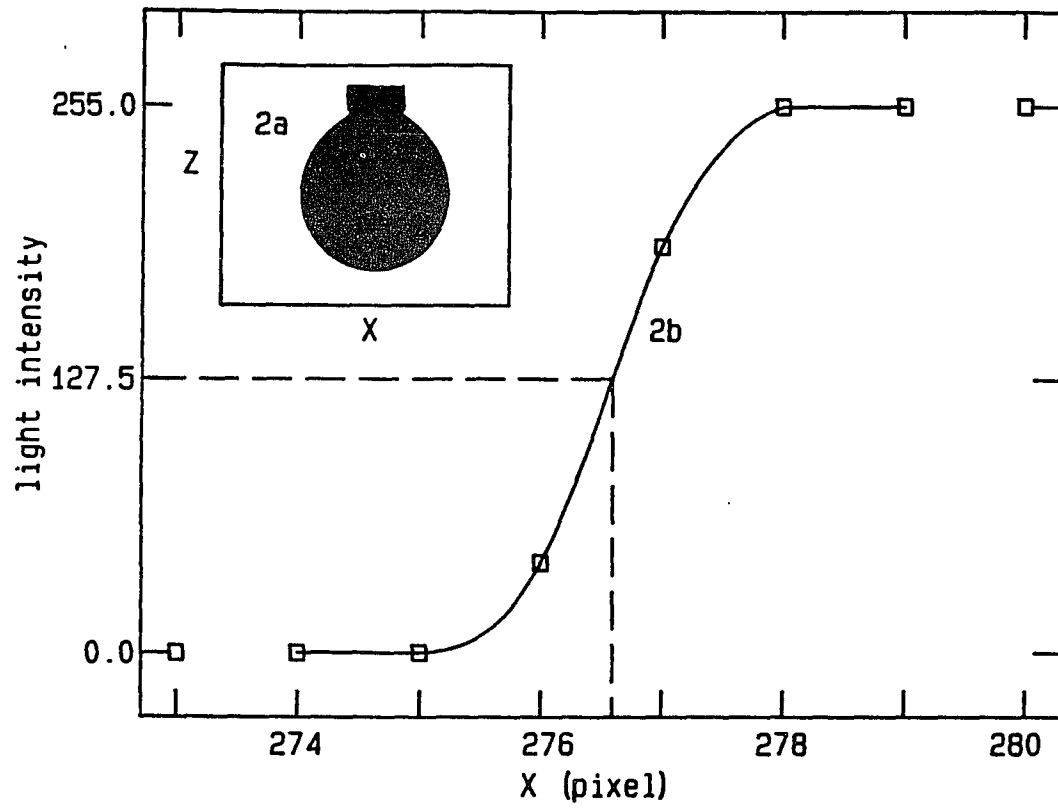


Figure 2 Sample digitized image of air/water interface and edge location determination from digitized image profile.

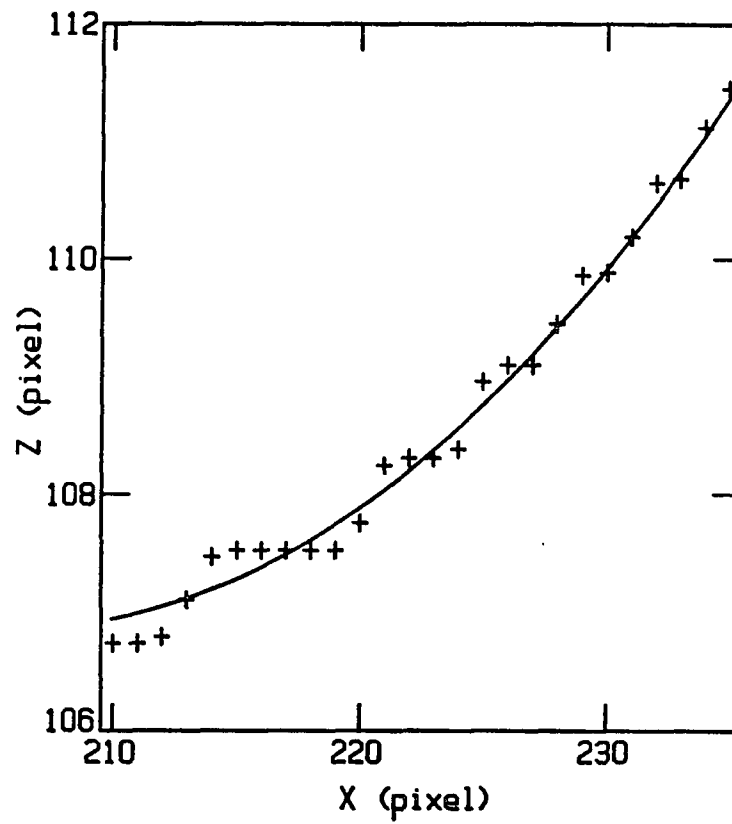


Figure 3a. Young-Laplace fitting of the region near the apex for the sample digitized image of Figure 2a.

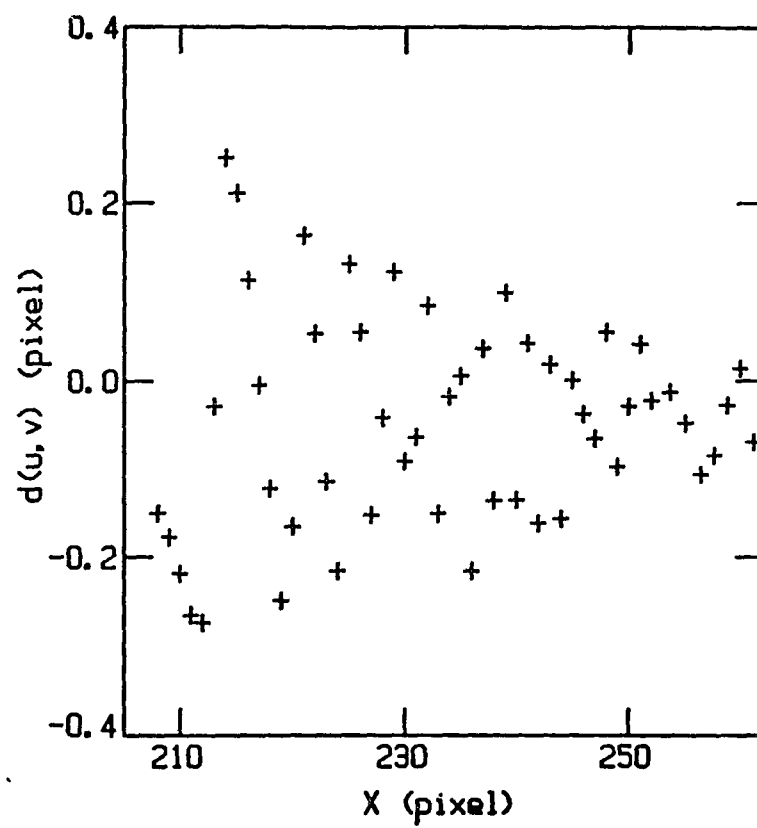


Figure 3b. Error analysis of sample image. Maximum error = 0.28% (of R_0);
Standard error = 0.13% (of R_0)

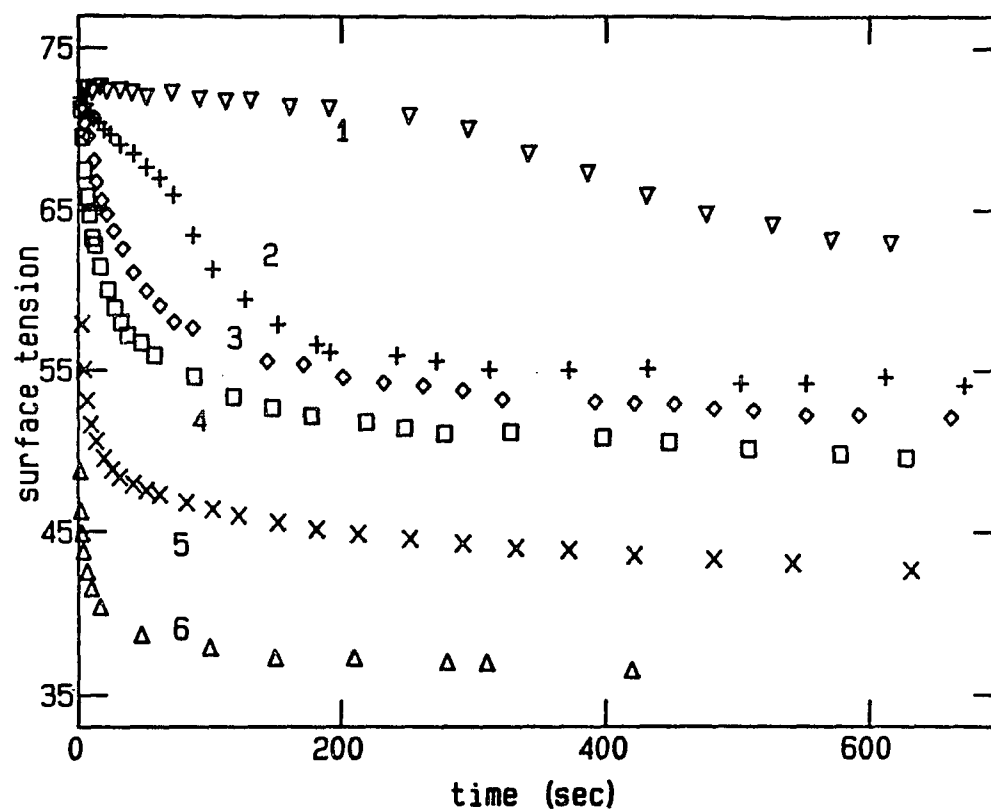


Figure 4. Representative dynamic surface tensions (γ =mN/m) of Triton X-100 solutions for C_0 - (1) 1.55×10^{-9} , (2) 9.89×10^{-9} , (3) 1.55×10^{-8} , (4) 2.32×10^{-8} , (5) 4.64×10^{-8} , and (6) 1.24×10^{-7} mol/cm³.

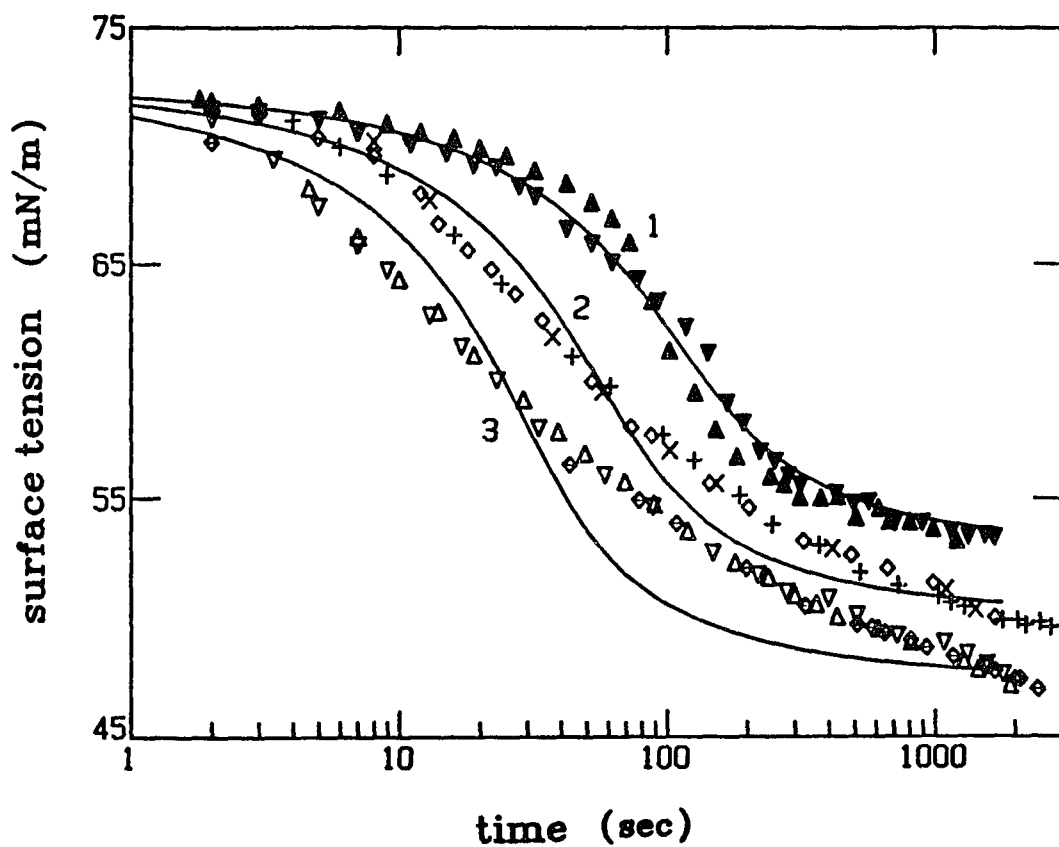


Figure 5. Dynamic surface tensions (γ -mN/m) of Triton X-100 solutions and the theoretical profiles for C_0 = (1) 9.89×10^{-9} , (2) 1.55×10^{-8} , and (3) 2.32×10^{-8} mol/cm³. $D = 2.6 \times 10^{-6}$ cm²/s. Each symbol represents a separate bubble.

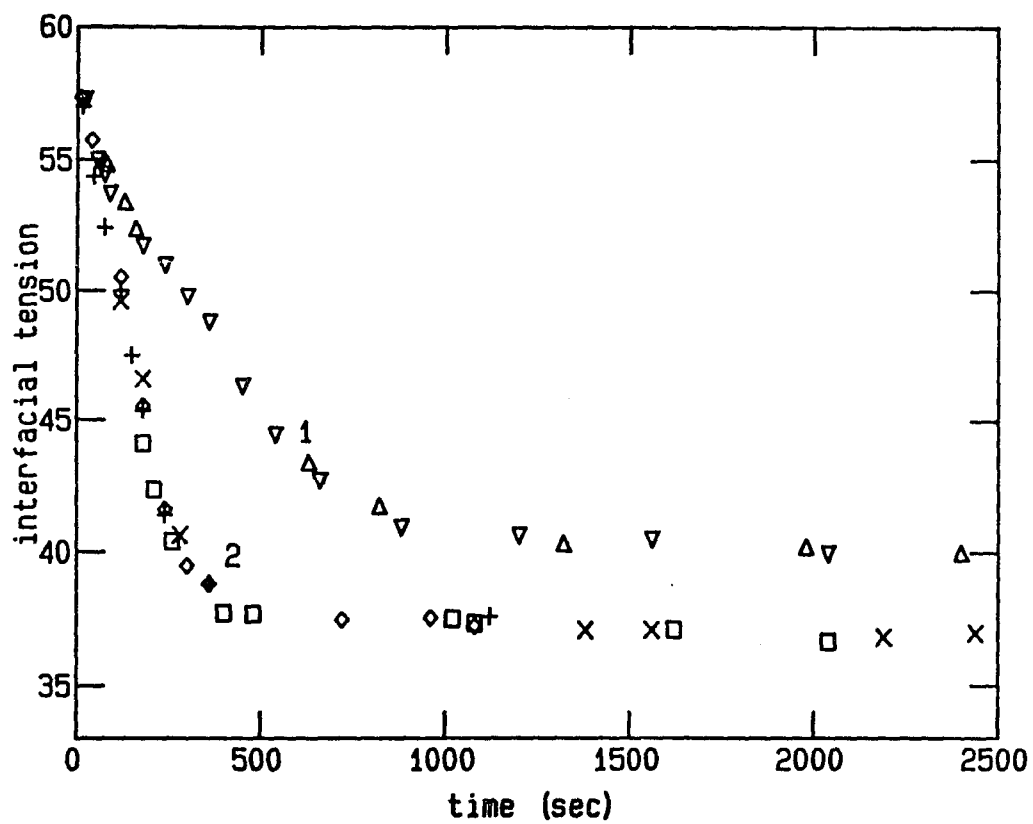


Figure 6. Dynamic interfacial tensions (γ -mN/m) of Triton X-100 aqueous solution against fluorocarbon oil: C_o - (1) 6.18×10^{-10} , and (2) 1.55×10^{-9} mol/cm³.

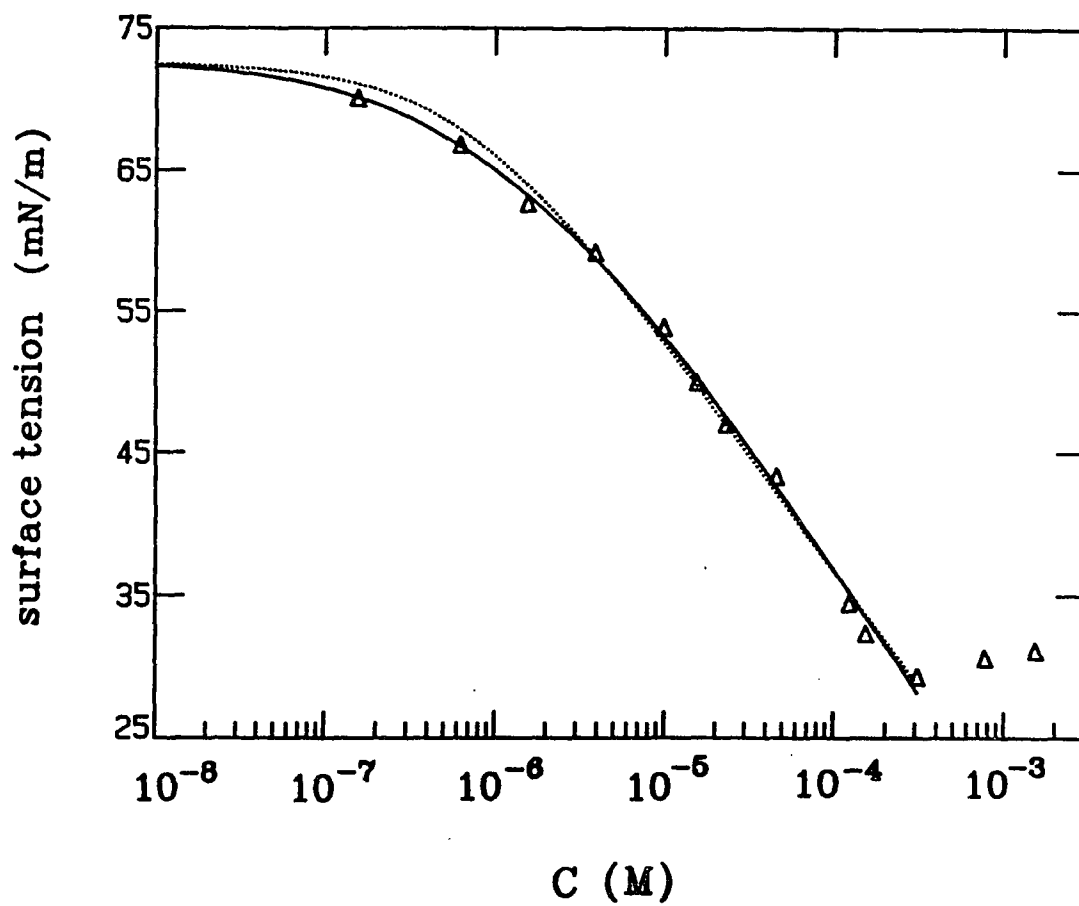


Figure 7. Equilibrium surface tension (γ -mN/m) for air/Triton X-100 aqueous solution. Theoretical fitting by Eqs.(7) and (8) (Frumkin isotherm; solid line) and Langmuir isotherm (dotted line).

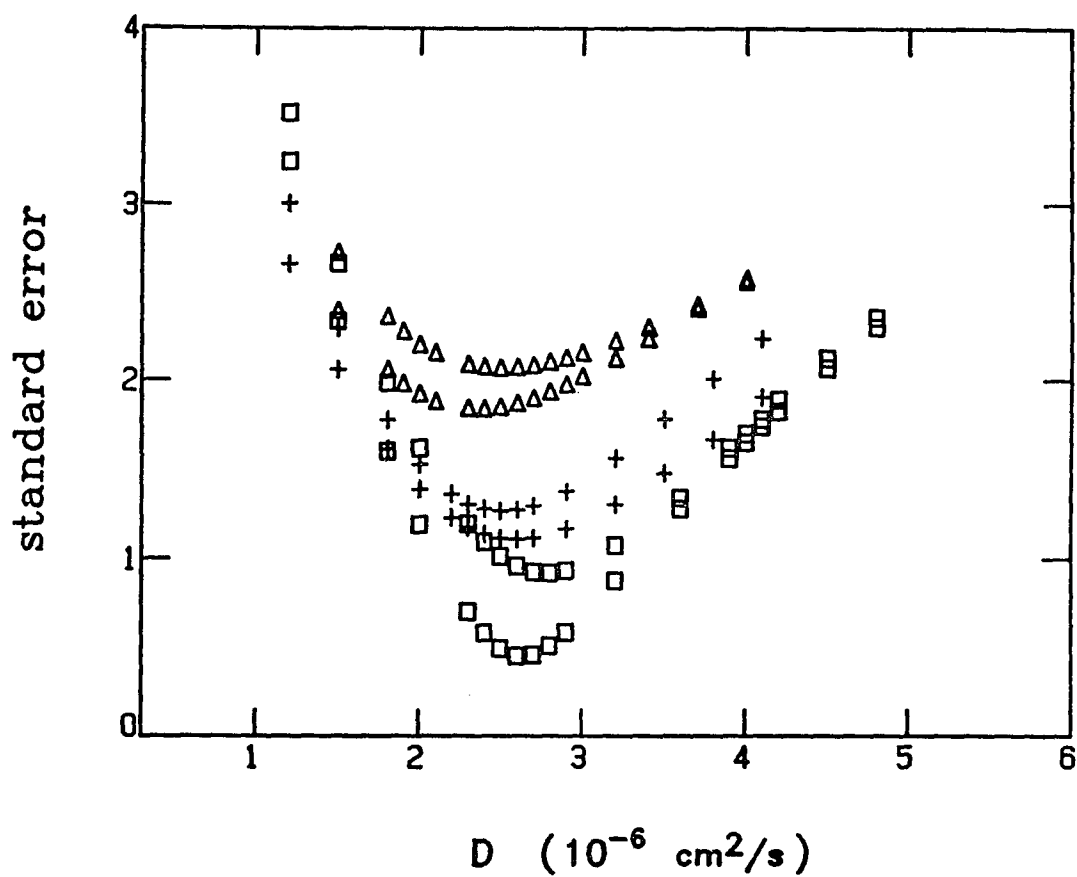


Figure 8. Sensitivity of the standard error of the theoretical solution and the experimental data to the value of the diffusion coefficient.
 (□) 9.89×10^{-9} , (+) 1.55×10^{-8} , (Δ) 2.32×10^{-8} mol/cm³.

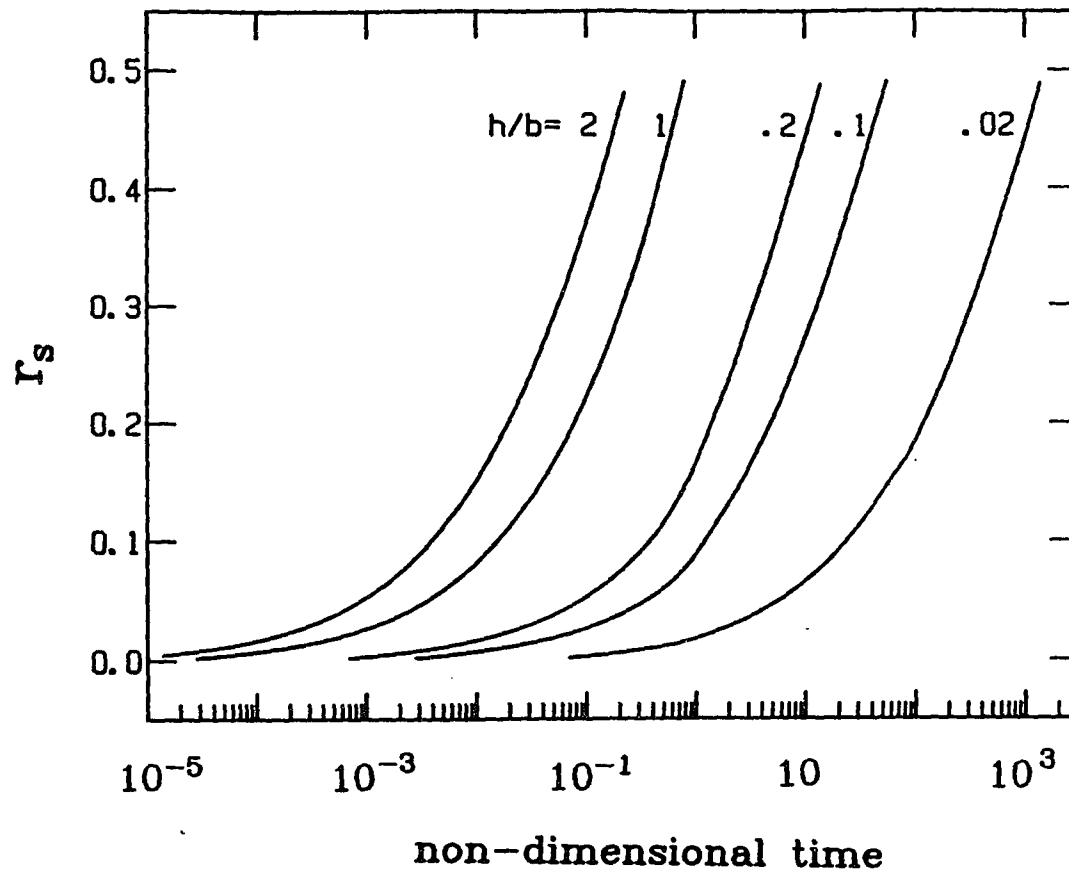


Figure 9. Effect of the spherical term of Eq.(5) in the diffusion controlled adsorption process: $h/b =$ (a) 2, (b) 1, (c) 0.2, (d) 0.1, and (e) 0.01 with $b = 1$ mm, $\Gamma_s = 2.91 \times 10^{-10}$ mol/cm² and $a = 6.62 \times 10^{-10}$ mol/cm³

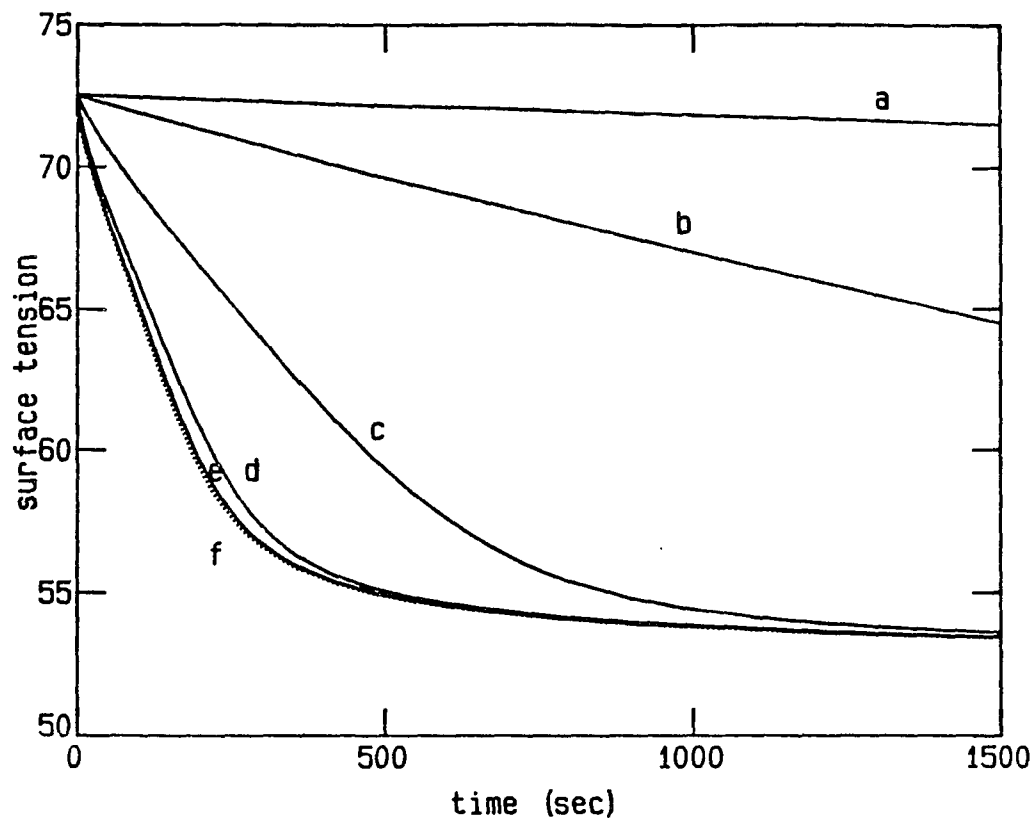


Figure 10. Numerical solutions for the surface tension (γ =mN/m) as a function of time for the mixed transport equation for β = (a) 10^4 , (b) 10^5 , (c) 10^6 , (d) 10^7 , (e) 5×10^7 ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and diffusion limited (f; dotted line). $C_0 = 9.89 \times 10^{-9} \text{ mol/cm}^3$.

CHAPTER 4

Diffusion-Limited Interpretation of the Induction Period in the Relaxation in Surface Tension Due to the Adsorption of Straight Chain, Small Polar Group Surfactants: Theory and Experiment

4.1 Introduction

The relaxation in the surface tension due to surfactant adsorption on a freshly created interface can exhibit a shoulder or plateau region extending from the time of interface formation. This behavior is usually realized under conditions of low bulk concentration and (or) short times after interface creation and usually with surfactants with long, unbranched hydrophobic chains and small sized polar group. After the induction period, the surface tension decreases quickly until it levels off at an extended time during which the equilibrium value is approached. Although they did not call attention to this behavior, the induction period can first be observed in Defay and Hommelen's extrapolation⁴ (toward the clean surface value) of their surface tension relaxation data for the adsorption of higher chain n-alcohols (C_7 - C_{10}) and capric acid at the water-air interface using the oscillating jet and the falling meniscus methods (cf. also the discussion of this work by Defay and Petre⁵). This induction period was first noted and measured in the study of Lucassen-Reynders *et al.*^{40,64} on the adsorption of hexadecyl dimethylammonio propanesulfonate. Several other recent studies have also shown evidence for this behavior in the adsorption of long chain

surfactants: Hua and Rosen²⁷ using both Aerosol OT-100 and N-dodecyl-N-benzyl-N-methylglycine, and the maximum bubble pressure method, Joos *et al.*^{18,19} using lower chain alcohols (C_7 - C_8) and the oscillating jet technique: Zhang and Zhao⁶⁵ using an anionic and cationic mixture (C_8 PyBr- C_{10} SNa) and oscillating jet technique.

The purpose of this paper is to provide an explanation for this shoulder behavior. In general, the relaxation in surface tension due to surfactant adsorption can be understood in terms of an underlying mass transport problem consisting of sorption and bulk diffusion. When a surface is freshly formed in a medium containing a bulk soluble surfactant, surfactant molecules adsorb onto the clean interface and decrease the surface tension. This creates a depletion of surfactant in the sublayer adjacent to the interface, and material therefore diffuses from the undisturbed bulk toward the sublayer. The central argument of this study is that the shoulder behavior reflects a cooperative adsorption/ phase transition process occurring on the surface for these long, straight chain surfactants and that the relaxation rate is determined solely by bulk diffusion with the sorption rates being much faster than those of diffusion. The origins of this argument lie in an examination of the dependence of the equilibrium surface tension (γ) against the bulk concentration (C); this dependence is denoted in this study as γ - $\ln C$ curves.

Consider the isotherm for n-octanol as given in Luckenheimer *et al.*⁴³ and Aratono *et al.*⁶⁶ The data of Luckenheimer *et al.* are reproduced in our Figure 5a and Figure 7 further on as γ against $\ln C$. The slope of this curve increases greatly (in absolute value) over a short concentration range about 10^{-7} mol/cm³. The slope of the γ - $\ln C$ curve, from the Gibbs adsorption equation, is proportional to Γ , the equilibrium surface concentration ($\Gamma = \frac{-1}{RT} \frac{d\gamma}{d\ln C}$). Therefore, the curve

for n-octanol indicates that at a critical surface coverage Γ_c , the surface concentration increases greatly with little change in the bulk concentration and the surface tension. This type of behavior is also observed in the γ - $\ln C$ curves of other long, slender surfactants: n-alcohols in paraffinic oil against water by Lin *et al.*,⁶⁷ tetradecyltrimethylammonium bromide and alkylpolyethoxy sulfate between water and nonpolar oil by Mehreteab and Loprest,⁶⁸ potassium oleate by Somasundaran *et al.*,⁶⁹ and several n-octyl adducts by Aratono *et al.*⁶⁶

The cusp, or near cusp behavior in the γ - $\ln C$ curve is evidence of the development of strong attractive energies between surface adsorbed molecules at increasing surface coverage: As Γ_c is approached, it can be surmised that because of the crowding occurring, the octanol molecules begin to align themselves perpendicular to the interface, thereby creating the geometry for strong van der Waals intermolecular attraction between the hydrocarbon chains. This increasing attraction lowers the desorption rate, and leads to cooperative adsorption as the ratio of the desorption to the adsorption rate decreases with coverage. The intermolecular cohesion, if strong enough, can also lead to the formation of a surface liquid phase. Because of the strong attraction, additional material can exist on the surface with little change in the surface chemical potential. This adsorption at nearly constant chemical potential has two consequences: First, since the bulk is in equilibrium with the surface, the bulk potential and thus the bulk concentration change by only a small amount. Second, the association or phase transition causes the surface pressure to remain nearly constant. Thus the γ - $\ln C$ curve develops a near cusp (or cusp, if a phase transition occurs) as the slope (proportional to Γ) changes greatly with little change in surface tension. Finally after sufficient adsorption (or complete

condensation to a liquid state), it is no longer possible to add surfactant to the surface without large changes in chemical potential. For this region the bulk chemical potential and concentration increase with little change in surface coverage, and the surface tension decreases greatly as the addition of surfactant to an already crowded interface increases significantly the surface potential.

From this point of view, the induction period can be rationalized within the context of diffusion control and continuous equilibrium between the subsurface and surface. At time zero when the surface is created, the surface and sublayer concentrations are both zero, and diffusion begins to bring surfactant toward the surface. Both the sublayer and the surface concentration increase slowly with time, and the surface tension relaxes slowly. At some point the critical concentration is reached on the surface, and additional diffusion increases the surface concentration while maintaining the surface tension and the sublayer concentration as nearly constant. After the surface coverage reaches some higher value, diffusion brings additional material to the surface, but most of this material serves to increase the sublayer concentration with only a small change in coverage. This causes the surface tension to decrease rapidly, signaling the end of the induction period in the relaxation curve, and the beginning of rapid relaxation towards the equilibrium value of γ .

To date, no studies have attempted to specifically ascribe the origin of the induction period to the effects of cohesive forces. Fainerman and Lylyk¹², and Miller and Lunkenheimer¹⁰ recognized that describing the adsorption of octanol, nonanol, decanol and decanoic acid required a surface concentration dependent activation energy for sorption, and they used the Frumkin model. These authors obtained surface tension relaxation data for these surfactants using the static ring method and maximum bubble pressure method, and obtained a mean diffusion coefficient by comparing the data to diffusion limited

theoretical solutions with the Frumkin model for intermediate and short times. Joos and co-workers^{18,19} also examined the relaxation of long chain alcohols. In constructing theoretical models these authors used the Langmuir adsorption model in which sorption activation energies are independent of surface concentration. Specifically, for octanol, nonanol and decanol, they found that the data can be explained by diffusion control. However, the agreement between theory and experiment is not especially good in the short time induction period, presumably because of the neglect of cohesive forces. (Note that in some cases the use of Langmuir isotherm and diffusion control has been shown to give theoretical relaxations in good agreement with experiment, presumably because cohesive effects are not important due to large polar groups or possibly electrostatic repulsion. Examples include sodium myristate and laurate,⁸ dimethyl dodecyl amine oxide,⁹ polyethoxy surfactants,^{9,63} and phosphine oxides.¹¹)

In this paper, the effect of the cohesive forces on diffusion limited relaxation profiles is studied in detail, and, in particular, the way in which cohesion gives rise to an induction period is clearly explained. Two new equilibrium adsorption isotherms (and corresponding equations of state) are constructed to incorporate the influence of cohesion: The first is a cooperativity model in which enhanced adsorption at increasing surface coverage is accounted for by formulating the activation energies for sorption as a power law function of Γ . The second is a phase transition model in which at a critical value of the surface coverage, a liquid phase begins to coexist with monomer state on the surface. The model development is compared with equilibrium and relaxation data for n-decanol (hereafter referred to simply as "decanol") obtained as part of this study using video digitization enhanced pendant bubble tensiometry.

An outline of this chapter is as follows. The model development is given in the next section (Section 4.2). Adsorption isotherms and

equations of state in the absence of phase transition are discussed generally in Section 4.2.1, and from this discussion the power law cooperativity model is developed. Phase transition models have not been extensively studied in the literature, and the one developed for this study is presented in Sec. 4.2.2. Section 4.3 describes briefly the pendant bubble experimental technique, and details the equilibrium and relaxation curves. In Sec. 4.4, the model development is compared with the equilibrium data, and model constants are determined. These fitted models are then used in Sec. 4.5 to predict surface tension relaxation profiles, and these theoretical profiles are compared with the experimentally ascertained ones. This chapter ends with discussion (Sec. 4.6) and summary (Sec. 4.7) sections.

4.2 Model Development

4.2.1 Power Law Cooperativity Model

Molecular adsorption onto a fluid surface forming a single adsorbed phase is usually studied statistically mechanically in terms of "site" models in which adsorption occurs onto particular sites. There are two types of site models,^{6,70} localized models in which the barrier for movement from one site to another on the surface is much greater than the thermal energy, and nonlocalized models where the converse is true and molecules equilibrate among the surface sites.

Consider first the nonlocalized models. The simplest of these is the two dimensional perfect gas law, $\Pi(1/\Gamma) = NkT$, where $\Pi = \gamma_0 - \gamma$ is the surface pressure (γ_0 is the value of the surface tension in the absence of surfactant), Γ is the surface concentration and N and k are, respectively, Avogadro's number and Boltzmann's constant. As in the case of three dimensions, the perfect gas law assumes the adsorbed molecules possess no area, and no intermolecular attraction; the reduction of surface tension arises from the collisions of the adsorbed species. The effect of the finite area of the adsorbed

molecules size is incorporated in the Volmer equation, $\Pi = \Gamma_{\infty} NkT \left(\frac{\Gamma}{\Gamma_{\infty} - \Gamma} \right)$ where $(N\Gamma_{\infty})^{-1}$ is the area per site, and the consideration of the excluded area $(N\Gamma)^{-1}$ elevates the surface pressure. Finally, intermolecular interaction is incorporated in the van der Waals model, $\Pi + N^2 \Gamma^2 \xi = \Gamma_{\infty} NkT \left(\frac{\Gamma}{\Gamma_{\infty} - \Gamma} \right)$ where ξ is a constant which accounts for the intermolecular interaction energies, and is positive for attraction. Adsorption isotherms are obtained by substituting these equations of state into the Gibbs adsorption equation and integrating; the results are compared in Table I, where x denotes the ratio Γ/Γ_{∞} .

Consider next the class of localized models, where the energetic barrier for transfer of surfactant between sites is much larger than the thermal energy. Localized models can be derived from an activation energy-rate framework as well as a statistical mechanical theory^{17,18}. The activation energy-rate framework is much simpler, and is sufficient for use here. The simplest localized model is the Langmuir adsorption isotherm; the rates of adsorption and desorption in this model are given by:

$$\frac{d\Gamma}{dt} = \beta \exp(-E_a/RT) C_s (\Gamma_{\infty} - \Gamma) - \alpha \exp(-E_d/RT) \Gamma \quad (1)$$

where t denotes time, C_s is the sublayer concentration and β , α , E_a , and E_d are, respectively, the pre-exponential factors and the energies of activation for adsorption and desorption. In the Langmuir model, the activation energies (E_a and E_d) are independent of the surface coverage. The adsorption isotherm which follows from Eq. 1 is

$$\frac{\Gamma}{\Gamma_{\infty}} = x = \frac{C}{C+a} \quad (2)$$

where $a = (\alpha/\beta) \exp[(E_a - E_d)/RT]$.

Although the Langmuir model takes into account an excluded area effect by making the adsorption proportional to the percentage of

unoccupied area, $1-\Gamma/\Gamma_\infty$, this type of model is unable to explain cooperativity where activation energies for adsorption and desorption change with surface coverage. To account for enhanced intermolecular attraction at increasing surface coverage, the activation energies are assumed to be Γ dependent. In this development, this dependence is assumed to be of a power form; thus

$$\begin{aligned} E_a &= E_a^0 + \nu_a \Gamma^n \\ E_d &= E_d^0 + \nu_d \Gamma^n \end{aligned} \quad (3)$$

where E_a^0 , E_d^0 , ν_a and ν_d are constants. At equilibrium, the time rate of change of Γ vanishes and the adsorption isotherm which follows is given by:

$$\frac{\Gamma}{\Gamma_\infty} = x = \frac{C}{a \exp(Kx^n) + C} \quad (4)$$

where $K = (\nu_a - \nu_d)\Gamma_\infty^n/RT$ and $a = (\alpha/\beta)\exp[(E_a^0 - E_d^0)/RT]$

The presence of cohesive intermolecular forces which increase with the surface coverage and which lower the desorption rate (relative to that of adsorption) are described by $K < 0$. Accounting for the dependence of the activation energies on Γ through a power law has been undertaken in the literature^{20,71,72} for $n=1$, and corresponds to the Frumkin isotherm. As will be shown in Sec. 4.4 and 4.5 when the experimental results for decanol are compared with the cooperativity models, the consideration of a power other than one is necessary in order to best account for the surface tension relaxation profiles. Note also that this power law approach to the activation energy with n other than one has been used recently to model the adsorption of proteins onto a gas-liquid interface.⁷³ The localized adsorption isotherms, and the equations of state which follow, are summarized in Table I.

4.2.2 Phase Transition Model

As mentioned in the Introduction in the context of the discussion of the equilibrium γ - $\ln C$ curve for n-octanol, in the vicinity of a particular surface coverage (Γ_c), Γ increases greatly with little change in the bulk concentration or the surface tension. It was commented on that this indicated cooperative adsorption due to enhanced intermolecular attraction, and the possibility of a phase transition to a liquid phase. In this section, a model framework for a surface phase transition is detailed.

Prior to the critical surface coverage, intermolecular attraction is not significant, except for coverage in the immediate vicinity of Γ_c , and therefore the adsorbed state is essentially gaseous. Therefore for $\Gamma < \Gamma_c$, the adsorption rate may be approximately described by the Langmuir isotherm. Denoting the Langmuir constants for this gaseous monomer phase by α_m , β_m and a_m , the surface monomer concentration (Γ_m) in the gaseous phase is given by:

$$\begin{aligned} \frac{d\Gamma_m}{dt} &= \beta_m C_s (\Gamma_\infty - \Gamma_m) - \alpha_m \Gamma_m \quad ; \quad a_m = \alpha_m / \beta_m \\ \frac{\Gamma_m}{\Gamma_\infty} &= x_m = \frac{C}{a_m + C} \end{aligned} \quad (5)$$

Alternatively, if a more exact treatment is necessary for adsorption near Γ_c , then a model which includes intermolecular interaction would be required (eg. Frumkin or van der Waals). However, it will be shown later that to fit the equilibrium and relaxation data of decanol, inclusion of the intermolecular attraction is not necessary, and therefore Eq. 5 proves adequate from this point of view. At the critical surface coverage aggregation commences, and a liquid expanded type phase (L_1) begins to develop on the surface and coexist with the gaseous monomer phase. It is assumed that as more surfactant is added to the system in a quasistatic series of equilibrium states, the

liquid expanded phase grows at the expense of the gaseous phase with the surface tension and bulk sublayer concentration remaining fixed. Since the surface tension remains fixed, the formation of the L_1 phase is a first order phase transition⁷⁴. With continuing addition of surfactant, the gaseous phase disappears completely, and the surface coverage is uniform and of the liquid expanded type.

The liquid expanded phase is presumed compressible, and to describe monomer exchange between this phase and the subsurface of the bulk a Langmuir isotherm can be used with different rate constants than those characterizing the gaseous state, but with the same limiting area per molecule $(N\Gamma_\infty)^{-1}$. Thus,

$$\frac{d\Gamma_\ell}{dt} = \beta_\ell C_s (\Gamma_\infty - \Gamma_\ell) - \alpha_\ell \Gamma_\ell \quad (6)$$

where Γ_ℓ denotes the surface density in the liquid expanded state, and β_ℓ and α_ℓ are constants for, respectively, surfactant molecules adsorption into and desorption out of L_1 . Eq. 6 defines the following equilibrium adsorption:

$$\frac{\Gamma_\ell}{\Gamma_\infty} = x_\ell = \frac{C}{a_\ell + C} \quad (7)$$

where $a_\ell = \alpha_\ell / \beta_\ell$.

In this phase transition model, the equilibrium dependence of the surface tension on the bulk concentration may be obtained from the Gibbs adsorption equation, and is summarized below:

$$\gamma(C) = \gamma_0 - \Gamma_\infty RT \ln(1 + C/a_m) \quad (C < C_c)$$

$$\gamma(\Gamma) = \gamma_0 + \Gamma_\infty RT \ln(1 - x_m)$$

$$\gamma(C_c) = \gamma_c = \gamma_0 - \Gamma_\infty RT \ln(1 + C_c/a_m)$$

$$\gamma(C) = \gamma_0 - \Gamma_\infty RT \ln\left(\frac{(a_\ell + C)(a_m + C_c)}{(a_\ell + C_c)a_m}\right) \quad (C > C_c)$$

$$\gamma(\Gamma) = \gamma_0 + \Gamma_{\infty} RT \ln \left(\frac{(1-x_{\ell})(a_{\ell}+C_c) a_m}{(a_m+C_c) a_{\ell}} \right) \quad (8)$$

where C_c is the bulk concentration corresponding to the critical surface coverage, and is given by $\frac{\Gamma_c}{\Gamma_{\infty}} = \frac{C_c}{a_m + C_c}$. This model is summarized alongside the single phase models in Table I.

4.3 Experimental Measurements

4.3.1 Materials

1-Heptanol (purity 99.5+ %) and 1-decanol (purity 99+ %) were obtained from Aldrich Chemical Co. and used without modification. The water with which the aqueous solutions were made was purified via a Millipore water purification system, with the output water having a specific conductance of 0.071 $\mu\text{S}/\text{cm}$. The value of the surface tension of water, using the pendant bubble technique described below, was 72.5 mN/m. All experiments were undertaken under atmospheric pressure at $22.0 \pm 0.5^{\circ}\text{C}$.

4.3.2 Pendant Bubble Apparatus Design and Experimental Procedure

Pendant bubble tensiometry enhanced by video digitization was employed for the measurement of the n-alcohol surface tension relaxation profiles, and the equilibrium tensions. This particular application of the pendant bubble technique is described in detail in a previous study,⁶³ and therefore only a brief description is given here.

The equipment shown in Figure 1 is used to create a silhouette of a pendant bubble, to video image the silhouette, and to digitize the image. The image forming and recording system consists of a light source (a halogen lamp with constant light intensity), a plano-convex lens system for producing a collimated beam, a quartz cell enclosed in a thermostatically controlled chamber, an objective lens, and a solid state video camera (CCD-71 series, Dage-MIT Inc.). The bubble-forming

system consists of a stainless steel inverted needle (ID=0.016") which is connected to the normally closed port of a three-way miniature solenoid valve (Lee Co.) via 1/16" ID teflon tubing. The common port of the valve is connected by the same teflon tubing to a gas-tight Hamilton syringe placed in a syringe pump (Sage Instruments). The valve is controlled by the output signal of a D/A Data Translation card (DT2801) installed on a IBM-PC AT. The video-image digitizer (DT 2861 Arithmetic Frame Grabber, Data Translation), also installed on the backplane of the AT, digitizes the picture into 480 lines $\times$ 512 pixels and assigns to each one a level of grey with eight bit resolution.

An edge detection routine was devised to locate the interface contour from the digitized image, and a calibration procedure using a stainless steel ball was used to calculate the length between pixels along a row, and along a column. The calibration procedure yielded values of 0.10096 pixel/ μ m horizontally and 0.12817 pixel/ μ m vertically.⁶³

The experimental protocol was as follows: The quartz cell was initially filled with the aqueous alcohol solution, and the bubble forming needle was positioned in the cell in the path of the collimated light beam. At this point, the solenoid valve was not energized. The syringe pump was turned on, and the air in the syringe was allowed to pass through the normally open port of the valve. Via input from the keyboard, the D/A card energized the valve, and allowed the gas to pass through the needle, thereby forming a bubble of air. The valve was then closed (also by input from the keyboard) when the bubble achieved a diameter of approximately 2 mm. The time required to create an air bubble of this size is $\approx$ 1 - 2 s. The bubble so created is one of constant mass. The change in volume, as the surface tension relaxes, is only a few percent over a time period of at least one hour. After the solenoid is closed and the bubble is formed,

sequential digital images were then taken of the bubble, first at intervals of approximately 1 s, and then later in intervals of the order of tens of seconds. After the surface tension relaxation was complete, the images were processed to determine the bubble edge coordinates.

The classical Laplace equation relates the pressure drop across a curved interface

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \quad (9)$$

where γ is the surface tension, R_1 and R_2 are the two principal radii of curvature of the surface, and ΔP is the pressure difference across the interface. For the pendant bubble geometry, Eq. 9 can be recast as a set of three first-order differential equations for the spatial positions x_1 and x_2 and turning angle ϕ of the interface as a function of the arc length s . Nondimensionalizing by the radius of curvature at the apex ($x'_1 = x_1/R_0$, $x'_2 = x_2/R_0$, and $s' = s/R_0$), the first-order equations have the following form (Rotenberg *et al.*⁵²):

$$\begin{aligned} \frac{d\phi}{ds'} &= 2 + Bx'_2 - \frac{\sin\phi}{x'_1} \\ \frac{dx'_1}{ds'} &= \cos\phi \\ \frac{dx'_2}{ds'} &= \sin\phi \end{aligned} \quad (10)$$

where B defines the Bond number or capillary constant and is given by

$$\frac{\Delta\rho \ g \ R_0^2}{\gamma} \quad \text{and } \Delta\rho \text{ is the density difference between the gas and solution}$$

phases, and g is the gravitational acceleration constant. The equations are subject to the boundary conditions $x'_1(0) = x'_2(0) = \phi(0) = 0$.

Eq. 10 is integrated by using a fourth-order Runge-Kutta scheme initialized with the approximate solution $x'_2 = \frac{-2}{B} [1 - J_0((-B)^{1/2} x'_1)]$

which is valid near the apex where $\phi \ll 1$ (Huh and Reed⁵³). (Here $J_0(x'_1)$ is the Bessel function of the first kind.)

The surface tension is computed from the data and the theoretical curve in the following way. An objective function E is defined as the sum of squares of the normal distance d_j between the measured points u_j and the calculated curve v obtained from the integration of Eq. 10 (i.e., $E = \sum_{j=1}^M [d_j(u_j, v)]^2$; M is the total number of experimental points). The objective function depends on four unknown variables, X_{10} and X_{20} , the actual location of the apex, R_0 and B . To obtain the optimal congruence between the theoretical curve and the data points, the objective function is minimized with respect to the four parameters ($\frac{\partial E}{\partial q_i} = 0$, $i=1,2,3,4$). Minimization equations are solved by applying directly the Newton-Raphson method, and from the optimal values of R_0 and B the tension γ can be computed. As demonstrated in Lin et al.,⁶³ the accuracy and reproducibility of the surface tension measurements obtained by this procedure are ± 0.1 mN/m.

4.3.3 Experimental Results

Relaxations in the surface tension due to decanol adsorption were measured at the air/water interface. Data was recorded from one second up to a few hours from the moment (referenced as $t=0$) in which the valve is closed and the bubble is formed. Shown in Figure 2 are representative dynamic surface tension profiles (for one selected bubble) of decanol aqueous solutions at four different bulk concentrations, $C = 4 \times 10^{-8}$, 7×10^{-8} , 1.0×10^{-7} and 1.586×10^{-7} mol/cm³. The reproducibility of these profiles is demonstrated in Figure 3, where the results of several pendant bubbles at these four concentrations are given. Observe from Fig. 2 that the shoulder behavior is evident for the lowest concentration using a linear time

scale, and it is evident for this and each of the higher concentrations when a log time scale is used (Figure 3).

4.4 Comparisons of the Equilibrium Data and the Model Predictions

4.4.1 Single Phase Models

The equilibrium surface tensions corresponding to the relaxations given in Figure 3 are obtained by averaging the longtime behavior; the results are plotted in Figure 4. Consider first comparisons of the decanol equilibrium data with single phase models, specifically the nonlocalized Volmer and van der Waals equations, and the localized Langmuir and Frumkin isotherms, all of which were described in Sec. 4.2.1. Figure 4a presents the predictions of the nonlocalized models alongside the data; the model constants are obtained by adjustment so as to minimize the error between the predictions and experimental values. The more exact agreement of the van der Waals relation indicates clearly the necessity of incorporating into the equation of state for decanol an increase in intermolecular attraction with surface coverage. The same conclusion is also obtained when the localized Frumkin and Langmuir models are used to correlate the data (Figure 4b); the Frumkin model (for $K < 0$), which describes the behavior of strong intermolecular attraction at increasing surface coverage, is in much better agreement with the data than that of Langmuir (for which activation energies are independent of coverage). The results of Figure 4 confirm the initial supposition in the Introduction that the relatively long, slender hydrocarbon chain of the decanol molecule can give rise to strong intermolecular attraction as the surface coverage increases. It should be noted that (negative) critical values (K_c) exist for the van der Waals or Frumkin parameter "K" below which discontinuities develop in the adsorption isotherm and the equation of state becomes non-monotonic. This behavior leads to non-monotonic surface tension relaxation curves,

which have not been observed. Thus, in fitting the data, the K parameters of these two models have been constrained to be larger than the critical one. This point is discussed more carefully in Sec. 4.6(ii). Note finally that the optimal values of the model constants are summarized in Table II.

The conclusion that it is necessary to incorporate increasing intermolecular attraction at increasing surface coverage in order to model decanol adsorption can also be shown to be true for *n*-octanol. Plotted in Figure 5a is a comparison of the fit of *n*-octanol data by Lunkenheimer *et al.*⁴³ for the Langmuir and Frumkin models, and the better agreement with the Frumkin equation is evident. As might be expected for the series of *n*-alcohols, as the hydrocarbon chain becomes smaller, the van der Waals intermolecular attraction is reduced (K negative, but smaller in magnitude), and lower chain alcohols ought to be described by equations not including attraction with increasing Γ ($K=0$ or Langmuir). Figure 5b demonstrates that the Langmuir model agrees reasonably well with the equilibrium data of *n*-heptanol, which was obtained as part of this work and also by Hommelen,⁷⁵ and inclusion of intermolecular interaction as in the Frumkin model (with a negative value of K whose absolute value is small) offers only marginally better agreement. These ideas are also confirmed in the equilibrium adsorption data of Fainerman and Lylyk.¹⁶ In their study, the Frumkin adsorption isotherm was used to describe the equilibrium adsorption of *n*-alcohols in the range $C_3 - C_{10}$, and the value of K in this model became increasingly negative as the chain length increases.

Reconsider the comparison of the model predictions of the van der Waals and Frumkin models and the equilibrium decanol data (Figure 4). Although the predictions of both models are close to each other, and in agreement with the data, the Π -A equations of state ($A=(N\Gamma)^{-1}$)

which correspond to these models differ substantially. The equations of state for all the single phase models considered are shown in Figure 6 where the disparity between the van der Waals and Frumkin relations is evident. Surface tension relaxation curves are obtained theoretically by computing Γ first as a function of time, and then determining γ through the Π -A curve (cf. Sec. 4.5.1). Thus it would be expected that the van der Waals and Frumkin models would result in considerably different $\gamma(t)$ profiles. It will be shown in the following section that this is indeed true, and that, in fact, neither model fits the relaxation data well despite the agreement with the γ - $\ln C$ data. To obtain theoretical surface tension relaxations in better agreement with the data, the Frumkin equation was modified by incorporating a power law dependence for the activation energy. This generalized Frumkin model has been described in Sec. 4.2.1. Plotted in Figure 4b are the predictions of the generalized model, and it is clear that this model is as accurate in correlating the data as the van der Waals and Frumkin models. (Note also that as indicated in Figure 5a, the generalized Frumkin model predicts the equilibrium results for octanol as well as the Frumkin model.) The Π -A curve for the generalized model for decanol is shown in Figure 6, and, as expected, it differs from the other single phase models, in particular the van der Waals and Frumkin models.

In discussing the model constant values, one important conclusion is that for the models which are in good agreement with the γ - $\ln C$ data (i.e. the van der Waals, Frumkin and generalized Frumkin models), the limiting area per molecule $(N\Gamma_{\infty})^{-1}$ is 18.4, 23.6, 23.6 Å² (cf. Table II), respectively. This is in good agreement with the range of 20 - 22 Å² obtained for insoluble monolayers of saturated normal alkyl chain molecules with small polar groups such as alcohols, carboxylic acids, amines and amides.⁷⁰

4.4.2 Phase Transition Model

Consider the γ - $\ln C$ data for decanol from the point of view of a phase transition: It is clear that the slope of the γ - $\ln C$ curve, which is proportional to the surface coverage, is discontinuous in the vicinity of the data point corresponding to the second highest equilibrium surface tension, 70.4 mN/m. Therefore the transition to a surface liquid phase should occur at an equilibrium surface tension near this value. Using the model of Sec. 4.2.2 in which the gaseous and liquid states are both described by Langmuir model, the theoretical curve shown in Figure 7 is obtained. The model constants are summarized in Table II, and were obtained, as before, by minimizing the deviation between the data and the model results. The agreement is as good as that achieved using the van der Waals and generalized Frumkin models.

In discussing the phase transition results, note first from the values of the model constants that the value of the surface tension during which the phase transition occurs (γ_c) is equal to 70.8 mN/m, and is, as expected, in the vicinity of the second data point on the γ - $\ln C$ curve. A second result is that the limiting area per molecule $(N\Gamma_\infty)^{-1}$ is equal to 23.0 Å² which is nearly equal to that obtained from the single phase models. A third result concerns the fairly significant compressibility of the liquid state. The Π -A curve corresponding to the phase transition model is presented in Figure 6 alongside the single phase models. The slope of the portion of the Π -A curve to the left of the horizontal line is a measure of the compressibility of the liquid state. Quantitatively the surface density of the liquid state formed during the phase transition is equal to the value of Γ at the point at which the Π -A curve departs from horizontal behavior (This value is denoted by Γ_{lc}). From the Langmuir model constants of the liquid phase, Γ_{lc} can be computed, and is equal to $0.65\Gamma_\infty$. The value of the surface density of the liquid at

the highest surface pressure is $0.96\Gamma_{\infty}$, so the liquid is compressed about fifty percent relative to Γ_{lc} .

A final result concerns the relatively low value, $0.09\Gamma_{\infty}$, for the coverage in the gaseous necessary for the commencement of the phase transition. This value is reasonable for two reasons. First, the value obtained is, on an area per molecule basis, equal to $256 \text{ \AA}^2/\text{molecule}$. This number is close to the areas per molecule observed for phase transitions for insoluble monolayers of similar structure. For example, for pentadecylic acid spread on a pH 2 water substrate (and therefore unionized), the value as given by Kin and Cannell⁷⁶ is approximately $500 \text{ \AA}^2/\text{molecule}$. Second, the value obtained for the area per molecule necessary for the phase transition of decanol is not large in light of the area swept out on the interface per molecule in the gaseous state. To estimate this swept out area, consider the following theoretical estimation: In the gaseous state, although the -OH group of the adsorbed decanol molecule must remain immersed in (or in contact with) the aqueous phase, the hydrocarbon chain is free to lie on the surface or dangle above the liquid in the air space. The mean radius of this extension may be approximated by the statistical relation used in three dimensions for the random walk extension of a molecule⁷⁷ composed of n links of unit length ℓ which are free to rotate about an angle θ . That value, denoted by $\langle r^2 \rangle$, is equal to $n\ell^2(1-\cos\theta)/(1+\cos\theta)$. Neglecting the difference in lengths between C-H, C-C and C-O bonds, the decanol molecule can be considered as a series of 11 links from the pivoting oxygen molecule which lies on the surface. Assuming a length of $1.54 \text{ \AA}$ for these links (the length for the C-C bond), and noting that the bond angle is the tetrahedron angle 109.5° , the mean extension ($\langle r^2 \rangle^{1/2}$) is estimated to be $7.2 \text{ \AA}$. Hence the swept out area is $164 \text{ \AA}^2$. Assuming that a phase transition cannot occur until the swept out areas begin to overlap, the value $164 \text{ \AA}^2$

represents an estimate for the critical coverage. This value is in reasonable agreement with the experimental value of $256 \text{ \AA}^2$.

With regards to this phase transition model, it is important to note that the equilibrium γ - $\ln C$ octanol data of Lunkenheimer *et al.*⁴³ cited previously can also be correlated successfully assuming a phase transition. This correlation is presented in Figure 7, again confirming the importance of intermolecular attraction at increasing surface coverage for the octanol molecule.

4.5 Comparison of Experimental Relaxation Curves and Theoretical Profiles Derived From the Models

5.1 Numerical Solution of the Diffusion Controlled Surfactant Transfer

The theoretical framework which describes the unsteady bulk diffusion of surfactant towards an initially clean pendant bubble, and its effect on the surface tension has been formulated previously⁶³, and therefore only a brief outline is given here. The pendant bubble is treated as a sphere surrounded by an infinite, quiescent medium which at the time $t=0$ contains a uniform concentration C_0 of surfactant. The surfactant is assumed not to dissolve into the gas phase of the bubble, and at $t=0$ the concentration of surfactant on the bubble surface is assumed to be equal to zero. Bulk diffusion from this initial state is assumed to be spherically symmetric, and convection effects are neglected. With reference to the experiments, $t=0$ of the numerical simulations is taken to be the time at which the valve is closed (marked as $t=0$ in the experimental curves). The neglect of convective transport deserves special comment: As was mentioned in Sec. 4.3.2 on the bubble apparatus design, the time necessary to create the air bubble was between 1 and 2 seconds. Certainly in that time interval radial convection of surfactant, in addition to radial diffusion, is important. The convection soon dissipates, and the time scale for this dissipation may be estimated

by the time scale for the diffusion of the vorticity surface disturbance through the surrounding liquid medium. This scale is b^2/ν , where ν is the kinematic viscosity of the aqueous alcohol solution and b is the bubble radius. As $b \approx 10^{-1}$ cm and $\nu \approx 10^{-2}$ cm², the time necessary for convection effects to disappear is of the order of one second, and therefore convection is only important for the first second or so in the relaxation.

The bulk diffusion equations can easily be solved by the Laplace transform technique, and from this solution the surface concentration can be formulated in terms of the unknown subsurface concentration $C_s(t)$:

$$\Gamma(t) = \frac{D}{b} [C_o t - \int_0^t C_s(\tau) d\tau] + 2 \left(\frac{D}{\pi} \right)^{1/2} [C_o t^{1/2} - \int_0^{t^{1/2}} C_s(t-\tau) d\tau^{1/2}] \quad (11)$$

where b is the bubble radius (assumed to be equal to the radius of curvature at the apex, R_o , in the computations to follow), and D denotes the diffusion coefficient. The above expression is the spherical surface analogue of Ward and Tordai's result for diffusion toward a planar surface.³

When the adsorption process is controlled solely by bulk diffusion (as is assumed in this development), the solution for the surface concentration is completed by specifying an adsorption isotherm. For the single phase models, it is a simple manner to relate $\Gamma(t)$ to $C_s(t)$ (cf. Table I). Once this relation is specified a numerical profile for $\Gamma(t)$ is computed in the following way. First, the convolution integral of C_s in Eq. 11 is integrated by first partitioning the interval $(0, t)$ into intervals of size δ in time, and integrating separately each interval by assuming a linear relation in time for C_s .

$$\int_0^t C_s(t-\tau) \tau^{1/2} d\tau = \sum_{i=0}^{n-1} \int_{i\delta}^{(i+1)\delta} \{ [C_s((n-i-1)\delta) - C_s((n-i)\delta)] \tau / \delta$$

$$\begin{aligned}
& + [(i+1)C_s((n-i)\delta) - iC_s((n-i-1)\delta))] / r^{1/2} dr \\
& = \left[\frac{4}{3} C_s(n\delta) + \frac{2}{3} C_s((n-1)\delta) \right] \delta^{1/2} \\
& - \sum_{i=1}^{n-1} \frac{2}{3} [C_s((n-i)\delta) - C_s((n-i-1)\delta)] [(i+1)^{3/2} - i^{3/2}] \delta^{1/2} \\
& + \sum_{i=1}^{n-1} 2 [(i+1)C_s((n-i)\delta) - iC_s((n-i-1)\delta)] [(i+1)^{1/2} - i^{1/2}] \delta^{1/2} \quad (12)
\end{aligned}$$

After integration and evaluating the spherical integral term in the same manner, Eq. 11 is of form

$$C_s(t_n) = b_1 \Gamma(t_n) + b_2 \quad (13)$$

where $t_n = n\delta$. The next step in the numerical procedure is to substitute C_s as given in Eq. 13 into the adsorption isotherm, and then solve for $\Gamma(t_n)$. Finally from the equation of state the surface tension at t_n is obtained.

The computation of the relaxation using the phase transition model is a modification of the above procedure. For $\Gamma(t) < \Gamma_c$, the Langmuir isotherm (Eq. 5) is used to relate $C_s(t)$ to $\Gamma(t)$, and $\gamma(t)$ is computed as described above. For $\Gamma_c < \Gamma(t) < \Gamma_{lc}$, $C_s(t)$ is fixed at the value C_c , and $\Gamma(t)$ is computed from Eqs. 11 & 12 with $C_s(t) = C_c$. Note that although the sublayer concentration is fixed, diffusion still proceeds since $C_o > C_c$, and all the material reaching the sublayer vicinity adsorbs onto the surface. For $\Gamma_c < \Gamma(t) < \Gamma_{lc}$, $\gamma(t) = \gamma_c$ and therefore the numerical profile contains a plateau region. After $\Gamma(t)$ exceeds Γ_{lc} , the relationship between the sublayer and surface concentrations is once again described by a Langmuir model (Eq. 7), $C_s(t)$ increases from C_c , and the surface tension relaxes to its equilibrium value.

4.5.2 Comparison of Relaxation Data and Model Profiles

Consider first the computed relaxation profiles using the single phase models. These are shown in Figure 3 for the Langmuir, Frumkin, van der Waals and generalized Frumkin models. The model constants used in obtaining the computed profiles represent the optimal fits of the γ - $\ln C$ equilibrium data, and are summarized in Table II. The numerical profiles are computed by adjusting the diffusion coefficient individually for each model and for each of the four bulk concentrations to achieve the best agreement with the data. Table III lists the values of the diffusion coefficients obtained. First note from Figure 3 that the agreement between the theoretical relaxation profile using the Langmuir isotherm and the data is very poor (at all four concentrations), and this reflects the inadequate fit between the equilibrium γ - $\ln C$ data and the Langmuir model predictions (cf. Figure 4b). The inadequacy of the Langmuir model is also evident from the fact that the values of the diffusion coefficient increase greatly with the bulk concentration, a result which is unreasonable considering the fact that hydrodynamic interactions and aggregate formation in the bulk tend to reduce the diffusion coefficient at increasing C . Although not shown, the behavior of the Volmer relaxation profile is similar.

The Frumkin and van der Waals numerical profiles fit the experimental data much better than the Langmuir model, but each of these is not very effective at predicting the data at the short, shoulder behavior times where the surface tension is larger than approximately 69 mN/m. Thus, although the van der Waals and Frumkin models fit the equilibrium γ - $\ln C$ data very well, it does not necessarily follow that the relaxation data will be predicted with as good an agreement. A reason for this was alluded to in Sec. 4.2: Although the equilibrium values of the surface tension for each bulk concentration are correctly predicted, the slope, which is proportional to Γ , may not be as well predicted, and hence the equation of state may be in error. If the equation of state is in

error, then it follows that the relaxation profiles cannot be correctly predicted. Figure 6 presents the Π -A curves for the van der Waals and Frumkin models, and it is clear that these equations of state do not agree well with the generalized Frumkin curve. As will be shown below, the latter model leads to numerical profiles which agree closely with the relaxation data.

The numerical relaxations constructed from the generalized Frumkin model are shown in Figure 3, and it is clear that the agreement with the data is superior to that of the other single phase models, especially in the shoulder region. The major conclusion which can be drawn from the better agreement (with the data) of the generalized Frumkin relaxation profile as compared to the Frumkin curve is that cooperative adsorption is best described using a power dependence for the activation energy. Note also that the diffusion coefficients obtained using the generalized Frumkin model, as expected, decrease with bulk concentration. This dependence is weak, however, presumably due to the fact that the bulk concentrations studied are extremely low. The average value is 6.5×10^{-6} cm²/s, and values close to this are obtained by the van der Waals (6.9×10^{-6} cm²/s) and Frumkin (7.4×10^{-6} cm²/s) models despite the lack of agreement of the model and data in the shoulder region.

The relaxation profiles corresponding to the phase transition model are also shown in Figure 3, and it is clear that the agreement with the data is comparable to that of the generalized Frumkin model. With this model, the shoulder behavior of the data is described precisely as a straight line, and corresponds to the state of the surface where a liquid state is forming at constant surface pressure. The diffusion coefficients obtained are listed in Table III and these are almost identical in value (6.3×10^{-6} cm²/s) to that obtained using the generalized Frumkin model.

4.6 Discussion

In this section four specific points concerning the results will be discussed. These are: (i) the nature of the condensed phase which forms in the phase transition interpretation of the shoulder behavior, (ii) zero-slope conditions in the equation of state of single phase models, (iii) arguments concerning the possibility of a sorption-diffusion mixed model interpretation of the induction period, and (iv) the use of the short time approximation to the diffusion equation in interpreting the relaxation data and obtaining the diffusion coefficient. These points are addressed separately below.

(i) The Nature of the Condensed Phase

In the phase transition model, intermolecular attraction among the hydrocarbon chains existing in the gaseous state leads to the formation of a separate liquid type phase which eventually occupies the entire surface. This phase was presumed to be an L_1 liquid expanded phase, in analogy with the first phase transition from the gaseous state which occurs with an insoluble monolayer. The details of the molecular configurations of the adsorbed molecules in the L_1 state have not been precisely documented. It is generally surmised that this state is an incoherent arrangement in which some molecules lie with their chains along the liquid substrate, while others are arranged somewhat more perpendicular to the substrate plane, and are intermolecularly bound to other neighboring out-of-plane molecules. The limiting area per molecule extrapolated from the slope of the Π -A curve for the L_1 state of decanol ($a_{L_1}^0$) is $\approx 37 \text{ \AA}^2/\text{molecule}$. This value falls slightly below the range, $45 - 55 \text{ \AA}^2$, which is generally accepted for amphiphatic molecules with saturated, unbranched, alkyl chains.⁷⁷

In the modelling undertaken in this study, the compressibility of the L_1 state has been described by the equation of state derived

from the Langmuir isotherm. Although the agreement of this model with the γ - $\ln C$ curve and the relaxation profiles are very good, this agreement does not conclusively establish the nature of the phase forming from the gaseous state. It is possible that the intermolecular attraction can lead to the formation of small area per molecule hemi-micelles rather than the L_1 state. An alternative picture, assuming the presence of hemi-micelles, is that at Γ_c aggregates in which the area per molecule is very small begin to form. These aggregates grow at constant surface pressure and constant monomer number density, and eventually a hemi-micelle population emerges in which most aggregates contain the same number of monomers. This state of constant surface pressure and monomer number density persists with addition of more bulk surfactant until the hemi-micelle number density becomes so large that addition of more surfactant to the surface cannot be done at constant chemical potential. At this point, the equation of state leaves the horizontal line of the Π -A curve, and addition of more surfactant to the surface increases both the hemi-micelle and monomer surface density. If it is assumed that the equation of state for this alternative condensed state of free monomer and hemi-micelle can be described by the Langmuir model (as was done for the L_1 phase), then the same relaxation curves as those of the L_1 transition are obtained.

(ii) Zero-slope Conditions in the Equation of State of Single Phase Models

When single phase models with cooperative adsorption are used (i.e., Frumkin, generalized Frumkin and van der Waals), values (K_c) exist for the intermolecular interaction parameter K for which, below these values, γ becomes a non-monotonic function of Γ . This point is derived by setting $\frac{\partial \gamma}{\partial \Gamma}$ and $\frac{\partial^2 \gamma}{\partial \Gamma^2}$ equal to zero. For the generalized Frumkin model, it can easily be shown that the value of K_c is equal to

$-(1+\frac{1}{n})^{1+n}$, and it can similarly be demonstrated that for the van der Waals model, critical behavior occurs for $K < -6.75$. When $K = K_c$, because $\frac{\partial \gamma}{\partial \Gamma}$ and $\frac{\partial^2 \gamma}{\partial \Gamma^2}$ are zero, the equation of state predicts an inflection point in the γ - Γ plane. When $K \leq K_c$, nonmonotonic behavior is obtained. This dependence on K is analogous to the behavior of three dimensional equations of state in the P - V plane, and the two dimensional results are illustrated in Figure 8 using the Frumkin model.

Original attempts at fitting the equilibrium decanol γ - $\ln C$ curve using the van der Waals and Frumkin equation demonstrated that the best congruence was achieved for $K < K_c$. Note however that the behavior which results when $K < K_c$ predicts non-monotonic surface tension relaxation curves. Since this behavior was not observed in the experimental relaxations, the values of K were constrained to be above K_c . These values are tabulated in Table II. It is important to emphasize that with the generalized Frumkin model, parameter optimization leaving K free resulted in a value which was significantly greater than K_c .

(iii) The Applicability of Mixed Model Interpretations

The relaxation predictions shown in Figure 3 were computed assuming that bulk diffusion is the rate controlling step. While this assumption certainly appears adequate in view of the good agreement achieved with a reasonable value for the diffusion coefficient, it is possible that sorption can still play a role. Specifically, if the diffusion coefficient were in fact larger than the value obtained from the diffusion limited assumption, then the diffusion limited curve would fall below the experimental profile. For this case, finite values of the sorptive rate constant could be used to moderate the relaxation, and thereby achieve just as reasonable an agreement with

the data. However, given the fact that the diffusion coefficient of the decanol molecule in water has not been established by other techniques due to difficulties in measurement at such low concentrations, and the fact that there is no evidence that the coefficient should be much larger than $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$, the diffusion limited theory presented here is the simplest possible to explain the experimental data.

(iv) The Short-time, Diffusion Limited Approximation for Measuring the Diffusion Coefficient

Short time experimental relaxation data has usually been interpreted in the literature using a simplified diffusion limited approach, and it is instructive to verify the applicability of this approach to the cooperative/phase transition equations of state developed in this study. In this simplified approach, an equation of state is used to translate the surface tension relaxation $\gamma(t)$ into a plot of surface concentration relaxation, i.e. $\Gamma(t)$. Theoretically, a simple relation for the short time adsorption can be derived by an asymptotic development of Eq. 11; the result is given by:

$$\Gamma(t) = 2C_0(Dt/\pi)^{1/2} + (D/b)C_0t + O(t^{3/2}) \quad (t \rightarrow 0) \quad (14)$$

Note from the above equation that the first term is identical to that which would have been obtained for adsorption onto a planar surface, and this reflects the fact that for short times diffusion gradients exist only in the very proximity of the surface and hence the surface geometry is not important.

The above asymptotic equation predicts that initial adsorption should be proportional to $t^{1/2}$. As shown in Figure 9 and more clearly in the inset to this figure, using the generalized Frumkin model and an average value for the diffusion coefficient of $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ and $C_0 = 4 \times 10^{-8} \text{ mol/cm}^3$, the numerical solutions do indeed follow this asymptotic behavior for Γ , but only at extremely low surface coverage

($< 0.02 \Gamma_0$). However most of the data obtained lie outside of the region in which the numerical solution and the asymptotic equation agree. This is also shown in Figure 9 using the data for $C_0 = 4 \times 10^{-8}$ mol/cm³. Constructing a straightline through this short time data without cognizance of the numerical curve (and therefore the range of validity of the $t^{1/2}$ behavior) can seriously underestimate the value of the diffusion coefficient. This is clearly shown in the figure where the diffusion coefficient corresponding to the slope of the best-fitting straightline is equal to 2.0×10^{-6} cm²/s. Miller and Lunkenheimer¹⁰, in a study also using n-decanol, obtained approximately this same value (0.2×10^{-6} - 3.7×10^{-6} cm²/s) of the diffusion coefficient using this short-time straight-line approximation. It is important to note that the region of overlap between Eq. 14 and the numerical solution is a function of a/C_0 , K and h/b . However for the concentrations used in this study the region of overlap is always small, and Figure 9 is typical. Other values for a/C_0 , K and h/b can result in larger regions of validity; an example of a more extended region of validity using the Frumkin equation with positive K is shown elsewhere in a study of the polyethoxy surfactant Triton X-100.⁶³

At extended times, the diffusion process is affected by the geometry of the surface, and the importance of including the bubble sphericity in the numerical solutions is shown in Lin *et al.*⁶³ The fact that the actual shape is not exactly spherical, but has a radius of curvature which changes was not incorporated into the model. Changes in curvature will affect the local rate of diffusion to the surface, and create a nonuniform surface tension distribution. This effect is not assumed to be important: The comparisons of the theoretical Young-Laplace solution (assuming a constant surface

tension) and the digitization data does not exhibit any systematic deviations which would indicate a nonuniform surface tension.

4.7 Summary

This study has examined both theoretically and experimentally the induction period in the surface tension relaxation profile of long chain small polar group surfactants. When a molecule with a long, slender, hydrophobic chain and a small polar group adsorbs onto an aqueous-gas interface, strong intermolecular attraction between adsorbed species arises when the surface coverage reaches a critical value. Because of this affinity, subsequent adsorption occurs with little change in the bulk concentration, and therefore little change in the surface tension. This behavior leads to a cusp (or near cusp) in the equilibrium γ - $\ln C$ curve, and to a shoulder behavior in the relaxation in surface tension. Two new equations of state were developed to describe this cooperative attraction: a generalized Frumkin model in which the activation energy for adsorption is proportional to a power of the surface coverage, and a phase transition model in which the attraction leads to the formation of a condensed liquid phase.

Experimental data for the equilibrium γ - $\ln C$ curve and the relaxation profile were obtained for n-decanol using pendant bubble tensiometry enhanced by video digitization. The experimental results confirmed the presence of a cusp in the γ - $\ln C$ curve, and an induction period in the relaxation profile. The equilibrium data was accurately fitted using either the generalized Frumkin or phase transition models. Numerical solutions of the bulk diffusion equation coupled with the adsorption isotherm corresponding to either model predicted very well the relaxation curves for values of the diffusion coefficient equal to 6.5×10^{-6} cm²/s. No evidence for sorption barriers for sorption was observed, although sorption kinetics could play a secondary role in the relaxation profiles if the diffusion coefficient

of the n-decanol molecule in water was slightly higher than the value obtained assuming only diffusion as the controlling step.

Acknowledgement

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Table I. Adsorption Isotherms and Equations of State

Isotherm	Henry	Langmuir	Volmer
Formula	$\Gamma = k'C$	$x = \frac{C}{C + a}$	$x = \frac{C}{C + a \exp(\frac{x}{1-x})}$
Parameters	k'	Γ_{∞}, a	Γ_{∞}, a
Equation for Π	$\Pi = RT\Gamma$	$\Pi = -\Gamma_{\infty}RT\ln(1-x)$ $= \Gamma_{\infty}RT(x+\frac{x^2}{2}+\frac{x^3}{3}+\frac{x^4}{4}+\dots)$	$\Pi = \Gamma_{\infty}RT(\frac{x}{1-x})$ $=\Gamma_{\infty}RT(x+x^2+x^3+\dots)$

Frumkin	van der Waals
$x = \frac{C}{C + a \exp(Kx)}$	$x = \frac{C}{C + a \exp(\frac{x}{1-x}+Kx)}$
Γ_{∞}, a, K	$\Gamma_{\infty}, a, K(=-2\xi N\Gamma_{\infty}/kT)$
$\Pi = -\Gamma_{\infty}RT[\ln(1-x) - \frac{K}{2}x^2]$ $= \Gamma_{\infty}RT[x+(1+K)\frac{x^2}{2}+\frac{x^3}{3}+\dots]$	$\Pi = \Gamma_{\infty}RT(\frac{x}{1-x} + \frac{K}{2}x^2)$ $= \Gamma_{\infty}RT[x+(1+\frac{K}{2})x^2+x^3+\dots]$

General Frumkin	Phase Transition
$x = \frac{C}{C + a \exp(Kx^n)}$	Gaseous $x_m = \frac{C}{C + a_m}$
	Liquid $x_l = \frac{C}{C + a_l}$
Γ_{∞}, a, K, n	$\Gamma_{\infty}, a_m, a_l, C_c$
$\Pi = -\Gamma_{\infty}RT[\ln(1-x) - \frac{Kn}{n+1} x^{n+1}]$ $= \Gamma_{\infty}RT(x+\frac{Kn}{n+1} x^{n+1}+\frac{x^2}{2}+\frac{x^3}{3}+\dots)$	Gaseous $\Pi = -\Gamma_{\infty}RT\ln(1-x_m)$ Liquid $\Pi=\Gamma_{\infty}RT(\ln(1-x_l)+\ln[\frac{a_m(a_l+C_c)}{a_m(a_m+C_c)}])$

Table II. Constants of Optimal Fit for n-Alcohol Aqueous Solution.

		Γ_{∞} ($\mu\text{mol}/\text{m}^2$)	a ($\mu\text{mol}/\text{cm}^3$)	K	n	K_c	$(N\Gamma_{\infty})^{-1}$ ($\text{\AA}^2$)
Volmer	(a)	26.68	0.153				
van der Waals	(a)	9.01	0.190	-6.73		-6	7.5
18.4							
Langmuir	(a)	14.58	0.0835				
	(b)	11.30	0.8258				
	(c)	7.58	1.531				
Frumkin	(a)	7.03	0.1297	-3.90	1	4	
23.6	(b)	6.81	0.9690	-2.56	1	-4	
	(c)	5.81	1.795	-1.70	1	-4	
General	(a)	7.05	0.4092	-4.62	0.5	-5.196	23.6
Fumkin	(b)	7.14	2.135	-2.83	0.4476	-5.469	

		Γ_{∞} ($\mu\text{mol}/\text{m}^2$)	a_m ($\mu\text{mol}/\text{cm}^3$)	a_l ($\mu\text{mol}/\text{cm}^3$)	C_c ($\mu\text{mol}/\text{cm}^3$)	$\gamma_c^{\dagger}$ (mN/m)	$\Gamma_c/\Gamma_{\infty}^{\dagger}$
Phase	(a)	7.23	0.1485	0.00800	0.01461	70.84	0.0896
Transition	(b)	8.07	2.726	0.3155	0.1148	71.68	0.0425

(a) Decanol, (b) Octanol, (c) Heptanol

[†]Calculated from Eq. 8, Eq. 5 respectively.

Table III. The Values of Diffusion Coefficient.

D ($10^{-6}\text{cm}^2/\text{s}$)	$C = 4 \times 10^{-8}$	7×10^{-8}	1×10^{-7}	$1.586 \times 10^{-7} (\text{mol}/\text{cm}^3)$
van der Waals	7.24	7.05	6.69	6.48
Langmuir	1.38	4.4	5.14	7.68
Frumkin	8.3	7.45	7.0	6.75
Generalized				
Frumkin	6.65	6.6	6.33	6.25
Phase Transition	6.18	6.65	6.25	5.97

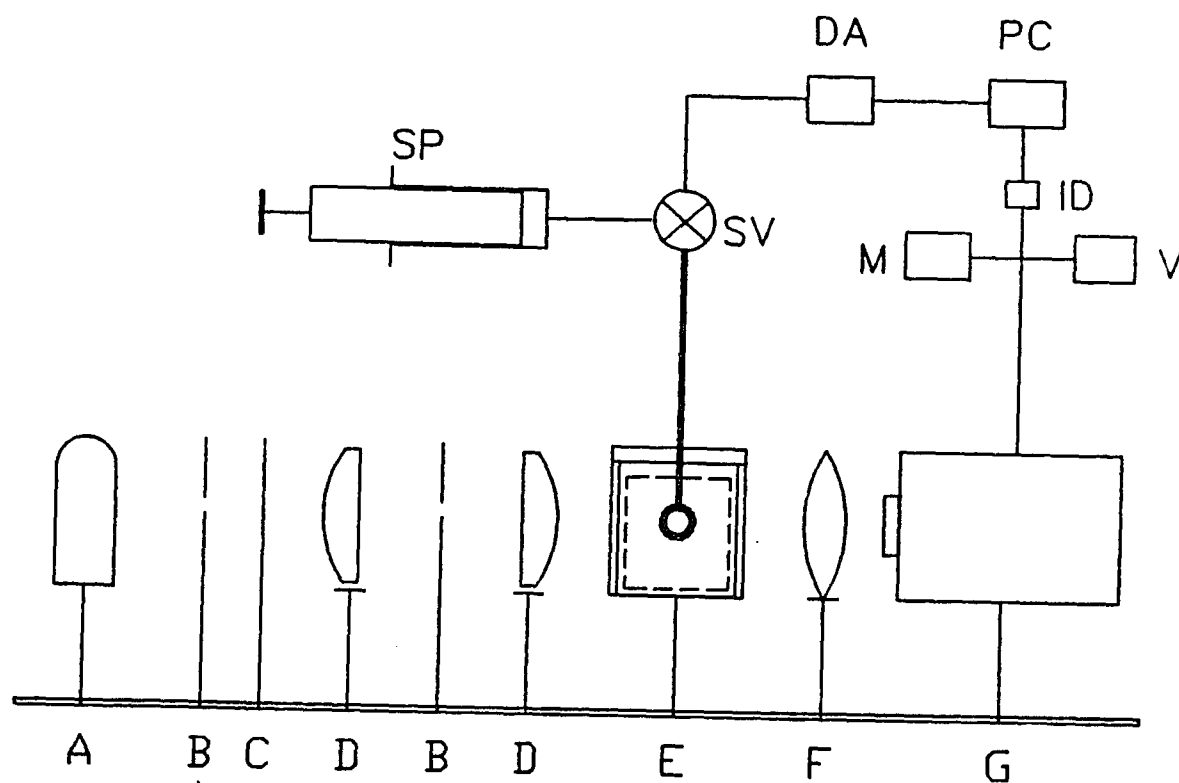


Figure 1. Schematic of the pendant drop tensiometry apparatus and the video image digitization equipment.

A: Light source. B: Pin hole. C: Filter.

D: Plano-convex lens. DA: D/A Data Translation card.

E: Thermostatic chamber, Quartz cell, and suspending needle.

F: Objective lens. G: Video camera. ID: Image digitizer.

M: Monitor. PC: IBM-PC AT. SP: Syringe and syringe pump.

SV: Solenoid valve. V: Video recorder.

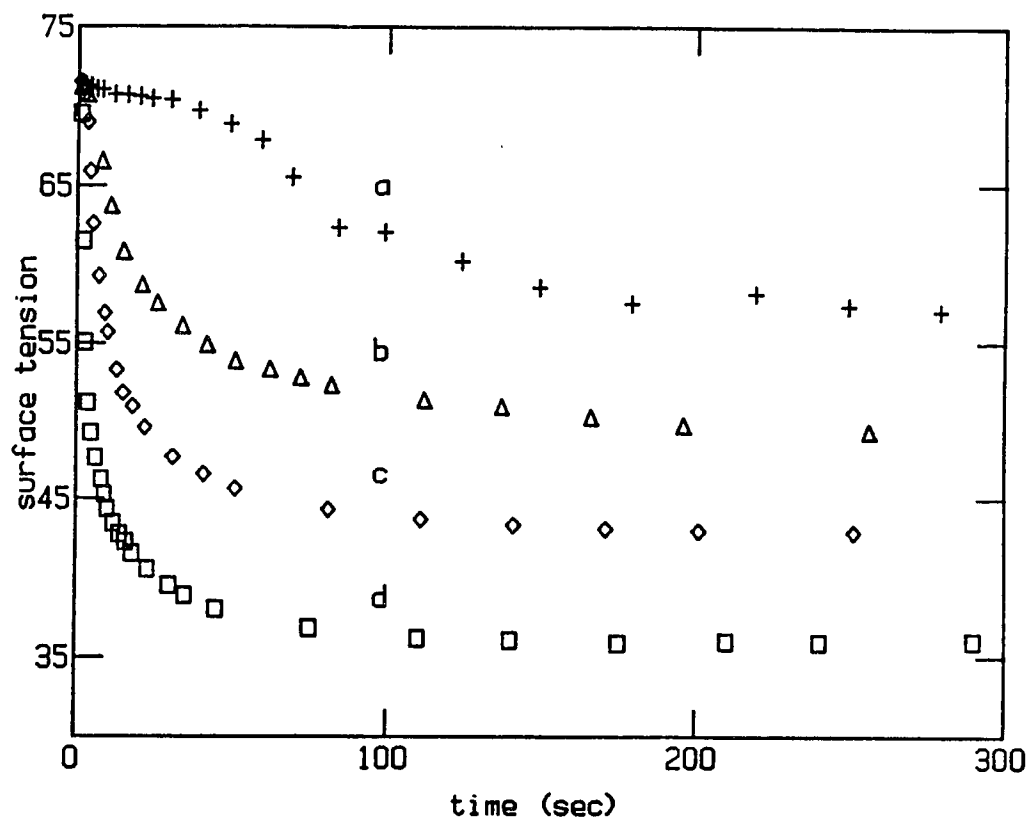


Figure 2. Representative dynamic surface tensions (mN/m) of n-decanol aqueous solutions for C_0 = (a) 4.0×10^{-8} , (b) 7.0×10^{-8} , (c) 1.0×10^{-7} , (d) 1.586×10^{-7} mol/cm³.

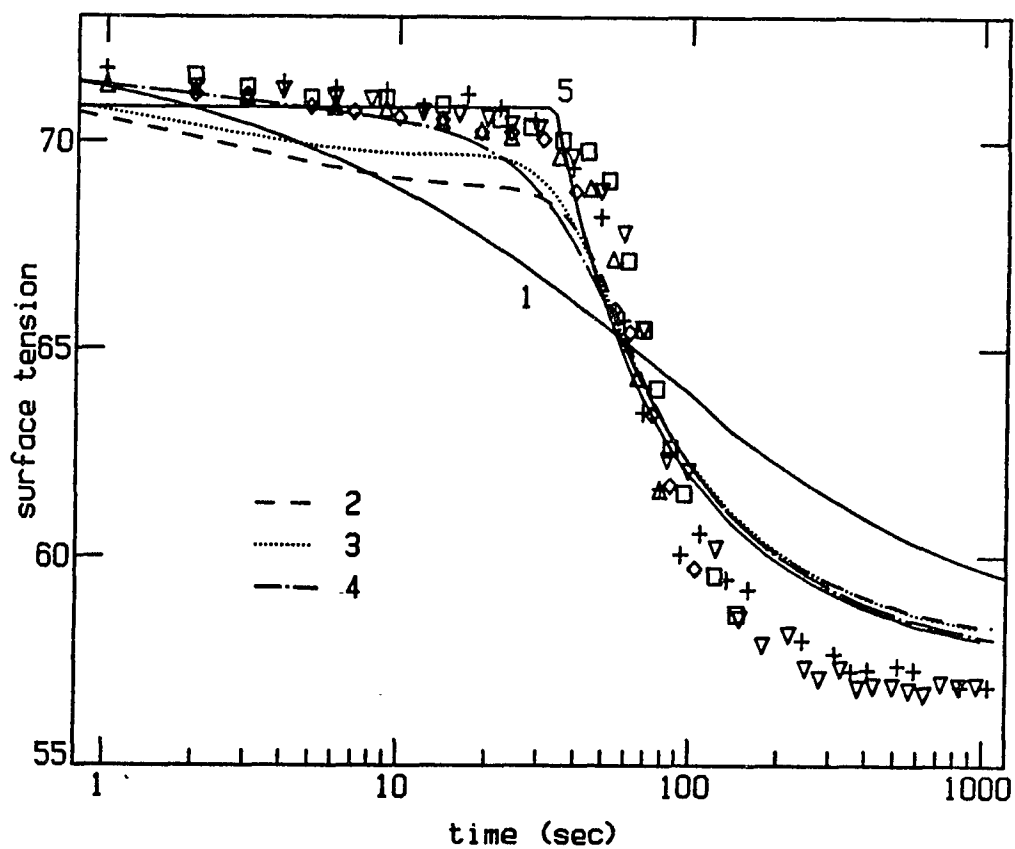


Figure 3a. Experimental values of the dynamic surface tensions (mN/m) of decanol solutions and the theoretical predictions of the models (1-Langmuir, 2-Frumkin, 3-van der Waals, 4-Generalized Frumkin, 5-Phase transition) for $C_0 = 4.0 \times 10^{-8}$ mol/cm³. Each symbol represents a separate bubble.

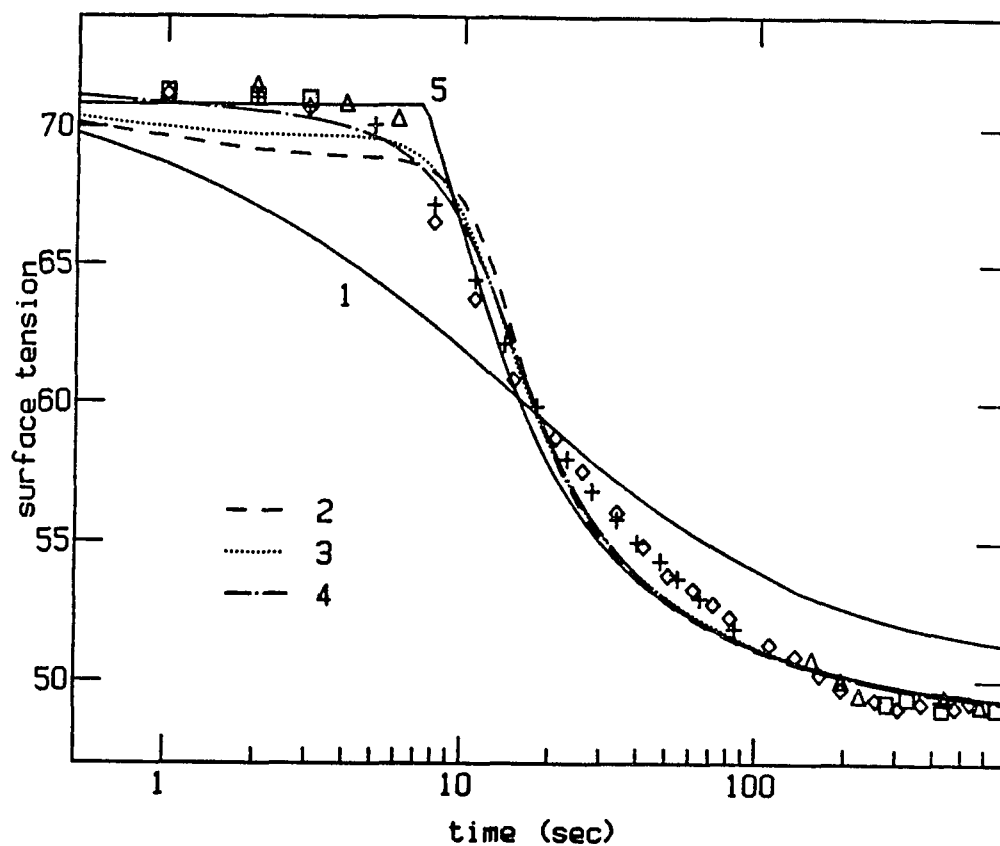


Figure 3b. Experimental values of the dynamic surface tensions (mN/m) of decanol solutions and the theoretical predictions of the models (1-Langmuir, 2-Frumkin, 3-van der Waals, 4-Generalized Frumkin, 5-Phase transition) for $C_0 = 7.0 \times 10^{-8}$ mol/cm³. Each symbol represents a separate bubble.

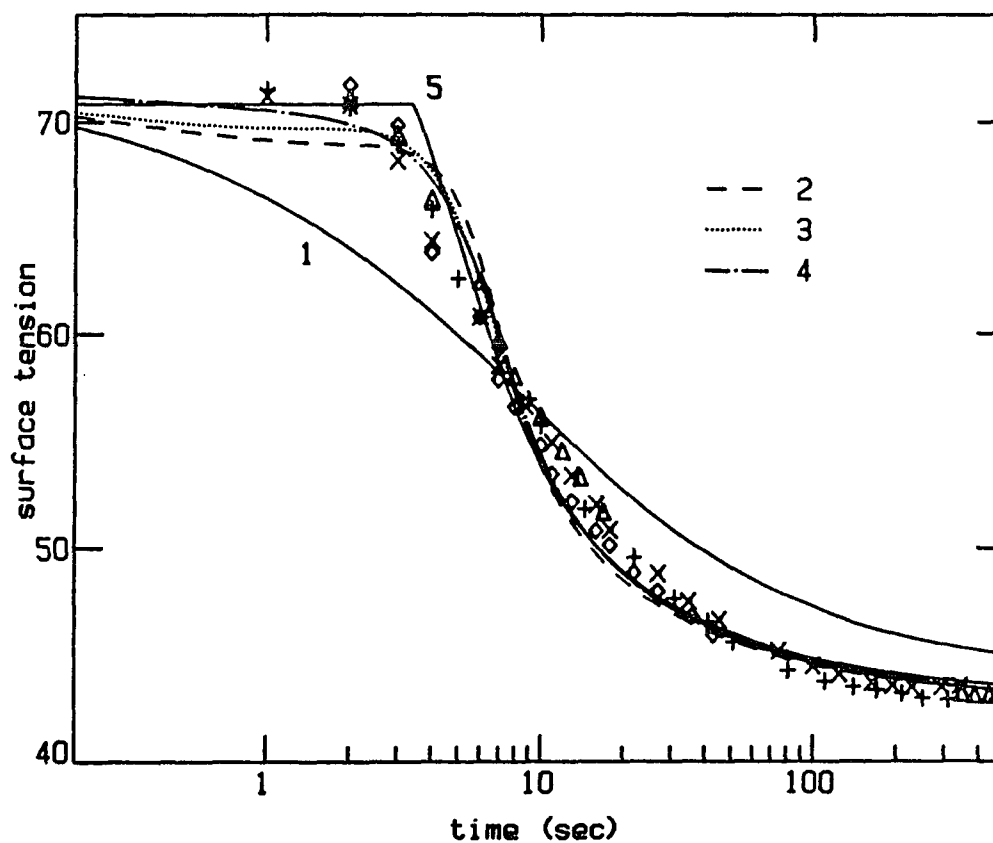


Figure 3c. Experimental values of the dynamic surface tensions (mN/m) of decanol solutions and the theoretical predictions of the models (1-Langmuir, 2-Frumkin, 3-van der Waals, 4-Generalized Frumkin, 5-Phase transition) for $C_0 = 1.0 \times 10^{-7}$ mol/cm³. Each symbol represents a separate bubble.

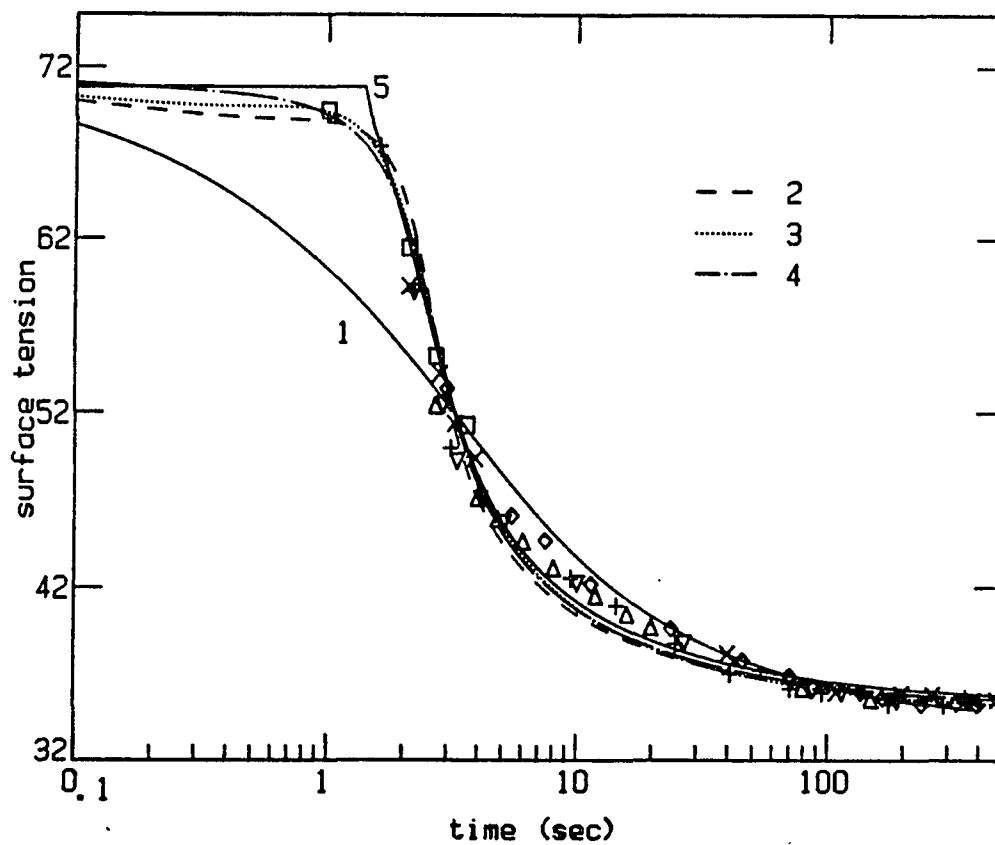


Figure 3d. Experimental values of the dynamic surface tensions (mN/m) of decanol solutions and the theoretical predictions of the models (1-Langmuir, 2-Frumkin, 3-van der Waals, 4-Generalized Frumkin, 5-Phase transition) for $C_0 = 1.586 \times 10^{-7}$ mol/cm³. Each symbol represents a separate bubble.

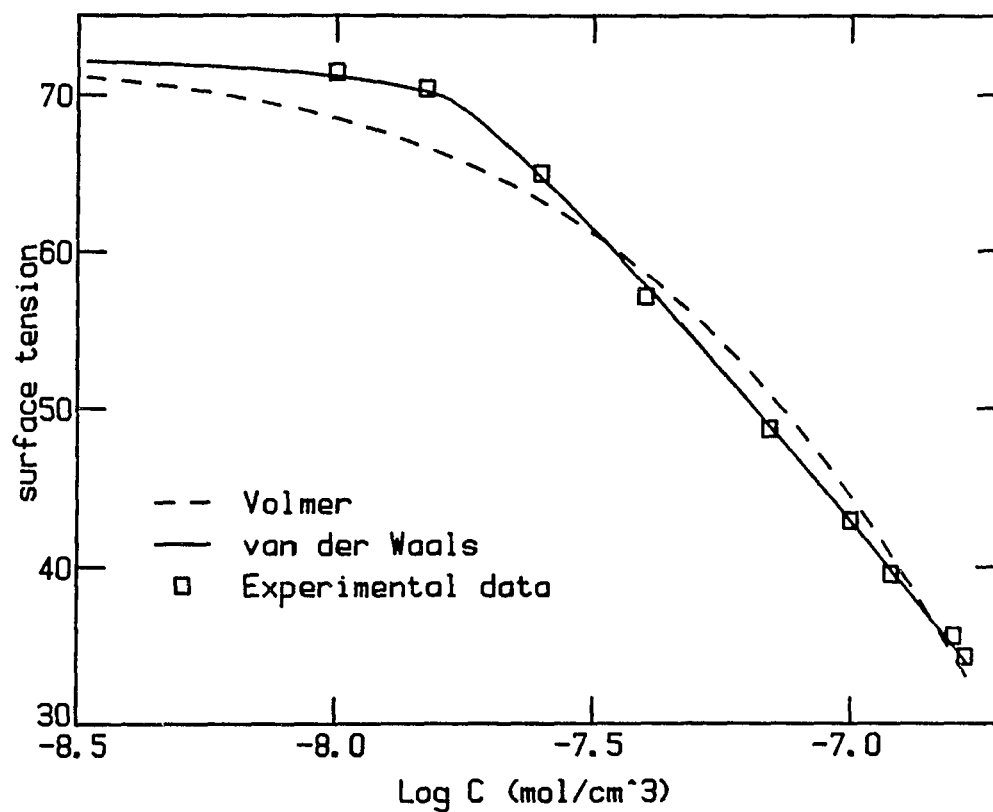


Figure 4a. Equilibrium surface tension (mN/m) for air/n-decanol aqueous solution and theoretical predictions of nonlocalized Models: Volmer and van der Waals equations of state.

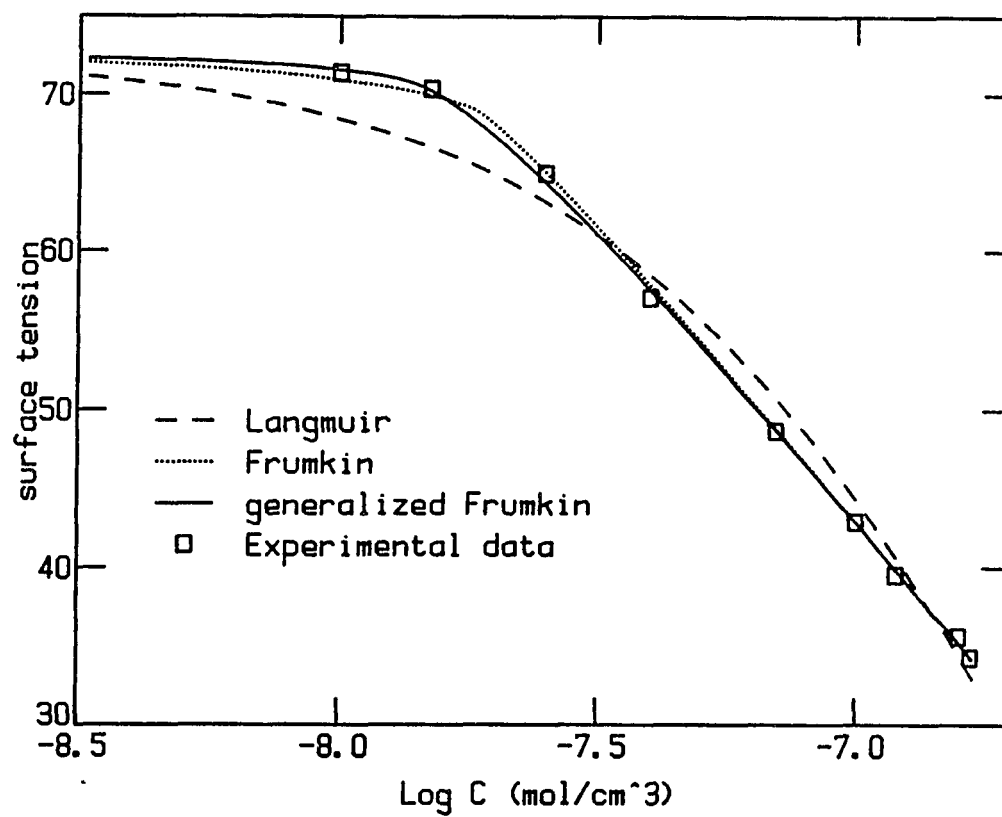


Figure 4b. Equilibrium surface tension (mN/m) for air/n-decanol aqueous solution and theoretical predictions of localized Models: Langmuir, Frumkin, and generalized Frumkin adsorption isotherms.

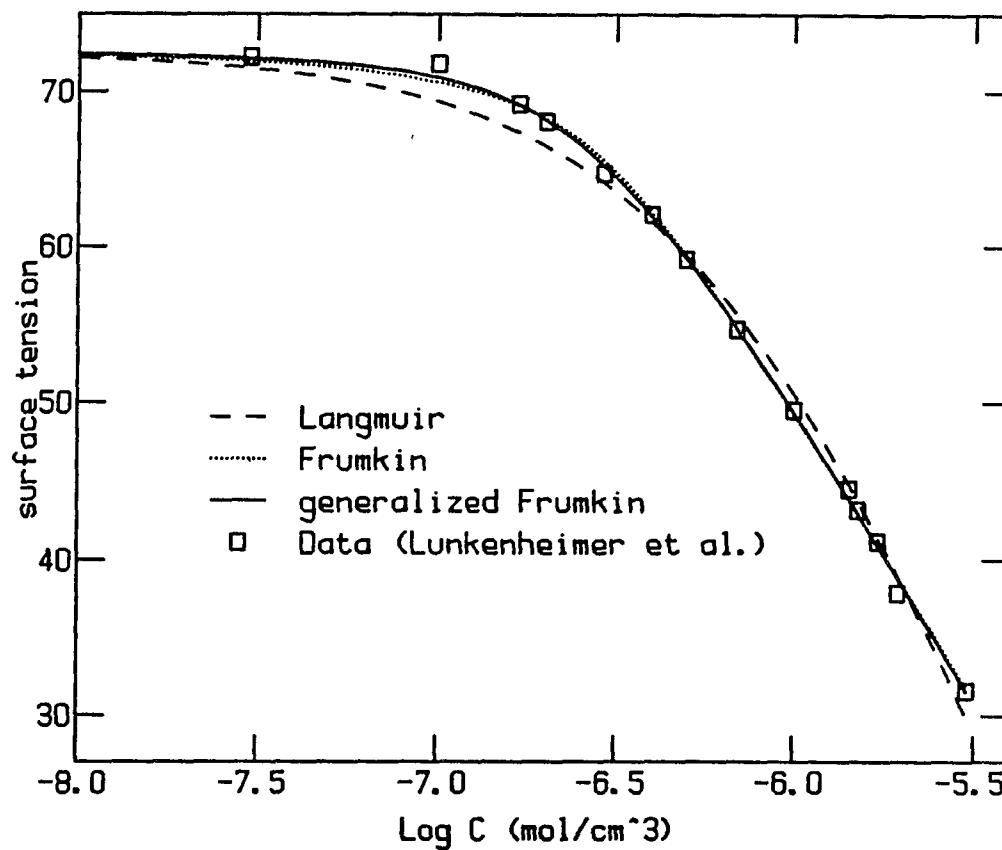


Figure 5a. Equilibrium surface tension (mN/m) data and localized model theoretical predictions for n-octanol (data from Lunkenheimer et al.¹⁰); Langmuir, Frumkin, and generalized Frumkin adsorption isotherms.

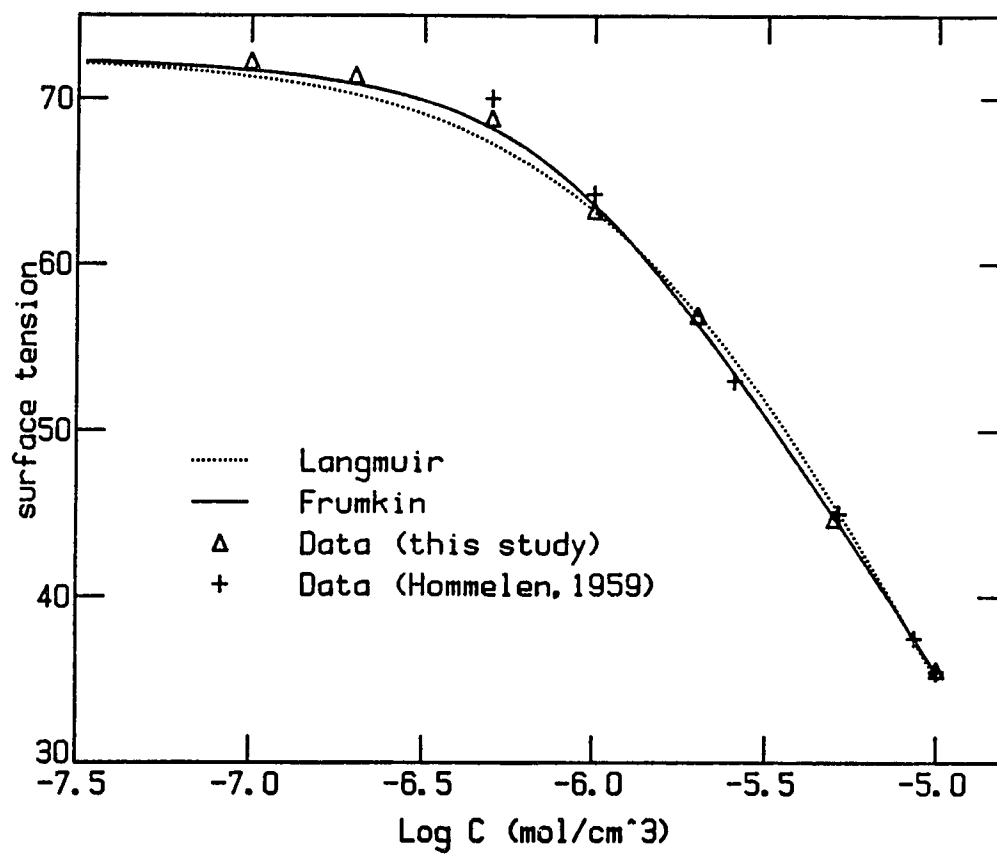


Figure 5b. Equilibrium surface tension (mN/m) data and localized model theoretical predictions for n-heptanol (data from this study and Hommelen³⁰; Langmuir, and Frumkin adsorption isotherms).

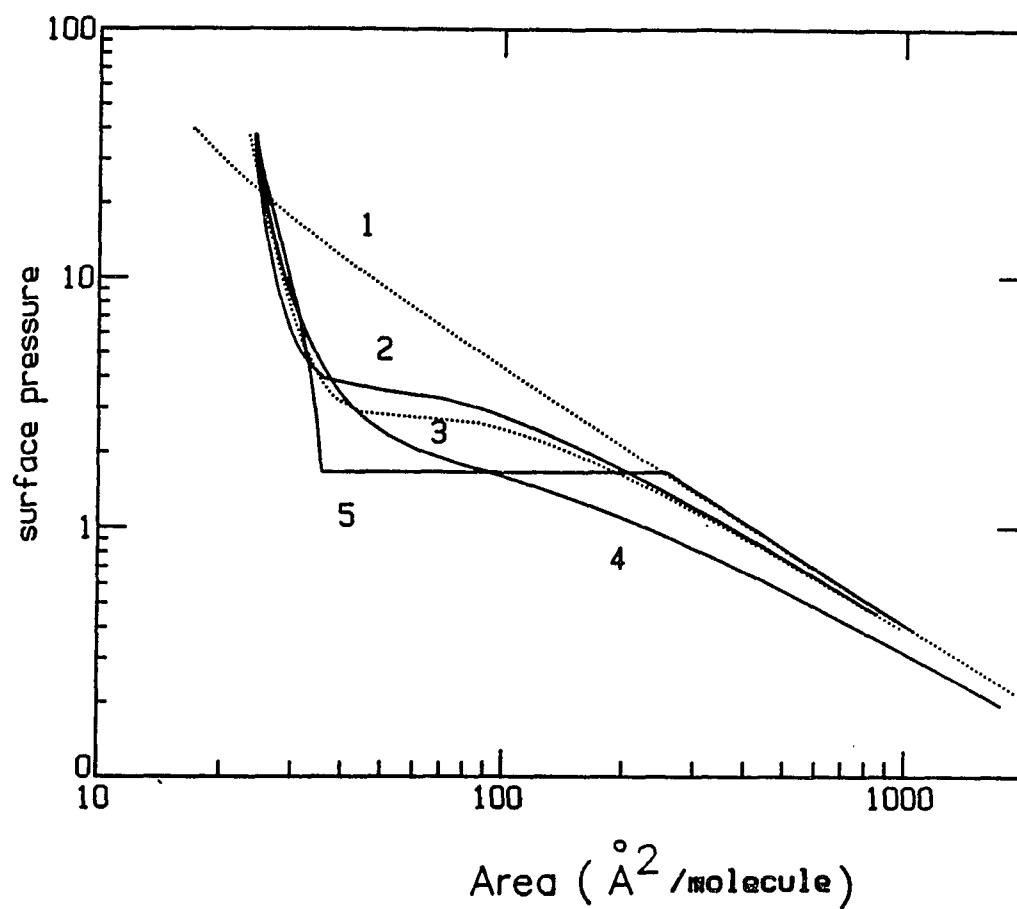


Figure 6. Surface pressure versus area per molecule relationships for the interface of air/n-decanol aqueous solutions using (1) Langmuir or Volmer, (2) Frumkin, (3) van der Waals, (4) generalized Frumkin, (5) Phase transition models.

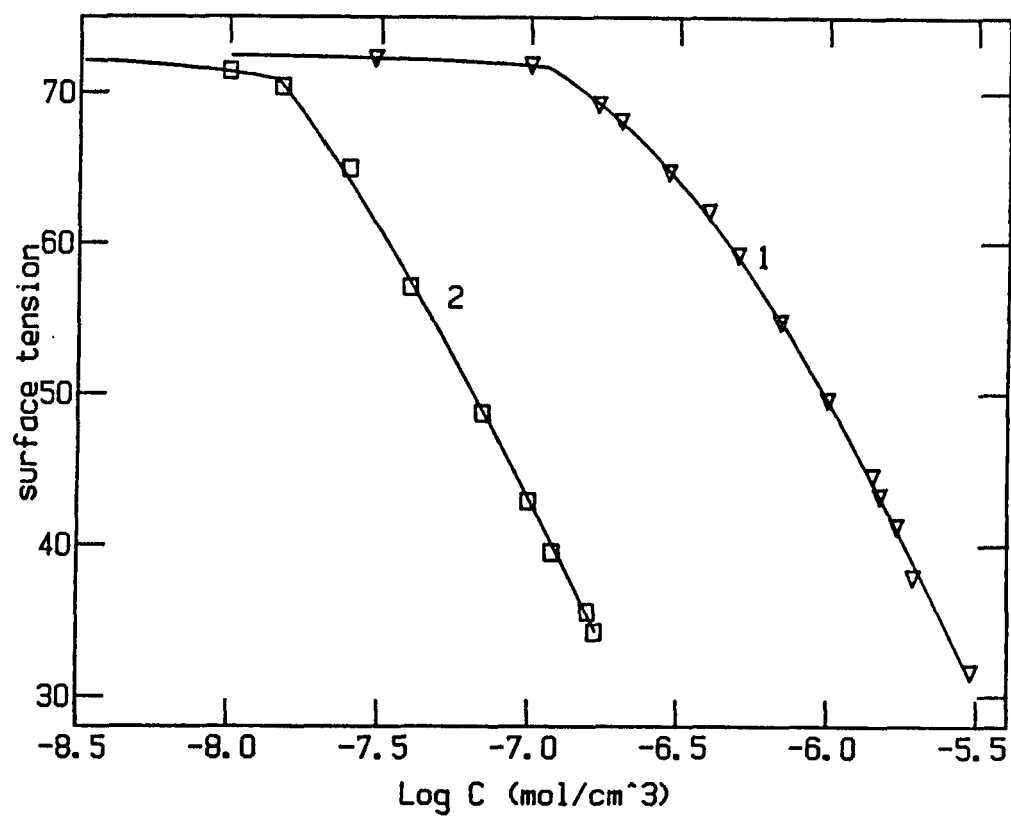


Figure 7. Equilibrium surface tension (mN/m) for (1) air/n-octanol and (2) air/n-decanol aqueous solution and theoretical predictions of the Phase Transition model.

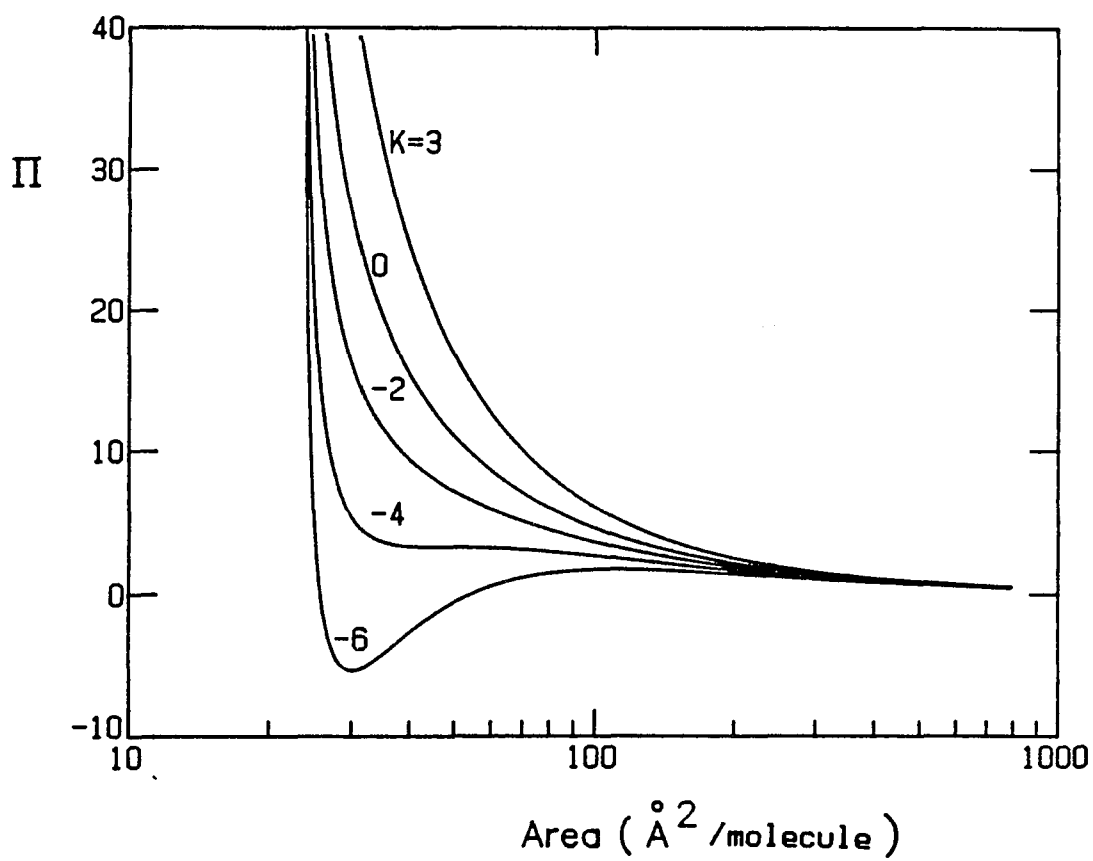


Figure 8. Surface pressure versus area per molecule relationships for the Frumkin isotherm demonstrating spinoidal behavior for K less than a critical value $K_c = -4$.

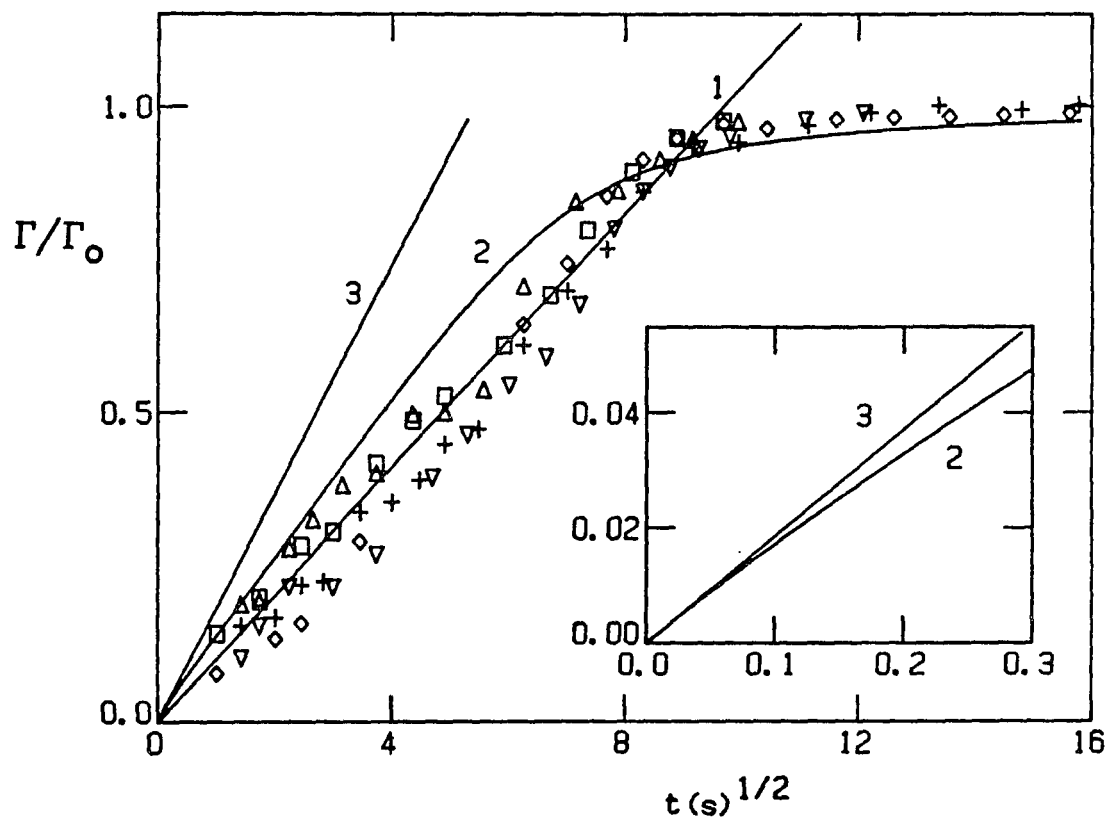


Figure 9. Surface concentration (Γ) versus $\sqrt{t}$ behavior: experimental data, (1) best-fit straightline ($D=2.0 \times 10^{-6} \text{ cm}^2/\text{s}$), (2) numerical relaxation using the generalized Frumkin isotherm and (3) the short time approximation ($\Gamma/\Gamma_0 = (2C_0/\Gamma_0)(Dt/\pi)^{1/2}$) for $C_0=4 \times 10^{-8} \text{ mol/cm}^3$ and $D=6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ (for 2,3). The inset details the small coverage behavior with $t^{1/2}$.

CHAPTER 5

The Effect of Cohesive Energies Between Adsorbed Molecules on Surfactant Exchange Processes: Shifting From Diffusion Control for Adsorption to Kinetic-Diffusive Control for Re-equilibration

5.1 Introduction

Bulk soluble surfactant molecules exchange between a fluid interface and the adjoining bulk sublayer through the kinetic processes of adsorption and desorption. The description of these rate processes, and the evaluation of the kinetic constants are important in understanding the influence of surfactant adsorption on many processes, particularly those involving the motion of fluid particles. Surfactant adsorbed onto the interfaces of moving fluid particles are convected to stagnation regions on the particle surface where they accumulate and give rise to Marangoni stresses which retard the surface flow. This loss in interfacial mobility significantly affects the physicochemical hydrodynamics of the fluid particle flow.⁷⁹

To date, kinetic rate constants have been primarily determined by measuring the surface tension relaxation when a initially clean interface is formed in the surfactant solution. Some examples include the oscillating jet,^{4,21,22} pendant drop,^{63,80,81} maximum bubble pressure,²⁴⁻²⁷ drop weight,^{30,31} Wilhelmy plate and Du Nouy ring³⁴ and falling film methods.²⁸ In determining from these relaxations the kinetic constants, it is important to note that the relaxations are determined by the the series processes of bulk diffusion and sorption kinetics. In principle, the kinetic constants can be determined by

comparing the numerical solutions to the experimental relaxations. In practice, however, the diffusion coefficient is not known precisely, and therefore fitting the data involves determining two constants, and this cannot often be done uniquely. The solution is to assume the process is either diffusion controlled or sorption kinetic controlled, and therefore to evaluate only one parameter. A second relaxation curve can be obtained by measuring the surface tension following a sudden contraction (or expansion) of an interface originally at equilibrium. Experiments of this kind have been done for small deviations on the surface of a Langmuir trough and in the geometry of a (reversed) funnel^{16,32} for a single expansion or contraction, and on the surface of a Langmuir trough for a periodic cycle of expansion and contraction. In principle, the relaxations obtained from deviations from equilibrium coverage along with relaxations corresponding to adsorption onto a clean interface can be used to simultaneously resolve the diffusion coefficient and the kinetic parameters.

When the adsorbing species consists of long slender hydrocarbon chains and small polar groups such as long chain n-alcohols, strong cohesive forces can be created at high surface concentrations. As the interface becomes crowded, the molecules become oriented perpendicular to the interface facilitating strong van der Waals bonding.^{72,78} In this case the desorption becomes very slow because of the large energy barrier it is necessary to overcome to move the surfactant from the surface into the bulk. This effect bears significantly on developing an accurate methodology for measuring simultaneously the diffusion coefficient and the kinetic rate constants. When such surfactants adsorb onto a clean interface, this deceleration in the adsorption rate only effects the latter stages of the surface tension relaxation for which the accumulated surface coverage is reasonably high. On the other hand, when the interface is compressed or expanded from an equilibrium, relatively high surface coverage, the effective

desorption rate governing the surface tension relaxation is much smaller than in the adsorption case. Therefore this re-equilibration relaxation is more kinetically limited than the adsorption relaxation. Ideally one may choose conditions for which the adsorption relaxation is diffusion controlled, and the re-equilibration relaxation is of mixed control, i.e. governed by both diffusion and sorption kinetics. Determination of the diffusion coefficient and the kinetic constants is then straightforward. The adsorption surface tension relaxation data is used to obtain the diffusion coefficient, and the mixed re-equilibration relaxation is used to obtain the kinetic constants using the already determined value of the diffusion coefficient.

In this study we examine theoretically the concept that surfactants with strong cohesion can have diffusion controlled adsorption and mixed re-equilibration relaxations. We adopt a simple surface geometry in which surfactant present in a semi-infinite liquid phase absorbs onto a planar surface, and we solve numerically for the mixed surfactant transfer consisting of one dimensional bulk diffusion and sorption exchange. We obtain solutions for adsorption onto a clean surface and re-equilibration of a perturbed equilibrium monolayer. To incorporate the influence of intermolecular cohesion on the sorption kinetics, a Frumkin expression is used in which the activation energy for desorption increases with the surface concentration.

Previous theoretical studies of the adsorption of surfactant onto a interface have neglected the influence of cohesive forces, and have used the Langmuir model to formulate the kinetics. Ward and Tordai³ developed, for a semi-infinite planar geometry, a linear convolution integral solution for the surface concentration as a function of time in terms of the unknown subsurface concentration. For the case of diffusion control, the surface concentration is obtained by simultaneously solving the integral equation and the adsorption isotherm, while for mixed kinetics the sorption kinetic expression

must be solved alongside the integral expression. For low bulk concentrations the equilibrium and kinetic expressions derived from Langmuir kinetics is linear, and Sutherland⁸² and Hansen¹⁷ present analytical solutions for the diffusion limited and mixed regimes respectively of adsorption onto a clean interface. Numerical solutions for moderate bulk concentrations and again adsorption onto a clean interface using Langmuir kinetics and the Ward and Tordai expression were obtained by several authors.^{18,19,56} The inclusion of cohesive forces were undertaken by Miller⁸³ for diffusion controlled adsorption by solving the convolution integral with the Frumkin and van der Waals isotherms. This study was extended by Borwankar and Wasan²⁰ to include the solution for mixed adsorption using a modified Frumkin kinetic expression. While these last two studies clearly demonstrate the influence of the cohesive energy interaction parameter on the adsorption relaxation, they do not compare these curves with the corresponding re-equilibration relaxations. Therefore no information can be obtained on the central premise of this paper that for the same value of the kinetic constants adsorption can be diffusion controlled while re-equilibration mixed. Finally, re-equilibration curves have been discussed by Van hunsel *et al.*,¹⁵ but only in the context of diffusion control and small perturbations from equilibrium. In this case the relaxations can be described by a modification of Sutherland's equations since the kinetics is linear for small deviations,.

This chapter is divided into four sections. Section 5.2 uses an activation energy approach to include the decelerating effect of cohesive energies on the rate of desorption. Section 5.3 gives the governing surfactant transport equations necessary to describe clean interface adsorption and re-equilibration, and discusses the numerical solution procedure. The simulation results are discussed in Sec. 5.4,

and consist of an examination of the influence of the cohesion interaction parameter and the surface activity on the surface tension relaxations. The chapter ends with a conclusions section which describes how these simulations can be used in identifying the proper experimental conditions necessary to measure both the diffusion coefficient and the sorption rate constant.

5.2 Adsorption Isotherms and Equations of State

In order to describe an adsorption-desorption kinetic process in which the kinetic rates are dependent on the surface coverage, an activation energy framework^{70,78} can be used. Thus the rates of adsorption and desorption are expressed in terms of Arrhenius type equations in which the activation energy is a function of the surface concentration:

$$\frac{d\Gamma}{dt} = \beta \exp(-E_a/RT) C_s(\Gamma_\infty - \Gamma) - \alpha \exp(-E_d/RT)\Gamma \quad (1)$$

In the above, t denotes time, C_s is the sublayer concentration and β , α , $E_a(\Gamma)$, and $E_d(\Gamma)$ are, respectively, the pre-exponential factors and the energies of activation for adsorption and desorption. To describe the functional dependence of the activation energies on the coverage, a general power law form is used:

$$\begin{aligned} E_a &= E_a^0 + \nu_a \Gamma^n \\ E_d &= E_d^0 + \nu_d \Gamma^n \end{aligned} \quad (2)$$

where E_a^0 , E_d^0 , ν_a and ν_d are constants. Eq. 1 in nondimensional form becomes:

$$\frac{dx}{d\tau} = K_a \exp(-\nu'_a x^n) C'_s(1-x) - K_d \exp(-\nu'_d x^n) x \quad (3)$$

where $x = \Gamma/\Gamma_\infty$, $\tau = tD/h^2$, $h = \Gamma_\infty/C_o$, $K_a = \beta C_o/(D/h^2)$, $K_d = \alpha/(D/h^2)$,

$\nu'_a = \nu_a \Gamma_\infty^n/RT$, $\nu'_d = \nu_d \Gamma_\infty^n/RT$, and $C'_s = C_s/C_o$.

At equilibrium, the time rate of change of Γ vanishes and the adsorption isotherm ($\Gamma(C)$) which follows is given by:

$$\frac{\Gamma}{\Gamma_{\infty}} = x = \frac{C}{a \exp(Kx^n) + C} \quad (4)$$

where $k = (\nu_a - \nu_d)\Gamma_{\infty}^n/RT$ and $a = (\alpha/\beta)\exp[(E_a^0 - E_d^0)/RT]$

Note from Eq. 4 cooperativity or enhanced adsorption at increasing surface concentration occurs when $K < 0$ or $\nu_d > \nu_a$. The corresponding equation of state is

$$(\gamma - \gamma_0)/(\Gamma_{\infty}RT) = [\ln(1-x) - \frac{kn}{n+1} x^{n+1}] \quad (5)$$

When $n=1$, Eq. 4 reduces to Frumkin adsorption isotherm⁷¹, and when $\nu_a = \nu_d = 0$, the Langmuir adsorption isotherm is obtained. In this theoretical study, attention is focused on the case of $n=1$ which is the simplest for describing the phenomenon.

An expression for the surface tension (nondimensionalized by $\Gamma_{\infty}RT$) as a function of C_0/a can be obtained by first numerically solving Eq. 4 to obtain Γ_e/Γ_{∞} , and then substituting this result into Eq. 5. Figure 1a plots the nondimensional surface tension as a function of the logarithm of C_0/a for different decreasing values of k starting with $k=0$ (Langmuir adsorption). Recall that the slope of these curves is proportional to the equilibrium surface concentration. Figure 1a shows that as k decreases the curves begin to develop a cusp like behavior in which the slope (and therefore the surface concentration) increases rapidly in absolute value with only a very small change in C_0/a . This represents the effect of intermolecular attraction: As soon as the surface concentration reaches some critical value, attractive energies between the adsorbed molecules lowers the desorption rate and therefore raises the equilibrium adsorption with an incremental change in C_0/a . This effect is shown in Figure 1b,

where near step like increases in the surface concentration begin to occur as a function of C_0/a when k is decreased sufficiently. However the cohesive energy also lowers the surface pressure (this is described by the second term in Eq. 5), and hence the increased adsorption does not lower the surface tension that significantly. This is the origin of the cusp. Eventually, after the concentration is raised to values nearing Γ_∞ , the repulsive attraction represented by the $1-\Gamma/\Gamma_\infty$ term dominates, and the surface tension decreases rapidly. This phenomenon of large adsorption with little change in the surface tension is more clearly evident in the Π -A curve which is plotted nondimensionally in Figure 1c as $(\gamma_0 - \gamma_e)/RT\Gamma_\infty$ against Γ_∞/Γ . Note that if the value of k is small enough, this type of Π -A behavior begins to resemble a phase transition in which a region of constant surface tension separates liquid expanded and gaseous phases as in the case of insoluble monolayers. The description of the effect of intermolecular attraction by the formation of a second phase represents an alternate way of describing this phenomena.

5.3 Governing Mass Transfer Equations and Numerical Solution Procedure

We shall consider only the case of one dimensional diffusion and adsorption onto a planar surface from a bulk phase containing initially a uniform distribution of the surface active solute. At $t=0$, the surface is considered to have a specified surface concentration Γ_b , which can be equal to zero (for adsorption to an initially clean surface), or nonzero (for desorption from an overcrowded interface). Diffusion of surfactant in the bulk continuous phase is described by the nondimensional Fick's law

$$\frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial \tau} \quad (z > 0, \tau > 0) \quad (6)$$

where z , the distance away from the interface, has been nondimensionalized by the adsorption depth h , and the bulk

concentration $C(z, \tau)$ and the time τ have been nondimensionalized, respectively, by the far field bulk concentration (C_0) and the diffusion time scale in the adsorption depth (h^2/D). The boundary and initial conditions for Eq. 6 are:

$$\begin{aligned} C(z, \tau) &= 1 & (z > 0, \tau = 0) \\ C(z, \tau) &= 1 & (z \rightarrow \infty, \tau > 0) \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{dx(\tau)}{d\tau} &= \left(\frac{\partial C}{\partial z} \right) & (z = 0, \tau > 0) \\ x(\tau) &= x_b & (\tau = 0) \end{aligned} \quad (8)$$

To complete the solution for the surface concentration, the diffusive flux is equated to the net rate of kinetic adsorption as given by the right hand side of Eq. 4.

The above system of field Eq. 6, boundary conditions (Eqs. 4&7) and initial condition (Eq. 8) is solved in the following manner. By the Laplace transform, a general solution to the field equation which incorporates Eqs. 7 & 8 may be formulated in terms of the unknown subsurface concentration $C'_s(\tau) = C(z=0, \tau)$:

$$x(t) - x_b = \left(\frac{2}{\sqrt{\pi}} \right) \left[\sqrt{\tau} - \int_0^{\sqrt{\tau}} C'_s(\tau - \tau') d\sqrt{\tau'} \right] \quad (9)$$

The subsurface concentration is determined numerically from Eq. 4 by a modification of a technique used by Miller and Kretzschmar.¹⁰ First, the convolution integral of C'_s in Eq. 9 is integrated by first partitioning the interval $(0, \tau)$ into intervals of size δ in time, and integrating separately each interval by assuming a linear relation in time for C'_s .

$$\begin{aligned} \int_0^{\tau} C'_s(\tau - \tau') / \sqrt{\tau'} d\tau' &= \sum_{i=0}^{n-1} \int_{i\delta}^{(i+1)\delta} \{ [C((n-i-1)\delta) - C((n-i)\delta)] \tau' / \delta \\ &\quad + [(i+1)C((n-i)\delta) - iC((n-i-1)\delta)] \} / \sqrt{\tau'} d\tau' \\ &= \left[\frac{4}{3} C(n\delta) + \frac{2}{3} C((n-1)\delta) \right] \sqrt{\delta} \end{aligned}$$

$$\begin{aligned}
& - \sum_{i=1}^{n-1} \frac{2}{3} [C((n-i)\delta) - C((n-i-1)\delta)] [(i+1)^{3/2} - i^{3/2}] \sqrt{\delta} \\
& + \sum_{i=1}^{n-1} 2[(i+1)C((n-i)\delta) - iC((n-i-1)\delta)] [(i+1)^{1/2} - i^{1/2}] \sqrt{\delta} \quad (10)
\end{aligned}$$

After integration, Eq. 9 is of form

$$C'_s(\tau_n) = b_1 x(\tau_n) + b_2 \quad (11)$$

where $\tau_n = n\delta$ and the constants b_1 and b_2 are a function of the concentrations $C'_s(0)$, $C'_s(\delta)$... $C'_s(\tau_{n-1})$. Eq. 3 is then solved numerically by first separating the variables and then integrating from $x(\tau_{n-1})$ to $x(\tau_n)$ using Simpson's 1/3rd rule.⁸⁴ In this numerical integration, C'_s is assumed to be a constant value during the small integration time step δ , and is set equal to the average value of $C'_s(\tau_{n-1})$ and $C'_s(\tau_n)$. By using Newton's method,⁸⁴ a value for $x(\tau_n)$ is found for which the surface concentration integral is equal to δ . The dynamic surface tension at time τ_n is obtained from Eq. 5 once the surface concentration $x(\tau_n)$ is known.

5.4 Results

Two types of numerical simulations are presented. The first is an *adsorption* simulation in which surfactant adsorbs onto an initially clean planar surface ($\Gamma_b=0$) from a bulk phase of uniform concentration ($C'(\tau=0, z)=1$, $z \geq 0$). The second is a *desorption* simulation in which a planar surface with a surface concentration, Γ_e , in equilibrium with a uniform bulk concentration C_o , is instantly compressed ($\Gamma_b > \Gamma_e$), and surfactant overcrowding causes desorption into the uniform bulk. The overcrowding is taken to be 10% (case I, fixed C_o/a) or 3% (case II, fixed k) of the equilibrium value, i.e. $\Gamma_b = 1.1\Gamma_e$. The reason for

selecting the same contraction ratio is because it is experimentally the most feasible.

The adsorption simulations are discussed first. The relaxation in surface tension is presented nondimensionally in terms of the variable θ defined as follows:

$$\theta(\tau) = \frac{\gamma - \gamma_e}{\gamma_b - \gamma_e} \quad (12)$$

where γ_b is the surface tension at time $t=0$ when the surface concentration is Γ_b ; therefore, $\gamma_b = \gamma(\Gamma_b)$ and $\gamma_e = \gamma(\Gamma_e)$ is, as before, the equilibrium tension. Here, only the case $\nu'_a=0$ and $n=1$ is considered in order to illustrate the basic ideas. For this case, the nondimensional relaxation $\theta(\tau)$ is a function of C_o/a , k , and K_d ($K_a = K_d(C_o/a)$). Consider first diffusion limited curves ($K_d \rightarrow \infty$); these are shown in Figure 2 for a fixed value of C_o/a ($=1.5$) and four values of k ($0, -1, -2$ and -3.5). The curves are approximately the same, but on closer examination it is clear that as k decrease, the relaxation develops a shoulder or induction period which extends from the initial time $t=0$ and which precedes a rapid decay period. This reflects the presence of strong intermolecular interaction. All curves begin with the same relaxation rate. However as surfactant molecules with strong intermolecular attraction begin to collect on the surface, the cohesive energies tend to keep the surface tension constant and this creates an induction period. This is the same phenomena which gave rise to the development of a near level region in the Π -A curve, and the adsorption process can be viewed during the induction period as proceeding along the nearly level line of constant surface pressure. Finally at sufficiently high concentrations, further addition results in strong repulsion, and the relaxation curves drop sharply down as the Π -A curves rise sharply.

Consider next the influence of finite sorption kinetics. Simulations of θ as a function of r for a fixed value of C_o/a (1.5, the same value as above) are presented in a set of four figures (3a-c) in which, for each figure, k is fixed at one of four values (0, -1 and -2) and K_d is varied from diffusion control ($K_d \rightarrow \infty$) to mixed control ($K_d=100, 10, 1, 0.1$) to sorption kinetic control ($K_d=0.01$). The relaxation in each of these figures has the same general dependence on K_d : The diffusion limited curve ($K_d \rightarrow \infty$) shows the fastest relaxation, and subsequently smaller values of K_d (which correspond to smaller values of K_a as well since $K_a=(C_o/a)K_d$ and C_o/a is fixed) show slower relaxations because of the increasing kinetic barrier. The separation between the diffusion limited relaxation and the curve for a particular value of K_d is approximately the same from figure to figure; thus $K_d=100$ is virtually indistinguishable from the diffusion limited relaxation.

The desorption simulations are discussed next. All desorption simulations use the same value of C_o/a (1.5) as was used for the adsorption relaxations. Consider first the diffusion limited behavior which is presented in Figure 4 for $k=0, -1, -1.5$ and -2 . These show quite clearly that initially, the rate of relaxation is fastest for the lowest value of k (-2), and the initial rate decreases as k increases towards the Langmuir value of 0. The reason for this behavior is due to the selection of the initial condition. At time $t=0$, the surface concentration is increased by 10 percent. The equilibrium surface concentrations for this fixed value of C_o/a are shown as the triangular points in Figure 1b. The surface concentrations at time $t=0$, which are 1.1 of these, are shown as the square points in Figure 1b. Thus for $k=0$, x is increased from 0.60 to 0.66, for $k=-1$, x is increased from 0.76 to 0.84 and finally for $k=-2$,

x is increased from 0.90 to 0.99. However, because the sorption kinetics is infinitely fast, the sublayer concentration C_s takes on immediately the value ($C_s(t=0)/a = 1.9, 2.3, 15.2$ respectively) in equilibrium with x_b . This starting value for $C_s(\Gamma_\infty)$ is much larger for the more negative values of k ; these square symbols represent the values of C_s/a corresponding to the ten percent equilibrium increase. The value for C_o/a for $k=-2$ is nearly an order of magnitude larger than the value for $k=0$. since the initial subsurface concentration is the driving force for the relaxation, the $k=-2$ curve is much faster than the Langmuir curve.

The mixed desorption curves are shown in Figures 5a-c with each figure corresponding to the same value of k (0, -1 and -2) and different values of K_d . As was the case with the adsorption simulations, smaller values of K_d cause slower relaxations relative to the diffusion limited curve. However, unlike the adsorption results, the separation distance between the finite kinetic curve for a particular value of K_d and the diffusion controlled curve increases as k becomes more negative (compare, for example, Figures 5a and 5c for $K_d = 100$). This result is caused by the effect of intermolecular attraction, as may be explained in the following way. As k is decreased and intermolecular attraction increases, the equilibrium concentrations increase: Thus for $k=0$, $x_e=0.60$, for $k=-1$, $x_e=0.76$ and finally for $k=-2$, $x_o=0.90$. Recall that the desorptions pictured in Figures 5a-c are driven by an initial ten percent increase in the surface concentration imposed by a surface shrinkage at $t=0$. Thus surface concentrations are throughout the relaxations much higher in Figure 5c than in 5a. Two competing effects come into play: On the one hand, the desorption rate is proportional to the surface coverage; this is described by the x term multiplying the brackets in the

desorption term of Eq. 3. This effect will tend to increase the desorption rate in going from Figure 5a to 5c. On the other hand, the increase in the intermolecular attraction parameter together with the increase in the surface concentration, lowers significantly the desorption rate as cohesive forces act to retain the molecule in the monolayer. This effect is described by the e^{kx} term within the brackets of the desorption term of Eq. 3. This effect dominates, and causes the markedly slower relaxation of Figure 5c.

Comparison of the adsorption and desorption simulations for the same value of k demonstrates the principal result of this study that as the importance of intermolecular interaction increases, an adsorption can be diffusion controlled, while a desorption can be controlled by both diffusion and sorption kinetics. To illustrate this principle with these figures consider the value of $K_d=100$; the mixed adsorption relaxation for this value is indistinguishable from the diffusion limited curve for the entire range of k . However the desorption curves for this value of K_d become increasingly removed from the diffusion limited relaxations as k decreases. Thus for $k=0$, the desorption curve for $K_d=100$ is nearly indistinguishable from the diffusion limited, while for $k=-2$, the departure is quite distinct.

The above simulations establish the result that if intermolecular attraction is sufficiently strong, for certain values of the kinetic parameters, adsorption relaxations can be diffusion controlled, while desorption relaxations can be mixed. This result was shown for a value of C_o/a equal to 1.5. From the point of view of designing an experiment to measure both the diffusion coefficient and the kinetic constants by taking advantage of this difference, it is important to examine the role of C_o/a . Note first, that if C_o/a is small enough, then the equilibrium adsorption Γ_e/Γ_∞ will be much less than one, and the influence of cohesive forces will not be very

important. This noninteracting state can be identified from Figure 1a, and is basically the range of C_o/a before the appearance of the cusp. From the Figure, this range is $C_o/a < (10^{-1})$. If the surface contraction in the desorption experiment is only of the order a few percent, then the surface coverage remains in the region in which intermolecular interactions are negligible. For this case, the reduction in the desorption rate due to cohesion will not be effective, and adsorption and desorptions will depart similarly from the diffusion limited curve. Alternatively if C_o/a is sufficiently large so as to be away from the cusp point, then the effect of the cohesive forces on the desorption rate become very significant, and the adsorption and desorption curves should differ considerably for the same kinetic parameters. This role of C_o/a is shown in the simulations of Figures 6a-c (adsorption curves) and 7a-c (desorption curves). In all of these simulations, the value of k is equal to -1, and C_o/a is set equal to 0.1 for Figures 6a & 7a, 1 for 6b & 7b and 10 for 6c & 7c. The desorption curves are for a three percent contraction of the surface area, i.e. $(\Gamma_b - \Gamma_e)/\Gamma_e = 0.03$. Comparing adsorption and desorption relaxations for the smallest value of C_o/a , 0.1 which is well before the cusp, we see from Figures 6a & 7a that the separation distances between the mixed kinetic curve and the diffusion limited curve is the same for the same value of K_d . Differences begin to arise as C_o/a is increased, and we see that for $C_o/a = 1$ and $K_d = 100$ (Figures 6b & 7b), the adsorption is essentially diffusion limited, while the desorption is distinctly mixed. This difference becomes even more exaggerated for $C_o/a = 10$ (Figures 6c & 7c). In this case all adsorption relaxations for $K_d > 10$ are diffusion controlled, while the

desorption relaxation is clearly mixed for values of K_d equal to or less than 10^3 .

5.5 Discussion and Conclusions

In order to successfully use these ideas to measure a kinetic constant, careful attention must be paid to the relationship between the real time scales and the actual differences in the surface tension predicted from the nondimensional plots and the sensitivity of the instrument. Figures 6a-c and 7a-c show that the desorption curves depart most significantly from the diffusion limited ones at the higher bulk concentrations. However, at these higher concentrations, the time scale used for nondimensionalization ($h^2/D = \Gamma_\infty^2/(C_0^2 D)$) is inversely proportional to the square of the bulk concentration. As the bulk concentration increases, the nondimensional scale becomes very small, and one nondimensional unit can be very short in real time. For example, the adsorption of straight chain alcohols at the air-water interface display intermolecular attraction.^{18,19} For this case, a is on the order of 10^{-7} mol/cm², D is approximately equal to 5×10^{-6} cm²/s, $\Gamma_\infty \approx 5 \times 10^{-10}$ mol/cm², C_0 ranges up to order of 10^{-6} mol/cm³ and K ranges from 0 to the critical value of -4. Thus for Figure 7c where $C_0/a=10$, the curves all relax in one nondimensional time unit, and this is of the order of 10^{-2} sec. This time scale is too short for many experimental techniques capable of desorption as well as adsorption experiments such as the pendant bubble or drop and reversed funnel methods. In addition for large values of C_0/a , the critical micelle concentration may be reached, and incorporating the diffusion of micelles in the bulk phase alters the mass transfer picture. Thus very high values of C_0/a are not necessarily desirable. Alternatively, if

C_o/a is too small, the absolute change in the surface tension may be too low for the instrument to measure accurately. Therefore values of C_o/a of order one appear optimal.

When C_o/a is small, the mixed curves for adsorption and desorption are, for the same value of K_d , the same distance away from the diffusion limited curves. The major reason for the similarity is that for small C_o/a , the equilibrium surface concentration is much less than Γ_∞ ; since the surface is only contracted by a few percent, the maximum concentration is too low to allow cohesive forces to decelerate the desorption. However, since surface concentrations Γ_e/Γ_∞ is much smaller than one, the surface can be contracted to a much greater extent than a few percent allowing intermolecular cohesion to reduce the desorption rate. Such an experiment would provide another way of demonstrating the effect of cohesion on the kinetic desorption rate.

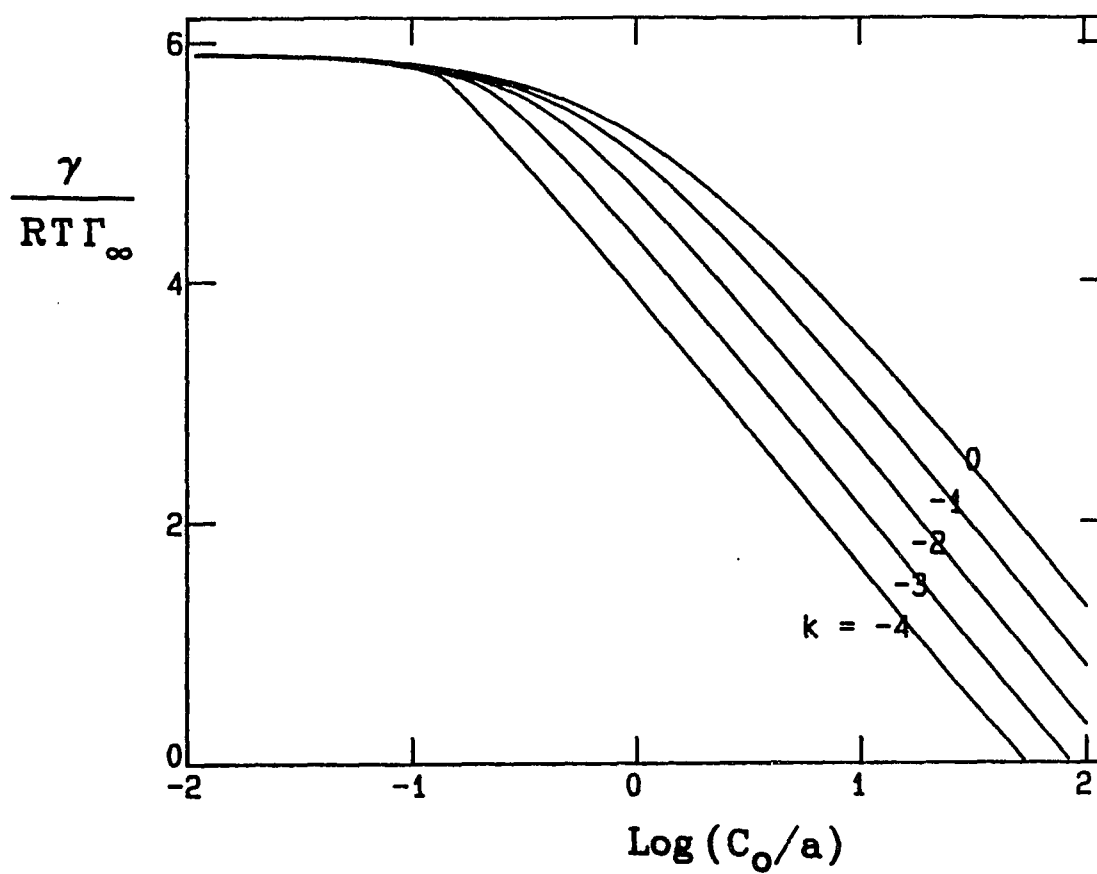


Figure 1a. The influence of the cohesion constant k on the equilibrium surface tension $\frac{\gamma}{RT\Gamma_{\infty}}$ as a function of C_0/a .

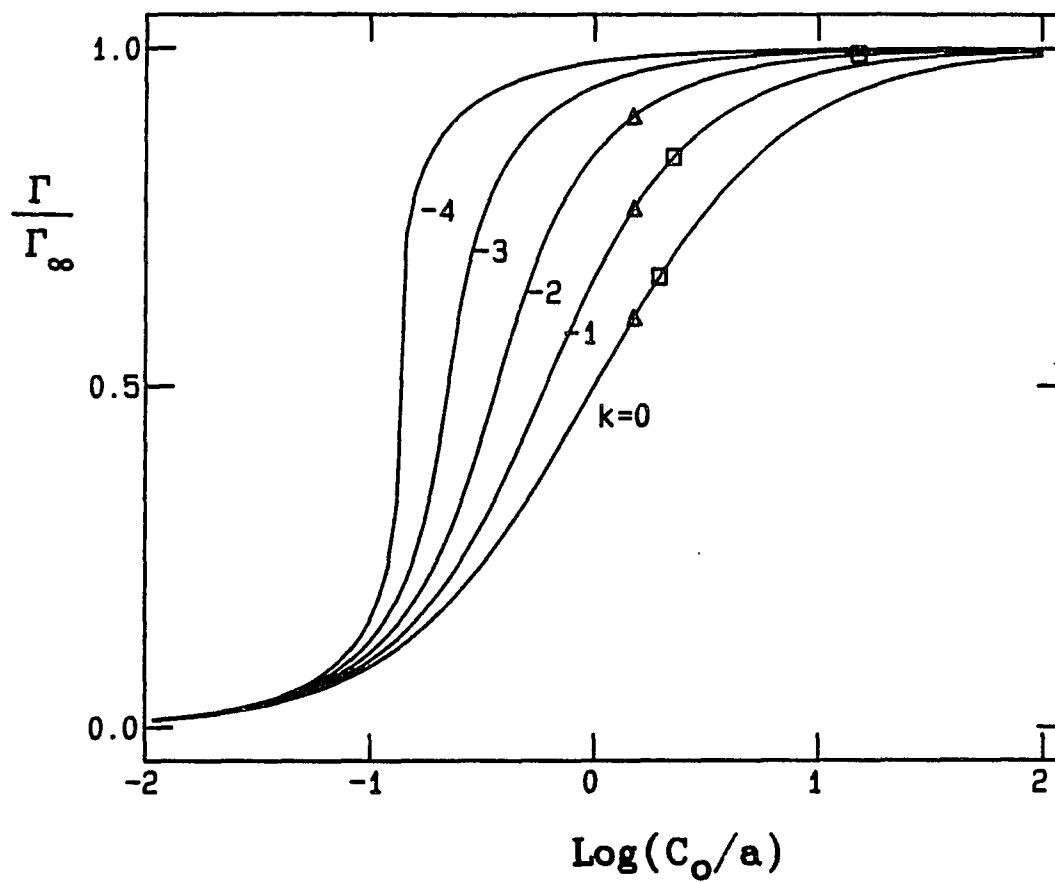


Figure 1b. The influence of the cohesion constant k on the surface concentration Γ/Γ_{∞} as a function of C_0/a .

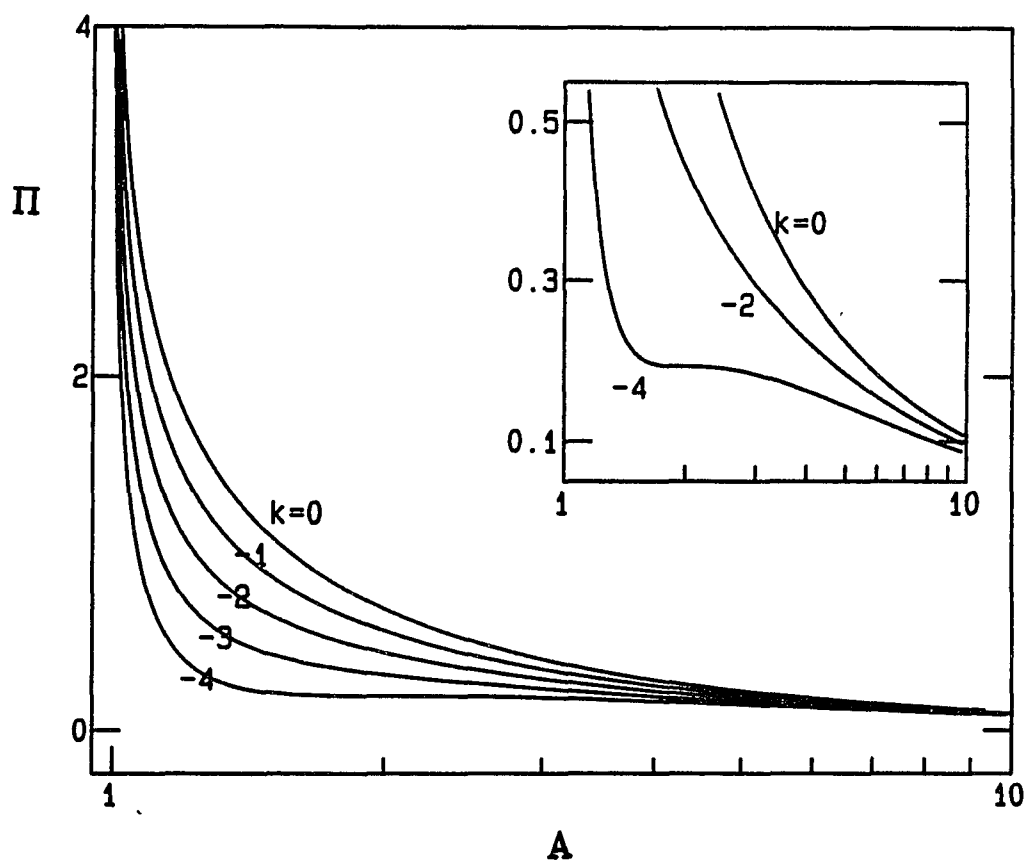


Figure 1c. The influence of the cohesion constant k on the surface pressure

$$\left(\Pi - \frac{\gamma_0 - \gamma}{RT\Gamma_\infty}\right) \text{ as a function of surface area } \left(A - \frac{\Gamma_\infty}{\Gamma}\right).$$

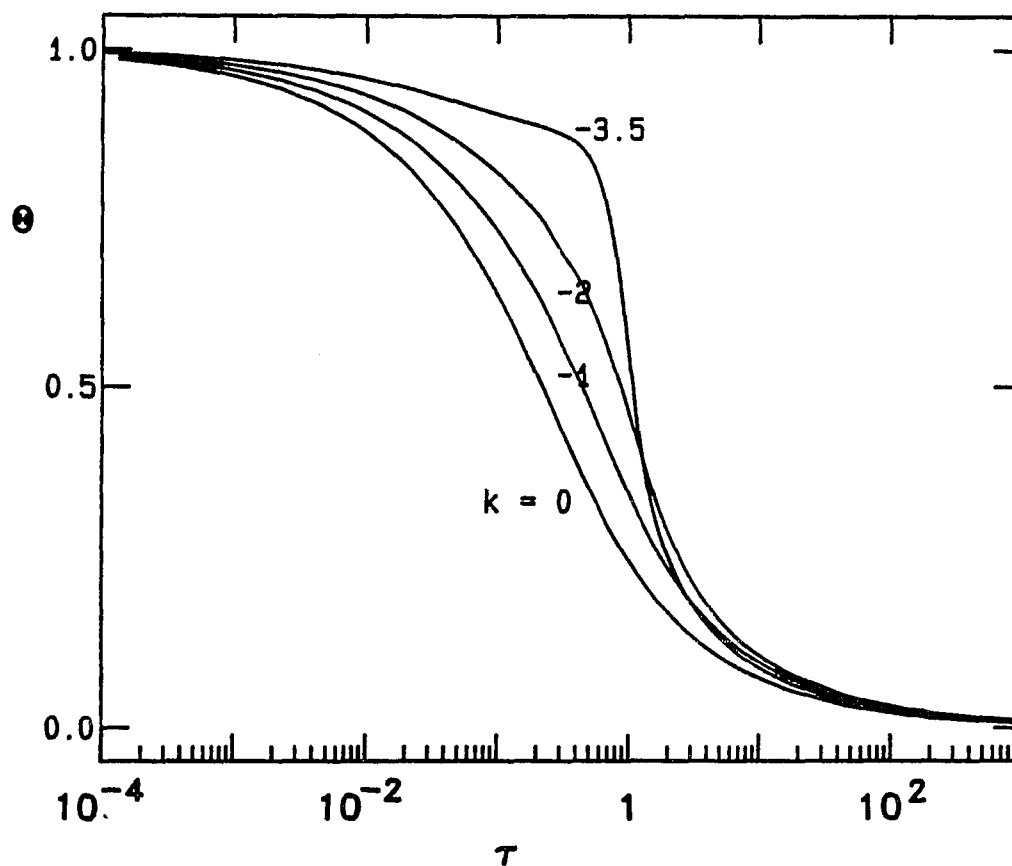


Figure 2. The influence of the cohesion constant k on diffusion controlled dynamic surface tensions ($\theta \frac{\gamma - \gamma_e}{\gamma_0 - \gamma_e}$) for adsorption onto a clean interface with $C_0/a = 1.5$

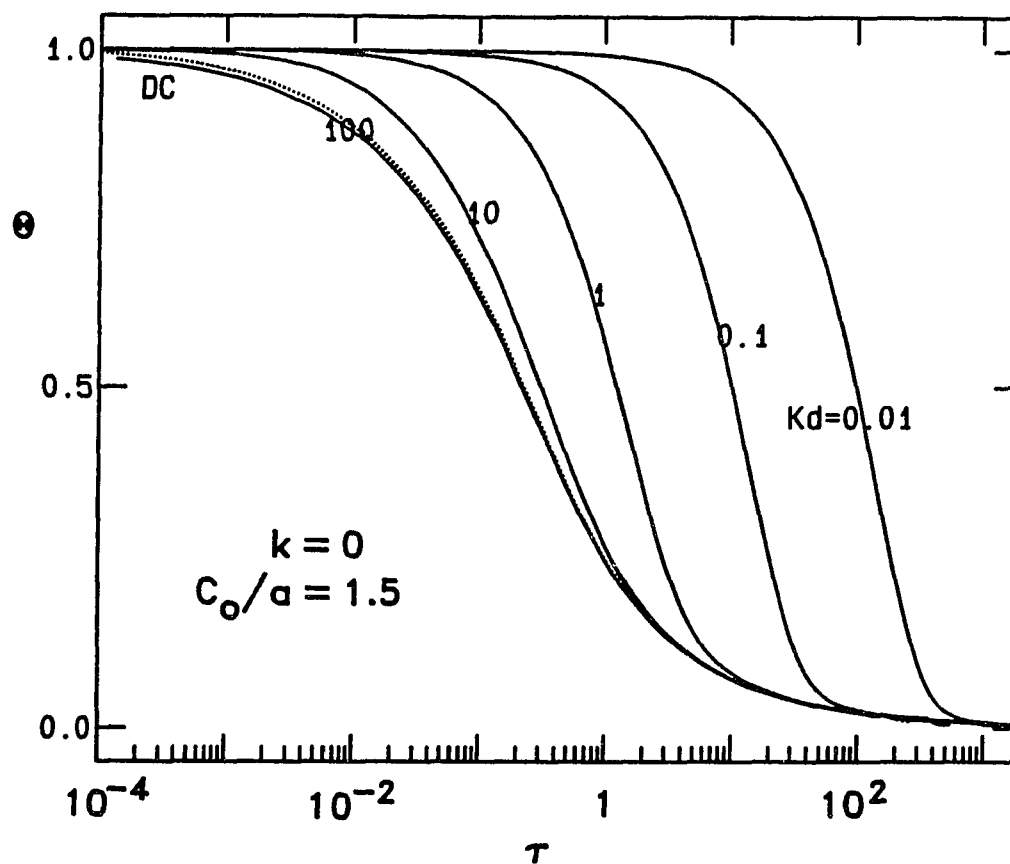


Figure 3a. The influence of the cohesion constant k on the dynamic surface tension for clean interface adsorption under the conditions of kinetic-diffusive control, $C_0/a = 1.5$ and $k = 0$. DC denotes diffusion control.

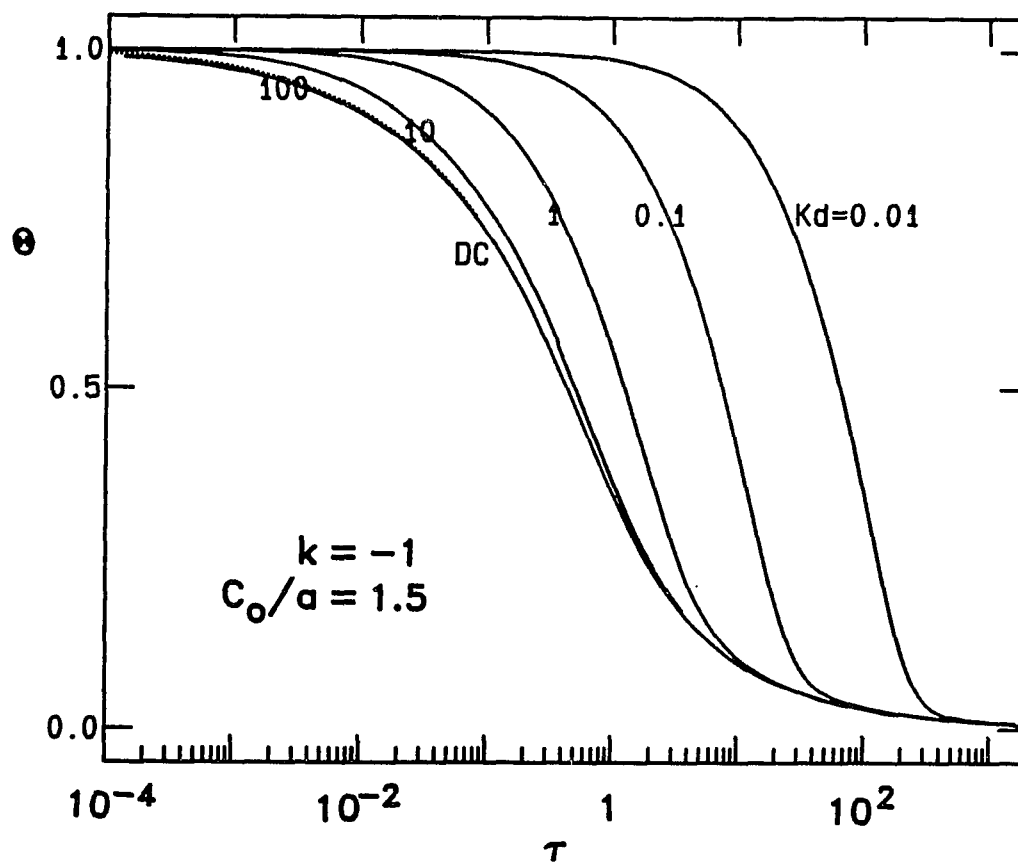


Figure 3b. The influence of the cohesion constant k on the dynamic surface tension for clean interface adsorption under the conditions of kinetic-diffusive control, $C_0/a = 1.5$ and $k = -1$. DC denotes diffusion control.

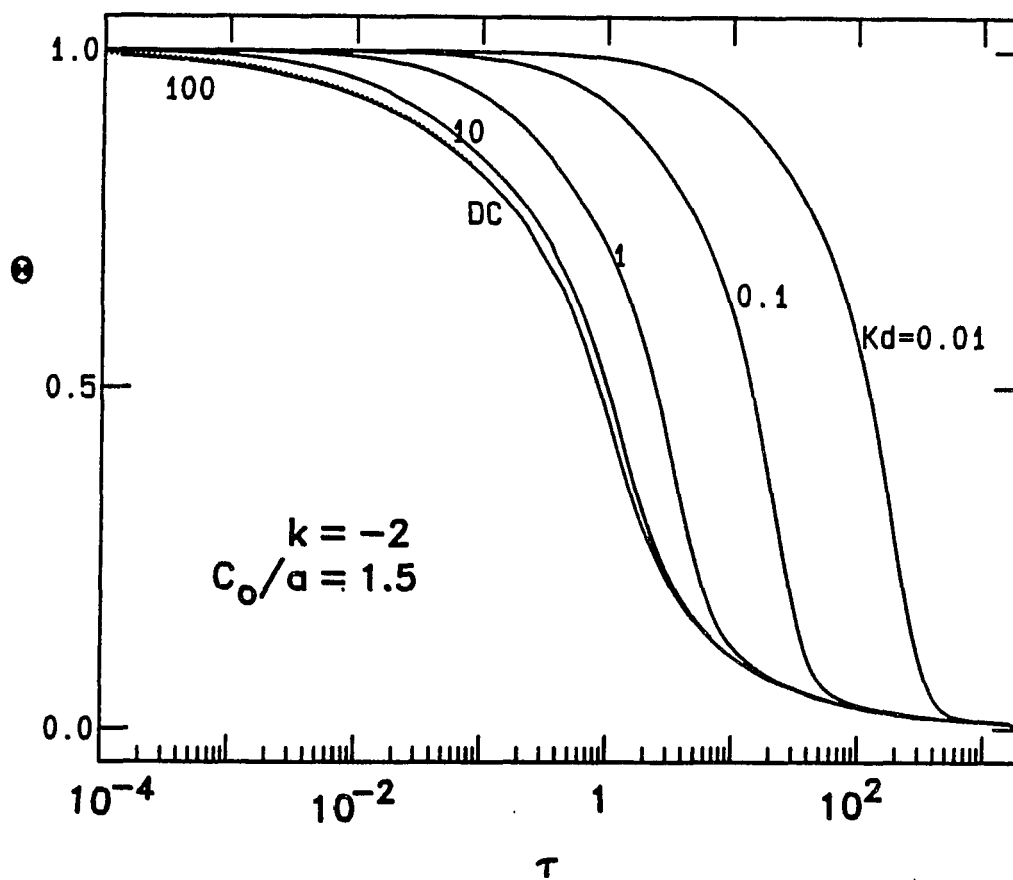


Figure 3c. The influence of the cohesion constant k on the dynamic surface tension for clean interface adsorption under the conditions of kinetic-diffusive control, $C_0/a = 1.5$ and $k = -2$. DC denotes diffusion control.

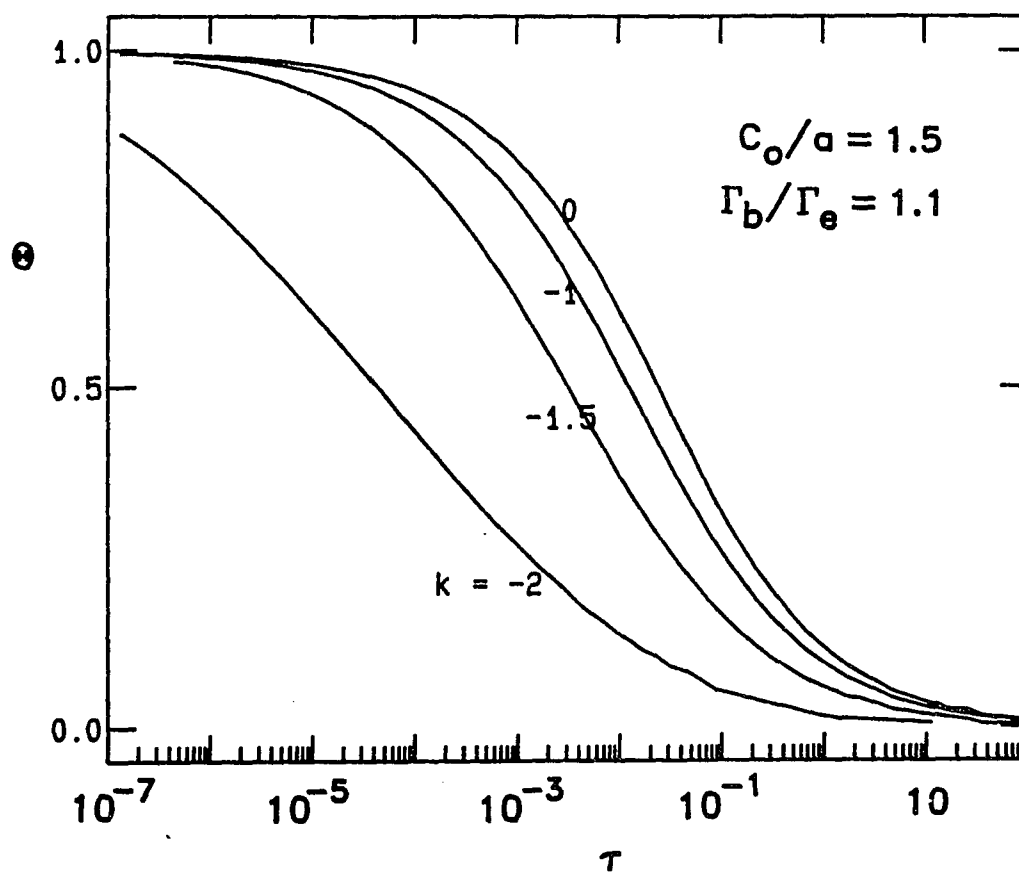


Figure 4. The influence of the cohesion constant k on the diffusion controlled dynamic surface tension $\theta \frac{\gamma - \gamma_e}{\gamma_0 - \gamma_e}$ for re-equilibration.

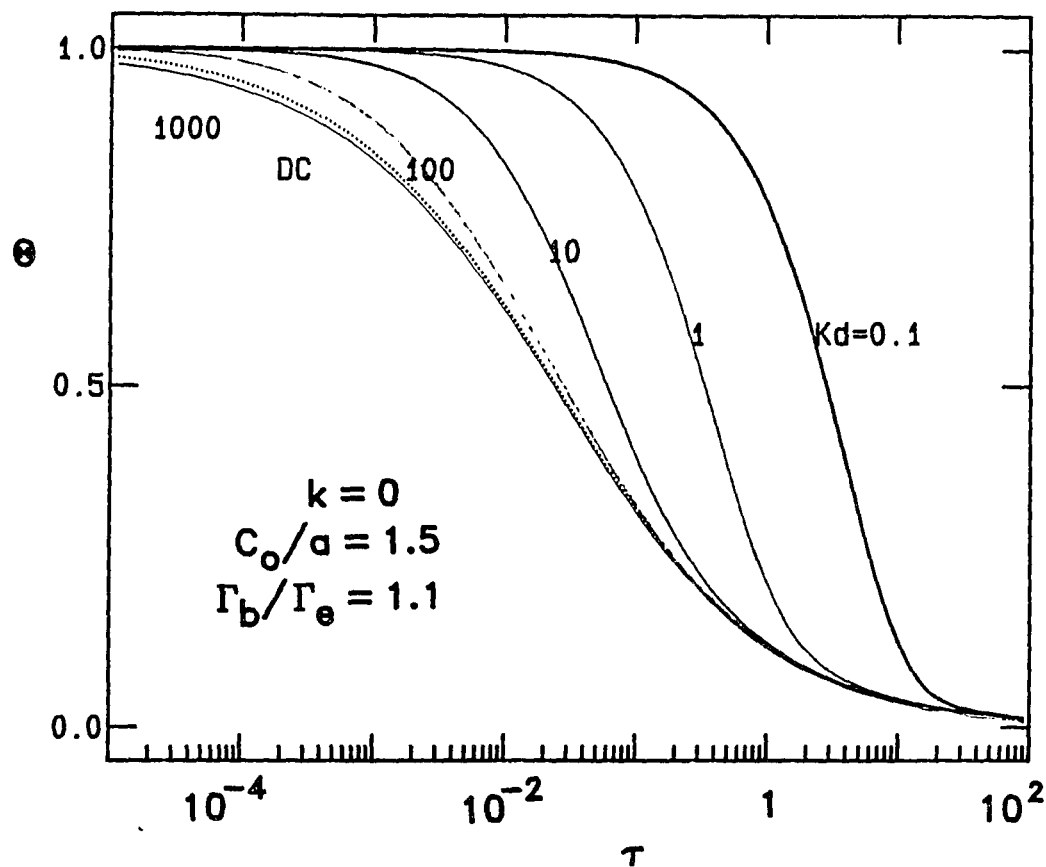


Figure 5a. The influence of cohesive effects on dynamic surface tensions corresponding to re-equilibration controlled by mixed sorption kinetics and diffusion for $C_o/a = 1.5$, $\frac{\Gamma_b}{\Gamma_e} = 1.1$ and $k = 0$. DC denotes diffusion limited curves.

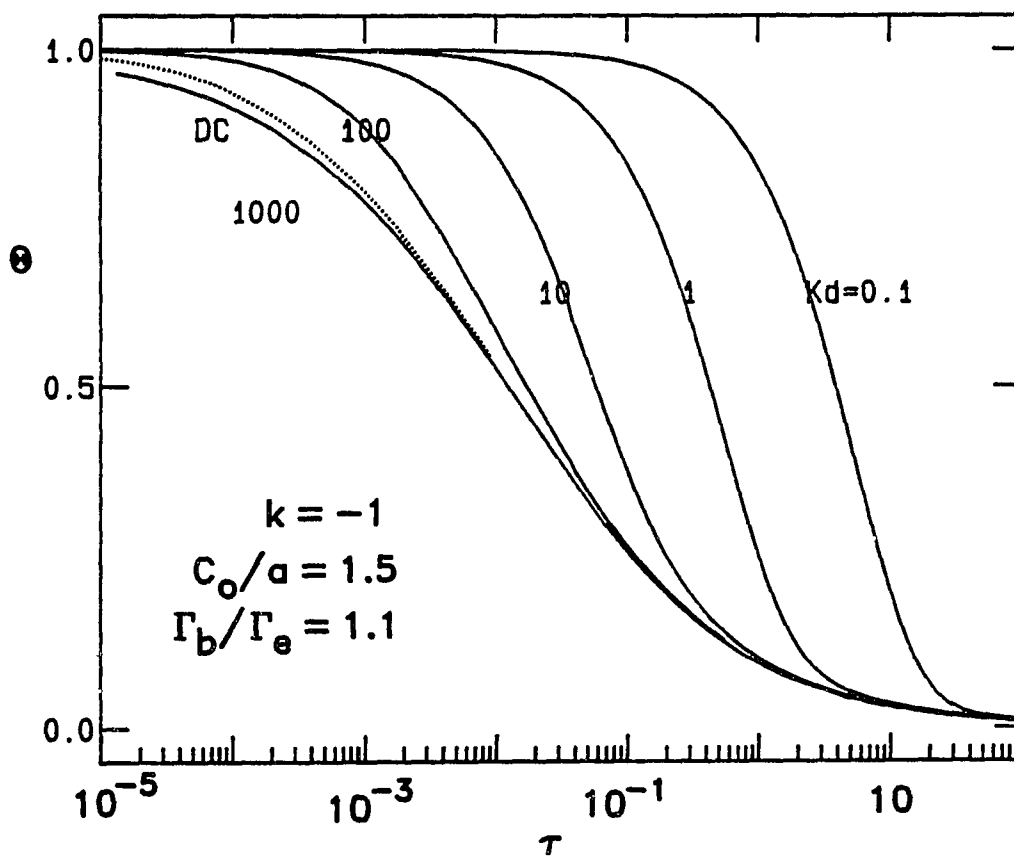


Figure 5b. The influence of cohesive effects on dynamic surface tensions corresponding to re-equilibration controlled by mixed sorption kinetics and diffusion for $C_0/a = 1.5$, $\frac{\Gamma_b}{\Gamma_e} = 1.1$ and $k = -1$. DC denotes diffusion limited curves.

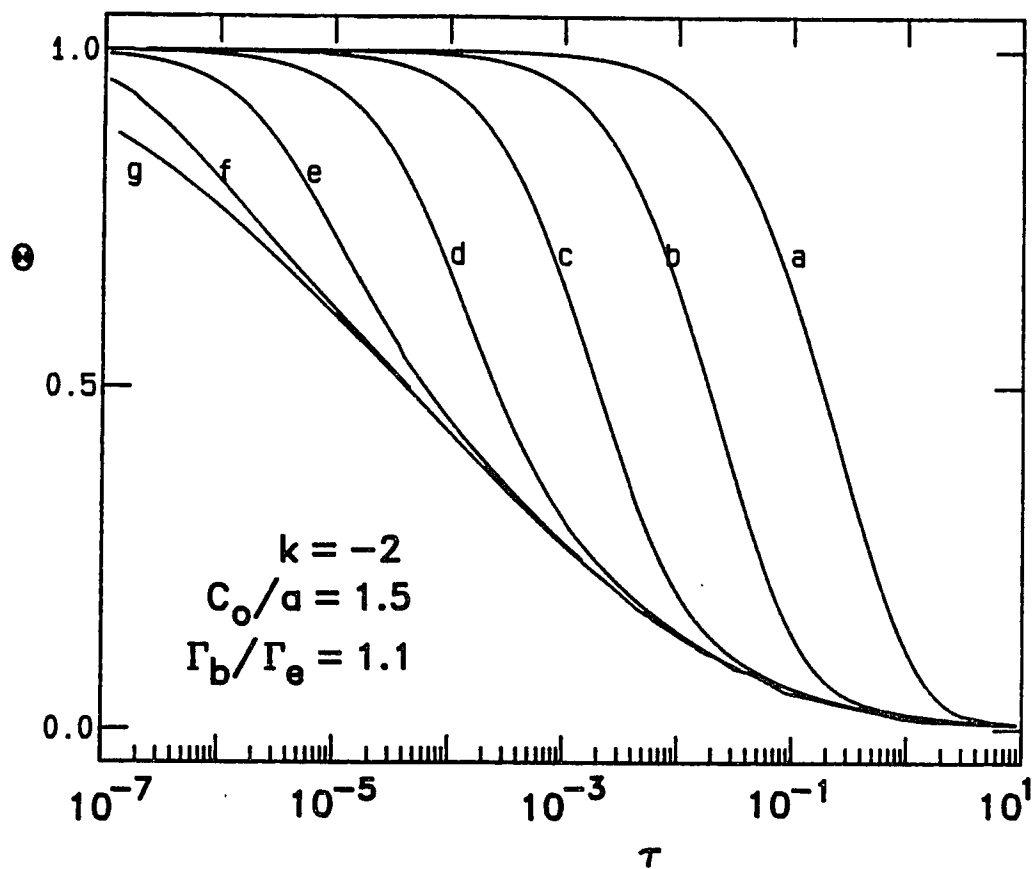


Figure 5c. The influence of cohesive effects on dynamic surface tensions corresponding to re-equilibration controlled by mixed sorption kinetics and diffusion for $C_o/a = 1.5$, $\frac{\Gamma_b}{\Gamma_e} = 1.1$ and $k = -2$.

$K_d =$ (a) 1, (b) 10, (c) 10^2 , (d) 10^3 , (e) 10^4 , (f) 10^5 and (g) denotes diffusion limited curves.

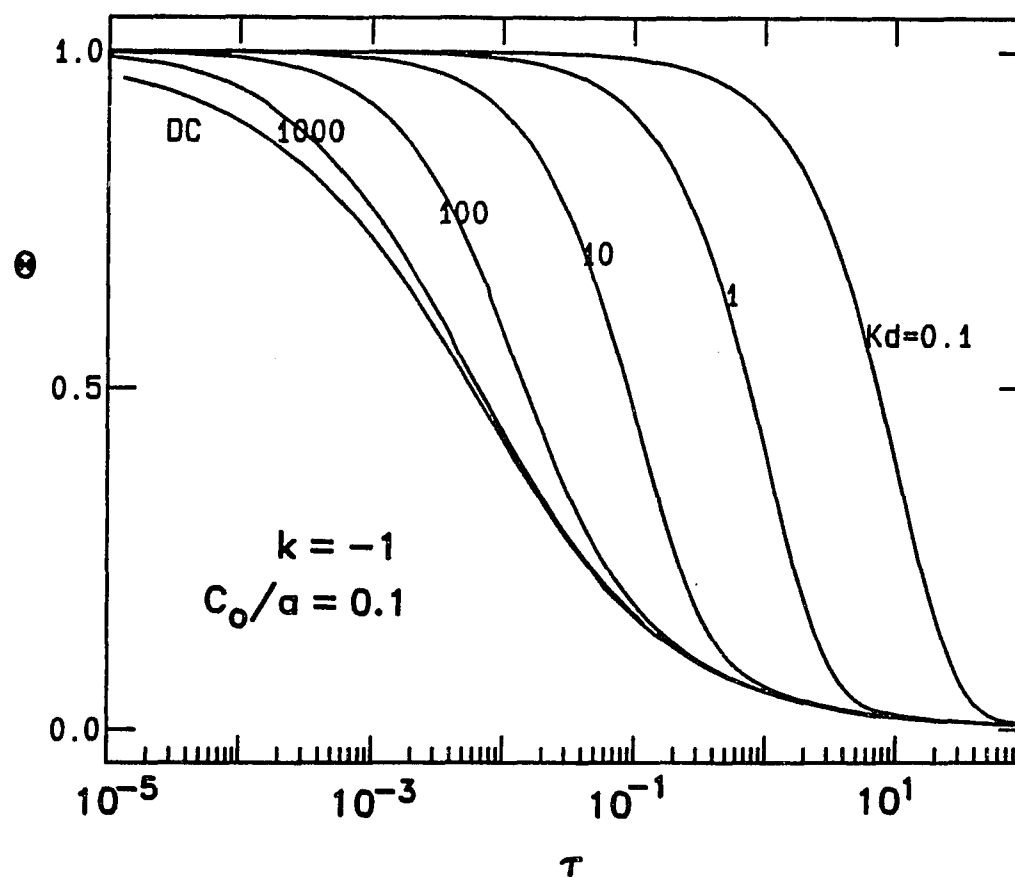


Figure 6a. The influence of surface activity on mixed control dynamic surface tension corresponding to clean interface adsorption for $k=-1$ and $C_0/a = 0.1$. DC denotes diffusion limited curves.

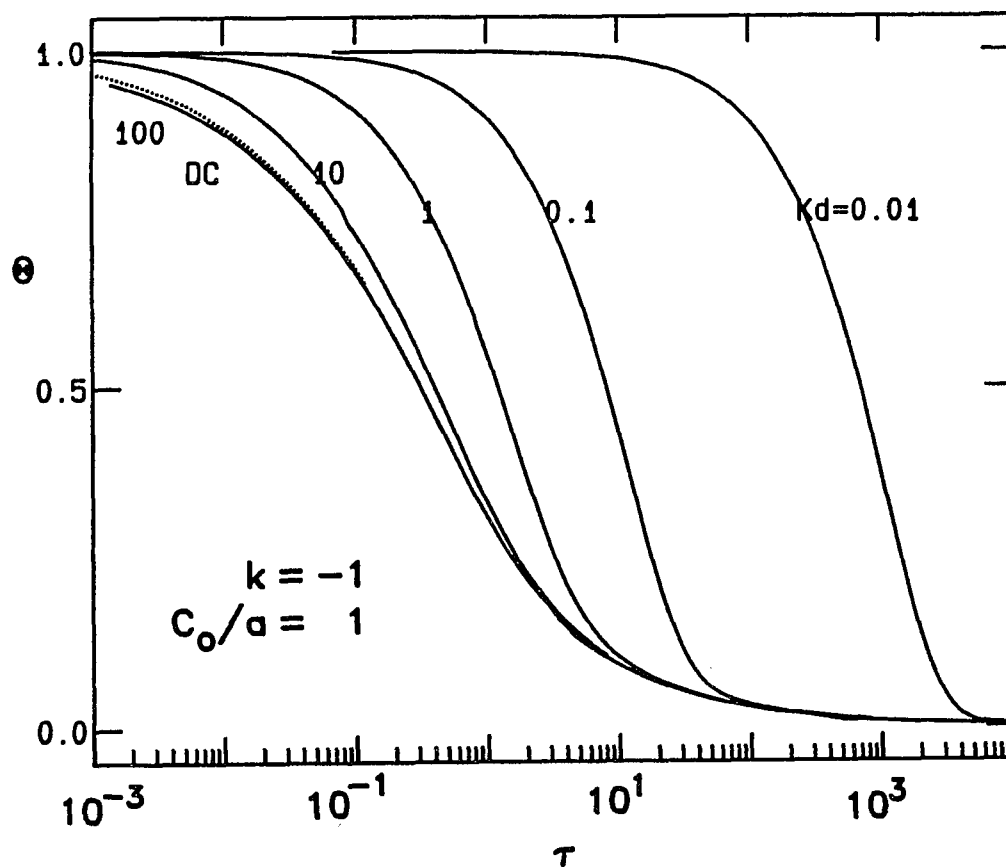


Figure 6b. The influence of surface activity on mixed control dynamic surface tension corresponding to clean interface adsorption for $k=-1$ and $C_0/a = 1$. DC denotes diffusion limited curves.

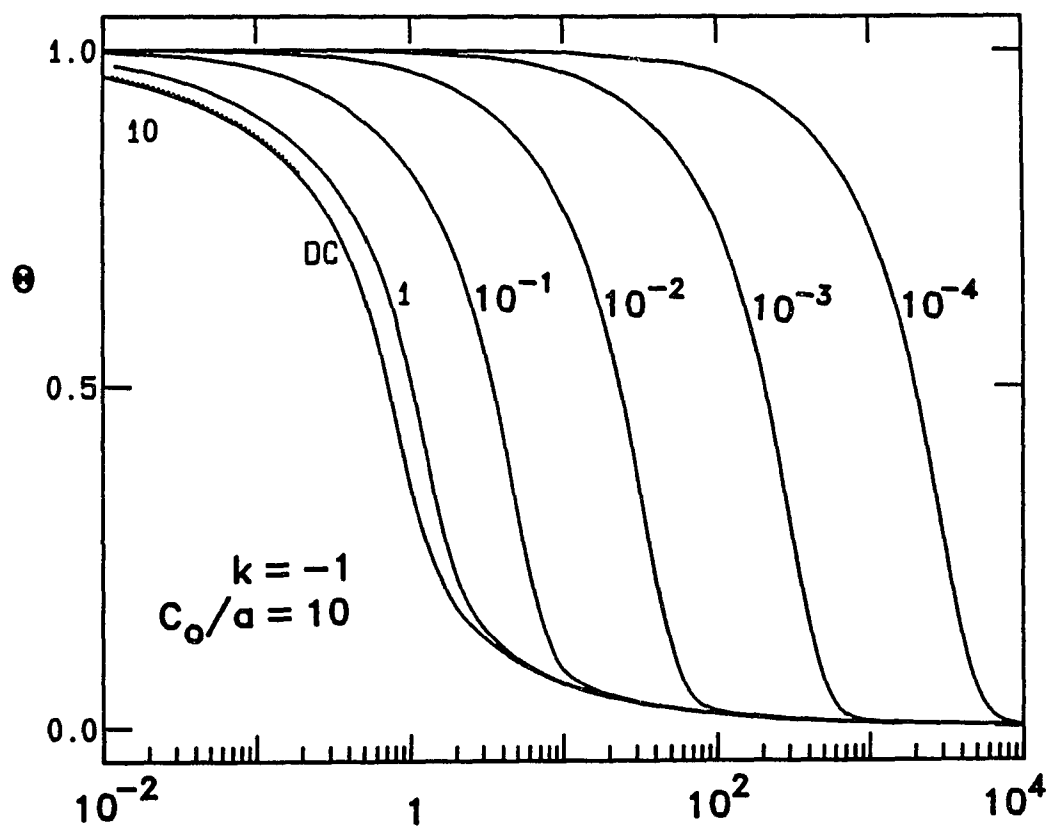


Figure 6c. The influence of surface activity on mixed control dynamic surface tension corresponding to clean interface adsorption for $k=-1$ and $C_0/a = 10$. DC denotes diffusion limited curves.

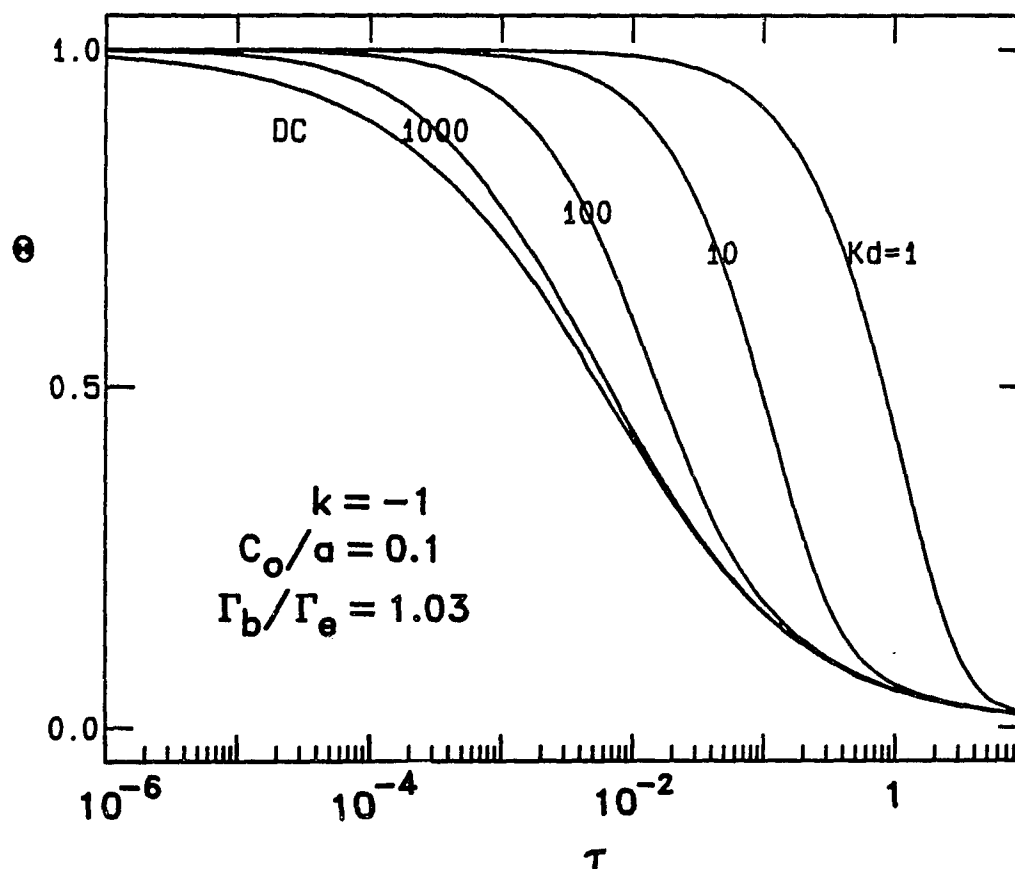


Figure 7a. The influence of surface activity on mixed control dynamic surface tension corresponding to re-equilibration for $k=-1$ and $C_0/a = 0.1$. DC denotes diffusion limited curves.

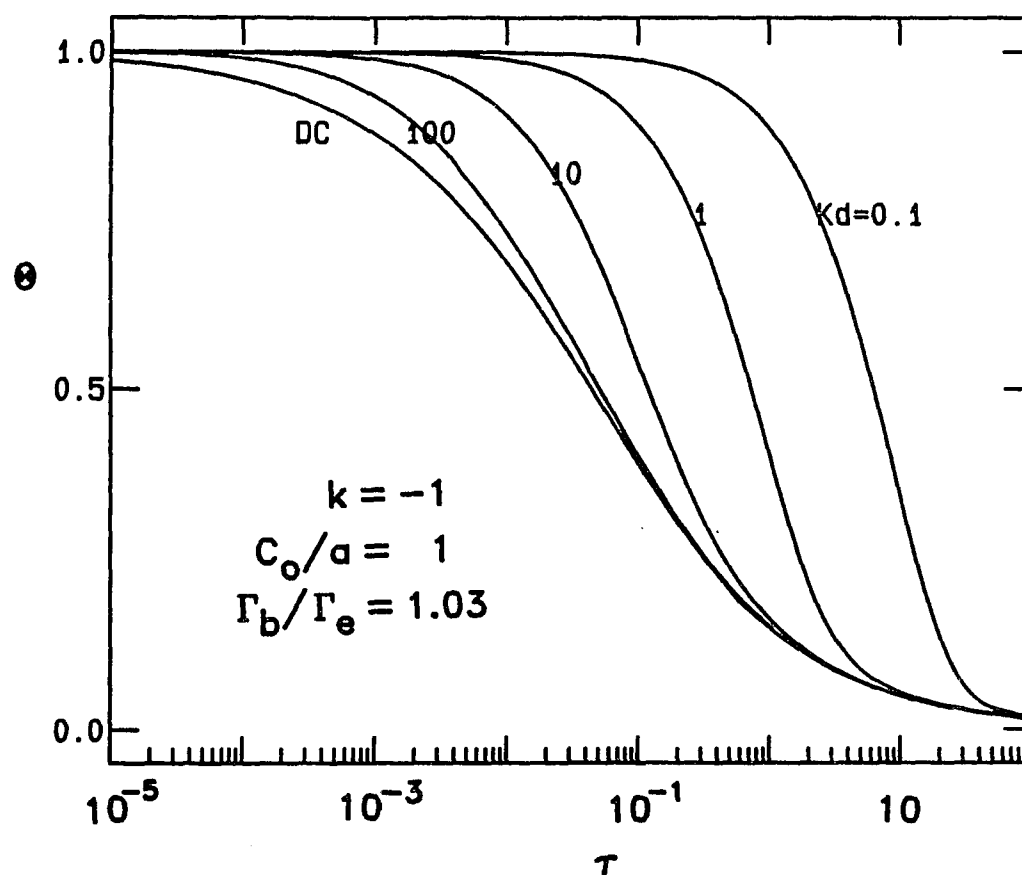


Figure 7b. The influence of surface activity on mixed control dynamic surface tension corresponding to re-equilibration for $k=-1$ and $C_0/a = 1$. DC denotes diffusion limited curves.

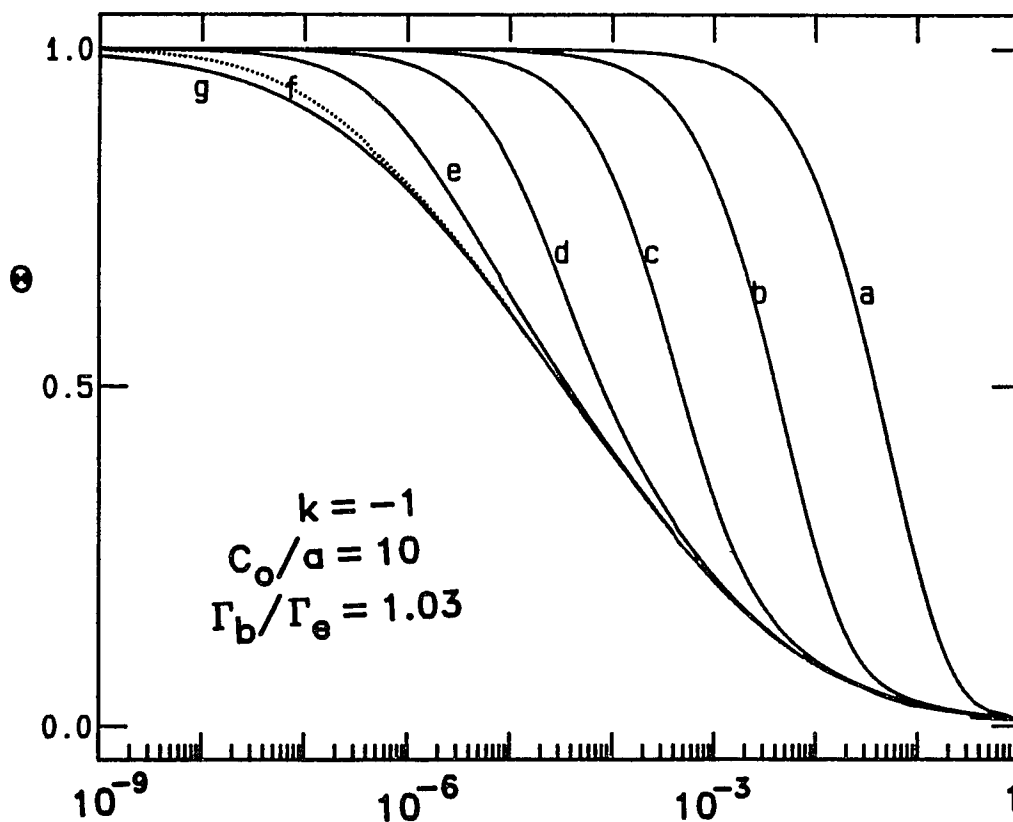


Figure 7c. The influence of surface activity on mixed control dynamic surface tension corresponding to re-equilibration for $k=-1$ and $C_o/a = 10$. K_d - (a) 1, (b) 10, (c) 10^2 , (d) 10^3 , (e) 10^4 , (f) 10^5 and (g) denotes diffusion limited curves.

CHAPTER 6

CONCLUSIONS

6.1 Summary

Taken together, the preceding three chapters constitute a theoretical and experimental study of the effect of strong cohesive energies on the sorption kinetics and dynamic surface tensions of surfactant adsorption. In what follows below, the main results are summarized.

The pendant drop apparatus used to measure the dynamic surface tension is described in Chapter 3. For clean interface adsorption, a precise dynamic surface (interfacial) tension measurement is achieved for a test surfactant, Triton X-100, for which cohesive energies are not important. A reproducible diffusion coefficient is obtained from the comparison of the entire experimental and diffusion limited theoretical relaxation curves. In addition, lower bounds on the kinetic constant for the sorption process are estimated for the Triton X-100.

In Chapter 4, kinetic models incorporating cohesive effects are developed, and clean interface adsorption in the presence of cohesion is studied theoretically through simulations and experimentally by pendant drop tensiometry. Two models are constructed to account for the cohesion: In the phase transition model, intermolecular attraction leads to the formation of a liquid phase from a gaseous phase. In the generalized Frumkin model, the intermolecular attraction causes a cooperative adsorption as the activation energy for desorption increases faster with surface coverage than adsorption. It is shown that, in clean surface adsorption simulations, an induction period in

the early surface tension relaxation arises as the presence of cohesion lowers the surface pressure.

Experimental verification of these ideas is obtained by studying the adsorption of aqueous solutions of n-decanol at the air/water interface. Surface tension relaxation profiles for n-decanol are obtained by using pendant bubble tensiometry enhanced by video digitization. These profiles compare favorably with the numerical solutions obtained using the developed models, the phase transition and the generalized Frumkin models, and particularly the induction period is observed.

The effect of cohesive energies between adsorbed molecules on surfactant exchange processes in re-equilibration is investigated in Chapter 5. The cohesive forces between surfactant molecules adsorbed onto a fluid interface raise the energy barrier for desorption of the molecule into the bulk sublayer, and correspondingly lower the desorption rate. For adsorption onto an initially clean interface, the reduction in the desorption rate affects the tail end of the process because it is only at these extended times that the surface concentration becomes high enough for the cohesive energy effect to become important. However when a concentrated equilibrium monolayer is perturbed, the subsequent re-equilibration is affected by the lower desorption rate during the entire period of the process.

These ideas are illustrated by theoretical simulations of the relaxation in surface tension due to adsorption onto an initially clean planar interface, and re-equilibration onto an interface containing a monolayer which has been perturbed. For these two relaxation processes, comparative studies are made of the relationship between the relaxation limited only by diffusion and that controlled by both diffusion and sorption kinetics. Novel regions are identified where the surface tension relaxation for adsorption onto a clean interface is diffusion controlled, and that for re-equilibration is mixed.

6.2 Suggestions For Future Research

Scientific research inevitably produces more questions than answers. During the course of this work many questions have been raised which might be answered through future research. Two major points are discussed here, first improvements in the experimental technique and secondly further investigations of the cohesive energy effect.

Some ways for improving the pendant drop technique are:

(i) Re-equilibration experiments have very short real time scales because the driving force is larger; therefore, it is necessary to examine closely the video image of the bubble during the first few seconds of the process. The video camera used in this study captures only 30 frames per second. For re-equilibration studies, it would be advisable to have a much faster camera.

(ii) The bubble edge is presently defined as the point at which the grey scale achieves half the difference between the black reading for the bubble interior and the white reading for the background. Although the results using this approach are very reasonable, the method does not guarantee that the halfway point is the true position of the interface. This question needs to be examined more closely.

(iii) Presently, the surface tension is computed by generating numerically the Young-Laplace solution for different parameters, and then comparing with the experimentally determined loci to determine the best fitting parameters. The speed of this procedure can be improved by tabulating in look-up tables in computer memory Young-Laplace solutions for various parameters, and then interpolating.

Some further investigations of the effect of cohesive energies are:

(i) All experiments were undertaken at room temperature. Experiments at increasingly higher temperatures can be used to identify the temperature above which the liquid expanded phase does

not form. Also, the additional data at other temperatures can be used to refine the values for the kinetic constants.

(ii) The techniques developed here can be used for other surfactants, particularly surface active block co-polymers and biological surface active species such as lung surfactants, to determine if cohesive effects are important.

(iii) The re-equilibration experiments were undertaken by a small contraction of the interface. The theoretical studies suggest that the dynamic surface tensions from large contractions at low initial coverage can also be of mixed diffusive-kinetic control. Thus large contraction experiments should be done to refine and make more reliable the values for the kinetic constants.

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