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**The Measurement of Wetting Layers in Two Phase Flows in
Capillaries and The Effect of Surfactant
on the Wetting Layer Thickness**

by

Wei Huang

**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**

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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.

1/30/97
Date

Charles Maldarelli
Professor Charles Maldarelli
Chair of Examining Committee

1/30/97
Date

Gerard G. Lowen
Professor Gerard G. Lowen
Executive Officer

Professor Charles Maldarelli

Professor Andreas Acrivos

Professor Gabriel Tardos

Dr. Syed Ahmed

Dr. Less Oppenheimer

Supervisory Committee

The City University of New York

ABSTRACT

The Measurement of Wetting Layers in Two Phase Flows in Capillaries and the Effect of Surfactant on the Wetting Layer Thickness

by

Wei Huang

Advisor: Professor Charles Maldarelli

When a capillary tube is filled with a fluid which strongly wets the tube wall, and a slug of a second nonwetting immiscible fluid is forced to move through the tube, the slug moves over a thin annular layer of the wetting fluid. This flow finds applications in foam displacement of oil or contaminants in rock pores, where surfactant is added to stabilize the foam. The effect of surfactant adsorption on the wetting layer thickness is a crucial but not well understood effect and is the focus of this thesis. A model for this flow is studied consisting of a 1 mm circular quartz capillary tube, with aqueous solutions of a polyethoxylated surfactant as the continuous phase and air or decane as the slug phase arranged in a periodic train flow.

The thesis consists of two parts. In the first, a new optical adsorbance technique is developed to measure the thickness. In the absence of surfactants,

measurements agree with the asymptotic low capillary number theory. In the second part the thickness of wetting layers as a function of surfactant concentrations and velocities are measured. At high velocities and low bulk concentrations, surfactant is swept into a stagnant zone at a back ring of the slug, and the measured thickness is the value for the clean interface. As the velocity decreases or the concentration increases, the surfactant monolayer extends over the entire surface, and the increase in deformability and rigidification increases the film thickness. For a further reduction in the velocity or increase in concentration, an additional increase in the film thickness is measured. The increased importance of bulk diffusion relative to surface convection increases the interfacial mobility, and depletes the surfactant concentration in the film. This creates a Marangoni force as the tension in the film is larger than at the slug ends, which draws fluid into the film accounting for the thickness increase. Finally, at fixed velocity, as the bulk concentration increases beyond the critical micelle concentration, increased rates of bulk eliminates depletion and the measured thickness is of a clean interface with a tension equal to the equilibrium surfactant tension.

Preface

And we know that in all things God works for the good of those who love him, who have been called according to his purpose. For those God foreknew he also predestined... And those he predestined, he also called; those he called, he also justified; those he justified, he also glorified

Romans 8:28

I can do everything through him who gives me strength

Philippians 2:13

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Chapter I

Introduction

1.1. Background and Motivation

When a circular capillary tube is filled with a fluid which strongly wets the capillary wall, and a second nonwetting immiscible fluid is forced to move steadily through the tube, the nonwetting, displacing fluid moves over a thin annular layer of the wetting fluid which is constant in thickness in the axial direction (Fig. I-1). If we denote by U the steady velocity of the advancing meniscus in a tube of radius R , by γ the interfacial tension between the two immiscible liquids, by μ and $\lambda\mu$, ρ and $\kappa\rho$ the viscosity and density of, respectively, the continuous liquid and the displacing fluid, then, apart from the property ratios l and k , the flow is prescribed by three dimensionless groups, the Weber number ($We = \rho U^2 R / \gamma$, a measure of inertial to capillary forces), the capillary number ($Ca = \mu U / \gamma$, a measure of viscous to capillary forces), and the Bond number ($Bo = \Delta \rho g R^2 / \gamma$, a measure of gravitational to capillary forces). In this study we focus our attention on tube radii small enough, and (or) fluids matched close enough in density, so that the Bond number is small. In this case gravitational effects are negligible and the displacing motion is axisymmetric

with the annular wetting layer surrounding the advancing core fluid of uniform thickness. In addition we are interested in the case in which the flow is slow enough and the tension large enough so that the Weber and capillary numbers are much smaller than one. We restrict our attention to these limits because the technological processes in which this flow serves as a model, processes which motivate this study and which we will presently describe below, operate in these limits.

The hydrodynamics of the displacement flow in the limit of small Weber and capillary numbers and negligible gravitational effects is fairly well understood, and the asymptotic analysis of Bretherton (1961), as clarified and placed in the context of the modern theory of matched asymptotic expansions by Park and Homsy (1984), provides the clearest picture. Because inertial and viscous forces are negligible with respect to the surface tension, the shape of the advancing meniscus is determined to leading order by surface tension alone, and therefore advances as a hemisphere of constant curvature equal to the tube radius R . The cylindrical interface of the thin uniform wetting layer connects to the hemispherical shape of the advancing meniscus by a transition region. In this region, the flow in the liquid film of the continuous phase underlying the interface is described by viscous lubrication theory, and solutions for the local flow field in the film can be developed analytically. By matching the interfacial shape in this region to the hemispherical interface of the capillary static region, and to the cylindrical interface of the constant thickness wetting layer,

Bretherton showed that the constant thickness, h , of the wetting layer scales to leading order with $Ca^{2/3}$ and is given by

$$\frac{h}{R} = 1.337Ca^{2/3} \quad Ca \rightarrow 0 \quad (I-1)$$

Thus as the viscous forces increase with respect to capillarity, the film thickens as viscous forces increasingly bend the interface. To this order in Ca inertial effects play no role as long as $We \ll 1$. Since the flow in the transition layer is a viscous lubrication flow, tangential stresses exerted by the film are large compared to the traction exerted by the displacing core, and therefore the core dynamics does not affect the transition layer interfacial shape (and therefore the constant wetting layer thickness) to leading order. Core dynamics begins to contribute when the core viscosity becomes large; Park and Homsy show precisely that as long as $l < Ca^{-1/3}$, equation (I-1) is valid.

It is important to note the flow in the uniform wetting layer: If the displacing fluid is inviscid, then in the reference frame of the tube, and in the absence of gravitational effects, the wetting layer is at rest, and is simply a deposited uniform layer. When the displacing fluid is viscous, the core fluid entrains the film liquid and the film is moving in the tube frame. Flow visualization experiments by Goldsmith and Mason (1962) in which talc particles are dissolved in the film clearly indicate that the film is nearly at rest for inviscid displacement, and moving for viscous displacement.

Exact numerical solutions of the Stokes (inertialess) equations for the case of an inviscid bubble advancing in a liquid for Ca between 10^{-3} and 10 by finite element (Shen and Udell (1985) and Westborg and Hassager (1989)), finite difference (Reinelt and Saffman (1985)), and boundary integral (Liu and Chang (1988)) and Martinez and Udell (1989)) methods demonstrate that Bretherton's equation is valid for $Ca < 0.1$. For larger Ca and $We \ll 1$, the film thickness rapidly asymptotes to a value equal to approximately 0.3 of the tube radius. Experimental measurements of the wetting layer thickness for capillary numbers in the range 10^{-3} - 10^{-2} by Bretherton (1961) based on the measurement of the volume change of a liquid slug advancing in a dry capillary show agreement with eq. (I-1). However, for Ca in the lower range of 10^{-5} - 10^{-3} , measurements of the film thickness by this method by Bretherton and later Schwartz *et al.* (1986), and by conductivity measurements (Marsessault and Mason (1960) and Chen (1986)) are consistently larger than the asymptotic expression, and this disparity increases as the capillary number decreases. For the larger film thicknesses of greater capillary numbers, $Ca > 10^{-2}$, the film thickness is determined by direct microscopic examination of long slug trains (Goldsmith and Mason (1963)), or by the measurement of the liquid volume expelled when air displaces a liquid which wets and fills a capillary (Taylor (1961) and Cox (1963)). The experimental studies in this range are in good agreement with the numerical studies, and in particular validate the high Ca asymptote. They also agree fairly well (although are slightly larger than) with the Bretherton asymptote for capillary number between 10^{-2} and 10^{-1} . Thus the only paradoxical result is the increasing disagreement between Bretherton's expression and the experimental

measurements of the wetting film thickness as Ca decreases beyond 10^{-3} . In the range of capillary number between 10^{-5} - 10^{-2} , an empirical correlation of Fairbrother and Stubbs (1935),

$$\frac{h}{R} = 0.5Ca^{1/2} \quad (I-2)$$

which is based on their own film thickness measurements. They obtained thicknesses in slug flows by measuring the difference between the slug velocity and the mean velocity of the poiseuille flow ahead of the slug. This correlation is uniformly in closer agreement with the data than the Bretherton expression.

Capillary displacement flows serve as models for the flow regimes of many processes of technological interest. These processes usually involve the motion of trains of long slugs of a nonwetting phase moving through a tube or a pore filled with a wetting phase. The movement of the leading edge of the slug sets the wetting layer thickness. Examples include, from the petrochemical industry, the displacement of oil in rock pores by foam, and, from the medical diagnostics industry, continuous flow spectrophotometry. We provide a brief description of these applications below, as they provide the motivation for our study.

Oil residing in the void spaces of porous media may be recovered by displacing the oil with a second fluid. Substantial removal requires that the displacing fluid have a greater resistance to flow in the porous media than the oil; otherwise large volumes of the oil can be bypassed. Gas drive recovery,

either by steam or carbon dioxide, has not been proven successful because of the higher mobility of the gas relative to the oil (Holm (1976) and Prats (1976)). Displacing the oil with an aqueous foam has been suggested since foam has a lower mobility than gas in a porous media. Foam in a porous media is a dispersion of a gas in the aqueous phase in which the liquid is continuous (i.e. connected), and at least some part of the gas is made discontinuous by thin liquid films called lamellae. In field practice, this two phase structure is generated in situ. When gas and liquid are forced through a porous media, and especially under the conditions in which the liquid wets the pore walls, the gas channels into and flows at the center of the pore cross section, and the liquid runs as a film along the pore wall. Visual experiments with transparent beadpacks have shown that the liquid lamellae separating gas segments are created from this core-annular flow by a snap-off mechanism at the pore constrictions (Mast (1972), Owette and Bringham (1987), Ransohoff and Radke (1988), Falls et al. (1988), Huh et al. (1988), Shirley (1988) and Gauglitz and Radke (1990)). The lamellae formed by snap-off can subdivide at junctures to create additional lamellae, and it is this combination of snap-off and division which fills the pore spaces with a finally textured foam in which the gas slugs are roughly of the order of the pore size and, when mobilized, snake through the porous media over a cushion of an aqueous film (see Fig. I-2; Mast (1972), Huh et al. (1988), Ransohoff and Radke (1988) and Falls et al. (1988)).

Continuous flow spectrophotometry is a method for the rapid spectrophotometric analysis of aqueous chemical samples(see Fig.(I-3)).

Samples and air are alternately aspirated into a transparent capillary to form a slug train, with the air slugs acting as spacers to keep separated the chemical samples. In the simplest case, the tube material is selected to wet the aqueous sample fluids (e.g. glass), so the train consists of air slugs moving over a wetting layer of the sample fluids. The train is passed in front of a light beam, and the spectroscopic adsorbances of each sample are measured and recorded.

In each of these examples, maintenance of a sufficient thickness is crucial to maintaining the integrity of the flow. If the film thickness becomes too thin, then capillary or flow inhomogeneities can lead to the rupture of the film and the attachment of the nonwetting slug phase to the tube wall. Under ideal conditions this attachment should not be troublesome since the continuous phase should rewet the surface. However, if contamination of the capillary surface has altered the capillary wall wettability to the wetting phase, then the attachment can persist as contact line forces adhere the nonwetting phase to the tube wall. In this case, the flow regime is distorted as nonwetting segments attempting to bypass the attached slug begin to coalesce with the obstacle allowing only the continuous phase to pass in a narrowed channel. For foam transport, these attached nonwetting phases can choke the flow. In the case of spectrophotometric flow, the coalescence of the continuous phase slugs combines different samples together, and accurate individual readings are not possible

1.2. Research Scope

In the above examples it is clear that it is important to know what the wetting layer thickness is as a function of the flow. Moreover, it would be very useful if the thickness could be adjusted so that sufficiently large values are realized. Flow velocities in these examples are of the order of a few centimeters per second or less, and therefore capillary numbers are usually small. The Bretherton expression provides a guideline for gauging what we might expect for the wetting layer thickness. But Bretherton's analysis indicates that the thickness is sole a function of the capillary number, and once the tension, wetting phase viscosity and train velocity are fixed, the thickness scaled by the radius is determined.

One possible way of exerting active control on the wetting layer thickness in an effort to increase its value is to dissolve surface active materials into the two phase system. Surfactant molecules contain a polar moiety and a nonpolar group (usually a hydrocarbon chain). Dissolved surfactant partitions itself at the meniscus and wetting layer interface, where the polar moiety contacts the more polar of the two immiscible phases, and the nonpolar group the less polar of the phases. Adsorption lowers the tension of the interface in proportion to the amount adsorbed onto the surface. The amount adsorbed, in turn, is proportional to the bulk concentration, and the surfactant affinity to the surface. Thus by varying the bulk concentration the overall tension can be reduced. From Bretherton's analysis and formula (eq.(I-1)), reduced tensions

lead to thicker films as viscous forces are allowed to further bend the interface in the transition region.

In the examples discussed above of foam flow in porous media and continuous flow spectrophotometry, surfactant is added to the system for reasons other than in an attempt to increase the film thickness. In the case of foam flow surfactant is added to the aqueous phase to stabilize the lamellae which separate the gas slugs (i.e. the interface between the trailing meniscus of one slug and the advancing meniscus of the slug immediately behind). Stabilization maintains the foam texture and the high foam viscosity which is necessary for mobility control. When adjoining gas slugs move out of a pore constriction, the liquid segments separating the slugs are forced to thin lamellae in order to accommodate the increased cross section, and they can snap if they thin to the point where intermolecular instabilities can cause the film to rupture. If surfactant is adsorbed from the bulk onto the lamellae interfaces, then, as the lamellae thins, steric interactions and electrical double layer repulsions (if the surfactant is charged) between the surfactant adsorbed on opposite ends of the film stabilizes the film against rupture. In the case of continuous flow spectrophotometry, the addition of surfactant to the chemical samples insures proper wetting of the tube by the samples.

As pointed out above, the addition of surfactant should decrease the tension and provide a means for increasing the wetting layer film thickness increase. However, reduction in tension is not the only way in which surfactant

adsorption will affect the wetting layer thickness. Surfactant gradients can also develop on the surface in the transition region between the advancing meniscus and the wetting film, and these gradients will create interfacial tension gradients which exert tangential traction (Marangoni stresses) on the underlying lubrication film. If the tension in the film is larger than the tension at the meniscus, then the interface is pulled in the direction of the film, and this action will draw wetting liquid into the film, and thereby increase the thickness. Alternatively, if the tension gradients pull the interface towards the capillary static region of the advancing meniscus, then fluid will be drawn out of the wetting layer and the thickness will decrease.

Surface concentration gradients develop for two reasons. The first occurs when the bulk concentration of surfactant in the continuous phase far ahead of the meniscus, C_o , is low. As the meniscus advances more cylindrical interface of the wetting film is created, and surfactant adsorbs from the underlying liquid film onto the surface. This depletes the bulk concentration in the wetting film. If the bulk concentration ahead of the advancing meniscus is small enough, this adsorption can deplete the bulk concentration in the film (C_F) to values below C_o . In this case, the surface concentration in the film far from the meniscus (Γ_F), which is in equilibrium with C_F , is less than the value at the surface of the advancing meniscus. The interface in the film tugs on the front end drawing fluid into the film and increasing the wetting layer thickness. Ratulowski and Chang (1990) and Park (1992) first illustrated this mechanism in their studies of the effect of low concentrations (trace amounts) of surfactant

on the wetting layer thickness. Their results do not contain the effect of the overall reduction in the surface tension due to surfactant adsorption because the low concentrations only marginally reduce the surface tension. A second reason for surface concentration gradients to develop is because of convection along the surface. For the clean interface, in the transition region, in a reference frame fixed to the slug velocity, a stagnation ring exists, and flow diverges from this ring towards the film and the advancing meniscus. This causes a repartitioning of surfactant along the surface. Flow convection is balanced by kinetic adsorption off of the surface, and diffusion into the film. Stebe and Barthes-Biesel (1995) (see also Ginley and Radke (1989)) studied this repartitioning for the case in which the bulk concentration in the continuous phase is large enough so that no depletion occurs in the wetting layer (as described by Ratulowski and Chang (1990) and Park (1992)), and the surfactant concentration in the continuous phase is in fact constant and equal to the bulk concentration far ahead of the meniscus (C_0). Kinetic exchange was assumed to be fast so that the surface concentration deviates only slightly from the equilibrium surface concentration. Stebe and Barthes-Biesel show that a minimum in the surface concentration exists near the clean interface stagnation ring, and hence Marangoni forces draw fluid from the meniscus into the transition region, and also from the film into the transition region. They show that the net effect is to increase the wetting layer thickness, so that the Marangoni stress between the transition region and the meniscus appears to dominate. This effect is in addition to the overall tension reduction.

Aside from these theoretical studies for trace surfactant concentrations of surfactant or surfactant whose kinetic rates are extremely large, no other theoretical studies have been undertaken on how the surfactant adsorption affects the film thickness. These theoretical studies are quite limited because if surfactant are to be used to control film thicknesses, the concentrations must be larger than trace amounts. More importantly, no experimental studies have systematically documented the effect of surfactant adsorption on the wetting layer thickness. Given the encouraging results of the theoretical studies that Marangoni forces and the overall tension reduction can increase the film thickness, it appears likely that we may use surfactant to develop robust film thicknesses. The aim of this study is to examine this possibility more carefully by studying both theoretically and experimentally the effect of surfactant on the wetting layer thickness. The study consists of two parts, as described below.

In the first part, we develop an optical adsorbance technique to measure the wetting layer thickness in an experimental two phase flow. The flow consists of the movement of long air or decane slugs in a water-filled, water-wetting quartz capillary 1 mm in diameter. The wetting layer thickness is determined by measuring the adsorbance of an aqueous soluble dye dissolved in the wetting phase. This part of the research is described in Chapter II. We demonstrate that the absorbance technique we developed provides measurements of the film thickness of both water\air and water\decane systems in agreement very well with Bretherton's solution for capillary numbers in the range of 10^{-4} - 10^{-2} .

In the second part of this research, we use this optical adsorbance technique to study the effect of surfactant on the wetting layer thickness. The study is conducted for air slugs. We use a polyethoxylated surfactant $C_{12}E_6$ which is soluble in the aqueous phase, and whose equilibrium adsorption parameters and diffusion and kinetic transport coefficients are measured by the pendant bubble technique. We studied convection and diffusion effects by varying both the flow velocity and surfactant bulk concentration. For a low bulk concentration, and high velocity, surfactant on the surface is compressed to a small region in the rear and the front tip, forming stagnant caps. For this case, surface convection is much faster than bulk diffusion. (the kinetic exchange is fast.) We find the measured thickness of the wetting layer around the slugs is equal to Bretherton's prediction for a surfactant free system. As the velocity decreases or concentration increases, the surfactant monolayer at the rear extends along the cylindrical interface overlying the film towards the front of the slug, and the monolayer at the front tip extends to the transition region between the cylindrical section and the front hemispherical section. The thickness of the film under the immobile layer is larger than that over the mobile film, so the average thickness increases. In addition, the extension of the monolayer from the front tip to the front transition region, allows the slug to be compressed and this also increases the thickness. Immobilizing the transition region also increases the thickness. To factor out the effect of deformability, we measure the film thickness relative to the predicted thickness assuming a uniform reduced tension equal to the equilibrium tension corresponding to the bulk concentration. (We call this thickness h_{eq}). We find the thickness (relative to

h_{eq}) increases as the velocity is lowered or the concentration increases due to the jump and the immobility in the transition region. Finally, at higher bulk concentrations or lower velocities, the film eventually becomes mobile as the diffusive exchange becomes comparable to the convection rate. Mobility depletes the bulk concentration in the film, raising the tension in the film and causing the thickness to increase (beyond the deformability effect) as surface tension traction brings more fluid into the film. We confirm the increase in thickness relative to the equilibrium Bretherton thickness. When the surfactant concentration is very high, large bulk diffusion rates reduce the depletion, the Marangoni force disappears, and the interface remobilizes so that the thickness of a clean interface with a reduced uniform tension is achieved (i.e. h_{eq}). These results are described in Chapter III.

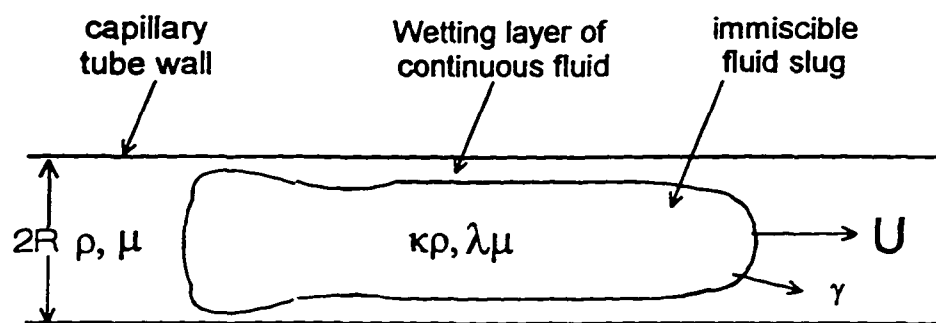


Fig I-1: Schematic of the two-phase slug flow regime illustrating the wetting layer of the continuous phase, the immiscible fluid slug and the parameters of the system.

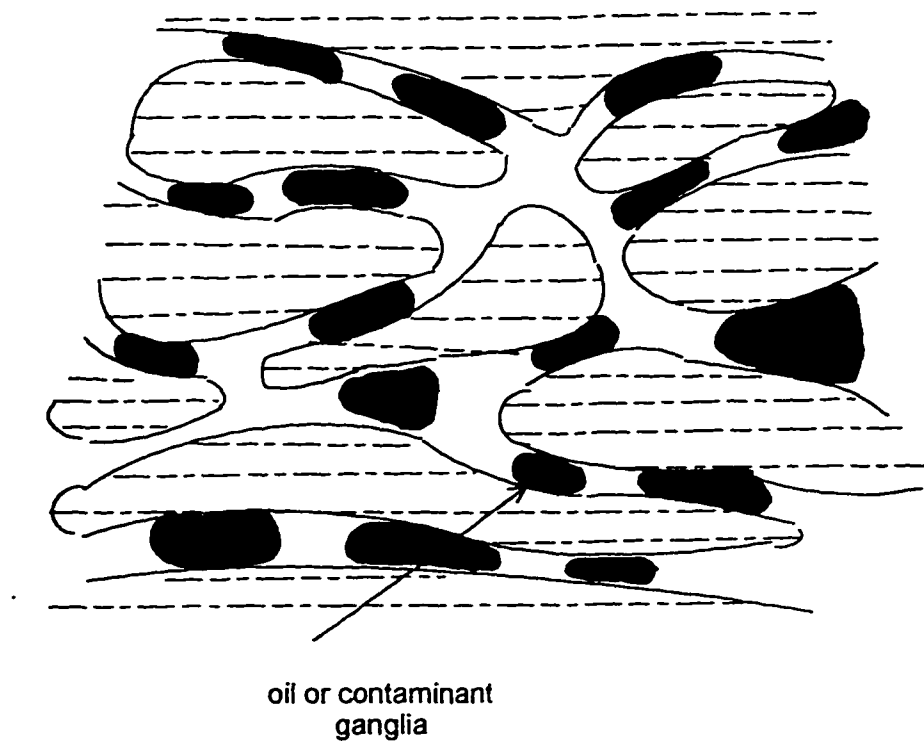


Fig. I-2: Schematic of foam flow in porous media displacing saturating oil. The foam moves as a contiguous train of gas bubbles separated by thin lamellae and moving over a water wetting layer.

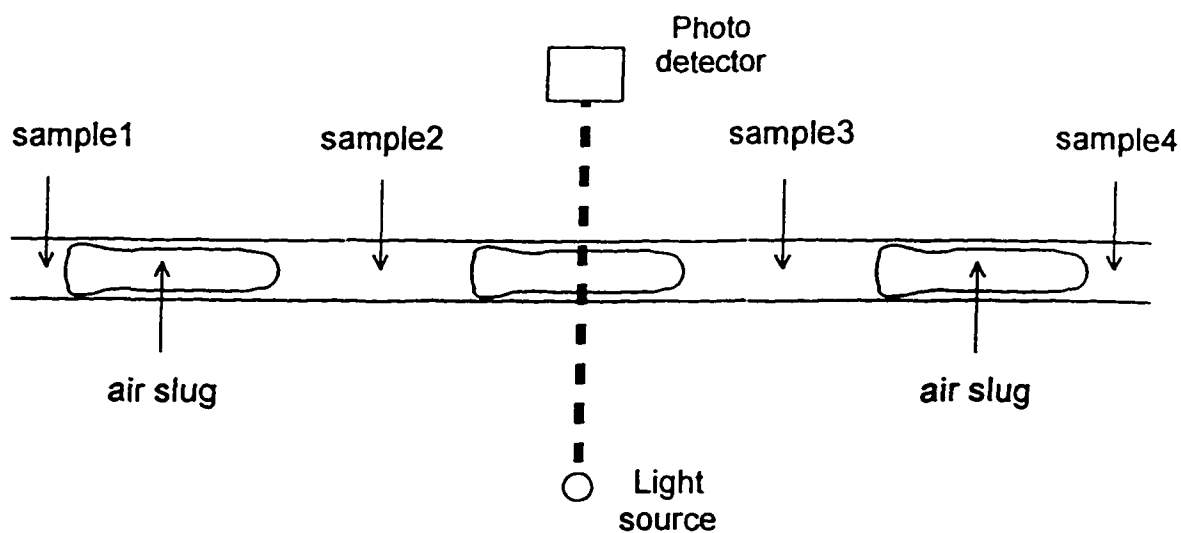


Fig. I-3: Continuous Flow Spectrophotometry: A technique for rapid spectrophotometric analysis of samples, a slug train is assembled by alternately aspirating into a tube different samples and oil spacers..

Chapter II

Measurements of the Wetting Layer Thickness for Surfactant Free System using a Newly Developed Optical Adsorbance Technique In Capillary Slug

II.1. Introduction

When a long liquid or gas slug moves through a continuous liquid phase wetting the inside surface of a capillary tube, the slug moves over a film of the wetting fluid. This idealized flow regime has generated significant interest, principally because it serves as a model for aqueous foam flow in water-wetting porous media. Due principally to capillary snap-off at throat constrictions (Mast (1972), Ransoff and Radke (1988), Falls *et al.* (1988), Huh *et al.* (1988), Shirley (1988) and Gaugilitz and Radke (1990)), air and an aqueous surfactant phase introduced into a water-wetting porous media arrange themselves into a flow geometry consisting of gas slugs which are separated by thin (surfactant stabilized) aqueous lamellae, and which move over a layer of water spread on the inside surface of the pore walls. Interest in porous media foam flow derives from the fact that each slug in the foam train contributes, in an additive way, a resistance to the foam flow, and therefore the foam permeability can be made

very low for high enough foam texture or interfaces per unit volume. (cf., for example, the foam model of Ratulowski and Chang (1990).) Foam's low permeability makes it an ideal choice as a mobilizing agent to displace oil ganglia in narrow rock pores for oil recovery in the petroleum industry (see for example Hirasaki (1989) and Hirasaki and Lawson (1985)), and soil contaminants in remediation procedures (Wilson *et al* (1990)). Other applications of this idealized flow geometry are as models of red blood cell flow in capillaries (see for example Evans and Skalak (1980) and Secomb *et al* (1986)) and meniscus closure in lung airways (Halpern and Grotberg (1992)).

The aim of this chapter is to describe the development of a new optical method for measuring the thickness of the wetting layer, and the use of this method to measure thickness for flows in which inertial and viscous forces are small relative to capillary forces (i.e. small capillary (Ca) and Weber (We) numbers). Several techniques have been used to measure the wetting layer thickness. However, as will be evident in the brief review which follows, these measurements increasingly disagree, as the capillary number decreases, with a low Ca asymptotic theory first developed by Bretherton (1961) which predicts a reduction in the film thickness as the $2/3$ power of the capillary number as Ca decreases. We establish that measurements from our new optical technique remain in excellent agreement with the asymptotic theory as the capillary number decreases, until at very low Ca the theory is no longer appropriate because the tube cannot be considered smooth relative to the film lengthscales, and intermolecular forces should be included in the asymptotic theory. We

begin with a review of the asymptotic theory, and then detail the existing experimental studies of the film thickness.

Theoretically the problem of a gas slug moving at a velocity U in a circular tube of radius R filled with a liquid of density ρ and viscosity μ was first studied by Bretherton in the limit in which the inertial forces are smaller than viscous forces ($Re = \rho RU/\mu \ll 1$) and gravitational forces are smaller than surface-tension ($Bo = \rho g R^2/\gamma \ll 1$, where γ is the surface tension). In this regime, the two competing forces are viscous force and surface-tension, and the ratio of their magnitude is defined as capillary number ($Ca = \mu U/\gamma$). Bretherton studied asymptotically the limit of low capillary number ($Ca \rightarrow 0$), by matched asymptotic expansions. In the limit of small Ca , surface tension forces are dominate at the front and rear ends of the slug and consequently hold the interfaces as sections of spheres. Viscous forces are important in a thin layer which connects the front and back ends to a long uniform wetting layer of thickness h . Because the gas slug is assumed to be inviscid, this uniform wetting layer is at rest in the tube frame. To leading order the thickness of the layer is given by

$$\frac{h}{R} = 1.337 Ca^{\frac{2}{3}} \quad (\text{II-1})$$

Park and Homsy (1984) extended Bretherton's study for the case of an immiscible liquid slug rather than a gas slug moving through continuous phase.

They found that Bretherton's analysis is still valid as long as the viscosity ratio of slug phase to the continuous phase is asymptotically smaller than $Ca^{-2/3}$.

Recent numerical solutions of this problem have been studied at low to order 1 capillary numbers, again in the limit of creeping flow, axisymmetric motion and an inviscid slug. These are exact solutions obtained by solving the full creeping motion equations with the continuity stress conditions on the free surface. Shen and Udell (1985) employed finite element method to calculate the film thickness for capillary numbers from 5×10^{-3} to 10^{-1} . They find that for this capillary number range, their solution for the film thickness is smaller than values obtained from Bretherton's eq. (II-1), but approach Bretherton's value for Ca between 10^{-2} and 10^{-3} . The same conclusion for this low capillary range was found by Reinelt and Saffman (1985) using finite-differences, Martinez and Udell (1989) using a boundary integral analysis, and Westborg and Hassager (1989) applying a Galerkin finite element method. These latter studies extended the solution for the film thickness for Ca up to 1 or 10 and find that the film thickness tends to a constant value which is equal to approximately 0.3 of the capillary radius. Finally, Westborg and Hassager studied the case in which the slug is viscous with the viscosity equal to the continuous phase. They find that for given capillary number the film thickness is larger than the value of the inviscid slug, and as the capillary number becomes smaller, the value approaches the inviscid slug film thickness confirming Park and Homsy's study. Calculations for smaller capillary numbers (i.e. $Ca < 10^{-2}$) have not been computed because of difficulties of convergence due to small values of the film

thickness. The inclusion of inertial forces in the calculation of the thickness was undertaken by Edvinsson and Irandoust (1996); they find for a Reynolds number of 200, the film thickness increases in the Ca range between 5×10^{-3} - 10^{-2} .

Several studies have attempted to measure the wetting layer thickness. Fairbrother and Stubbs (1935) measured the film thickness by measuring the difference between the slug velocity and the mean velocity U_m of the Poiseuille flow ahead of the slug (the latter by determining the flow rate and dividing by the cross sectional area); since in the slug frame, the liquid around the slug is at rest, it can easily be shown that the film thickness is given by $\frac{U - U_m}{U} = \frac{2h}{R}$. Fairbrother and Stubbs measured the film thickness as a function of the capillary number in a range of 10^{-4} to 10^{-2} , and correlated their results with the following equation

$$\frac{h}{R} = 0.5 Ca^{\frac{1}{2}} \quad (\text{II-2})$$

For capillary numbers larger than 10^{-3} , this correlation predicts smaller film thickness than Bretherton's expression, and larger film thickness when Ca is smaller than 10^{-3} . However, in the range of 10^{-3} to 10^{-2} , where Fairbrother and Stubbs' experiments were done, the two predictions are within 5%, so Fairbrother and Stubbs' results in this range are in fairly good agreement with Bretherton's theory.

Experiments at a lower range of capillary numbers were undertaken by Bretherton (1961) and Schwartz *et al.* (1984), using a shrinking slug method, and Marchessault and Mason (1960) and Chen (1985) using a conductivity technique. In the shrinking slug method, a wetting liquid slug is driven by an infinite gas slug at a certain speed through a dry tube for a known distance. As the slug moves, its length decreases because it deposits a stationary film on the tube wall. From the measurement of the reduction in slug length, the film thickness is calculated. For Ca range of 10^{-3} to 10^{-2} , Bretherton's results agree well with his expression eq. (II-1), as well as with Fairbrother and Stubbs' correlation eq. (II-2), since this is the range in Ca for which these equations agree. For Ca between 10^{-5} to 10^{-3} , his measurements become increasingly larger than his asymptotic prediction eq. (II-1), and fall within an envelope formed between the one-half power correlation eq. (II-2) (which is larger than Bretherton's expression in this range) and his asymptotic equation eq. (II-1). For $Ca < 10^{-5}$, the film thickness becomes nearly constant. The experiments of Schwartz *et al.* using the shrinking slug method were in the middle range in Ca that were studied by Bretherton ($10^{-5} < Ca < 10^{-3}$). Their measurements lie along the Fairbrother and Stubbs correlation, and therefore at the top of the envelope.

Conductivity measurements of the film thickness by Maresseault and Mason and Chen were undertaken by using a conducting aqueous electrolyte as the wetting phase, and either a gas or a nonconducting fluid as the slug phase. An electrical current was passed axially along the tube as the slug moves and the resistance is measured; since the electrical current must pass through the

film, the measured resistance is inversely proportional to the film thickness. Marchessault and Mason studied the middle range of Ca from 10^{-5} - 10^{-3} that was studied by Bretherton and Schwartz *et al*, and found film thickness which were slightly larger than the Fairbrother and Stubbs correlation, and thus just outside the envelope of eqs (II-1) and (II-2). Chen (1985) studied both the middle and low range ($Ca < 10^{-5}$) for gas and oil slugs. For gas slugs and Ca in the middle range his data, like that of Schwartz *et al*, lie on the Fairbrother and Stubbs correlation (and hence on the top of the envelope). For Ca in the lower range, the film thickness becomes constant with Ca . Recall Bretherton also found this result, although Bretherton's thickness in this low range are almost an order of magnitude smaller than Chen's data. Chen also measured the thickness of oils slugs, and found these to agree with Bretherton's expression in the middle range (and hence to be smaller than the gas slug values), and to tend to a constant value (equal to the gas slug values) in the low range.

With the exception of Chen (1986), the experimental studies at low capillary number were all for gas slugs moving in liquids. An extended study of liquid slugs was undertaken by Cachile *et al*. (1996) using a radioactive tracer technique. A tracer is dissolved in the continuous phase, and the continuous phase is then displaced by an infinite finger of an immiscible liquid. A scintillation detector above the tube then counts the radioactivity in the deposited film, from which the thickness can be calculated from the known concentration of the tracer. By movement of the tube, local variations in the thickness were calculated. They find that the average thickness in the capillary

number range of 10^{-5} - 10^{-3} is again in agreement with Fairbrother and Stubbs' correlation, although the slug phase viscosities are small enough to satisfy Park and Homsy's criterion for the validity of Bretherton's equation.

All of the above experimental studies were for capillary numbers less than 10^{-2} . Experiments for Ca in the range of 10^{-2} to 2 were done by Taylor (1961) and by Cox (1962). These authors expelled liquid from a capillary by air, and calculated the film thickness left behind from the measurement of the volume of recovered liquid. They find that for Ca in the range of 0.01 to 0.1, the thicknesses are less than the Bretherton value, and agree well with Fairbrother and Stubbs' correlation. For Ca larger than 0.1, both studies find that the thickness becomes constant with Ca, saturating to a value of 0.3 for h/R. The results of Taylor and Cox in the entire range of 0.01 to 2 agree well with the numerical solutions of Shen and Udell, Martinez and Udell, Westborg and Hassager and Reinelt and Saffman. Goldsmith and Mason (1963) measured film thicknesses of liquid slugs in the capillary number range of 0.01 to 0.1 by direct measurement of magnified photographic images of the films obtained with a microscope. For the cases in which the liquid viscosity is much smaller than that of the continuous phase, Goldsmith and Mason, like Taylor and Cox, find agreement with the Fairbrother and Stubbs' correlation.

The key features which emerge from this literature review are the fact that the experiments in the middle range ($10^{-5} < Ca < 10^{-3}$) gave thickness which became increasingly larger than Bretherton's asymptotic relation, and that

became independent of Ca in the low range ($<10^{-5}$). These results are ostensibly inconsistent with the asymptotic theory since this theory should become increasingly applicable as the capillary number is reduced. Several ideas have been suggested for the origin of this discrepancy. One possibility for the larger measured values in the middle range is the presence of surfactant in either the continuous (and, if a liquid) slug phases. Surfactant adsorption decreases the slug tension which would increase the deformability, and thereby the thickness.

Although this doesn't account for the effect of surface tension gradients (Marangoni forces) on the thickness, several theoretical studies demonstrate that Marangoni traction serves to increase the thickness. But the question remains, if proper precautions are undertaken to assure the system is interfacially clean of surfactant, would the measurements agree with Bretherton's expression as the capillary number is lowered? A second possibility for the disagreement as Ca is decreased, suggested by Chen (1986), is the presence of grooves in the tube which may become of the order of the film thickness as Ca decreases. For his 1 mm inner diameter tubes, Chen measured by electron microscopy surface grooves less than one micron. At a value of 5×10^{-5} , Bretherton's expression predicts a value for the film thickness of 1 mm. for a 1 mm tube. So it may make sense, at least for these imperfect tubes, to only extend the validity of the asymptotic equation to this value of Ca , since the thicknesses would be about one order in magnitude larger than the tube imperfections. Also the imperfections may explain the uniform values of the film thickness measured in Chen and Bretherton's experiments (also in 1 mm tubes) for $Ca < 10^{-5}$, but cannot explain the increasing disparity with theory as Ca is decreased from 10^{-3} - 10^{-5} .

A third reason for why Bretherton's expression may not be valid for $Ca < 10^{-5}$ is the fact that van der Waals attractions between the film and the wall become important as the film thickness becomes less than 0.1 micron (Teletzke *et al.* (1988)). The effect of this attraction to maintain a constant film thickness, despite the reduction due to viscous shear. Chen (1986) estimated the size of this film to be of the order of a few hundredths of a micron, so this effect may not be determining when grooves of the order of tenths of microns are present. Thus the essential question of the validity of Bretherton's expression in the range of $10^{-5} < Ca < 10^{-3}$ remains.

In this paper we introduce a new optical adsorbance technique for measuring the wetting layer thickness. The technique is accurate at low capillary numbers, is continuous and can be used for both conducting and nonconducting wetting phases. In this technique, an adsorbing dye is selected which, for a gas slug system is soluble in the continuous phase and for a liquid slug system is selectively soluble in either the slug or the continuous phase. A light beam is passed through the slug perpendicular to the tube axis, and the adsorbance of the beam is measured. From the change in the adsorbance due to changes in the dye path length, the film thickness is calculated. The primary advantage of this technique is that it is continuous, and therefore allows for the measurement of slug trains as well as single advancing menisci. The method can therefore be used for measuring the film thickness of foam flows in which the gas slugs are separated by thin lamellae. Bretherton and Schwartz *et al.*'s slug shrinkage method does not allow continuous measurement because the film has

to be removed after the passage of an individual slug. The conductivity method used by Marcessault and Mason and Chen is limited to a nonconducting slug phase, and cannot be used in the case in which the wetting layer is nonconducting

We will use our optical method in a 1 mm tube to measure the film thicknesses in the range $10^{-5} < Ca < 10^{-3}$ as it is in this range that the experimental measurements begin to disagree with the Bretherton asymptotic formulae. We explain in §2 how the thickness is calculated from the adsorbance measurements, and we also detail our experimental apparatus design and measurement procedure. The technique is illustrated using a system consisting of water as the continuous phase, and air or decane as the slug phase moving through a quartz tube. We present results in §3, and discuss these results and the merits and applicability of the technique in §4.

II.2. Calculation of Film Thickness From Adsorbance Measurements

We illustrate first the case in which the dye is dissolved in the wetting layer. Figure (II-1a) shows the adsorbance of a collimated light beam passing through the tube, without dye in the wetting layer. The intensity (I_F) emerging from the tube is given by:

$$\log\left[\frac{I_i}{I_F}\right] = \epsilon_w D\left[\frac{2h}{D}\right] + \epsilon_{nw} D\left[1 - \frac{2h}{D}\right] \quad (\text{II-3})$$

where (I_i) is the intensity of the incident beam impinging on the tube surface, D is the diameter of the tube, h is the film thickness and ϵ_w and ϵ_{NW} are, respectively, the adsorbance coefficients of the wetting and nonwetting phases. The two terms on the right hand side of eq. (II-3) represent, respectively, the adsorbance due to the wetting layer and the core; In eq. (II-3) we neglect the adsorbance of the light beam through the tube walls. When dye is added to the wetting layer, dye adsorption attenuates further the incident intensity (I_i). Dye adsorbance is given by the Beer-Lambert relation in which the differential change in intensity dI , over a path length dx , due to the dye, is given by $\frac{dI}{I} = \epsilon_D(C)Cdx$ where C is the concentration of dye, and $\epsilon_D(C)$ is the dye extinction coefficient, and becomes a function of concentration at high C . With dye in the wetting layer, the intensity now emerging from the tube is given by:

$$\log\left[\frac{I_i}{I_{DF}}\right] = \epsilon_D(C)CD\left[\frac{2h}{D}\right] + \epsilon_w D\left[\frac{2h}{D}\right] + \epsilon_{NW} D\left[1 - \frac{2h}{D}\right] \quad (\text{II-4})$$

Subtracting eq. (II-4) from eq. (II-3) yields the working equation for measuring the thickness:

$$\log\left[\frac{I_F}{I_{DF}}\right] = \epsilon_D(C)CD\left[\frac{2h}{D}\right] \quad (\text{II-5})$$

Thus in order to measure the film thickness, the adsorbance of the beam without dye (I_F) and then with dye (I_{DF}) is measured; from their quotient the film thickness is calculated from eq. (II-5) once the extinction coefficient of the dye is known. In fact, the entire product $\epsilon_D(C)CD$ can be measured in the same way by just measuring the attenuation of the beam through the continuous phase (i.e without the slug), first without the dye (I_O) and then with the dye (I_D); from the Beer Lambert law:

$$\log \frac{I_O}{I_D} = \epsilon_D(C)CD \quad (\text{II-6})$$

where $\log (I_O/I_D)$ is the optical density (OD) of the solution.

When the dye is dissolved in the nonwetting continuous phase, the extinction coefficient product $\epsilon_D(C)CD$ is measured first, by introducing only the nonwetting phase into the tube without dye (I_O), and then with dye (I_D), and then using eq. (II-6). Next the wetting phase is introduced, and the adsorbance of the beam through the wetting layer with dye in the slug phase is measured (I_{FD}); the film thickness is then given by eq. (II-5) where the last term

$$\log \left[\frac{I_{FD}}{I_D} \right] = \epsilon_D(C)CD \left[\frac{2h}{D} \right] + (\epsilon_{NW} - \epsilon_W)D \left[2 \frac{h}{D} \right] \quad (\text{II-7})$$

on the right hand side of eq. (II-7), the adsorption of the solvents, is negligible compared to the adsorption of the dye.

II.3. Experimental

II.3.A. Apparatus Design

We measured the wetting layer thickness in a straight 1 mm inner diameter quartz tube (Wilma Glass) approximately 170 cm in length, using water as the continuous phase, and air or decane as the slug phase. The use of a quartz capillary facilitates preferential wetting of the water continuous phase, and allows for excellent optical transmission. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) dissolved in water is used as the dye. This dye has several adsorbance peaks in the ultraviolet region of the spectrum. This dye is selected for two reasons. First as an inorganic salt, the dye is insoluble in the decane phase and is not surface active. For the range of concentrations used in the experiments reported here, surface tensions at the aqueous solution/air surface, and interfacial tensions the aqueous solution/decane interface (both measured by the pendant drop technique) show no surface aging, and tension values in agreement with literature values for the systems without the inorganic ion. Second, dichromate provides a stable adsorbance, and is used as a standard for spectrophotometric calibration.

Instead of measuring the thickness around a single slug, we measure thicknesses in a continuous slug train (see Fig. (II-2)) in which both the slug length and the distance between slugs is set to be 20 tube diameters. This separation distance and slug size are much larger than what is necessary to assure that the slugs are noninteracting and a uniform wetting layer develops around them. The continuous two phase slug flow is created by the pumping arrangement detailed in Fig. (II-3) using two computer-controlled digital syringe pumps (Cavro) equipped with solenoid valves with two ports, one for dispensing and one for aspirating (in order to refill the syringe). One pump is for air or decane and the other is for the aqueous phase. The dispensing port of the water pump is connected directly to the open end of the quartz tube by Teflon tubing. To insert decane slugs into the tube, a hole is bored through the tube a few centimeters from the open end, and a hollow platinum needle is inserted into the hole, and is arranged so that the needle projects into the cross sectional area for the flow. The output of the air or decane pump is connected by Teflon tubing to this needle. With the needle extending into the middle of the capillary, when air or decane is introduced into a water filled capillary, the nonwetting air or oil avoid the walls, and smoothly forms a slug surrounded by the water wetting layer. In addition to the fact that water wets quartz in preference to air or decane. This method of introduction facilitates the continued wetting of the quartz tube by water by eliminating any air or oil contact. The slug train is first formed in the capillary by alternately introducing water and air or decane into the tube such that when one pump is dispensing liquid into the tube, the other is aspirating so as to refill its syringe. The size of the nonwetting fluid slugs, and

the size of the aqueous segments separating the slugs, is controlled by the stroke volume of the Cavro pumps. After the train has been formed in the tube, the entire train is pushed by water from the water syringe pump at a prescribed velocity, insuring a smooth flow.

The optics used to measure the film thickness is diagrammed in Figure (II-4). The tube is held horizontally by a series of fasteners. A pair of 200 micron width rectangular slits 5 mm in length mounted into circular disks (Milles Griot) are fastened to the top of a stacked arrangement of micro translation stages (Newport) which allow x-y-z movement of the slit in front (or in back) of the tube. The slits are aligned parallel to the centerline of the tube. Alignment is accomplished by video imaging a silhouette of the tube without the slits, and then digitizing this image to locate and mark the tube centerline on a video screen. The slits are then aligned, one to each side of the tube, to the centerline mark.

The beam of a 2 mw UV helium cadmium laser (Omnichrome) laser, 0.22 mm in diameter and a wavelength of 325 nm, is then directed by a prism (A in Fig.(II-4)) to pass the tube through the two slits; this beam is then directed to a UV sensitive photomultiplier tube with a 2.54 cm (one inch) diameter active area housed in a thermoelectric cooler (Thorn Emi) by a second prism B (see the optical path detailed by the straight line in Fig. (II-4). The photomultiplier tube in the thermoelectric cooler is cooled to $-24 \pm 2^{\circ}\text{C}$ in order to reduce the dark

current, and thereby increase the sensitivity by increasing the signal to noise ratio.

II.3.B. Experimental method

The minimum film thickness which this experimental method is capable of measuring accurately is determined by the optical density of the dye solution. This may be seen as follows. As the film thickness decreases, the difference between the adsorbance readings through the film without dye (I_F) and with dye (I_{DF}) is very small, and equations (II-5) and (II-6) can be combined into the following form:

$$2.303 \cdot \frac{2h}{D} \cdot OD \approx \frac{\Delta I}{I_{DF}} \quad (\text{II-8})$$

where $\Delta I = I_F - I_{DF}$, and OD is the solution optical density. For accurate measurements, $\Delta I / I_{DF}$ should be at least five percent so that the adsorbance difference can be distinguished from the noise in the photomultiplier tube readings; therefore

$$\frac{2h}{D} > \frac{0.05}{2.303} \cdot \frac{1}{OD} \quad (\text{II-9})$$

Therefore, to be able to measure thin film thicknesses at very low capillary number, we need to use a high optical density ($\epsilon_D(C)CD$ large). Since the optical path length is fixed by the diameter of the tube, and the variation of the extinction coefficient is small (as we will demonstrate later), we use a high concentration of dye to increase the optical density. In order to accurately measure thicknesses for Ca as low as 10^{-5} , using Bretherton's correlation as an estimate for the film thickness in eq. (II-9), we find the concentration should be approximately 40g/L. In order to obtain exactly $\epsilon_D(C)CD$, measurements of (I_O) and (I_D) are needed. At the high concentration 40g/L, the measurements for single phase dye solution separating slugs (I_D) is not available because of high adsorbance of the dye. In this case, (I_D) is the intensity of the light beam passing high concentration absorbing dye through path length of tube diameter 1mm. Because of the strong absorbance, the intensity of the light beam is too weak to be measured accurately. To determine $\epsilon_D(C)CD$ at 40g/L, a 3.3g/L solution is prepared. (I_O) and (I_D) for the single phase separating slugs are measured for this lower concentration for a decane/water system at a velocity of 12.8 cm/sec by the procedure described below. From eq. (II-6), we find that $\epsilon_D(C)CD$ is equal to 2.00 for the concentration of 3.3g/L solution, and hence a value for the extinction coefficient of $6.03 (g^\circ cm/L^\circ sol)^{-1}$. The measurements of (I_F) and (I_{DF}) are obtained also from the same experiments at a velocity 12.8 cm/sec. Therefore, the wetting layer thickness can be determined from eq. (II-5). We measured h/R to be 0.0263 for this particular capillary number 2.6×10^{-3} which differs from Bretherton's prediction at this Ca for 3%. The experiments for decane/water system at the same capillary number are then conducted using

the high concentration solution 40g/L and $\log(I_P/I_{DF})$ is obtained from the measurements of (I_D) and (I_F) . Since we know the wetting layer thickness from the above measurement, from eq. (II-5), we found $\epsilon_D(C)CD$ is equal to 23.8, and hence the extinction coefficient is $5.94 \text{ (g}^\circ\text{cm/L}^\circ\text{sol)}^{-1}$ for concentration at 40g/L. Measurements reported in the literature for potassium dichromate dissolved in 0.001 perchloric acid for a much lower concentration range (0.02-0.1 g/Kg $^\circ\text{sol}$) are 5.8 at 322nm and 6.1 at 323nm, and for this concentration range the extinction coefficient does not vary with concentration. Extrapolating, we would expect in the lower concentration range an extinction coefficient of 6.7 at our laser wavelength of 325. Our smaller measured value (6.03) for the high concentration of 3.3g/L solution and the almost same value 5.94 for 40g/L indicate saturation at the higher concentrations, which is to be expected.

We now describe the experimental protocol for the measurement of the thickness. Experiments using 3.3g/L dye solution are begun by first pumping through the quartz capillary a cleaning solution (Nochromix in concentrated sulfuric acid) for about one hour, and then rinsing the solution by pumping deionized water (Millipore) for a few hours. The slug train is formed (either in water or the aqueous dye solution), and then pushed at a prescribed velocity by the aqueous pump as described in the Apparatus Design Fig. (II.3.A). Concomitantly, adsorbance measurements through the capillary are recorded at a uniform rate (dependent on the velocity) so that there are approximately 300 measurements per slug. Two intensities of the adsorption then can be obtained

by analyzing the recording, the intensity through the water phase itself (I_O) and through the slugs surrounded by water wetting layer (I_F), both without dye in the continuous water phase. For each reading, about fifteen slugs are averaged, and about ten readings are averaged for each intensity value. The same process is done only with the dye solution replacing the pure water. Again, two intensities are obtained, through the continuous phase itself (I_D) and through the slugs surrounded by continuous wetting layer (I_{DF}), both with dye in the continuous wetting phase. PM tube voltage readings are taken and stored in a computer using an A/D card (Data Translation). For the higher dye concentration, we follow the same procedure except we do not measure (I_D) but use the extinction coefficient as measured above to calculate the film thickness.

For the water/decane system, when the continuous phase is pure water without dye, the adsorbance of the slug surrounded by the wetting layer (I_O) is indistinguishable from the adsorbance readings through the separating water phases (I_F). If the index of refraction of decane and water were exactly identical, then there would be no reflection at the interface, which would imply that the absorbance readings (I_O) and (I_F) would be the same, and, the average of the intensity of the light detected by PM tube would be as same as the average of just the pure water reading. However, since two indices of refraction are very close but not matched here ($n_{\text{decane}} = 1.42$ and $n_{\text{water}} = 1.29$), the two averages (I_O) and $(I_O + I_F)/2$ which is denoted as $I_{F/O}$ are different. (as shown in Fig. (II-5) and is described in §II.4 Results and Discussion; note there are equal

numbers of equally sized water and decane slugs). Therefore, since two adsorbances (I_O) and (I_F) are different but not distinguishable, an average value ($I_{F/O}$) and the water phase (I_O) is recorded. Thus, (I_F) is determined by (I_F) = ($2I_{F/O} - I_O$). When the continuous phases is the aqueous dye solution, the strong adsorbance of the dye allows for the readings through the slugs to be distinguished from those through the aqueous phase separating the slugs. For each slug, measurements corresponding to the middle of the slug are averaged to calculate (I_{DF}).

As for air/water system, the index of refraction for air is different from water on the contrary of the water/decane system where the two are very close. Both readings through the slugs, (I_F) and (I_{DF}) with and without dye in the water phase, are distinguished from the signals through the single water phase only. They are averaged corresponding to the middle of the slugs. All experiments are carried out at room temperature (22 ± 3 °C).

To account for small, long term variations in the laser intensity or the sensitivity of the PM tube, we use a bracketing procedure to sequence our runs. At a particular velocity, first a water run is undertaken, followed by a dye run, and then a second water run. The two (I_F) are averaged and the average is used to compute the film thickness from eq. (II-4) so that the (I_F) is referenced to the conditions during the measurement of (I_{DF}).

II.3.C Surface and Interfacial Tensions

The interfacial tension of the air/water and decane/water interface were measured by using the pendant drop technique. A pendant drop of decane is formed by the injection of decane through an inverted needle immersed in water, or an air bubble is formed in water at the tip of the needle. A silhouette of the drop is imaged onto a video camera, and the video image is digitized. From the digitized field, the interface contour is numerically constructed and compared to solutions of the Young-Laplace equation. These solutions are parameterized by the interfacial tension, and we vary the tension until the Young-Laplace shape and the experimental curve agree (Girault *et al.* (1989), Lin *et al.* (1990) and Cheng *et al.* (1992)). The measured value for the air/water tension was 72.5 dyne/cm at 22.5°C, and was 48.8 dyne/cm for decane/water at 22.5°C (which is in good agreement with the literature value for this interfacial tension Hansen (1993)).

To confirm that the flow system remains contamination free, we collect the aqueous phase which is just used to measure the wetting film thickness at the outlet of the flow, and we measure its surface tension using the pendant drop technique to monitor the purity of the flow system. The surface tension measurements showed that there was no contamination of the system during the time that the film thicknesses were measured.

II.4. Results and Discussion

As mentioned in the experimental section, the optical density of our solution is approximately 23.8, hence, from eq. (II-9), $2h/D$ should be larger than 9.12×10^{-4} . By using either Bretherton's or Fairbrother and Stubbs' expression, we expect that the capillary number to give this film thickness is approximately 1.9×10^{-5} . Therefore we set the lower boundary in our experiments to be 1.45×10^{-5} , which corresponds to a velocity of 0.106 cm/sec for our air/aqueous solutions with an surface tension 72.5 dyne/cm at 22.5°C. Experiments were undertaken for capillary number over two decades. It is from 2.01×10^{-5} up to 2.61×10^{-3} , which corresponds to a velocity range of 0.106 cm/sec to 12.8 cm/sec for the decane/water system and from 1.48×10^{-5} to 1.67×10^{-3} for the air/water system, which corresponds to the same velocity range. At higher velocities, when capillary numbers approaches to 10^{-2} , the slug train begins to become unstable, with air or decane satellites of the order of the tube diameter separating from the back end of the moving slugs.

As we remarked in the Introduction, Bretherton's expression is valid in the limit for which $Ca \ll 1$ and $Re\ Ca \ll 1$. In the range of our experiments, while capillary number is certainly small (1.48×10^{-5} - 2.61×10^{-3}), Reynolds numbers range between 40 and 200 so that $5.92 \times 10^{-4} < ReCa < 0.522$. Thus in terms of inertial effects, we are at the upper range of validity of the Bretherton theory.

The Bond numbers for air/water flows is 0.03, and it is 0.013 for the decane/water system. So gravitational effects are negligible.

Typical values of the transmitted intensities (I_O), (I_{DF}) and (I_{FO}) are shown in Fig. (II-5) as a function of time during the progression of an experiment for decane/water and for four velocities (2.06 cm/sec (0-80 min), 4.2 cm/sec (80-160 min), 8.5 cm/sec (160-240 min) and 12.8 cm/sec (240-300 min). From (I_O) and (I_{FO}) we calculate (I_F) as described in Sec. II.3.B. Recall each point represents an average of fifteen slugs, and for each reading of (I_F) and (I_{FO}) to calculate the thickness, approximately ten points are taken. Besides bracketing corrects for any variation in the laser intensity or detector sensitivity, nevertheless the uniform values of (I_O) evident in Fig. (II-6a) provide an indication of the stability of the laser and PM tube over the approximately five hours of the experiment.

A similar plot of the transmitted intensities (I_O), (I_{DF}) and (I_F) are shown in Fig. (II-6) for an air/water system and two velocities (0.106 cm/sec (0-200 min) and 12.8 cm/sec (200-320 min)). The most difficult measurement, in terms of accuracy is at the lowest velocity, and we see from the figure a value for (I_{DF}) of 0.927 and for the bracketing value of (I_F) 0.996; thus a seven percent change in the signal is realized. We see this value to be much larger than the deviations from the mean at this lowest velocity.

In order to measure the wetting layer thickness, 39 runs were performed using both air and decane as the slug phase, at different velocities. The assembled data for the film thickness measured as a function of the capillary number is shown in Fig. (II-7) in the range of Ca between 1.48×10^{-5} - 2.61×10^{-3} . Since the quartz tube was not thermostated, and as we have remarked, the fluid temperatures varied by $22^{\circ} \pm 3^{\circ}C$. The primary effect of this variation on the film thickness is through the viscosity change of the water, which can be as large as 10 percent for this range in variation. Therefore the capillary numbers reported for each run is computed using the water viscosity at the experimental temperature of the run. The surface and interfacial tensions are not strong functions of temperature (for the air/water system, $d\gamma/dT = 0.15$ dyne/cm $^{\circ}C$), and therefore, the values at $22.5^{\circ}C$ are used for the calculations of capillary numbers.

The first issue with the data shown in Fig. (II-7) is the comparison with Bretherton's equation and Fairbrother and Stubbs' correlation. These relationships are shown in the figure, and we note for both the air/water and the decane/water systems, the film thickness is in close agreement with Bretherton's expression for Ca equal to 2.61×10^{-3} , and down to a capillary number of 5.41×10^{-5} where the measured thickness is $1.1 \mu m$. For values of Ca less than 5.41×10^{-5} , the measured thicknesses are between $0.65 - 0.95 \mu m$ and are larger than the Bretherton prediction, although less than Fairbrother and Stubbs' correlation. We attribute this discrepancy, as discussed in the Introduction, to the presence of grooves in the tubes with depths less than a micron. Although we have not measured the groove depths, these capillaries are from the same

manufacturer as those used by Chen (1986) who found these sized imperfections by electron microscopy. Note that in the range from 10^{-2} - 10^{-3} , the data also agrees with the Fairbrother and Stubbs correlation, because of the overlap of these expressions in this Ca range. However, between 5×10^{-5} - 10^{-3} the data is clearly lie far from Fairbrother and Stubbs' correlation, and this is in disagreement with prior existing research which finds agreement with both expressions between 10^{-3} - 10^{-2} , but agreement closer to Fairbrother and Stubbs for 5×10^{-5} - 10^{-3} . The wetting layer thicknesses around the air slugs are in closer agreement with Bretherton's prediction (to within a few percent) than those around the decane slugs,

While our result, that Bretherton's expression is valid as Ca decreases until the film thickness becomes of the order of the tube imperfections, is consistent with the asymptotic theory, it hasn't shown why previous research found increasing disagreement as Ca decreased. The effect of surfactant, mentioned in the Introduction, may be the reason, In this study, care was taken to check the air/water and oil/water tensions of the liquids exiting from the stream, and followed rigorous cleaning procedures to maintain these values equal to the surfactant free inlet values. If a surfactant impurity is present, it will be convected by the surface flow to the regions on the surface where the flow converges. Bretherton's solution demonstrates that there are two regions, one at the back end, and a second at the front tip. At high velocities, the partitioned surfactant collects in a belt at the converging zone at the back end, and a cap at the front end. For an impurity, the size of these belts are very small, and so much

of the surface is swept clean of surfactant. However, at lower velocity, the Marangoni tensions in the cap become large relative to the viscous forces, and the belt and cap sizes increase and begin to cover the entire surface. As such, the interface deformability increases and the thickness increases. This may explain why Bretherton's expression is found at high capillary numbers but thicker films at lower capillary numbers. Our attention to surfactant-free conditions may have avoided these difficulties and resulted in an agreement with Bretherton's solution over the entire range of Ca .

II.5. Summary

In this chapter, we have developed a new, general technique for measuring the thickness of the annular wetting layers surrounding long liquid or gas slugs moving through a continuous liquid phase in a capillary. The difference in adsorbance of a light beam passed perpendicular to the tube axis and through the slug and surrounding film with and without an adsorbing dye is measured. This difference is proportional to the dye path length, from which the film thickness is determined once the optical density of the solution is measured. Because of reflection off of the curved hemispherical sections of the meniscus at the front and back ends of the slug, the adsorbance is only proportional to the dye path length in the long cylindrical region of the slug where the film thickness is uniform. The technique can be used to measure the thicknesses of

aqueous wetting layers in two phase foam flows consisting either of isolated long gas slugs or foam trains in which the gas slugs are separated by flattened thin aqueous lamellae. The method is also useful in three phase systems consisting of oil and air slugs over a wetting water layer, or air and water slugs moving over an oil layer. As such, this technique is more versatile than previously developed ones, particularly the meniscus shrinking method and high speed air displacement technique, which is not continuous and cannot be applied to slug trains, the conductivity measurements, which is only applicable to water wetting capillaries, and the direct microscopic visualization measurements, which cannot resolve micron and sub micron thicknesses which occur at low capillary number.

In this chapter, we demonstrated the developed optical adsorbance method using air or decane slugs moving through an aqueous continuous phase in a quartz capillary tube with dichromate dissolved in the water film as the adsorbing dye. Measured thicknesses in the low capillary number range between 1.48×10^{-5} to 2.61×10^{-3} are compared with Bretherton's low capillary number asymptotic expansion and Fairbrother and Stubbs' correlation. The results are in much better agreement with Bretherton's solution than the later for capillary number range which is over two decades, from 2.61×10^{-3} to 5.34×10^{-5} . It is the first time this is reported while all other measurements are systematically higher than Bretherton's expression or reaching a constant in the lower range of capillary number from 10^{-3} to 10^{-4} . Our agreement with Bretherton's solution at lower Ca range is due to a very careful contaminant control of the experiments,

as well as the accuracy of the design of the system. The departure of the thickness from Bretherton's analysis in the Ca range lower than 2.23×10^{-5} is because of the film is so thin that it is in the order of the grooves size of the tube wall.

The experimental methods described in the first section in this chapter which have been used to measure the wetting layer thickness in a capillary tube have drawbacks which limit either their accuracy at low capillary number or their general applicability. Fairbrother and Stubbs' technique of measuring the thickness around a moving bubble by taking the difference between the slug velocity and the mean Poiseuille velocity becomes very inaccurate at low capillary numbers because the difference between these values is only a few percent. While the bubble velocity can be measured to less than a percent accuracy, the tube radius must also be known to this accuracy in order for the error in U_m not to exceed the difference between U and U_m . The method used by Taylor and Cox in which an infinite slug is forced through the tube and the volume collected is subtracted from the volume in the tube also becomes inaccurate at low Ca since these volumes differ by only a few percent, and the accuracy of the volume in the tube depends on an accurate measurement of the capillary radius. Bretherton and Schwartz *et al.*'s method of computing the thickness by measuring the shrinkage of a liquid slug pushed by air and wetting a dry tube is accurate at low Ca because it avoids taking the difference between two quantities that differ by only a few percent; measurement of the slug

shrinkage can be made as accurate as desired by using a long travel distance for the slug to shrink.

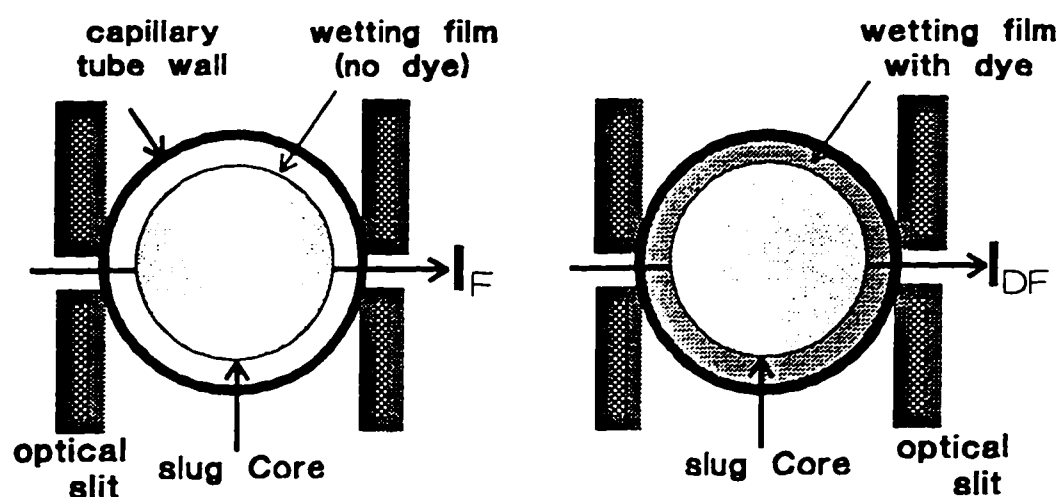


Fig. II-1. Schematic of the optical adsorbance technique for measuring the wetting layer thickness of a two phase slug flow in the capillary tube with the adsorbing dye dissolved in the continuous wetting layer phase

(a) Illustration of the measurements for I_F , the light intensity through the two phase slug flow without the dye dissolved in the continuous wetting phase.

(b) Illustration of the measurements for I_{DF} , the light intensity of the two phase slug flow with the dye in the continuous wetting phase.

The optical density is obtained with the same arrangement and the film thickness is computed from the log of the ratio of above two measurements

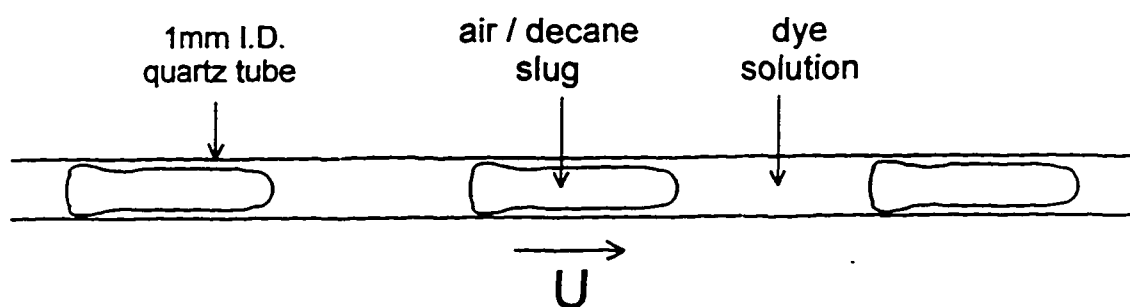


Fig II-2. Schematic of the two phase aqueous/air or aqueous/decane slug train flow in a capillary tube.

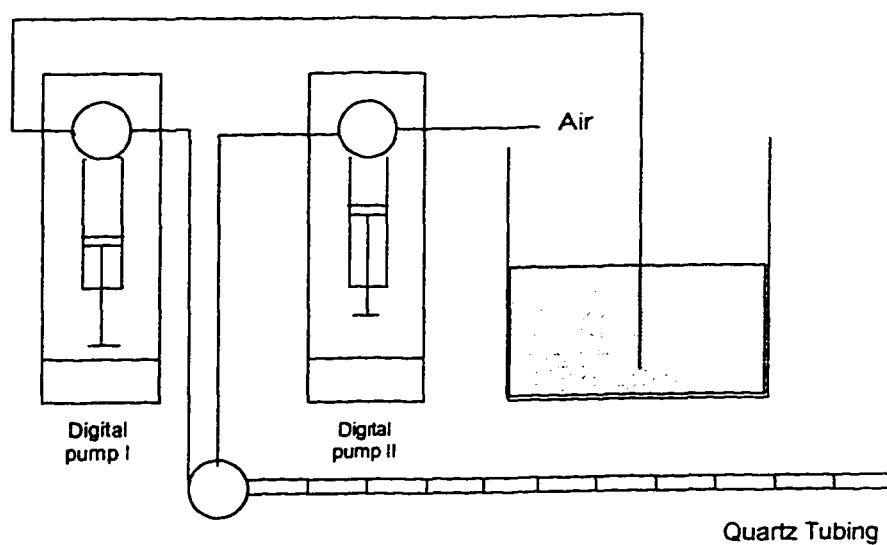


Fig II-3. Schematic of the pumping system employed to create the periodic flow regime

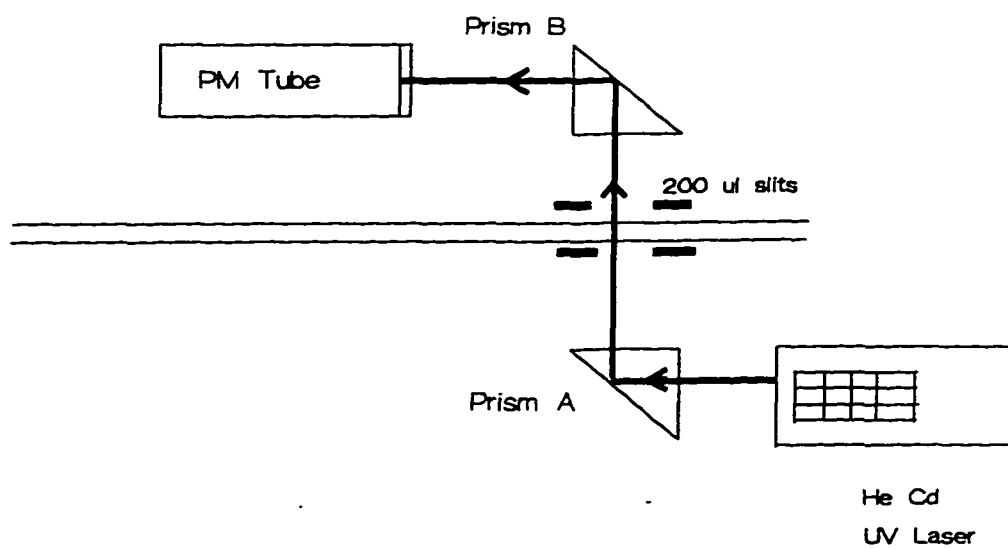


Fig II-4. Schematic of the arrangement of the optical components and the optical path for the adsorbance measurements

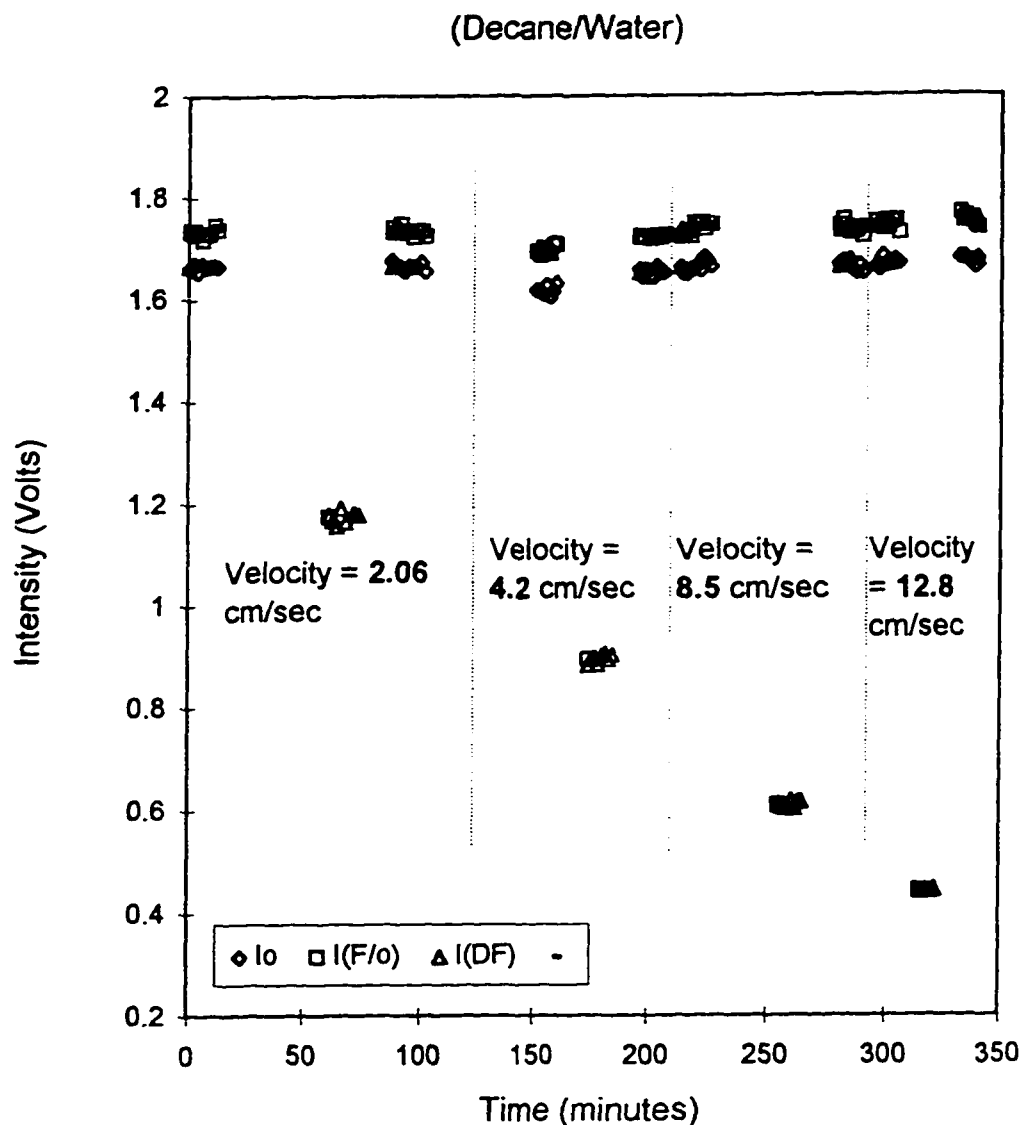


Fig II-5.

Sample of the optical adsorbance measurements data for decane/water system. Each point represents an average of the light intensity of the adsorbance for about fifteen slugs. (a) I_0 is the intensity of the light passing through the water phase

(b) $I_{(F/O)}$ is the average of the intensity of the light passing through water phase and decane slugs surrounded by the water wetting film.

(c) I_{DF} is the intensity of the light passing through decane slugs surrounded by the wetting film dye water solution.

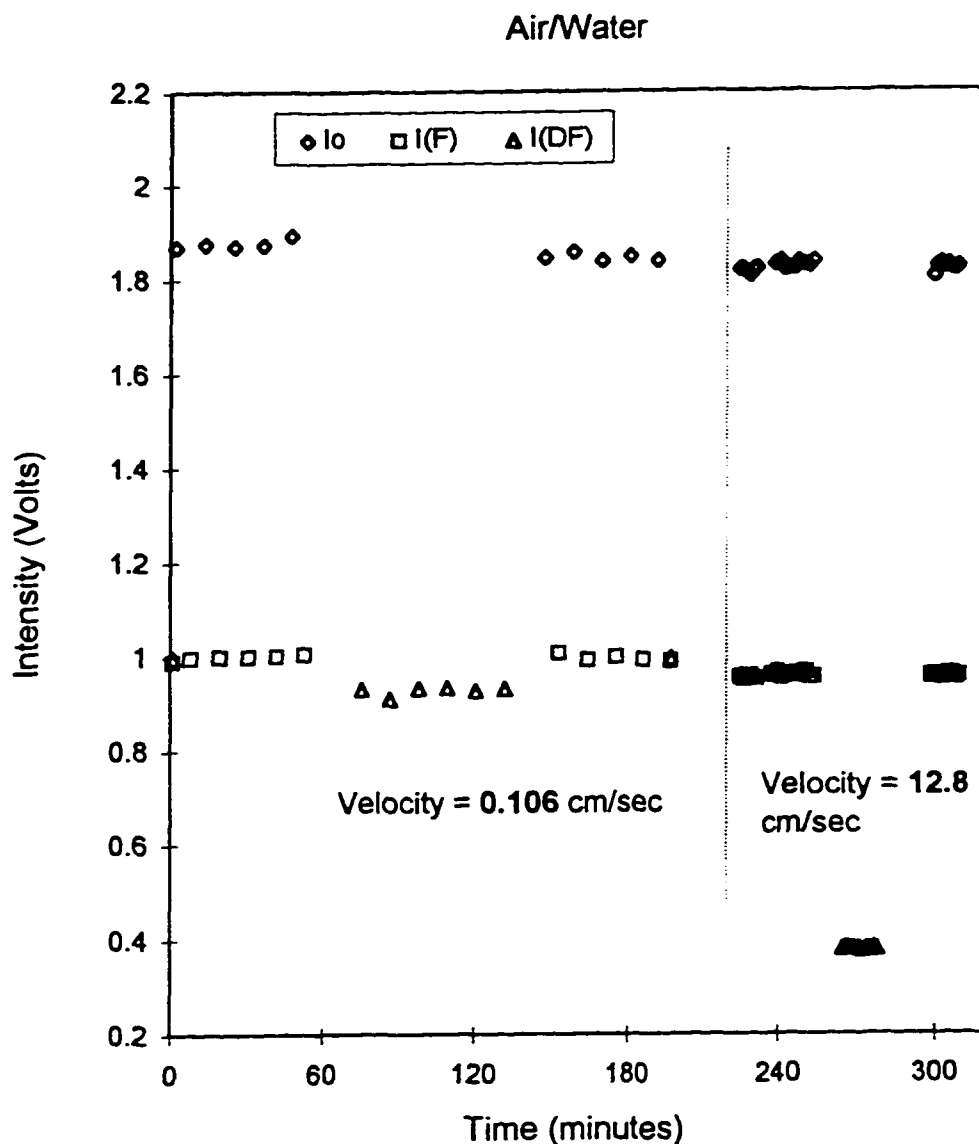


Fig II-6. Sample of the optical adsorbance measurements data for air/water system. Each point represents an average of the light intensity of the adsorbance for about fifteen slugs.

(a) I_O is the intensity of the light passing through the water phase

(b) I_F is the intensity of the light passing through slugs surrounded by the water wetting film.

(c) I_{DF} is the intensity of the light passing through air slugs surrounded by the wetting film of the dye solution.

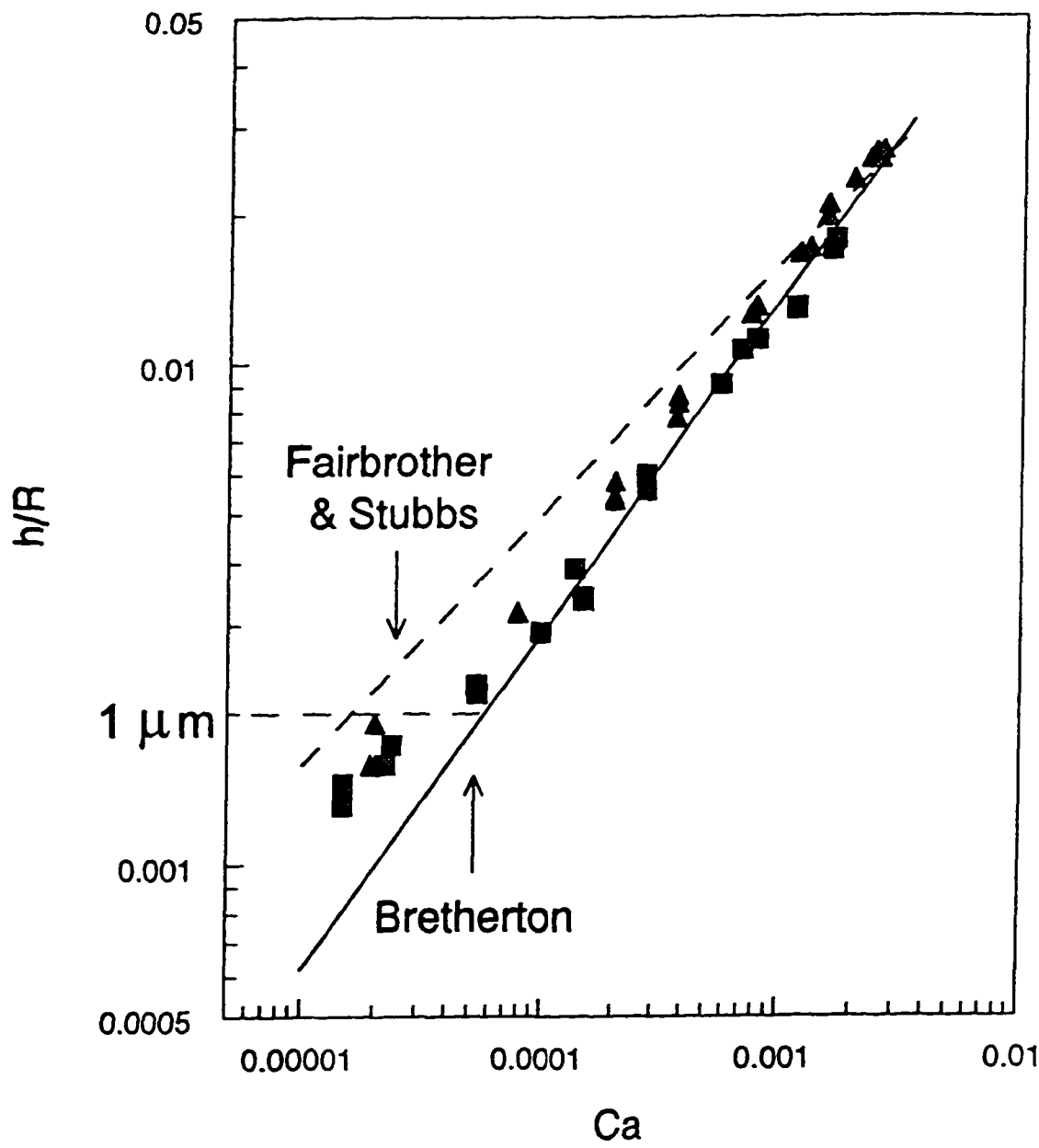


Fig II-7. Measured wetting layer thickness of the air/water and decane/water system as function of the capillary number using the optical adsorbance technique for Ca in the range of 10^{-5} to 10^{-3} . Squares represent data of the air/water system, triangles represent data of the decane/water system. Bretherton's solution and Fairbrother and Stubbs' Correlation in the same range are overlaid.

Chapter III

The Influence of Surfactant on the Wetting Layer Thickness in the Motion of Gas Slugs Through a Continuous Liquid in A Capillary

III.1. Introduction

When a long gas slug is forced to move through a capillary filled with a continuous phase which wets the tube wall more strongly than the slug phase, the nonwetting slugs move over a uniform annular wetting layer of the continuous phase. This motion has been studied both theoretically and experimentally as a model problem for understanding fluids distribution and hydraulic permeability of two phase flows, particularly aqueous foam flows, in finely-capillaried porous media. Aqueous foams move through narrow capillaries as a train of gas slugs, separated by thin lamellae. The gas slugs move over a cushion of a water wetting layer. The resistance of the foam to flow is proportional to the number of gas slugs per unit volume (the foam texture). For a finely textured foam, the flow resistance can be very large, and makes foam an ideal agent for displacing a fluid from porous media, as for example displacing oil from rock pores. To maintain the texture, it is important to stabilize the thin

lamellae which separate the slugs. These lamellae can be forced to drain, when, for example, the cross section through which the foam train is moving increases. If the drainage has reduced the lamellae thickness sufficiently, the lamellae may rupture due to intermolecular interactions. Surfactant is added to the aqueous phase for stabilization. Surfactant adsorbs from the aqueous phase onto the interfaces of the separating lamellae. Adsorbed surfactant can give rise to steric repulsions when the interfaces of the lamellae approach each other, which can stabilize the lamellae from rupture. If the surfactant is charged, electrostatic repulsion through extending double layers can also lead to stabilization.

The addition of surfactant raises the question of what is the effect of surfactant on the hydrodynamics of the slug motion, particularly the wetting layer thickness in the slug flow. The thickness of the wetting layer is relevant to the stability of the flow. If the wetting layer which form as the nonwetting fluid displaces the wetting liquid are too thin, then it can render the layer liable to rupture. This allows a portion of the nonwetting gas phase to become attached to the capillary wall, which upsets the stream motion, as the nonwetting segment, held by surface tension forces, blocks the flow. The wetting phase can respread, dislodging the attached nonwetting segment. However, if this process does not occur rapidly enough, the attached segment may act as a site for the continued attachment of the nonwetting phase which can lead to texture loss and a reduction in the foam resistance which is the important character of foam flow to be used as remobile agent.

Flows in porous media are usually at reduced velocities such that interfacial tension forces dominate over inertial or viscous forces (small capillary and Weber numbers). In the absence of surfactant and in this limit of dominant interfacial forces, this movement of an infinitely long gas slug in a circular capillary of radius R has been studied in considerable detail by Bretherton (1961). The film thickness (h_m) has been shown, by a matched asymptotic expansion at small capillary number, to be set by the advancing meniscus and is given by

$$\frac{h_m}{R} = 1.337Ca^{2/3} \quad (\text{III-1})$$

where Ca denotes the capillary number and is equal to $\mu U/\gamma_c$, where μ is the viscosity of the continuous wetting phase, U is the slug velocity and γ_c the clean interfacial tension. Thus in the absence of surfactant, the thickness is set by the balance of capillary and viscous forces as given by the capillary number. Park and Homsy (1984) have shown that the above expression is also true for viscous slugs as long as the ratio of the slug to the continuous phase viscosity is smaller than order $Ca^{-2/3}$.

The obvious way which surfactant can affect the thickness is by reducing the overall tension of the interface, allowing the front end of the slug to be more deformable to viscous forces (lower capillary number), and thereby increasing the film thickness. But surfactant can also exert an effect on the wetting layer thickness by creating interfacial tension gradients (Marangoni

traction) on the fluid interface which exert tangential traction on the fluids adjoining the interface. Interfacial tension gradients develop as surfactant partitions along the interface as a result of the convective surface flow, kinetic exchange between the sublayer and the surface, and diffusive exchange between the sublayer and the bulk. All the research on the influence of surfactants on the wetting layer thickness have been theoretical (Hirasaki and Lawson (1985), Ginley and Radke (1989), Ratulowski and Chang (1990), Park (1992) and Stebe and Barthes-Biesel (1995)), and have attempted to elucidate how the transport mechanisms of convection, diffusion and kinetic exchange determine the surfactant distribution on the surface, and, in turn, the interfacial tension gradients. These studies have focused on gas displacement and a surfactant only soluble in the wetting phase, which of course is the case with foam motion. Taken together, these studies indicate that the effect of the Marangoni forces is to increase the thickness apart from the increase which follows from the overall lowering of the surface tension. However, these theoretical studies are restricted to regimes of rapid exchange of surfactant between the bulk and the surface, so that surfactant gradients only develop in transition regions between the hemispherical shape and the cylindrical portion of the slug. The long cylindrical section of the slug is assumed to be in equilibrium with the liquid film, and no surfactant gradients exist. Accurate measurements of kinetic rate constants and diffusion coefficients suggest that while the kinetic exchange is fast enough for the assumption of rapid equilibrium in the wetting layer to hold, diffusive exchange is not fast enough.

This means that there is a slug length dependence to the effect of surfactant on the wetting layer thickness.

The aim of this study is twofold. The first is to outline a more general theoretical framework for how surfactants can affect the wetting layer thickness which accounts for the slow diffusive exchange and lack of equilibrium between the surface and the film. The second is to use the optical adsorbance technique which we have previously developed and described in Chapter II for measuring the wetting layer thickness to examine experimentally for the first time how surfactant affects the wetting layer thickness, and to interpret these results in terms of our theoretical framework. We have measured wetting layer thicknesses in a model flow consisting of a water-wetting 1 mm quartz circular capillary in which air slugs move in a continuous water phase. In our optical adsorbance technique, a dye is dissolved in the aqueous phase, and the adsorbance of a sheet of laser light passing perpendicularly across the tube and strongly adsorbed by the dye is measured for the flowing system in the absence and then the presence of the dye. The difference is related to the wetting layer thickness. To illustrate the surfactant effect, we use the polyethoxylated amphiphile $C_{12}E_6$ ($CH_3-(CH_2)_{11}(-OCH_2CH_2)_6-OH$). Measurements were undertaken in this flow system at different capillary numbers and surfactant concentrations.

This chapter is organized as follows. In the next section (Sec. III.2), we outline our proposed theoretical framework. The experimental technique is

discussed in the following Sec. III.3, and we present and discuss our results of measurements in Sec. III.4.

III.2 A Framework for Understanding Surfactant Distributions on the Surface of Gas Slugs and Their Effect on Wetting Layer Thicknesses

A general picture of the distribution of surfactant along the surface of a slug can be surmised from an examination of the surface flow pattern in the absence of surfactant. As we mentioned in the Introduction (III.1), Bretherton (1961) and later Park and Homsy (1984) used a matched asymptotic approach to solve for the hydrodynamic flow for low capillary number ($Ca = \mu U / \gamma_c$). Because the capillary number is small, at the front and back ends of the slug, viscous stresses on the interfaces (which scale as $\mu U / R$) are not as important as capillary forces (which scale as γ_c / R), and surface tension holds these menisci with constant curvature as sections of spheres. Away from ends, the slug moves over a uniform wetting layer of constant thickness which is at rest in the laboratory frame. In the reference frame of the slug, this layer is moving with uniform velocity $-U$, i.e. in the negative axial direction. The annular interface of this uniform wetting layer is connected to the spherical sections of the front and back menisci by transition regions overlaying a thin film in which both viscous and surface tension forces are important. For small Ca , Bretherton showed that the axial and thickness lengthscales in the transition layer film are of order $Ca^{1/3}$

and $Ca^{2/3}$, respectively. A composite picture of the five regions of the slug is shown in Fig. III-1.

Consider the flow in the front transition region. To leading order in this region, Bretherton derives the following equations for the nondimensional scaled film thickness h (nondimensionalized by R and scaled as $Ca^{2/3}$) and surface velocity u_s (nondimensionalized by U and an order one quantity) as a function of the scaled nondimensional axial coordinate z (nondimensionalized by R and scaled as $Ca^{1/3}$)

$$\begin{aligned} \frac{d^3 h}{dz^3} &= \frac{6[1 - u_s]h - 12h_\infty}{h^3} \\ u_s &= \frac{1}{2} - \frac{3h_\infty}{2h} \end{aligned} \quad (\text{III-2})$$

where h_∞ is the uniform wetting layer thickness. The above expression for the surface velocity clearly shows that there exists a stagnation ring in the flow on the surface of the transition layer, located to leading order at the point where the film thickness is 3 times of the uniform wetting layer thickness. This is a diverging stagnation point: Note from the above expression that for z to the left of this ring, $h < 3h_\infty$ and the surface velocity is negative, and to the right $h > 3/2h_\infty$ and u_s is positive. Thus to the left of the stagnation ring the flow is towards the wetting layer, and to the right surface elements convect to the tip of the meniscus. The origin of this diverging stagnation ring is the fact that the velocity of the advancing meniscus, U , is smaller than the centerline velocity of

the Poiseuille flow upstream of the advancing meniscus (see Fig. III-1). Thus in the meniscus frame of reference the fluid velocity of the continuous phase near the tube center and in front of the meniscus must be moving in the positive axial direction, while fluid near the wall is moving in the negative axial direction. This gives rise to the separation ring. Since in the uniform wetting layer, the flow is uniformly in the negative axial direction and equal to $-U$, the net flow rate across any cross section (termed the leakback and denoted dimensionally as q) is equal (to leading order) to $2\pi R U h_{\infty}$ and is in the negative axial direction. Integration of the film thickness equation, and matching to the annular interface of the wetting layer, and the spherical meniscus at the advancing front yields eq. (III-1) for h_{∞} to leading order in Ca .

At the back end, eq.(III-2) is also valid, and a stagnation ring is again located in scaled variables for $h = 3h_{\infty}$. However, at this ring fluid diverges because $h < 3h_{\infty}$ to the right ($u_s < 0$), and $h > 3h_{\infty}$ to the left ($u_s > 0$); see Fig. (III.1.) As with the front end, this separation ring arises because, in the slug reference frame, the continuous phase liquid is moving in the positive z direction, while near the wall it is moving in the negative z direction.

Surfactant adsorbed from the continuous phase onto the slug interface, as we have mentioned in Sec. II, the obvious way that surfactant can affect the thickness is by reducing the overall tension of the interface, increasing the film thickness. This can be easily seen by defining capillary number at equilibrium using γ_{eq} ($Ca_{eq} = \mu U / \gamma_{eq}$), and we then denote the film thickness evaluated at Ca_{eq}

using Bretherton's solution as ($h_{eq} = 1.337 Ca^{2/3}$) which is nothing more than the increased film thickness due to the effect of surfactant increasing the deformability of the slug. Instead of uniformly distributed on the interface, surfactant is partitioned by the surface convection. In order to focus on the effect of Marangoni traction, For the rest of this chapter, we are going to discuss the changing of the film thickness relative to h_{eq} . At the front stagnation ring surfactant is swept towards the rear ring, and the front tip, depleting the sublayer concentration in the front ring vicinity and creating a diffusive flux of surfactant to this part of the surface. At the front tip, surfactant accumulation gives a local flux away from the leading edge. The surface flow collects surfactant at the rear stagnation ring, raising the sublayer concentration in the neighborhood of this ring and creating a diffusive flux from the rear ring out into the continuous phase. In addition, at the trailing end, because surfactant is convected to the back ring and the sublayer concentration is low at the trailing end, surfactant diffuses towards the back end. Thus, as shown in Fig. (III-2), a general picture which we may anticipate of the surfactant distribution shows a high concentration at the back ring and the front tip, an increasing concentration from the front ring to the back ring and the front tip, and a decreasing concentration from the back ring to the back tip. The exact partitioning which is realized from the general picture in Fig. (III-2) is a function of the ratio of the diffusive flux to the surface and the convective flow of surfactant along the surface. This ratio is described the surfactant mass balance on the surface of the slug, which we formulate generally in the dimensional form:

$$-\nabla_s \cdot [\Gamma \mathbf{u}_s] = D \mathbf{n} \cdot \nabla c \quad (\text{III-3})$$

where ∇_s is the surface gradient operator, $\mathbf{u}_s$ is the surface velocity, D is the diffusion coefficient of the surfactant, $\mathbf{n}$ is the outward normal to the slug interface, Γ is the surface concentration of surfactant and c is the bulk concentration of surfactant. Nondimensionalization of eq. (III-3) allows for a formulation of the ratio of the diffusive to the convective rate. We nondimensionalize the bulk concentration by C_o , the bulk concentration of the continuous phase. To nondimensionalize the surface concentration Γ we use the surface concentration Γ_o in equilibrium with the bulk concentration C_o . As we mentioned in the Introduction Sec. (III.1), the surfactant we use for the experimental part of this study is the polyethoxylated amphiphile $C_{12}E_6$. Equilibrium measurements of the tension as a function of the bulk concentration ($\gamma(C_o)$), which we describe later (III.C.1), demonstrate that the adsorption can be described by the Langmuir adsorption and thus

$$\frac{\Gamma_o}{\Gamma_\infty} = \frac{k}{1+k} \quad (\text{III-4})$$

where Γ_∞ is the maximum packing concentration and k is equal to the adsorption rate βC_o divided by the desorption rate a :

$$k = \frac{\beta C_b}{\alpha} \quad (\text{III-5})$$

From the measurements of the equilibrium tension as a function of the bulk concentration, as we show in Sec. III.C.1 for the test surfactant used, we calculate Γ_∞ and β/α . We scale the surface velocity by the slug velocity U .

We first consider the cylindrically long section of the slug whose axial length scale is L and whose radial length scale is, from the Bretherton thickness for the clean system, $RCa^{2/3}$. Thus the scaling of the diffusive flux is $DCo/(RCa^{2/3})$ and for the axial convection along the surface $[U\Gamma_\infty]/L$. The diffusion coefficient has been measured for the test surfactant by dynamic tension measurements (Pan *et al.* (1995)). The dimensionless surface mass balance then becomes,

$$-\tilde{\nabla}_\perp \cdot [\tilde{\Gamma} \tilde{u}_\perp] = \Phi \mathbf{n} \cdot \tilde{\nabla} \tilde{c} \quad (\text{III-6})$$

where the tilde denotes a nondimensional variable, and Φ describes the ratio of diffusion to convection in the long cylindrical region and is given by:

$$\Phi = \frac{1+k}{Ca^{5/3}} \left[\frac{\mu D \alpha}{\beta \gamma_c \Gamma_\infty} \right] \frac{L}{R} \quad (\text{III-7})$$

We are now in a position to define our first regime of surfactant transport. Our interest is in small capillary numbers, and our experiments will have Ca in the range of 10^{-4} - 10^{-2} , and our L/R is of order 40. However, principally because of the small value of the diffusion coefficient, at the higher end of Ca and for low bulk concentrations (k small), $\Phi \ll 1$, and the convective rate is much larger than the diffusive rate over the length scale L . Because of this disparity, surfactant is swept to the trailing ring of the slug since with $\tilde{\nabla}_s \cdot [\tilde{\Gamma} \tilde{u}_s] = 0$, either the surface concentration or the surface velocity is equal to zero. It is important to note that when the convective rate is much faster than the diffusion rate in the long cylindrical region, it is certainly also true in the transition regions and the hemispherical (capillary statics) end regions. In the transition regions the axial length scale is much shorter, $R Ca^{1/3}$ instead of L , while the radial lengthscale is the same and therefore the ratio of diffusion to convection is given by:

$$\Phi_1 = \frac{1+k}{Ca^{4/3}} \left[\frac{\mu D \alpha}{\beta \gamma_c \Gamma_\infty} \right]$$

In the hemispherical cap regions, the axial and radial length scales are R , and the ratio of diffusion to convection becomes

$$\Phi_2 = \frac{1+k}{Ca} \left[\frac{\mu D \alpha}{\beta \gamma_c \Gamma_\infty} \right]$$

Clearly, since $Ca \ll 1$ and $L/R > 1$, if $\Phi \ll 1$ than Φ_1 and Φ_2 are both much smaller than one. Thus at the front tip in the hemispherical section, surfactant collects in an immobile cap, while in the front transition region the interface is swept clean of surfactant. At the back stagnation ring, surfactant collects in an immobile cap, that can extend into the long cylindrical region or the trailing hemispherical end of the slug. This stagnant cap regime of surfactant transport is illustrated in Fig. (III-3). As we discuss below, caps are compressed by the viscous flow in the film, and their sizes represent a balance between this compression and interfacial tension Marangoni forces which resist the compression.

The stagnant cap condition of relatively high Ca and small bulk concentration (small k) is the reference point for our changing of bulk concentration and velocity or capillary number. As the bulk concentration increases (but we assume Φ remains smaller than one), the amount of surfactant adsorbed onto the surface increases, and the caps shown in Fig. III-3 become larger. Similarly, as the velocity (Ca) decreases (assuming once again Φ remains small), interfacial tension forces become large relative to the viscous forces which tend to compress the caps, and the caps once again increase in size. To estimate the size of the caps (L_{CAP}), we equate the scale of the viscous compression to the Marangoni tension gradient which resists the compression. In the long cylindrical region of lengthscale L , the viscous traction is of order $\mu U/h_{\infty}$ since the monolayer is immobile and the wall is moving with velocity $-U$.

The Marangoni stress scales as $\left\| \frac{\partial \gamma}{\partial \Gamma} \right\|_{\Gamma} \frac{\Gamma_{max}}{L_{CAP}}$. Since the amount of surfactant in

the cap is equal to what is swept along the long cylindrical section,

$$\frac{\Gamma_{\text{MAX}}}{\Gamma_0} = \frac{L}{L_{\text{CAP}}} \text{ For Langmuir adsorption, the surface tension as a function of the}$$

surface concentration is given by:

$$\gamma(\Gamma) = \gamma_c - RT\Gamma_{\infty} \ln\left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) \quad (\text{III-8})$$

Equating the Marangoni and viscous forces, the cap length scales as

$$\left[\frac{L_{\text{CAP}}}{R}\right]^2 = \frac{k}{Ca^{1/3}} E \frac{L}{R} \quad (\text{III-9})$$

where E is the elasticity number ($E = \frac{RT\Gamma_{\infty}}{\gamma_c}$). Thus as Ca decreases or k

increases, the size of the cylindrical cap grows. By the same reasoning, the size of the cap at the front end scales as $\frac{k}{Ca} E$, and because of the stronger dependence on Ca grows quickly into the front transition region.

Thus in the stagnant cap regime ($\Phi \ll 1$), we expect the following behavior as Ca decreases or k increases, as illustrated in Fig. (III-4). At low k and high Ca , the caps are localized in and about the back transition region and the front tip Fig. (III-4.A). As k increases or Ca decreases, the caps grow. The front cap, which grows faster, reaches the front transition region, and therefore

this region is partially immobile and partially mobile. The back cap grows towards the back tip and along the cylindrical region Fig. (III-4.B). Finally, for large enough k or small enough Ca , the cap which grows from the back reaches the front transition region and the back tip, and the interface is completely immobile Fig. (III-4.C). Further increase in k or decrease in Ca will allow Φ to become of order one. This defines a second regime of partial interfacial mobility, and we describe this regime below.

The surfactant distributions depicted in Fig.(III-4) for the stagnant cap regime would result in the following measured thicknesses. When the caps are compressed, the measured thickness would correspond to the Bretherton clean interface value, since surfactant is not present in the critical front transition region or most of the long cylindrical region. As the caps grow with increasing k or decreasing Ca , we mentioned above that the immobile surfactant cap enters the front transition region from the front tip. This effects the film thickness in two ways. First, the interface becomes more deformable, and the thickness which is set for the cylindrical section of the wetting layer increases. Second, as shown by Bretherton, when the interface in the transition region becomes immobile, the thickness also increases. The growth of the cap in the cylindrical region has a separate effect. Because of the transition from a mobile to an immobile interface, the thickness must increase over the solid part of the interface to satisfy the continuity of the leakback. Therefore there is a jump in thickness; any technique (such as ours as we will describe subsequently) which measures an average thickness will therefore measure an increase in thickness.

This jump is shown in Fig. (III-4.B), and we may estimate the thickness jump to be a factor of two since we are going from a uniform to a shear velocity profile in the film. When the cap reaches the front transition region, this jump disappears, the thickness becomes more uniform (since the shear in the layer is constant), and deformability and immobility in the front transition region contribute to a thicker film than the Bretherton clean interface value. (III-4c).

With a further increase in k or a decrease in Ca , diffusion begins to compete with convection in the long cylindrical region and Φ becomes of order one. With Φ of order one, the interface in the cylindrical section is no longer immobile (as in Fig. (III-4.B)), but develops an axial velocity. It is important to note that when Φ becomes of order one, the transition regions can still be stagnant since $\Phi_1 < \Phi$. When Φ_1 becomes of order one, or $\Phi = O(\frac{L}{RCa^{1/3}})$, then the transition region becomes mobile and the cylindrical film region of length scale L reaches equilibrium. In this case the film is uniform since no Marangoni stresses exist, and the thickness is set by the mobility in the front transition region. This is the regime studied by Ratulowski and Chang (1990) and (for the kinetic controlled case) by Stebe and Barthes-Biesel (1995).

We term this regime in which the cylindrical interface just becomes mobile until the transition regions become mobile ($\Phi = O(\frac{L}{RCa^{1/3}})$) the “Partially Mobile Regime”. (Fig. III-5). As first discussed by Ratulowski and Chang (1990), the most important characteristic of the surfactant distribution in this

regime in terms of its influence on the film thickness is a depletion effect. A surfactant balance across any cross-section of the slug at position z , and an upstream section from the slug where the bulk concentration is uniform is given by

$$q(C_o - C_f) = 2\pi R \Gamma u_s \quad (\text{III-10})$$

where q is the leakback, and C_f is the average concentration of surfactant in the film at some location z , and the product Γu_s is also evaluated at the cross-section position z . From the above equation, we know that the film is depleted of surfactant, and therefore surface concentrations may be significantly smaller than the values at the hemispherical ends. This results in a Marangoni stress which draws fluid into the film in addition to the thickening due to increased deformability. Thus we may anticipate that as k increases or Ca decreases and Φ becomes of order one or larger, the film thickness relative to the clean Bretherton value will continue to increase.

A final regime occurs for fixed Ca as the bulk concentration increases still further. For this case, the large bulk concentration C_o diminishes the depletion effect described by eq.(III-10), and mobilizes the hemispherical caps ($\Phi_2 \gg 1$). The result is a completely mobile interface, and a value of the film thickness equal to the Bretherton value evaluated at the equilibrium tension (see Fig. (III-6)). (We denote this value h_{eq}). We term this regime "Completely Remobilized." In practice, it is usually achieved for concentrations of surfactant exceeding the

critical micelle concentration (CMC) in which case the surfactant micelles (aggregates of surfactant) provide the reservoir to maintain the surface in equilibrium, and maintain a constant monomer concentration in the film.

III.3 Experimental Measurements of the Film Thickness

The experimental method used to measure the wetting layer thickness was developed in Chapter II for a clean system, and the method is only briefly reviewed here. A horizontal, straight quartz capillary, 1 mm in inner diameter is mounted on a vibration isolation table, and a UV laser beam at 325 nm wavelength is arranged to pass across the tube, perpendicular to its axis. The beam passes through two optical slits, 200 mm in thickness, and 5 mm in length. The slits are arranged facing one another on either side of the tube with the centerline of each slit (in the long direction) parallel to the tube centerline, and all three centerlines lying in one plane which itself is parallel to the plane of the isolation table. The slits act to chop the laser beam in such a way that only light passing through the center of the tube passes out through the second slit. The laser beam is detected by a photomultiplier tube. A train of air slugs in a continuous water phase is assembled in the tube upstream from the slits by the alternating action of two dispensing/aspirating syringe pumps: One pump is connected to the reservoir containing water or the dye solution, and the second pump is connected to air. The length of the slugs is 20 capillary diameters, and they are separated by 20 diameters. After the train has been created, it is pushed

by the water syringe pump at a uniform prescribed velocity, causing the slug train to pass in front of the slits. Adsorbance measurements are recorded by computer through an AD board, first without dye dissolved in the aqueous phase and then with dye. When dye is not present, the adsorbance of the water film is measured as I_F . However, the dye strongly reduces the signal and an average value I_{DF} is measured. The film thickness is then obtained from the

$$\log\left[\frac{I_F}{I_{DF}}\right] = \epsilon_D(C)CD\left[\frac{2h}{D}\right] \quad (\text{III-11})$$

equation.

where $D=2R$, C is the concentration of dye and ϵ_D is the extinction coefficient. The extinction coefficient is measured separately in experiments as described in Chapter II.

It is important to emphasize that the measured thicknesses is an average value over the length of the slug. From the photomultiplier tube readings, the front and back of the slugs are located, and the photomultiplier tube readings are averaged over the length of the slug, starting with one radius from the front, and ending with one radius from the back of the slug.

As we mentioned in the Introduction, the surfactant used is $C_{12}E_6$. We have measured the surface tension at the air/water (γ_{AW}) surface by using the axisymmetric shape analysis of pendant bubbles or drops. A pendant bubble is

formed at the tip of an inverted needle in an aqueous solution, and a silhouette of the bubble is imaged onto a video camera, and digitized to locate the interface contour. By comparing the interface shape to solutions of the Young-Laplace equation, the surface or interfacial tension is obtained. In the case of oil/water tensions, we first pre-equilibrate the oil and aqueous phases. Shown in Fig. (III-7) are the air/water tensions as a function of bulk concentration in the aqueous phase. The air/water tensions range from 72.4 dyne/cm for the clean system to 33.5 dyne/cm at 40 mg/L. Above 40 mg/L the surface tension does not change, indicating the formation of surfactant aggregates or micelles in the bulk phase. These results confirm other literature studies (Carless *et al* (1964), Corkill *et al* (1964) and Lucassen and Giles (1975) for the air/water $C_{12}E_6$ system.

The equilibrium Langmuir constants are obtained by fitting the equilibrium γ -ln C_o measurements (Fig. III-7) to the equation of state, eq. (III-8) with the adsorption isotherm eq.(III-4) substituted for the surface concentration, the equilibrium data yields: $a/\beta = 0.0512\text{mg/L}$ and $\Gamma_{\infty} = 1.089 \times 10^{-4} \text{ mg/cm}^2$. Dynamic surface tension experiments in which a pendant bubble is quickly formed, and the reduction in surface tension is measured as surfactant adsorbs onto the initially clean surface have been used by Pan *et al.* (1995) to determine the rate constants using the above equilibrium parameters; they find $D = 8 \times 10^{-6} \text{ cm}^2/\text{sec}$ and $\beta = 4 \text{ m}^3/(\text{mole sec})$.

III.4 Experimental Results

Average film thicknesses in the cylindrical section of the slug (as explained in the experimental section above) were measured for four different slug velocities (6.4 cm/sec, 2.06 cm/sec, 0.744 cm/sec and 0.213 cm/sec) and a range of bulk concentrations C_o (0.32-80 mg/L; the CMC is 40 mg/L) of aqueous solutions of $C_{12}E_6$. In Fig. III-8 - III-11 we hold the velocity constant, and graph the measured film thickness as a function of increasing bulk concentration. In Figures III-8 and III-9 the two higher velocities are shown (6.4 and 2.06 cm/sec), and only results for concentrations less than the CMC are plotted. The bulk concentration is scaled as Φ . The film thickness is scaled with the equilibrium film thickness h_{eq} , which is the Bretherton thickness assuming the tension is uniform and equal to the equilibrium tension at the bulk concentration C_o employed. For these two velocities, values of Φ vary from 10^{-2} to values less than 10. From our discussion in Sec. III.2, we expect that for $\Phi < 10^{-1}$, we should be in the stagnant cap regime, and the thicknesses should be close to Bretherton's clean interface value. From the graphs in Figs. III-8 and III-9 we see that h/h_{eq} is indeed smaller than one, indicating measured values close to Bretherton's clean value since $h_{eq} > h_{clean}$. We also note that as the concentration (Φ) increases, the relative thickness increases as the measured thickness increases faster than h_{eq} . In accordance with the discussion in Sec. III.2, growth of the cap into the front transition region squeezes the slug and increases the thickness. In addition, the anticipated jump at the solid/mobile juncture would raise the average thickness. As Φ increases above 1 in Figs. III-8

and III-9, the cylindrical interface begins to become mobile, and depletion of surfactant in the film can begin to account for further increases in the film thickness. For these two velocities, if we restrict our measurements to concentrations less than the CMC, it is not possible for Φ to be sufficiently large enough to see the complete effects of depletion and complete remobilization.

However, at the two lower velocities (0.744 and 0.213 cm/sec) (Figure III-10 and III-11), achievable values of Φ for concentrations once again less than the CMC can be as large as 100. For these velocities, at the lowest concentrations employed, Φ is already of order one, so that we are already in the partially mobilized regime and h/h_{eq} begins larger than one, and increases due to the Marangoni forces arising from depletion. As the bulk concentration is increased further, and depletion becomes less significant, the scaled film thickness begins to decrease, and this is observed in both graphs in Figs. III-10 and III-11. In Fig. III-12 we assemble all the data below the CMC as a plot of the relative thickness against the diffusion to convection parameter Φ , and identify the two regions of surfactant transport, the stagnant cap regime (Region I) and the partially mobile regime (Region II).

To examine remobilization, we measured thicknesses for concentrations equal to or above the CMC for three velocities (0.213, 0.744, and 6.4 cm/sec; see Fig. III-12). We plot the scaled thickness as a function of the bulk concentration and find that at twice the CMC (80mg/L) which corresponds to Φ of 10^3 the scaled thickness becomes approximately equal to one. This

strongly suggests that the slug interfaces have become completely mobile, and the system is behaving as if it were surfactant free except for the uniformly lowered tension.

III.4 Conclusions

In this chapter we have studied experimentally the effect of surfactant dissolved in the continuous phase on the wetting layer thickness surrounding a gas slug moving through a tube, and we have analyzed the results in terms of surfactant distributions and induced Marangoni forces on the slug surface. We have used a model system consisting of a 1 mm quartz capillary wetted by an aqueous solution of the polyethoxylated surfactant $C_{12}E_6$. This is a useful model surfactant because its transport parameters - kinetic rate constants and the diffusion coefficient - have been measured previously using the pendant bubble technique, and the knowledge of these parameters allows for a more realistic understanding of the surfactant distribution. In the model system, the wetting layer thickness is measured by the laser adsorption technique we have developed previously in Chapter II, and have shown to give accurate experimental results for the surfactant-free (clean) system in which the thickness is given by Bretherton's expression.

Besides overall surface tension reduction which increases the deformability and thickens the wetting film, surfactant affects the thickness in

three regimes. It's a function of the ratio of diffusion effect and convection effect, which can be defined as a function of surfactant concentration C and velocity U , $\Phi(C, U)$, or $\Phi(k, Ca)$ in dimensionless.

The first is realized at low bulk concentrations or high velocities. In this regime, the diffusive flux of surfactant to the surface is much smaller than the convective flux, $\Phi \ll 1$, and surfactant collects in a stagnant ring at the back stagnation ring of the slug, and the front tip. In the stagnation zones the surface velocity is equal to zero, but the surfactant concentration is nonzero, and along the rest of the bubble surface the surfactant concentration is equal to zero. The wetting layer thickness above the stagnant ring is larger than that above the surfactant free zone, and thus there is a jump change in thickness. At relatively very low bulk concentrations and high velocities, the stagnant zones are small enough that the deformability of the overall reduction of surface tension in the transition region doesn't occur, the measured wetting layer thickness is simply Bretherton's expression, and our results verify this behavior. As the velocity decreases or the concentration increases, the size of the stagnation zones increases into the front transition region which sets the wetting film thickness, and it increases the film thickness for overall tension reduction and the jump increasing due to the immobile surface. Finally the entire surface is covered by the immobile surfactant layer, the thickness has increased further, and this represents the end of the first regime.

The second regime demarcates the transition from the slug whose surface is completely immobile. As the bulk concentration increases or the velocity decreases, diffusion and surface convection become of the same order, $\Phi = O(1)$. The distinguishing feature of this regime is that the larger diffusive flux allows the surface to be mobile, and this depletes the bulk concentration of surfactant in the wetting layer. As a result the surface concentration in the wetting layer is reduced, and this gives rise to Marangoni forces which raise the film thickness further from that measured for the completely immobile surface. Our measurements confirm this increase in thickness. As the bulk concentration increases still further, the effect of depletion is reduced, and this reduces the film thickness as Marangoni forces are diminished. The end of this second regime is at the critical micelle concentration (CMC).

The last regime is comprised of surfactant concentrations in excess of the CMC. In this case, $\Phi \gg 1$. Diffusion completely dominates, the reservoir of surfactant which micelles afford completely diminishes the depletion effect, and the interface is in a remobilized state in which the surface motion is the same as that of a surfactant free system except for the overall reduced tension. The reduced tension makes the interface more deformable, and the Bretherton thickness of a clean interface with reduced tension h_{eq} is measured.

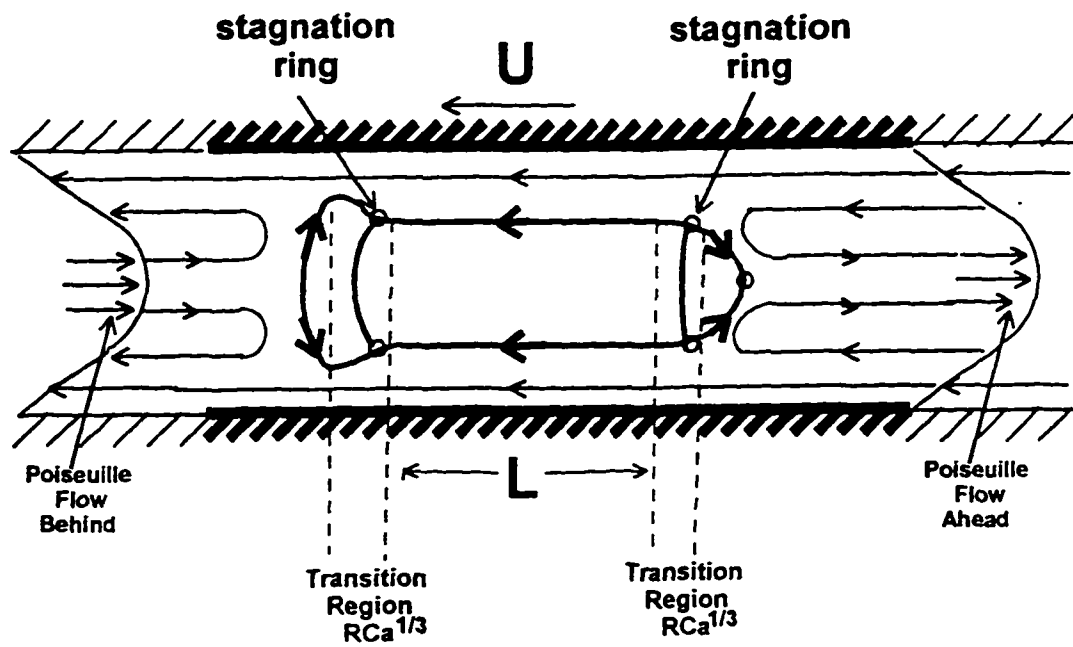


Fig III-1. Hydrodynamic flow pattern for the slug flow; stagnation rings develop at the leading and trailing ends due to the fact that the slug velocity is smaller than the centerline velocity of the far field Poiseuille flow.

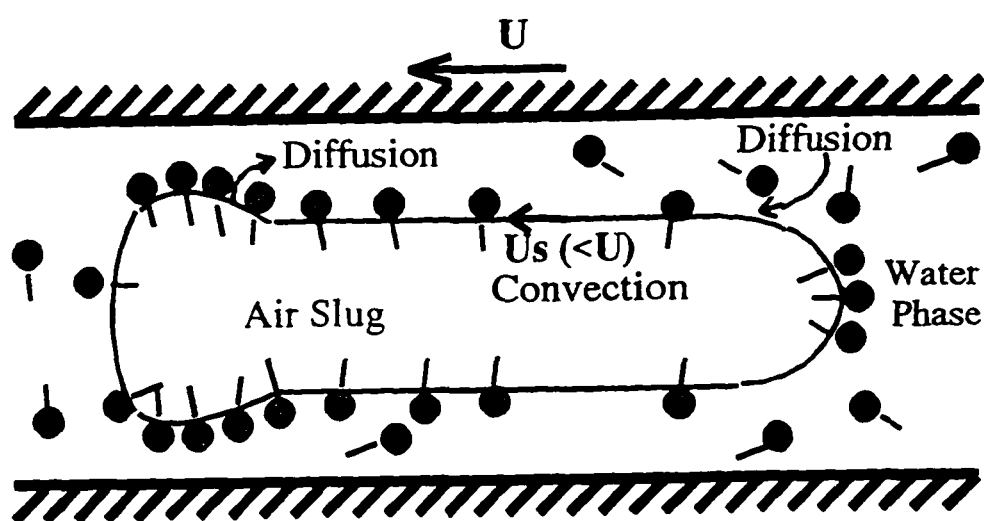


Fig. III-2 Generalized surfactant distribution on the bubble surface. Surfactant accumulates at the back stagnation ring and front tip, and the Marangoni force extending over the length of the bubble reduces the tangential velocity ($U_s < U$).

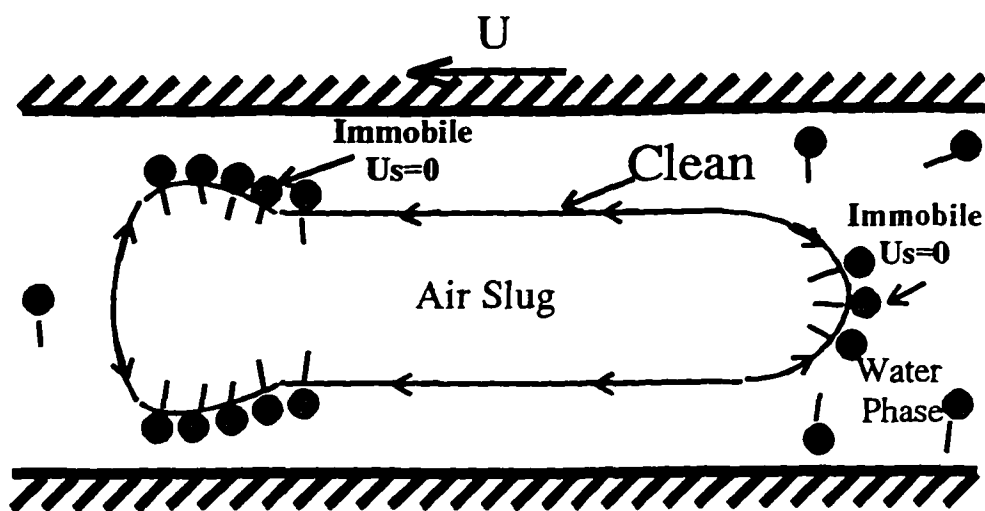


Fig. III-3 The stagnant cap regime of surfactant transport. Surfactant collects in an immobile ring at the back transition region, and a cap at the front end. The rest of the surface is swept clean of surfactant and is mobile.

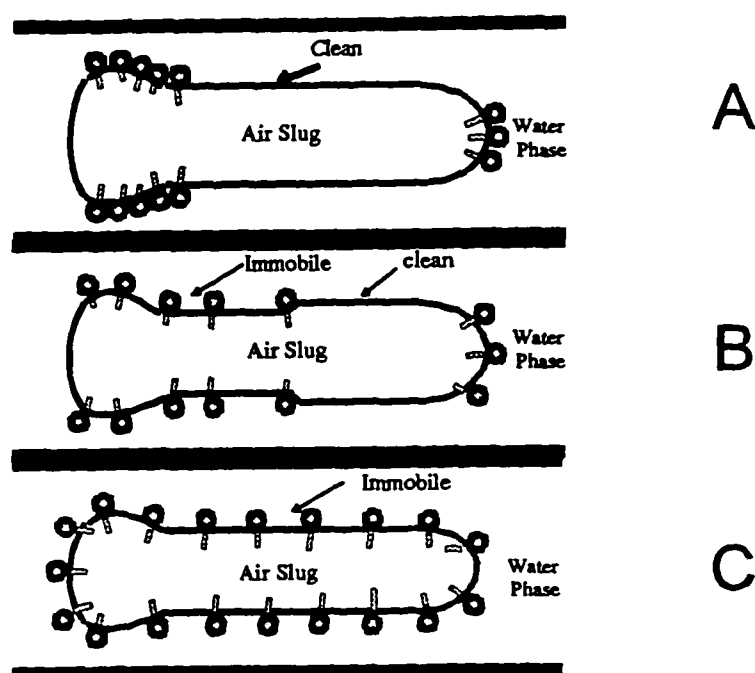


Fig. III-4 The growth of stagnation rings and caps in the stagnation cap regime. The reduction in capillary number, or increase in bulk concentration increases the size of the immobile regions. For high Ca or small k , the caps are localized; as Ca decreases or k increases the stagnation regions grow in size (B) until they occupy the entire surface (C).

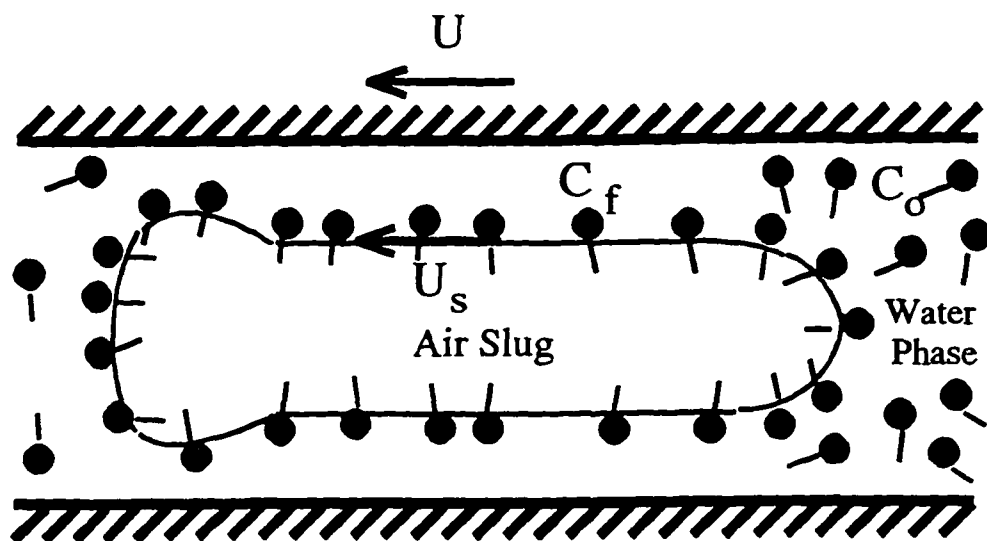


Fig. III-5 The partially mobile regime: Increased exchange of surfactant begins to mobilize the thin film region, and the axial velocity is nonzero ($U_s < U$) but not equal to the slug velocity.

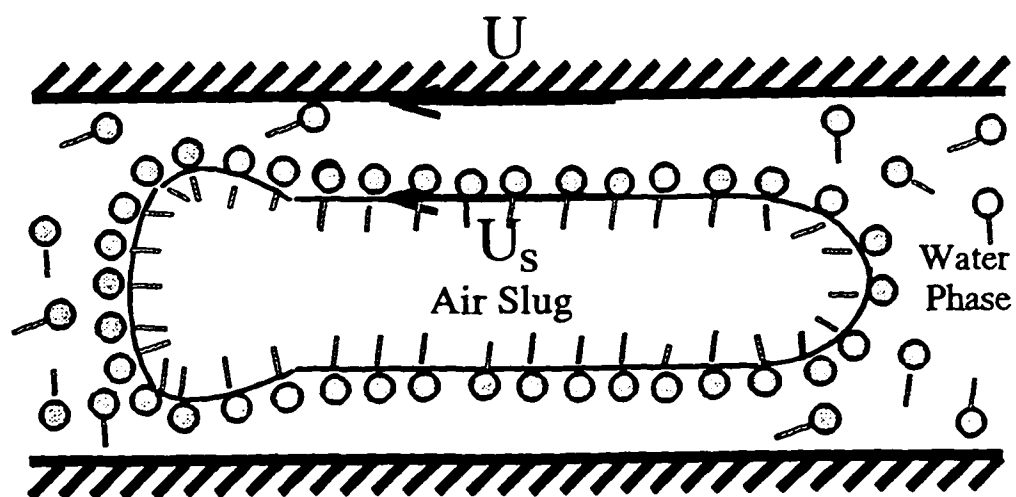


Fig. III-6 The completely mobile interface: Surfactant exchange is very fast at reduced Ca or large k , and the interface completely remobilizes with the thin film region velocity equal to the slug velocity U .

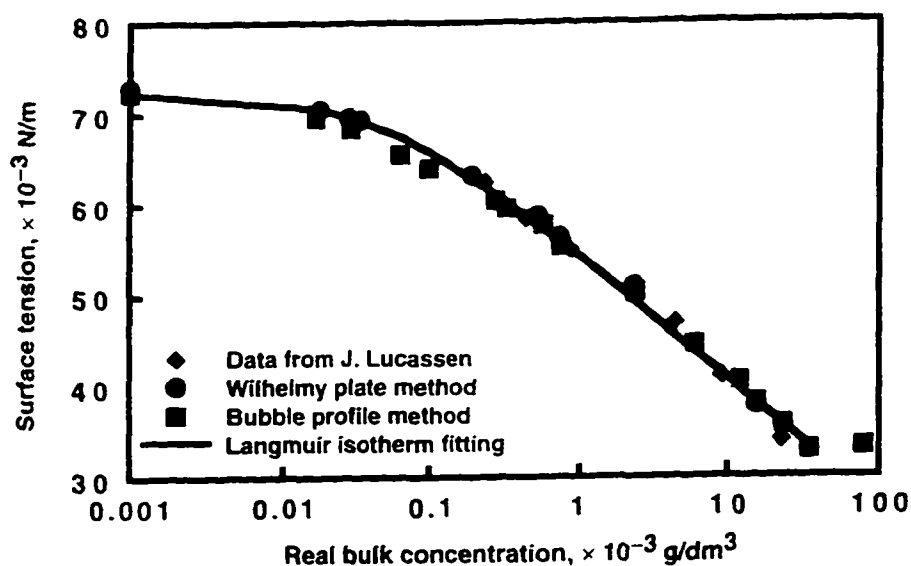


Fig. III-7 Surface tension as a function of bulk concentration for the surfactant C_{12}E_6 . Data is taken using the pendant bubble or Wilhelmy plate technique, as indicated; the data of Lucassen et al (1977) is also shown along with the Langmuir fit of the equilibrium tension.

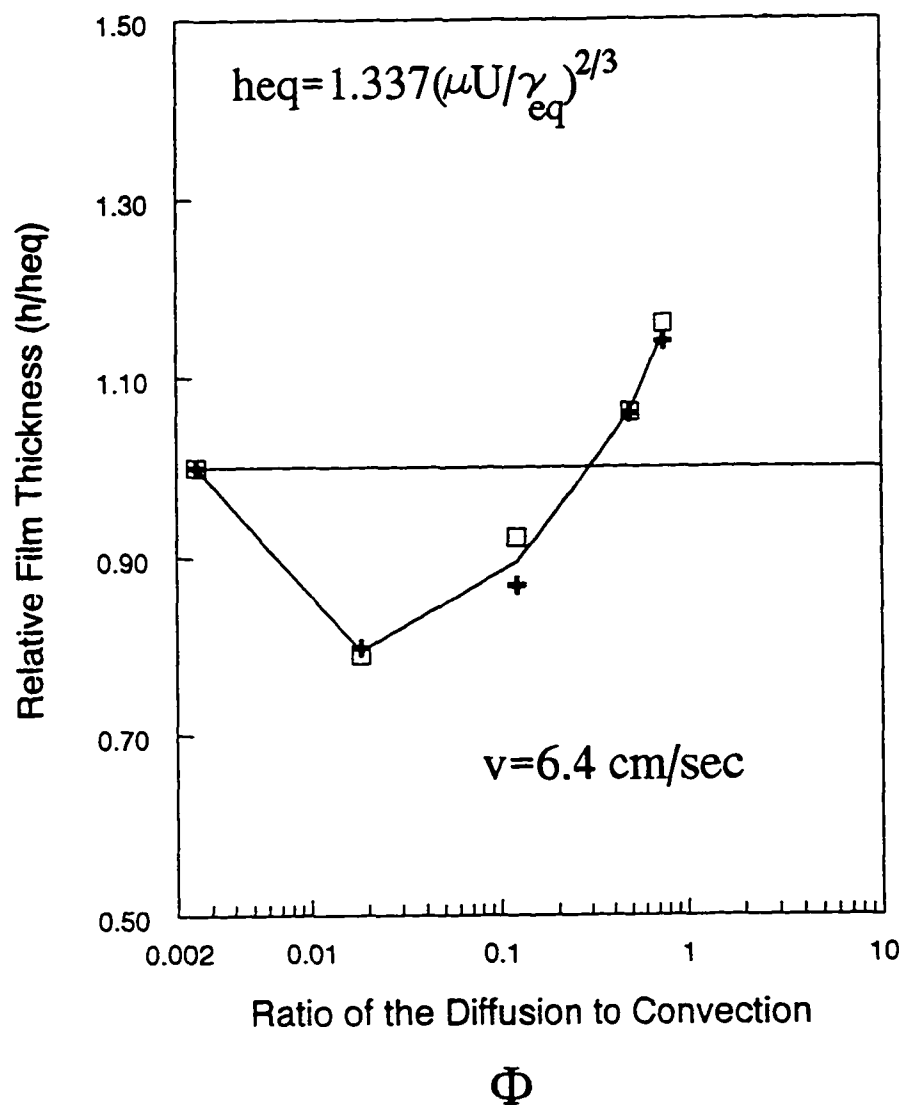


Fig. III-8 The first high velocity (6.4 cm/sec) measurement of the relative film thickness against the diffusion to convection parameter Φ . For $\Phi < 1$, the surfactant transport is in the stagnant cap regime, the interface is swept clean and thicknesses less than the equilibrium thicknesses are measured

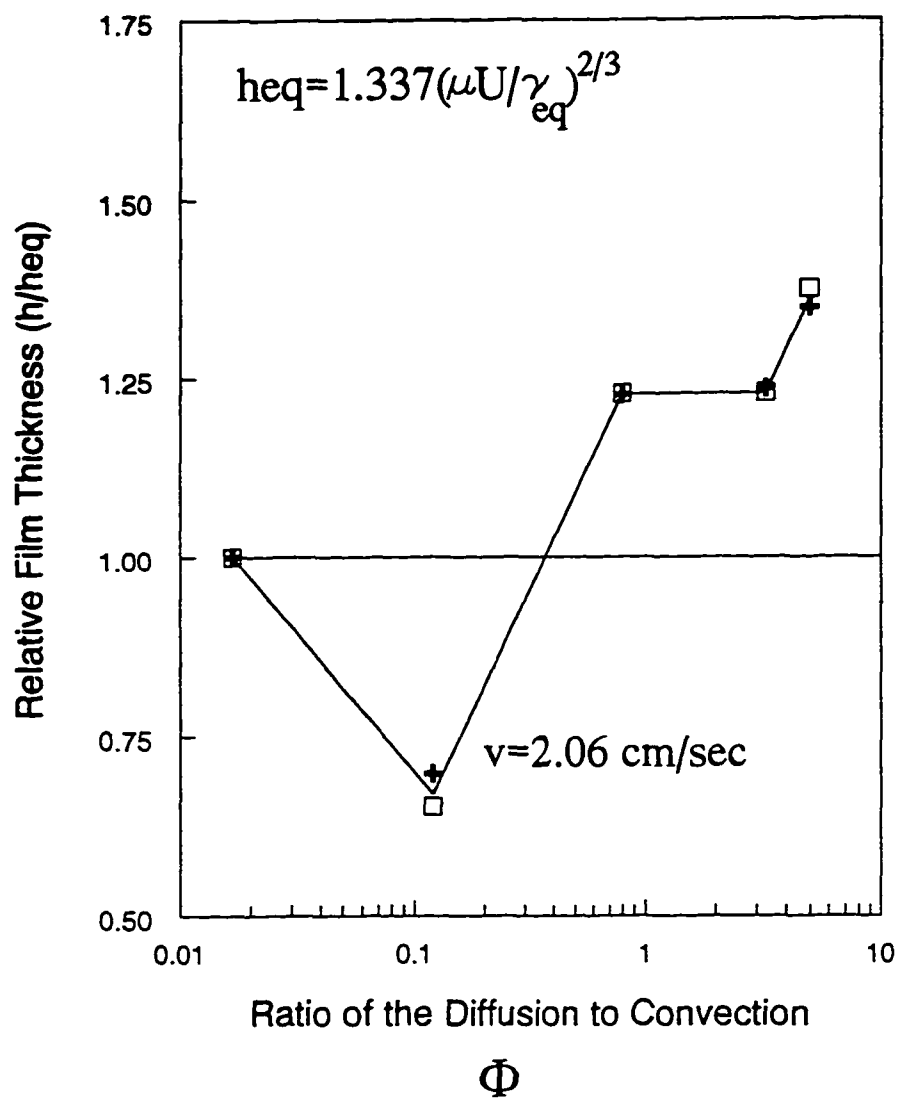


Fig. III-9 A second high velocity (2.06 cm/sec) measurement of the relative film thickness against the diffusion to convection parameter Φ . For $\Phi < 1$, the surfactant transport is in the stagnant cap regime, the interface is swept clean and thicknesses less than the equilibrium thicknesses are measured..

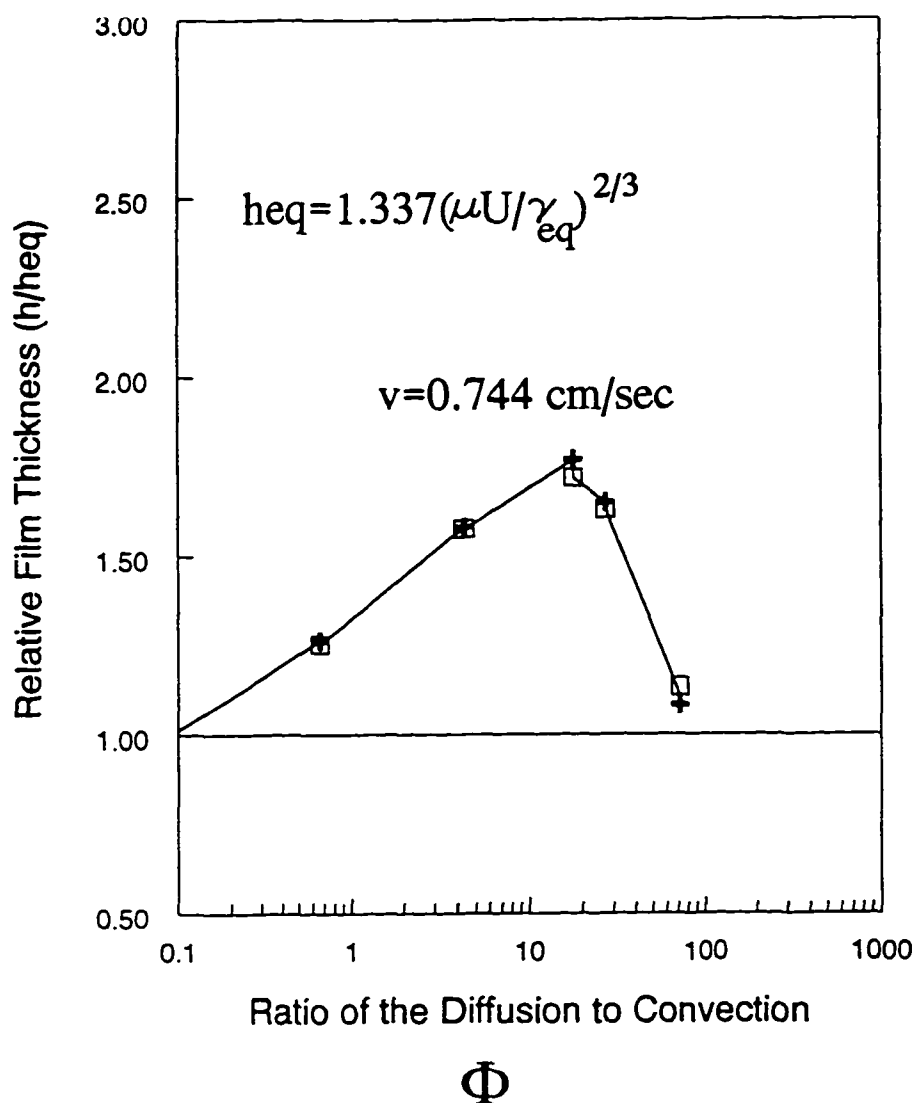


Fig. III-10 A low velocity (.744 cm/sec) measurement of the relative film thickness against the diffusion to convection parameter Φ . For $\Phi > 1$, the surfactant transport is in the partially mobile regime, the thickness becomes larger than the equilibrium value as depletion becomes effective. Further increase in concentration leads to a reduction in relative thickness as depletion becomes less effective

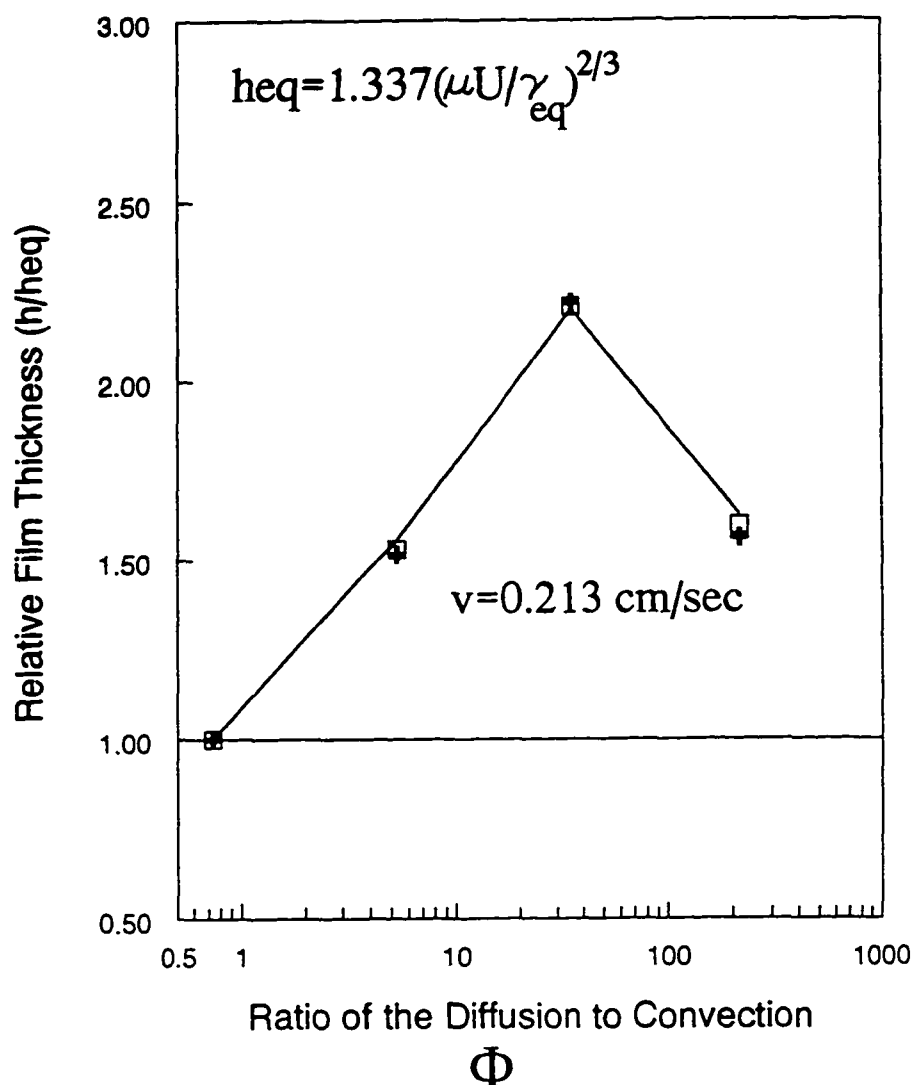


Fig. III-11 A second low velocity (0.213 cm/sec) measurement of the relative film thickness against the diffusion to convection parameter Φ . For $\Phi > 1$, the surfactant transport is in the partially mobile regime, the thickness becomes larger than the equilibrium value as depletion becomes effective. Further increase in concentration leads to a reduction in relative thickness as depletion becomes less effective

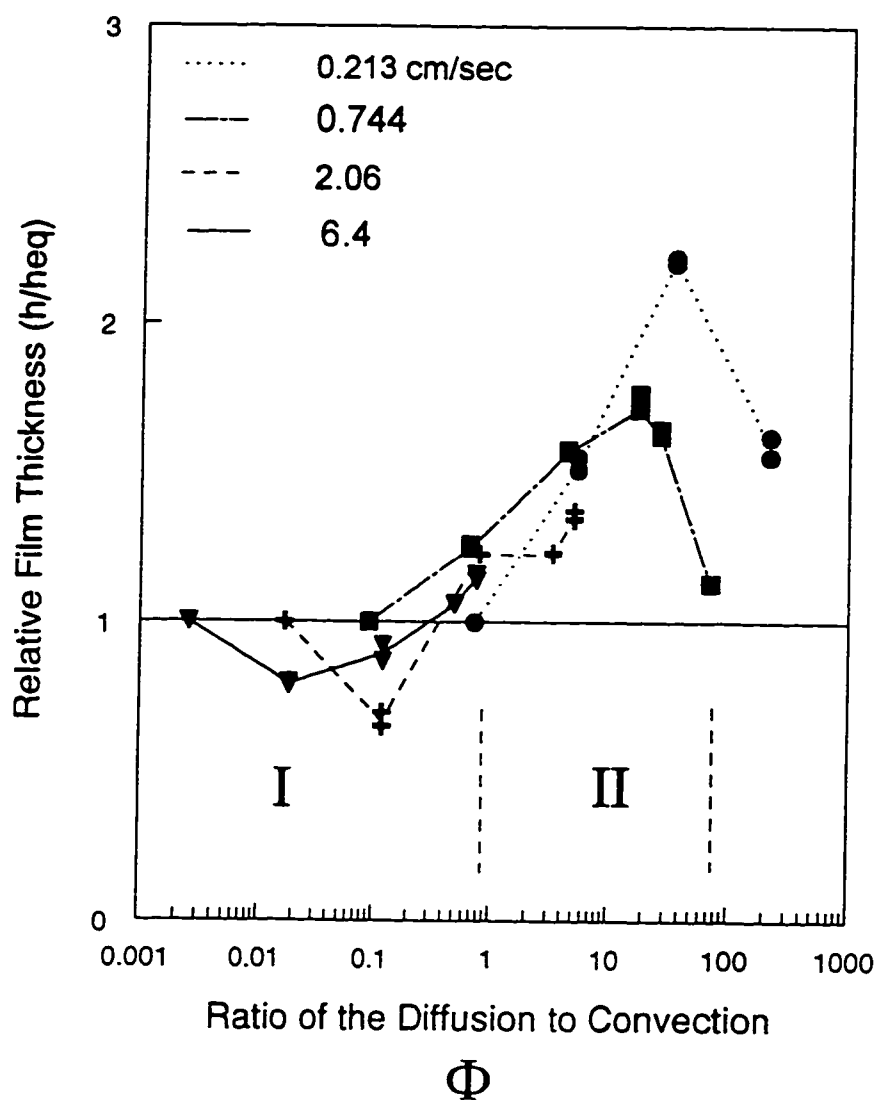


Fig. III-12 Recasting of all measured relative film thicknesses as a function of the diffusion to convection ratio Φ , and the demarcation of the stagnant cap regime (Region I) and the partially mobile regime (Region II).

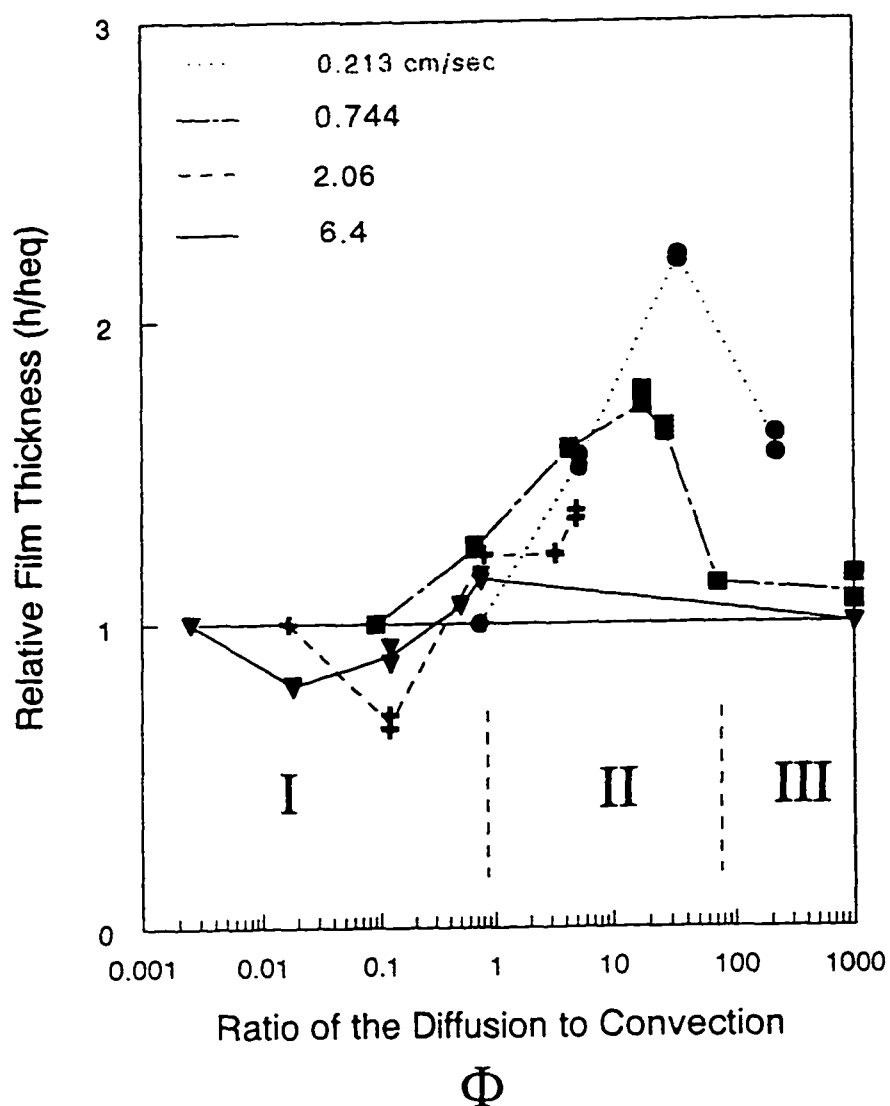


Fig. III-13 Remobilization: For concentrations larger than the critical micelle concentration, the diffusion to convection parameter Φ nominally exceeds 10^2 and the equilibrium Bretherton thickness is achieved with the relative thickness equal to one. This is Region III.

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