# Controlled Drop Tensiometer for Measuring Dynamic Interfacial and Film Tension

**R. Nagarajan, Kalman Koczo, Elemer Erdos, and Darsh T. Wasan**
Chemical Engineering Dept., Illinois Institute of Technology, Chicago, IL 60616

*A dynamic interfacial tensiometer described measures the tension of stressed liquid–liquid interfaces. In this accurate and controlled method, the time-dependent pressure difference across the curved interface of a spherical drop, immersed in a second immiscible phase, is measured as a function of time. Dynamic experiments are conducted by varying the drop size, thereby stressing the interface. The technique is eminently suited for the measurement of static and dynamic interfacial tensions, the study of the diffusion, adsorption, and desorption kinetics of surfactants, and the rheological behavior of liquid films. These capabilities are demonstrated for n-dodecane contacted with an aqueous solution of a nonionic surfactant. To explain the phenomena, diffusion models are developed that compare well with the experimental data. The noninvasiveness and versatility make this instrument a useful tool.*

## Introduction

In industrial processes, interfacial phenomena occur mostly under dynamic conditions. The stability and rheology of emulsions and foams, thin-liquid-film dynamics, the action of antifoams and demulsifiers, and petroleum recovery and refining processes are common practical examples where fluid interfaces are in a constant state of flux (Wasan et al., 1988).

In these examples, the interfacial behaviors are strongly controlled by surface active agents. The equilibrium (static) interfacial tension, although a fundamental property, is usually of limited value. Rather, in these dynamic situations, dynamic interfacial properties, and the diffusion, adsorption, and desorption properties of the surfactants are of paramount importance.

Much effort has been expended by researchers toward determining these properties, and a number of methods have been developed to study the dynamic interfacial properties (Defay and Petre, 1979; Edwards et al., 1991). These range from the dilatational methods using barriers (Lucassen and Giles, 1975; Van Voorst Vader et al., 1964) to the more recent longitudinal and transverse wave techniques (Maru and Wasan, 1979; Lucassen and Van den Tempel, 1972; Ting et al., 1985; Hard and Lofgren, 1977; Langevin, 1981). Some newer methods include the oscillating bubble (Lunkenheimer et al., 1984; Gottier et al., 1986; Hsu and Apfel, 1985), the maximum bubble/drop pressure techniques (Kao et al., 1992a,b; Garrett and Ward, 1988; Holcomb and Zollweg, 1990; Mysels, 1990), the growing drop technique (Van Hunsel et al., 1986), the funnel (Van Hunsel and Joos, 1987), and the overflowing cylinder (Bergink-Martens, 1993) methods.

This article describes a new, noninvasive, and versatile tensiometer to accurately measure static and dynamic tension of liquid–liquid interfaces under controlled conditions. In this technique, the capillary pressure in a near spherical liquid drop, immersed in another immiscible liquid, is measured (Passerone et al., 1991; Nagarajan and Wasan, 1993). For this geometry, the interfacial tension is related to the capillary pressure and drop radius by the Young-Laplace equation. Dynamic experiments are conducted by continuously varying the drop size, thereby stressing the interface. The corresponding capillary pressure and drop radius are monitored, and the dynamic interfacial tension is calculated. A variety of dynamic situations can be simulated by this computer-controlled instrument.

The operating principles of the method have been described by Nagarajan and Wasan (1993). In this article, the capabilities of the technique are fully described. Experimental data for a system of an aqueous solution of a nonionic surfactant contacted with dodecane are given. Theoretical

---

Correspondence concerning this article should be addressed to D. T. Wasan.

Present address of R. Nagarajan, Nalco Chemical Co., One Nalco Center, Naperville, IL; Elemer Erdos, Technical University of Budapest, Institute for Physical Chemistry, Budapest, H-1111, Egry J. u. 20–22, Hungary.

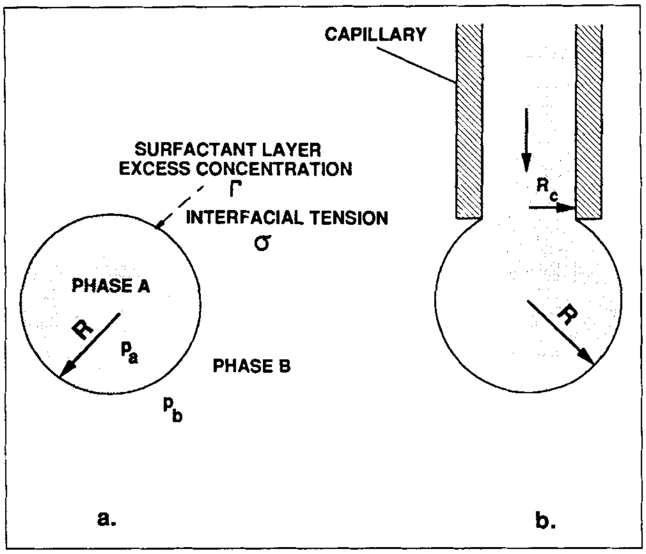

**Figure 1. (a) Tension of a liquid drop in an immiscible phase; (b) Principle of drop formation at the tip of a capillary.**

formulations to aid in understanding the underlying phenomena and to verify the measured data are also discussed.

## Description of the Technique

### *Principle of operation*

The instantaneous tension of the interface of a spherical drop suspended in another immiscible phase (Figure 1a) is related (Passerone et al., 1991; Edwards et al., 1991; Nagarajan and Wasan, 1993) by the Young-Laplace equation to the drop radius and the capillary pressure, which is the pressure difference across the curved interface:

$$p_a - p_b = \frac{2\sigma}{R}. \tag{1}$$

If chemical equilibrium exists and the drop radius is constant, the interfacial tension remains constant at the temperature and the interfacial excess, corresponding to the concentrations of surfactants present in the system. This value is the equilibrium interfacial tension for this system.

Dynamic experiments, conducted by either expanding or contracting the drop interface, cause a change in the interfacial composition, and the system deviates from equilibrium. The net interfacial composition is time dependent, and the interfacial tension and the capillary pressure vary with time. If the drop remains spherical, the capillary pressure is related to the dynamic interfacial tension by Eq. 1. In addition, rheological stresses, owing to the deformation of the interface, contribute to the capillary pressure, and the dynamic interfacial tension calculated is not a compositional thermodynamic quantity alone (Edwards et al., 1991; Edwards and Wasan, 1988).

In this technique (Figure 1b), the capillary pressure in a nearly spherical liquid drop, which is formed at the tip of a capillary and immersed in another immiscible phase, is measured by a sensitive pressure transducer. If the contact line is maintained at the inner capillary diameter, the interfacial tension is related to the capillary pressure and drop radius through Eq. 1. The size of the drop is varied by using a computer-controlled microsyringe attached to the capillary.

The sphericity of the suspended drop is determined by the balance between gravity, which deforms the drop, and the capillary forces, which act to keep the drop spherical. The ratio of these two forces is the characteristic Eötvös number (Holcomb and Zollweg, 1990; Mysels, 1990):

$$E\ddot{o} = \frac{\Delta \rho g l^2}{2\sigma}. \tag{2}$$

If $E\ddot{o}$ is small, the deformation due to gravity is much smaller than the capillary (interfacial) effects, and the drop is spherical with a radius $R$. In the technique described here, the effect of gravity distorting the sphericity of the drop becomes less than the accuracy of the measurement if $E\ddot{o} < 0.02$ (Hartland and Hartley, 1976).

The adsorption and desorption kinetics of surfactants are measured by monitoring the capillary pressure change with time for a drop immersed into the second fluid. An initial state of the interface is easily established. For instance, a "clean" interface, devoid of surfactants, is formed by rapidly expanding a new drop to the desired size. The relaxing interfacial tension as surfactants in the system adsorb at the interface is followed by monitoring the capillary pressure. The data provide key information about the diffusion and adsorption kinetics of the surfactants. Desorption kinetics can also be studied by contracting a drop from a known state to a new state. The sudden reduction in interfacial area causes desorption of surfactants deduced from the interfacial tension change over time.

Dynamic interfacial tension of dilating liquid–liquid interfaces is measured by monitoring the capillary pressure for an expanding (or contracting) liquid drop immersed in the second immiscible liquid. The interfacial tension, as a function of time, is computed from the capillary pressure and radius. In this mode, interfacial hydrodynamic stresses are important only at high rates of expansion (Nagarajan and Wasan, 1993).

This tensiometric technique, in its most advanced use, is applicable for film rheological studies. In this mode, a liquid film of one phase is formed by encapsulating a drop of another liquid and immersing both in a third liquid (or gas), thereby sandwiching the film between the inner drop and outer phases. These two, the outer and drop phases, may or may not be the same. The film tension is calculated by expanding or contracting the drop and monitoring the corresponding change in capillary pressure.

### *Instrument*

The main functional units of the apparatus are highlighted in Figure 2. The drop (or liquid film) is formed at the bottom tip of a vertical glass capillary. The size of the drop (or liquid film) is controlled by a microsyringe that is connected to the capillary and filled with the drop phase. The plunger movement of the syringe is driven by linear electromotors that are

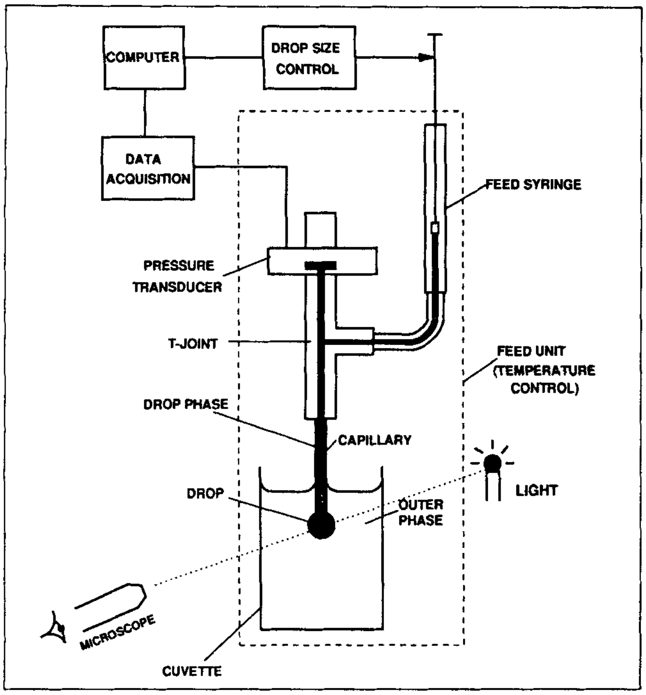

**Figure 2. Operation principle of the controlled drop tensiometer.**

controlled by the computer. The capillary pressure is measured by a sensitive piezoelectric pressure transducer, mounted directly above the capillary (see Figure 2). Data are logged by the computer, which is interfaced to the transducer as well. The capillary, the pressure transducer, and the feed syringe are built into a feed unit that is placed in a temperature-controlled water bath. The capillary tip with the drop or liquid film can be observed by a microscope.

Figure 3 shows the relation between the drop volume and the shape of the liquid-liquid interface, the capillary pressure, and the radius of curvature for a system without surfactants. The interfacial tension is constant, equal to the equilibrium value for the liquid pair. For the calculation of drop volume and capillary pressure, a reference point is defined as the point where the liquid-liquid interface is flat. At this point (Figure 3b), the radius of curvature becomes infinite, the capillary pressure is zero, and the drop volume is zero. The radius of curvature is calculated by solving

$$V_d = \frac{\pi}{3}(2R^3 + 2R^2B + R_c^2B) \tag{3}$$

where

$$B = \pm\sqrt{R^2 - R_c^2}.$$

The radius of curvature is minimum (Figure 3c) and the capillary pressure is maximum when the drop is hemispherical.

A necessary condition of the interfacial tension measurement is that the oil-water-glass, three-phase contact line should stay at the inner rim of the capillary during the whole expansion-contraction process (see Figure 1b). Therefore the internal capillary surface should be drop phase wetting, while the horizontal surface of the capillary tip should be outer phase wetting.

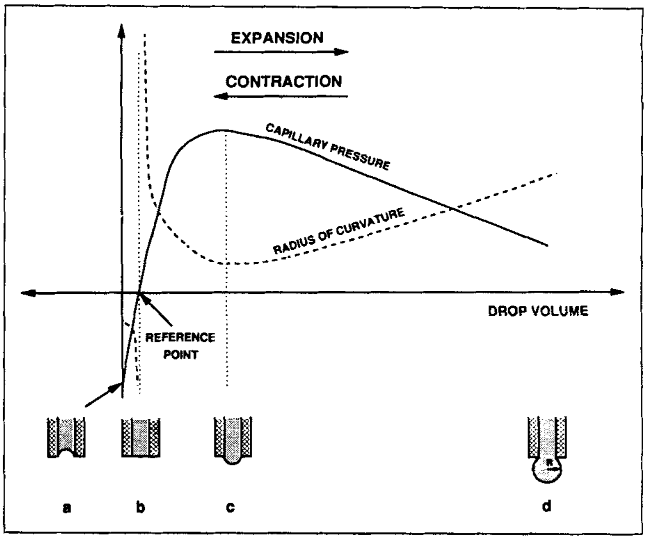

**Figure 3. Change of capillary pressure and radius of curvature during drop formation at the tip of a capillary as a function of drop volume.**

The sensitivity of the measurement is 0.05 mN/m. To avoid drop distortion by gravity, the Eotvos number was kept below 0.02 in the measurements. Thus, for systems with about $\sigma$ = 10 mN/m, $\Delta\rho = 250$ kg/m$^3$, the maximum drop radius was about $2.5\times10^{-4}$ m, which corresponds to $E\ddot{o} = 7.8\times10^{-3}$ using Eq. 2.

The viscous pressure loss during drop expansion or contraction can be directly measured by immersing the capillary into the same liquid as inside and measuring the pressure change under the same flow rate as in the interfacial tension measurement. With $n$-dodecane as drop liquid, the viscous pressure loss was negligible even with the narrowest capillary and the highest flow rates.

## Materials

The oil phase used in these experiments was $n$-dodecane (Gold Label, Aldrich). The oil was purified by treating with carbon black for several days. Water was deionized and doubly distilled in an all glass apparatus. A commercially available, nonionic surfactant, Brij 58, hexadecyl-polyoxyethylene ether with an average number of 20 ethoxy groups (Sigma), was studied. This surfactant, which is highly water soluble but practically insoluble in oil, was used without further purification. This common system (Van Hunsel et al., 1986; Van Hunsel and Joos, 1987) is known to display diffusion-controlled kinetics since the adsorption barrier at the interface is weak. In addition, the equilibrium tension is a function of the interfacial excess only, since molecular arrangements at the interface after adsorption are rapid. Prior to measurements, the aqueous and oil phases were preequilibrated.

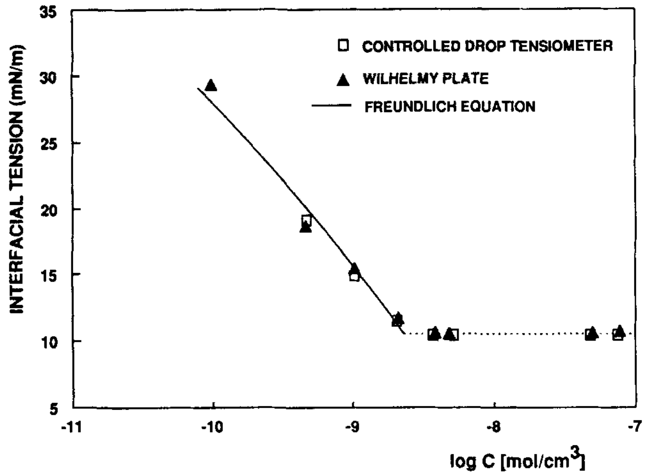

**Figure 4. Equilibrium interfacial tension of *n*-dodecane/ aqueous Brij 58 solution system at 297 K.**

## Results and Discussion

### *Equilibrium interfacial tension*

For the measurement of equilibrium interfacial tension, a drop is formed at the capillary tip and maintained at that size. From the recorded capillary pressure vs. time data, based on the reference point, the drop volume, radius of curvature, and the equilibrium interfacial tension are calculated. The equilibrium interfacial tension isotherm for an oil drop immersed into the aqueous solution is shown in Figure 4. For comparison, the interfacial tension was also measured using the Wilhelmy plate technique. Coincidence between the two techniques is good.

The shape of the isotherm is typical for such nonionic isotherms. The critical micelle concentration (CMC) was around $2.5 \times 10^{-9}$ mol/cm$^3$. The Freundlich adsorption isotherm (Davies and Rideal, 1969) was used to relate the surface excess concentration to the bulk concentration, below the CMC, as shown in Figure 4.

$$\Gamma = KC_b^m. \tag{4}$$

and using the Gibbs adsorption isotherm

$$\sigma_o - \sigma = \frac{R_g T \overline{\Gamma}}{m}$$

where $R_g$ is the gas constant and $T$ is the temperature.

Using the experimental isotherm data, the constant $m$ was found to be 0.2, while the empirical constant $K$ was found to be $2.1 \times 10^{-8}$ (Nagarajan and Wasan, 1993).

### *Adsorption kinetics*

To study the adsorption kinetics of surface-active materials, a reference point is formed by setting a horizontal interface (see Figure 3b). After this, a drop is rapidly formed (within a few seconds) and then maintained at this size. Initially, the interfacial tension is high, nearly equal to the interfacial tension between the pure solvents. The tension then decreases due to surfactant diffusion and adsorption until equilibrium is reached. The interfacial tension as a function of time is calculated.

The diffusion and adsorption kinetics for the present system were studied by rapidly forming a fresh drop of dodecane of $2.5 \times 10^{-4}$ m radius using a capillary with a $1.41 \times 10^{-4}$ m inner radius. The initial interfacial tension was near that for a clean interface.

The experiment described for the system studied can be modeled by assuming a spherical drop immersed in a second, immiscible phase that extends to infinity. Initially, the drop interface is devoid of surfactant, and the initial interfacial tension is that for the pure liquids at the given temperature. As surfactants diffuse to the interface and adsorb, the interfacial tension decreases, eventually reaching the equilibrium value corresponding to the concentration of surfactants in the two phases. The analysis of Ward and Tordai (as discussed by Davies and Rideal, 1969; Miller, 1981) is applicable here for the unknown diffusion kinetics of the water-soluble surfactants studied. The mass balance of surfactant species in the outer phase (the aqueous phase in this case) is governed by Fickian diffusion equation as

$$\frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left( r^2 \frac{\partial C}{\partial r} \right) \tag{5}$$

where $C(r, t)$ is the concentration at time, $t$ and the radial coordinate, $r$. The diffusivity is denoted by $D$.

If the initial bulk concentration is $C_b$, this equation is subject to the initial and boundary conditions:

$$\begin{array}{llll} \text{at } t = 0, & C = C_b & \text{for} & R < r < \infty \\ \text{as } r \to \infty, & C = C_b & \text{for} & \text{all } t. \\ \dfrac{d\Gamma}{dt} = D \dfrac{\partial C}{\partial r} & & \text{at} & r = R \\ \text{at } t = 0, & \Gamma = 0 & & \\ \Gamma = \Gamma(C) & & \text{at} & r = R. \end{array} \tag{6}$$

These conditions are obtained from the following considerations. Initially, the concentration is $C_b$ throughout the bulk. The infinite extent of the outer phase implies that the concentration remains constant far from the drop. The assumption of diffusion-controlled kinetics is implied in Eq. 6, which equates the diffusive flux to the adsorption flux at the subsurface $r = R$. Since a fresh drop is formed rapidly, the interfacial concentration initially is zero. In addition, the fast adsorption results in rapid attainment of equilibrium between the subsurface and interface at all times, so that the interfacial excess concentration is governed by Eq. 4 at $r = R$. This leads to the final boundary condition. This model is a limiting case of a more general formulation of a surfactant that is soluble in both phases and where adsorption–desorption kinetics at the interface are rate-determining steps as well. Such a general model for an oscillating drop has been given by Gottier et al., (1986).

A numerical solution of the preceding problem is straightforward, and an implicit finite difference scheme, devised so as to accommodate any adsorption isotherm (Miller, 1981), was adopted.

Figure 5 shows the experimental relaxation data for two

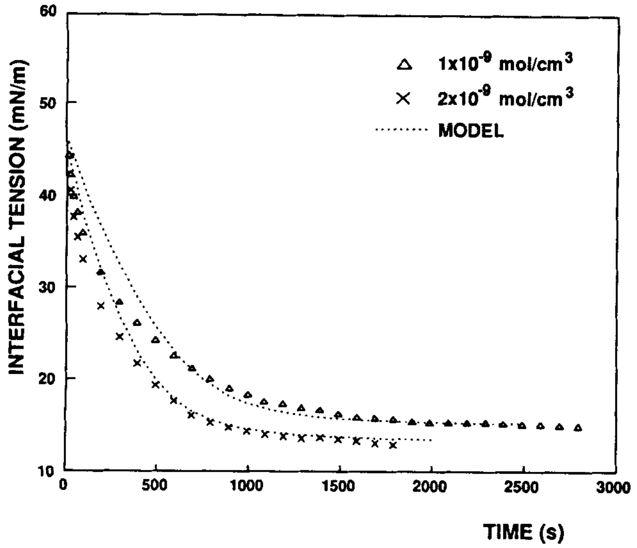

**Figure 5. Interfacial tension of a relaxing *n*-dodecane/ aqueous Brij 58 interface as a function of interface age for two surfactant concentrations.**

surfactant concentrations, both below CMC. An initial rapid relaxation process is followed by a slower tendency toward the equilibrium interfacial tension. Also shown are results of the diffusion model, calculated using a surfactant diffusion coefficient, $D$, of $5 \times 10^{-10}$ m$^2$/s. This value is reasonable for such surfactants. The coincidence between the data and model is good at later times, but not at early times where the model significantly overpredicts the interfacial tension. Overall, the data show that the assumption of diffusion-controlled kinetics is good. The failure at early times is probably due to the inapplicability of the Freundlich isotherm constants over such large concentration intervals. In addition, early time kinetics models in dynamic experiments are confounded by disturbances not accounted for in the isotherm. Van Hunsel and Joos (1987) reported the same findings for a similar system using the drop-volume technique for early time kinetics. They calculated diffusion coefficients one order of magnitude higher than normal.

This instrument is thus useful in the study and evaluation of the kinetics of interfacial adsorption for surfactants.

## Dynamic Interfacial Tension

To study the effect of dilatation of the interface under controlled conditions, a drop is formed and an initial equilibrium state is established by maintaining this drop size for sufficient time so that the capillary pressure and interfacial tension reach equilibrium values. In expansion experiments, the drop volume is increased with constant flow rate and the capillary pressure is monitored over time. In pure systems or in systems where surfactant adsorption is fast, the interfacial tension does not change during drop expansion and the capillary pressure decreases, as shown by Eq. 1. In surfactant systems, if the surfactant adsorption is not fast, the dynamic interfacial tension can be significantly higher than the equilibrium values and the capillary pressure will increase during interface expansion.

For diffusion-controlled kinetics, the model surfactant balance equations and corresponding initial and boundary conditions for the experiment described and for a system containing surfactant in the outer phase only are

$$\frac{\partial C}{\partial t} + v_r \frac{\partial C}{\partial r} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) \quad \text{for} \quad r > R \tag{7}$$

$$\text{at } t = 0, \qquad C = C_b \quad \text{for} \quad R_0 < r < \infty$$

$$\text{as } r \to \infty, \qquad C = C_b \quad \text{for} \quad \text{all } t.$$

$$\frac{d\Gamma A}{dt} = DA \frac{\partial C}{\partial r} \qquad \text{at} \quad r = R$$

$$\text{at } t = 0, \qquad \Gamma = \Gamma_b$$

$$\Gamma = \Gamma(C) \qquad \text{at} \quad r = R. \tag{8}$$

These conditions are similar to those derived for the relaxation experiment except that now the diffusion equation for the bulk aqueous phase Eq. 7 accounts for the convection owing to the radial drop growth, and the interface balance Eq. 8 accounts for area dilatation (Nagarajan and Wasan, 1993). Equations 7 and 8 assume a fast adsorption rate at the interface, and therefore rapid attainment of equilibrium between the interface and subsurface. Since the drop is initially in equilibrium, the initial interfacial condition is the static equilibrium interfacial tension and interfacial excess concentration ($\Gamma_b$) at the given bulk concentration. Also, since the experiment is started from equilibrium conditions, the initial interfacial concentration is in equilibrium with the bulk, in which the concentration is $C_b$. A numerical solution for this set is straightforward by finite-difference techniques.

## Systems without Surfactants

The accuracy of the apparatus was checked by measuring oil–water systems without surfactants. Figure 6 shows the capillary pressure as a function of $1/R$ for expanding drops of *n*-dodecane and 1-decanol in water. The data points are on a straight line, as given by the Young-Laplace equation (Eq. 1)

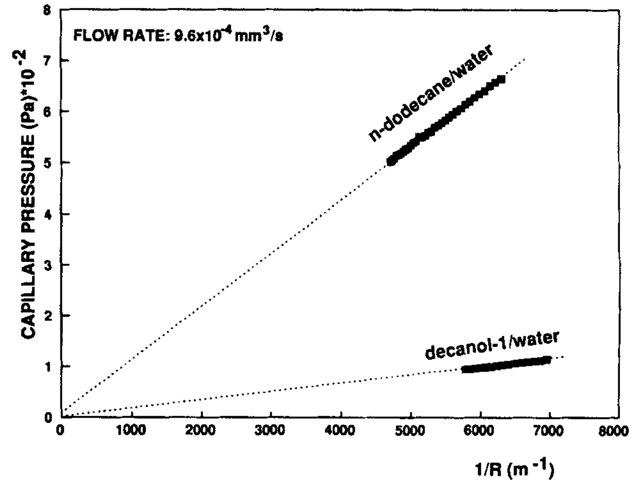

**Figure 6. Capillary pressure–drop radius relationship in pure systems, for expanding oil drops, at 297 K.**

Radius of capillary: $1.41 \times 10^{-4}$ m.

**Table 1. Interfacial Tension of Oil/Water Systems Without Surfactants**

| | Interfacial Tension (mN/m) | |
|---|---|---|
| System | Controlled Drop Tensiometer | Literature |
| Dodecane/water | 51.2±0.2 | 51.4* |
| 1-Decanol/water | 8.4±0.1 | 8.5** |

*Aveyard and Briscoe, 1972.
**Villers and Platten, 1988.

for a constant interfacial tension value. The calculated interfacial tensions (Table 1) are in good agreement with the literature values (Aveyard and Briscoe, 1972; Villers and Platten, 1988).

### *Surfactant systems*

Expansion and contraction experiments were conducted by first forming a drop with an initial radius of $2\times10^{-4}$ m and allowing it to reach equilibrium. The drop was then expanded or contracted, and the capillary pressure change in response to the change in interfacial tension was monitored over time. The rates of expansion were deliberately kept low so that interfacial rheological contributions to the dynamic interfacial tension were small (Nagarajan and Wasan, 1993).

Figures 7 and 8 show the results, at two bulk surfactant concentrations, of the dynamic interfacial tension vs. time for an expanding drop. The tension increases with time since the depletion of surfactant occurs faster than the diffusional flux in the bulk to the interface. Also shown are model numerical solutions. A diffusivity, $D$, value of $5\times10^{-10}$ m²/s was used. This value is typical (Lucassen and Giles, 1975; Van Hunsel and Joos, 1987) for such systems. The coincidence is very good, justifying the assumptions of diffusion-controlled kinetics.

Figures 9 and 10 show, at the same concentrations as earlier, the results for a contracting drop. In this case, the tension decreases with time since the surfactant desorbs as the interfacial area contracts, but being unable to diffuse into the bulk, it accumulates in the subsurface. Therefore, the local subsurface concentration is higher than the bulk, resulting in a lower interfacial tension. The numerical solutions coincide well with the measured data.

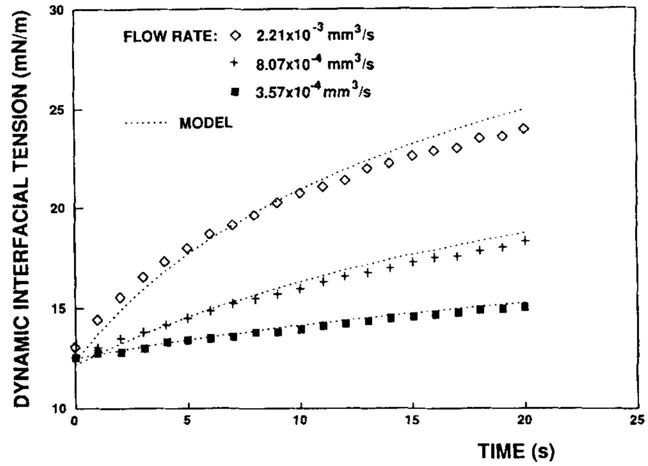

**Figure 8. Dynamic interfacial tension of $n$-dodecane/aqueous Brij 58 system at 297 K, with $C=2\times10^{-9}$ mol/cm³ Brij 58, for an expanding drop as a function of time.**

Radius of capillary: $1.41\times10^{-4}$ m. Numerical solutions of diffusion model, using $D=5\times10^{-10}$ m²/s.

## Film Tension

When two emulsion droplets interact, an emulsion film is formed from the continuous phase between the drops. The behavior of emulsions, for example, the rate of coalescence,

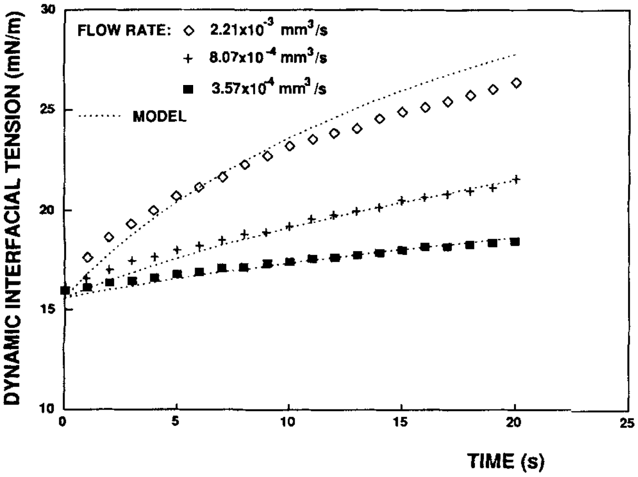

**Figure 7. Dynamic interfacial tension of $n$-dodecane/aqueous Brij 58 system at 297 K, with $C=1\times10^{-9}$ mol/cm³ Brij 58, for an expanding drop as a function of time.**

Radius of capillary: $1.41\times10^{-4}$ m. Numerical solutions of diffusion model, using $D=5\times10^{-10}$ m²/s.

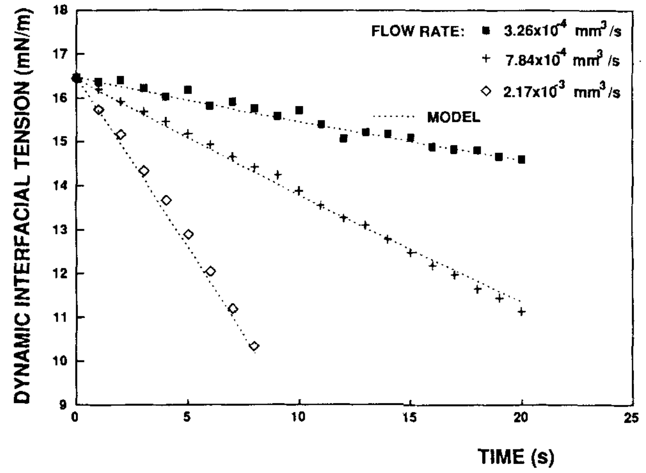

**Figure 9. Dynamic interfacial tension of $n$-dodecane/aqueous Brij 58 system at 297 K, with $C=1\times10^{-9}$ mol/cm³ Brij 58, for a contracting drop as a function of time.**

Radius of capillary: $1.41\times10^{-4}$ m. Numerical solutions of diffusion model, using $D=5\times10^{-10}$ m²/s.

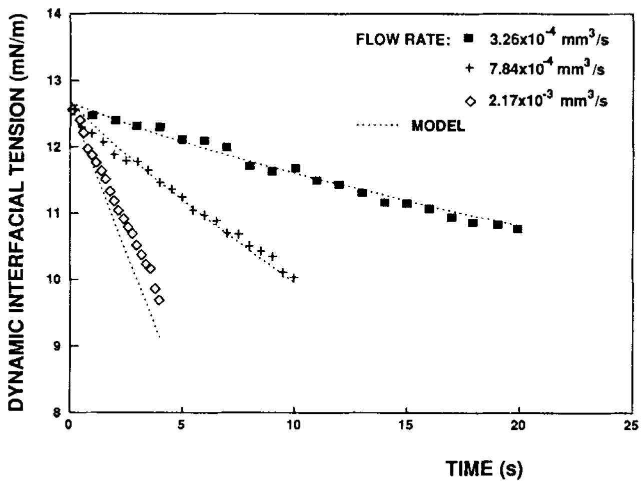

**Figure 10. Dynamic interfacial tension of *n*-dodecane/aqueous Brij 58 system at 297 K, with $C = 2 \times 10^{-9}$ mol/cm³ Brij 58, for a contracting drop as a function of time.**

Radius of capillary: $1.41 \times 10^{-4}$ m. Numerical solutions of diffusion model, using $D = 5 \times 10^{-10}$ m²/s.

strongly depends on the properties of these emulsion films. The interfacial rheological properties of thin liquid films (foam, emulsion, or pseudoemulsion films) control the stability of the respective colloidal systems, at surfactant concentrations below the CMC (Wasan et al., 1992).

The controlled drop tensiometer can be used to study the film tension of thin liquid films formed at the tip of the capillary (Figure 11). The pressure difference between the drop and the outer phase depends on the film radius, $R_f$, the interfacial tensions at the inner and outer interfaces ($\sigma_i$ and $\sigma_o$) and the film thickness. The thickness of a drained film is generally in the 30–100 nm range, and some systems form common or Newton black films with about 5–30 nm thicknesses (Ivanov, 1988).

For relatively *thick films* (higher than about 30 nm) the pressure drop at the film is the sum of the capillary pressures at the two film interfaces. In this case, the Young-Laplace equation for the film can be written as

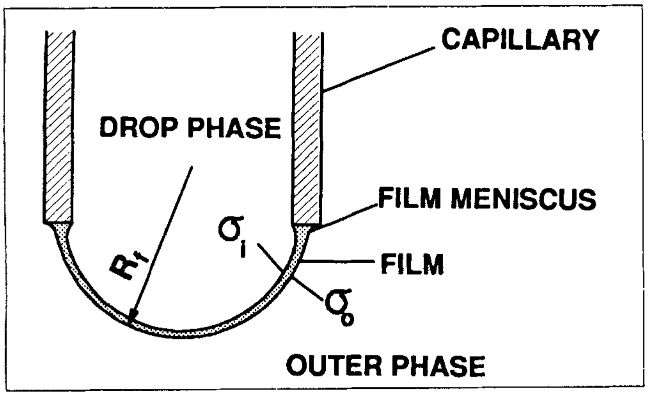

**Figure 11. Principle of thin-liquid-film investigation at the tip of capillary.**

$$p_c = \frac{2f}{R_f} \tag{9}$$

where the film tension is equal to the sum of the interfacial tensions

$$f = \frac{4\sigma_i\sigma_o}{\sigma_i\sigma_o} \tag{10}$$

and $R_f$ is the film radius. For emulsion (or foam) films: $\sigma_i = \sigma_o$.

In *black films*, the interactions between the film interfaces, as manifested in the disjoining pressure, become significant and Eq. 10 is not valid. A limitation of the film studies by the controlled drop tensiometer is that the film thickness cannot be measured. However, it can be observed, using the microscope of the apparatus, whether black film forms or not. It was found that in the system studied, black emulsion film did not form.

Figure 12 shows a method to form an aqueous emulsion film between two identical oil phases (such as in oil-in-water emulsions) at the tip of the capillary. Preconditions of the experiment are that the surface of the capillary must be well wetted by the film phase (by the continuous phase) and that the film must be stable during the time of measurement. Thus, in the case of an aqueous film, the capillary tip must be hydrophilic. The capillary is filled with oil and immersed in the aqueous solution (film liquid), and the oil phase is layered on top of the aqueous phase in the cuvette. Then an oil drop is formed (Figure 12a). After this, the level of the oil layer is slowly reduced by sucking out the lower, aqueous phase using a syringe. As the oil–water interface is reduced below the

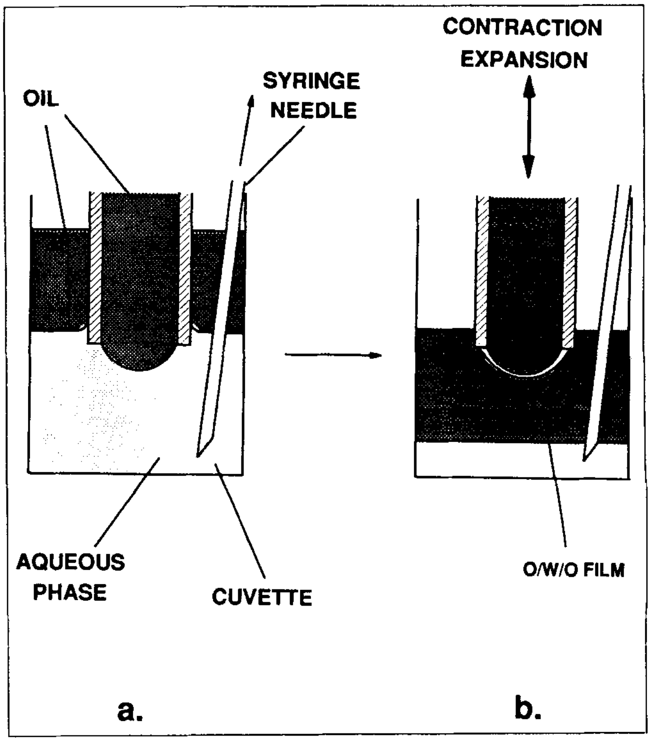

**Figure 12. Preparation of an aqueous emulsion film between oil phases at the tip of a capillary.**

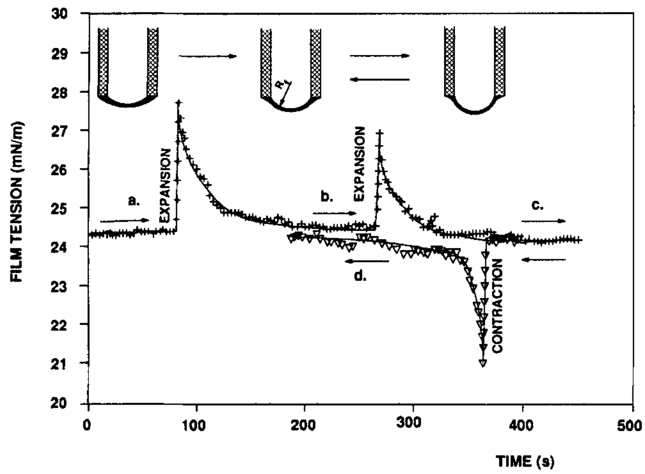

**Figure 13. Film tension of aqueous Brij 58 emulsion film between *n*-dodecane phases, under subsequent expansions and contractions.**

Surfactant concentration: $2\times10^{-9}$ mol/cm$^3$. Film radii: (a) $3.3\times10^{-4}$ m; (b) $2.8\times10^{-4}$ m; (c) $2.5\times10^{-4}$ m; (d) $2.8\times10^{-4}$ m.

drop, a water film bordered by a circular meniscus covers the oil drop owing to the hydrophilicity of the capillary tip (Figure 12b). The capillary pressure and the film tension are then measured, using similar procedures as before for studying adsorption kinetics (stress relaxation) or dynamic interfacial tension for expansion and contraction.

Figure 13 shows the results of preliminary, adsorption kinetics experiments with liquid films. Aqueous Brij 58 emulsion films, sandwiched between *n*-dodecane phases under expansion and contraction, were studied using a capillary with $5\times10^{-4}$ m inner diameter and $10^{-4}$ m wall thickness. The surfactant concentration was $2\times10^{-9}$ mol/cm$^3$.

A small film ($R_f = 3.3\times10^{-4}$ m) was formed and kept until equilibrium was reached (Figure 13a). The film tension was 24.5 mN/m, approximately two times higher than the interfacial tension of this system. The film was abruptly expanded to a radius $R_f = 2.8\times10^{-4}$ m, and this size was maintained. It is seen that the film tension jumps and then decreases with the aging time until the same equilibrium tension sets in again (Figure 13b). Then the film was expanded to a lower radius ($R_f = 2.5\times10^{-4}$ m), and the stress relaxation was measured again (Figure 13c). The equilibrium film tension was equal to the previous equilibrium values.

In the reverse relaxation experiments the large film ($R_f = 2.5\times10^{-4}$ m) was abruptly reduced to the second size ($R_f = 2.8\times10^{-4}$ m; see Figure 13d). As a result, the film tension (and the capillary pressure) dropped because both the film radius increased and the adsorbed surfactant layer was compressed. The film tension increased with aging time as the surfactant desorbed from the reduced film interfaced and finally approached equilibrium (Figure 13d) at the same value as in the case of the expanding film experiments.

These experiments demonstrate how the controlled drop tensiometer technique can be used to study the behavior of liquid films, as models of disperse systems. Further applications of the method will be published elsewhere.

## Summary

The operation and the various capabilities of the controlled drop tensiometer are described. A sensitive pressure transducer, coupled with accurate mechanical motion, allows for the determination of interfacial tension, with a sensitivity of 0.05 mN/m. With the automated instrument, a wide range of dynamic experiments is possible, demonstrated here for a nonionic surfactant system. Many other surfactant systems, including proteins, can be measured with our technique. The controlled geometry allows for the study of different time scales, so that both low molecular weight surfactants displaying rapid kinetics as well as the slow kinetics of macromolecular surfactants can be examined. These capabilities of the apparatus were demonstrated with oil as the drop phase, and aqueous surfactant solution phase as the outer phase (in the interfacial tension measurements), and an aqueous phase as the film phase between two identical oil phases (in the film studies). The technique is, however, more flexible. The drop phase can be any liquid, and the outer phase any immiscible liquid or gas (dynamic surface tension can be also measured). Similarly, the film phase can also be any liquid, the drop phase can be any immiscible liquid, and the outer phase can be any immiscible liquid or gas.

## Acknowledgments

This study was supported in part by the National Science Foundation and by the U.S. Department of Energy. The authors gratefully acknowledge the helpful comments provided by Dr. A. D. Nikolov. The film tension experiments were conducted by Young Ho Kim.

## Notation

$A$ = interfacial area
$C$ = surfactant concentration
$C_b$ = bulk surfactant concentration
$D$ = surfactant diffusivity
$Eö$ = Eötvös number (Eq. 2)
$f$ = dynamic or static film tension
$g$ = acceleration due to gravity
$K$ = empirical constant of Freundlich adsorption equation
$l$ = characteristic length scale (Eq. 2)
$m$ = empirical constant of Freundlich adsorption equation
$p_c$ = capillary pressure
$r$ = radial coordinate
$R$ = radius of curvature of drop
$R_0$ = initial radius of curvature of drop
$R_c$ = inner radius of capillary
$R_f$ = film radius
$t$ = time
$v_r$ = radial velocity of drop interface
$V_d$ = drop volume

### *Greek letters*

$\Delta\rho$ = density difference between immiscible liquids
$\sigma$ = dynamic or static interfacial tension
$\sigma_i$ = interfacial tension at the inner film interface
$\sigma_o$ = interfacial tension between pure liquids; interfacial tension at the outer film interface
$\Gamma$ = surface excess concentration

## Literature Cited

Aveyard, R., and B. Briscoe, "Adsorption of n-Alkanols at Alkane/Water Interfaces, *J. Chem. Soc., Farad. Trans.*, **68**, 478 (1972).

Bergink-Martens, D. J. M., "Interface Dilation. The Overflowing Cylinder Technique," PhD Thesis, Agricultural Univ., Wageningen, The Netherlands (1993).

Defay, R., and G. Petre, "Dynamic Surface Tension," *Surface and Colloid Science*, E. Matijevic, ed., Vol. 3, Wiley, New York (1979).

Davies, J. T., and E. K. Rideal, *Interfacial Phenomena*, Academic Press, New York (1969).

Edwards, D. A., and D. T. Wasan, "Surface Rheology: I. The Planar Fluid Surface," *J. Rheol.*, **32**(5), 429 (1988).

Edwards, D. A., H. Brenner and D. T. Wasan, *Interfacial Transport Processes and Rheology*, Butterworth-Heinemann, Boston (1991).

Garrett, P. R., and D. R. Ward, "A Reexamination of the Measurement of Dynamic Surface Tensions Using the Maximum Bubble Pressure Method," *J. Colloid Interf. Sci.*, **132**, 475 (1988).

Gottier, G. N., N. R. Amundson, and R. W. Flumerfelt, "Transient Dilation of Bubbles and Drops: Theoretical Basis for Dynamic Interfacial Measurements," *J. Colloid Interf. Sci.*, **114**, 106 (1986).

Hard, S., and H. J. Lofgren, "Elasticity and Viscosity Measurement of Monomolecular Propyl Stearate Films at Air-Water Interfaces Using Laser-Scattering Techniques," *J. Colloid Interf. Sci.*, **60**, 529 (1977).

Hartland, S., and S. W. Hartley, "Axisymmetric Fluid-Fluid Interfaces," Elsevier, Amsterdam (1976).

Holcomb, C. D., and J. Zollweg, "Improved Calculation Techniques for Interfacial Tensiometers," *J. Colloid Interf. Sci.*, **134**, 41 (1990).

Hsu, C., and R. E. Apfel, "A Technique for Measuring Interfacial Tension by Quadrupole Oscillation of Drops," *J. Colloid Interf. Sci.*, **107**, 467 (1985).

Ivanov, I. D., ed., "Thin Liquid Films. Fundamentals and Applications," *Surfactant Science Series*, Vol. 29, Marcel Dekker, New York (1988).

Kao, R. L., D. A. Edwards, D., D. T. Wasan and E. Chen, "Measurement of Interfacial Dilatational Viscosity at High Rates of Interface Expansion Using the Maximum Bubble Pressure Method. I. Gas-Liquid Interface," *J. Colloid Interf. Sci.*, **148**, 247 (1992).

Kao, R. L., D. A. Edwards, D. T. Wasan, and E. Chen, "Measurement of the Dynamic Interfacial Tension and Interfacial Dilatational Viscosity at High Rates of Interfacial Expansion Using the Maximum Bubble Pressure Method: II. Liquid-Liquid Interface," *J. Colloid Interf. Sci.*, **148**, 257 (1992).

Langevin, D. J., "Light-Scattering of Monolayer Viscoelasticity," *J. Colloid Interf. Sci.*, **80**, 412 (1981).

Lucassen, J., and M. van den Tempel, "Longitudinal Waves on Viscoelastic Surfaces," *J. Colloid Interf. Sci.*, **41**, 491 (1972).

Lucassen, J., and D. Giles, "Dynamic Surface Properties of Nonionic Surfactant Solutions," *J. Chem. Soc., Farad. Trans. I.*, **71**, 217 (1975).

Lunkenheimer, K., C. Hartenstein, R. Miller, and K. D. Wantke, "Investigations of the Method of the Radially Oscillating Bubble," *Colloids Surf.*, **8**, 271 (1984).

Maru, H. C., and D. T. Wasan, "Dilatational Viscoelastic Properties of Fluid Interfaces, II. Experimental Study," *Chem. Eng. Sci.*, **34**, 1295 (1979).

Miller, R., "On the Solution of Diffusion Controlled Adsorption Kinetics for any Adsorption Isotherms," *Colloid Poly. Sci.*, **259**, 375 (1981).

Mysels, K. J., "The Maximum Bubble Pressure Method of Measuring Surface Tension, Revisited," *Colloids Surf.*, **43**, 241 (1990).

Nagarajan, R., and D. T. Wasan, "Measurement of Dynamic Interfacial Tension by an Expanding Drop Tensiometer," *J. Colloid Interf. Sci.*, **159**, 164 (1993).

Passerone, A., L. Liggieri, N. Rando, F. Ravera, and E. Ricci, "A New Experimental Method for the Measurement of the Interfacial Tension between Immiscible Fluids at Zero Bond Number," *J. Colloid Interf. Sci.*, **146**, 152 (1991).

Ting, L., D. T. Wasan, and K. Miyano, "Longitudinal Surface Waves for the Study of Dynamic Properties of Surfactant Systems: II. Liquid-Liquid Interface," *J. Colloid Interf. Sci.*, **107**, 345 (1985).

Van Hunsel, J., G. Bleys, and P. Joos, "Adsorption Kinetics at the Oil/Water Interface," *J. Colloid Interf. Sci.*, **114**, 432 (1986).

Van Hunsel, J., and P. Joos, "Stress Relaxation Experiments at the Oil/Water Interface," *Colloids Surf.*, **25**, 251 (1987).

Van Voorst Vader, F., Th. F. Erkens, and M. van den Tempel, "Measurements of Dilatational Surface Properties," *Trans. Farad. Soc.*, **60**, 1170, (1964).

Villers, D., and J. K. Platten, "Temperature Dependence of the Interfacial Tension Between Water and Long-Chain Alcohols," *J. Phys. Chem.*, **92**(14), 4023 (1988).

Wasan, D. T., M. E. Ginn, and D. O. Shah, eds., "Surfactants in Chemical/Process Engineering," in *Surfactant Science Series*, Vol. 28, Marcel Dekker, New York (1988).

Wasan, D. T., A. D. Nikolov, L. A. Lobo, K. Koczo, and D. A. Edwards. "Foams, Thin Films and Surface Rheological Properties," *Progr. Surf. Sci.*, **39**(2), 119 (1992).

*Manuscript received Sept. 15, 1993, and revision received Apr. 25, 1994.*