THE KINETICS OF ADSORPTION AT THE AIR-WATER INTERFACE FOR A SERIES OF TWELVE CARBON SURFACTANTS

by

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Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Chemical Engineering

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October, 1970

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ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. Jerry A. Caskey, Assistant Professor of Chemical Engineering, for his continued guidance, assistance and encouragement, during the course of this study.

Financial assistance was provided by the Allied Chemical Company, to whom thanks are extended.

Finally, the author wishes to thank Miss Karen A. Gunning for her patience and understanding in typing the manuscript.

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I. INTRODUCTION

If the surface of a solution of surface-active agent is disturbed, a finite period of time is necessary for the equilibrium surface tension to again prevail. Surface tensions during this period are referred to as dynamic surface tensions. As the dynamic surface tension decreases to its static value more surfactant is adsorbed at the liquid-gas interface. Thus, it is possible to deduce adsorption kinetics through a study of dynamic surface tensions.

The dynamic surface tension is commercially important in processes such as detergency, which takes place under non-equilibrium conditions. More recently a knowledge of adsorption kinetics has become important in waste-water treatment facilities.

There is, unfortunately, a paucity of dynamic surface tension data available on surfactants of commercial importance. Most adsorption studies have been carried out with organic acids and alcohols. Furthermore, the reliability of much of this data is in doubt because of questionable techniques. The oscillating jet method has been the most widely used and, at this time, is the most refined for studying adsorption rates in the one to fifty millisecond range.

The purpose of this investigation was to study the rate of adsorption of commercially important surfactants for exposure times of five to thirty milliseconds. An anionic (sodium dodecyl sulfate), cationic (dodecyl trimethyl ammonium bromide), and nonionic (dodecyl diethanol amide) surfactant were all represented in this study.

II. LITERATURE REVIEW

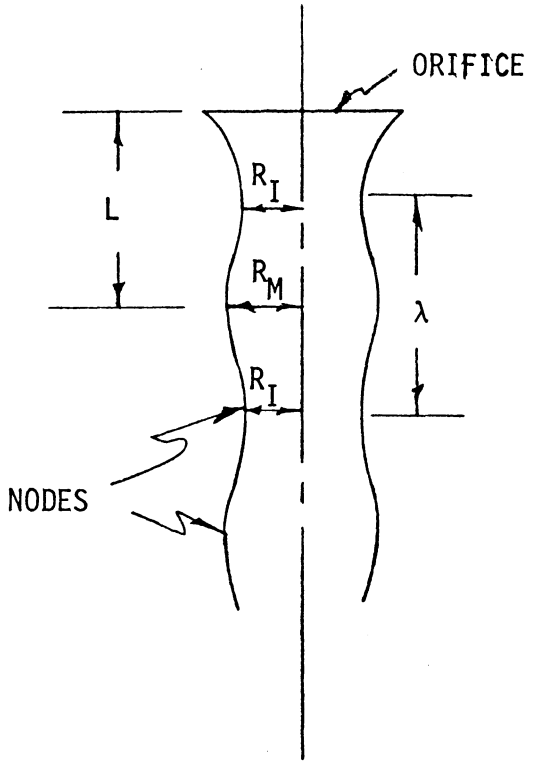
The purpose of this section is to acquaint the reader with previous studies on the kinetics of adsorption, as well as to present a brief survey of the development of dynamic surface tension measurement by the oscillating jet technique. In addition, a short review of the chemistry of surface-active agents is given.

Measurement of Dynamic Surface Tension

No less than eight different methods are available for measuring dynamic surface tensions [9,12]. Among these are jet, drop and channel methods. Defay and Prigogine [12] present an extensive bibliography of most of these methods, as well as a brief description of them. Davies and Rideal [9] describe several other methods along with their applicability. The most popular and reliable of the methods for measuring surface tensions in the one to fifty millisecond range is the oscillating jet technique.

When a liquid issues forth from an elliptical orifice, a standing wave pattern is observed, the waves oscillating about the equilibrium circular cross-section (Figure 1). The volumetric flow rate of the jet and the jet dimensions (wavelength and diameter of nodes) are sufficient to determine the surface tension of the jet at various surface ages.

Bidone [3] in 1854 was the first to note this phenomenon, although he mistakenly thought it was due to viscosity. Lord Rayleigh [28]



R_I = MINIMUM RADIUS

R_M = MAXIMUM RADIUS

λ = WAVELENGTH

L = DISTANCE FROM ORIFICE

FIGURE 1. DIAGRAM OF AN OSCILLATING JET

elaborated on Bidone's work and correctly attributed the oscillating form to capillary forces, i.e. surface tension. Rayleigh's work was more to illustrate the theory than to present an exact mathematical treatment. He did, however, derive an equation for the surface tension, for the crude approximation of an inviscid fluid with infinitely small wave amplitudes about the circular cross-section.

It remained for Niels Bohr [5] in 1909 to lay a solid theoretical foundation by solving the hydrodynamic equations of motion, subject to the appropriate boundary conditions. He obtained an equation for the surface tension which accounted for viscosity, finite wave amplitudes, and the effect of the ambient air. The one major assumption which he made is that there is no velocity profile in the jet. This is a significant restriction, since Bohr used a long capillary tube with an elliptical opening at the end. Recognizing this, he took his measurements a sufficient distance away from the orifice that the viscosity could damp out the velocity effects.

It should be noted that Bohr studied pure water. He, therefore, was not interested in the initial surface tension variation with time, since for a pure fluid there should be none. Subsequent workers, however, investigating the dynamic surface tension of solutions, were naturally interested in the initial surface tension lowering at small surface ages, i.e. near the orifice. It is for this reason that the one assumption of plug flow is so important.

Rideal and Sutherland [29] studied the dynamic surface tensions of aqueous solutions of heptanol and 3-methyl-1-butanol. Their

results indicated that their data were dependent on the particular orifice they used as well as the flow rate of the jet. Their orifices, however, were of the same type as Bohr's, yet they appear to have neglected the effect of velocity profiles.

Sutherland [31] extending this work, found no satisfactory way to account for this anomalous dependence on the apparatus. Sutherland also presented a useful simplification of the Bohr equation good to within 2 percent.

$$\gamma = \frac{4\rho D^2\left[1 + \frac{37}{24}\frac{b^2}{a^2}\right]}{\left(6r\lambda^2 + 10\pi^2 r^3 + 2.5\frac{\pi^4 r^5}{\lambda^2}\right)} \qquad (1)$$

where:

$$\frac{b}{a} = \frac{r_m - r_i}{r_m + r_i}$$

$$r = \frac{r_m + r_i}{2}$$

γ = surface tension, dynes/cm

ρ = density of the solution, gm/cm^3

D = volumetric flow rate, cm^3/sec

λ = wavelength, cm

r_m, r_i = maximum and minimum radii of the jet, cm

The assumptions inherent in this equation are:

"(1) The fluid is in laminar flow.

(2) All initial disturbances caused by ejection of liquid from the orifice are absent in that portion of the jet which is measured.

(3) The vibrational components of velocity of the jet are sufficiently small that second and higher order terms are negligible.

(4) The viscosity at the surface of the jet is the same as that in the interior of the jet.

(5) The diameter of the jet is small compared with the wavelength of the oscillation.

(6) The effect of amplitude in the frequency of oscillation may be calculated in the absence of viscous forces.

(7) The only effect of the surrounding medium is its inertia."(31)

(8) The orifice is elliptical.

All of the above assumptions apply to the original Bohr equation. The only additional restriction required for the simplified form is that the viscosity of the liquid does not exceed 0.01 poise.

Hansen, Purchase, Wallace and Woody [17] found one solution to the problem of having a non-uniform velocity profile. They deliberately promoted a profile which, however, was known, and then corrected for it in the equation for the surface tension. This worked well, giving values which were consistent for several different orifices. It also allowed accurate measurement of the surface tension at low surface ages.

Defay and Hommelen [10] measured the dynamic surface tensions of various organic acids and alcohols using capillary type orifices. Evidently unaware of the work of Hansen, et. al. [17], they appear to have run into the same problems as Rideal and Sutherland [28], not taking velocity effects into account. In order to bring their data into accord with literature values, they introduced an empirical correction factor which, they claim, worked fairly well.

Both Netzel, Hoch, Marx [20] and Vandegrift [32] studied the dynamic surface tension of pure water using a diaphragm type of orifice. This is a platelike orifice, having an elliptical hole bored out of gold or brass foil (0.005 centimeter thick). Owens [24] used a similar orifice, however it was 0.04 centimeter thick. The reason for using the diaphragm rather than the capillary orifice was to eliminate the troublesome velocity profiles.

The quantitative results for pure water for the above three investigators were all different. Qualitatively, however, they were identical; the surface tension was initially 80 to 100 dynes per centimeter and decreased monotonically to the static value of 72 dynes per

centimeter within approximately five milliseconds. Both Netzel, et. al. [20] and Owens [24] applied a correction factor to their water data which they then applied to surfactant solutions that they studied. Vandegrift [32] concluded that water does not have a time dependent surface tension but that the mathematical description for the process was inadequate.

Caskey and Barlage [6] used a diaphragm orifice made of two mil mylar film. In addition, they coated their orifice with paraffin to prevent wetting of the surface, a phenomenon that could cause velocity gradients in the jet. They obtained results which were consistent at short exposure times, giving a constant value for the surface tension of water at 25°C of 74 dynes per centimeter, not significantly different from literature values. They found, moreover that the surface tension was independent of the flow rate of the jet. One further innovation was made in this study. Rather than using complicated optical and photographic means to measure the jet dimensions, as in previous studies, a coordinate cathetometer was employed and the dimensions measured directly.

From the preceding survey it is concluded that meaningful data can be obtained from the oscillating jet method using a diaphragm orifice. Several precautions must be taken, however. The orifice must be elliptical and not just a symmetrical oval, and it should be coated with a non-wetting material so as to prevent non-uniform velocity effects.

Theory of Surface-Active Agents

This section provides a short review of surface chemistry as applied to aqueous solutions of surfactants. In addition, we will be specifically concerned with the gas-liquid interface.

The Surface "Phase". Whenever a system consists of two phases, there is a region in between which is labeled a surface. This is not a well defined boundary, and indeed its precise thickness is not known. Moreover, its properties will vary over the thickness of the surface and are different from either of the two bulk phases. (8,22)

It may be observed that the surface of a pure liquid, such as water, appears to be covered by an elastic membrane which tends to contract. This phenomena can be attributed to the unequal forces which act at the surface, as compared with the balanced forces that act on the molecules in the bulk. It is in this light that surface tension is defined as "....the work required to increase the surface by unit area, at constant temperature, pressure, and composition." (22)

Surfactants in Solution. If a surfactant is added to water the surface tension will be less than that of pure water, due to an adsorbed monolayer of solute at the surface. The surfactant tends to concentrate at the surface because of its hydrophobic-hydrophilic structure. That is, the hydrophobic hydrocarbon chain will resist being immersed in the water, whereas the hydrophilic end group is opposed to removal from the water. (9)

Mathematically, the surface tension lowering is expressed in terms of surface spreading pressure. (9)

$$\Pi = \gamma_0 - \gamma \tag{2}$$

where:

Π = spreading pressure, dynes/cm

γ_0 = surface tension of solvent, dynes/cm

γ = surface tension of solution, dynes/cm

Gibbs' Adsorption Isotherm. The amount of solute in the surface which is over and above that in the bulk is termed the surface excess. It was quantitatively deduced by Gibbs [14] and is given by

$$\Gamma = - \frac{1}{NRT} \frac{d\gamma}{d(\ln c)} \tag{3}$$

where:

Γ = surface excess, moles/cm^2

γ = equilibrium surface tension, dynes/cm

R = gas constant, ergs/mole °K

T = temperature, °K

c = bulk concentration, moles/liter

and N is a variable that depends on the nature of the solute.

Equation 3 is subject to several restrictions [9]:

(1) Because of the nebulous thickness of the surface an arbitrary boundary is chosen within the surface phase where the surface excess of solvent is zero.

(2) Activity coefficients are equal to unity and thus, concentrations may be used.

(3) Temperature, pressure, and chemical potential are constant throughout the system.

(4) The concentration is below the critical micelle concentration.

The factor N in the above equation arises from the differential form of Gibbs' isotherm, (9)

$$\partial\gamma)_T = - \Sigma\Gamma\partial\mu)_T \qquad (4)$$

where μ is the chemical potential. The summation on the right must include all adsorbed species, including counter-ions for long-chain ionic molecules. Thus, N is two for a monovalent ionic compound and one for a nonionic surfactant.

Micelle Formation. For aqueous solutions of surfactants the equilibrium surface tension reaches a constant value over some narrow concentration range (Figure 2). Moreover, there is an abrupt change in the physical properties of the solution in this region. These changes are generally attributed to the formation of aggregates of surfactant molecules or micelles. (23)

Surface tension-concentration curves will frequently show a minimum in surface tension rather than a smooth decline followed by a constant value. This minimum has been shown to be due to trace impurities, and can be removed through extensive purification. (1)

It was previously mentioned that Gibbs' adsorption equation is not applicable above the critical micelle concentration. If it were

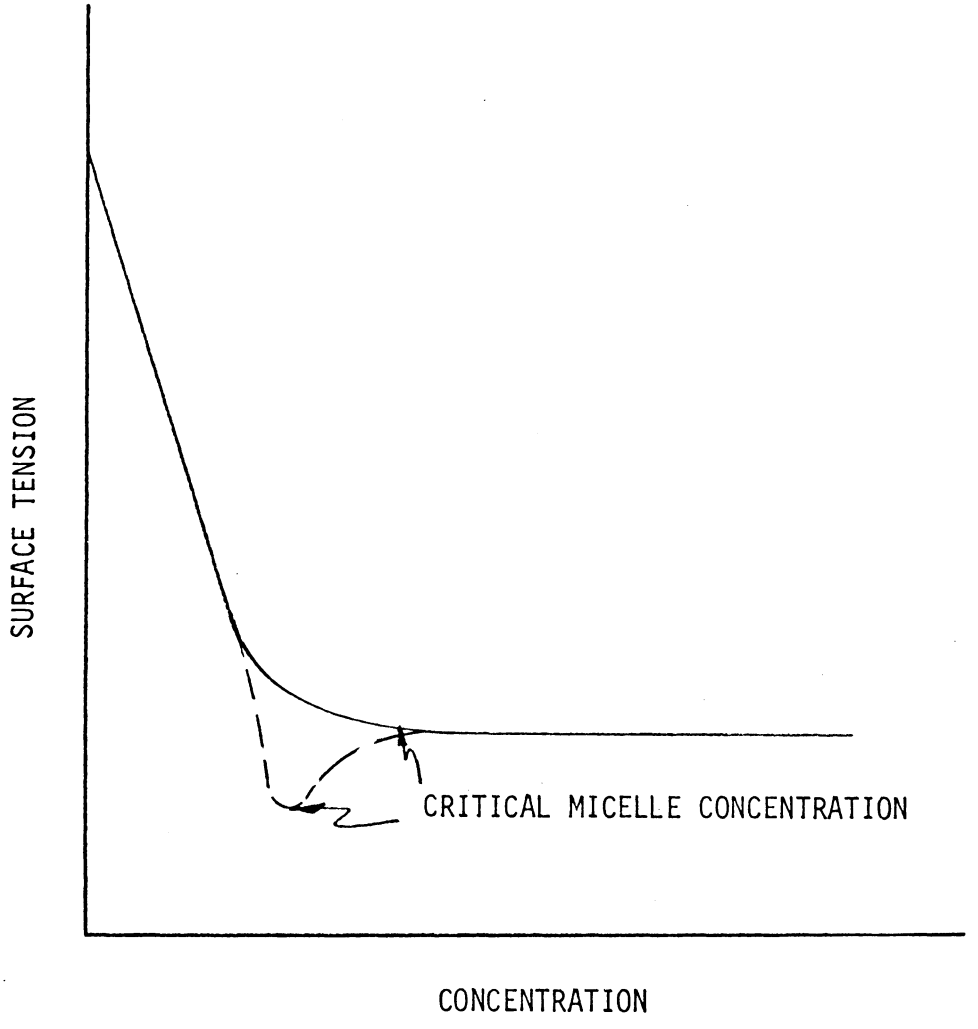


FIGURE 2. TYPICAL EQUILIBRIUM SURFACE TENSION CURVE

DAVIES, J.T., AND E.K. RIDEAL, "INTERFACIAL PHENOMENA", SECOND EDITION, P. 200. ACADEMIC PRESS, NEW YORK, 1963.

valid, then at high concentrations, where the slope of the γ-c curve is zero, Gibbs' equation would predict a zero surface excess. Obviously, this can not be so, since the surface tension is quite low. This is borne out by radioactive tracer studies, which indicate a strong adsorption over the entire curve. (9)

Adsorption Kinetics

This section presents a survey of previously postulated models for the kinetics of adsorption of surfactants at the air-water interface. These models fit into two categories; (1) pure diffusion controlled kinetics, and (2) kinetics limited by an energy barrier which hinders molecules from entering the surface. Included in this second group are first-order rate expressions. In general, these results have been deduced from studies on simple organic acids and alcohols.

Diffusion Theory. In a classic paper Ward and Tordai (33) have treated the case of diffusion controlled adsorption. They visualize a solution of uniform concentration at zero time. That portion of the bulk immediately adjacent to the surface and several molecular diameters thick is referred to as the sub-surface. Because the solute molecules are surface-active, (have a lower free energy in the surface than the bulk), the molecules in the sub-surface will initially all migrate to the surface where the chance of finding an empty "site" for adsorption is highly probable. It is assumed that equilibrium is established instantaneously between the sub-surface and surface, whereas the molecules in the bulk will migrate at a significantly slower rate

to the sub-surface. Thus, the sub-surface concentration will initially fall to zero.

As the adsorption continues the surface will become more fully occupied, the probability of a solute molecule finding a site will decrease, and the sub-surface concentration will start to increase. At this point the possibility of back-diffusion from the sub-surface to the bulk must be included in the model, so that at equilibrium the bulk and sub-surface concentrations are equal.

The equation that Ward and Tordai [33] developed follows:

$$\Gamma = 2\left(\frac{D}{\pi}\right)^{1/2}\left\{C_0 t^{1/2} - \int_0^{t^{1/2}} \phi(z)\, d[(t-z)^{1/2}]\right\} \qquad (5)$$

where:

Γ = surface concentration, moles/cm^2

D = the diffusion coefficient, cm^2/sec

C_0= the bulk concentration, moles/cm^3

z = an integration variable, sec

$\phi(z)$ = the sub-surface concentration, moles/cm^3

t = time, sec

Equation 5 allows, in theory, for the calculation of either Γ or D, if one of the two is known. Unfortunately, the integral term, which accounts for the back diffusion can not be integrated directly since $\phi(t)$ is not known explicitly. However, since it was assumed that no energy barrier exists between the surface and sub-surface and if it is further assumed that the surface tension corresponds to a

unique value of the sub-surface concentration, then the integral may be solved numerically. That is, the concentration in the sub-surface, in the dynamic case, will be the same as the bulk concentration of a solution at equilibrium which has the same surface tension.

For organic acids and alcohols, the diffusion model has generally been inadequate in describing experimental results. Defay and Hommelen [10,11] are the only authors whose data seem to support equation 5. Hansen and Wallace [18] investigating similar compounds, however, found that apparent diffusion coefficients increased with time and increasing concentration, yet in all cases was less than the classical diffusion coefficient, indicating an activation barrier.

Energy Barrier Limited Kinetics. Hansen and Wallace [18] developed a general theory of adsorption for the organic acids they studied and found that "The adsorption kinetics.....involve a dimeric transition state...." That is, the kinetics are barrier limited with a second order dependence on concentration.

Hansen [15] in a later article, compared the work of Defay and Hommelen [10,11] with that of Hansen and Wallace [18]. He found that, although the experimental data were quite similar, the interpretations were entirely different. After a lengthy theoretical development he concluded that diffusion can not be justifiably ignored, and that the proposed mechanism of Hansen and Wallace [18] must be incorrect. Hansen went on to present two possible hypotheses to explain the adsorption data: (1) there is a small barrier to surface entry, and diffusion is not initially rate-limiting, although it becomes so

eventually; (2) the dependence of dynamic surface tension on the number of solute molecules in the surface may be different in the dynamic and equilibrium situations.

Netzel, Hoch and Marx [20] investigating Triton X-100, a non-ionic surfactant, found that their data could be fitted to a first-order rate expression.

$$-d(\gamma - \gamma_e)/dt = k(\gamma - \gamma_e) \qquad (6)$$

where:

γ, γ_e = dynamic and equilibrium surface tensions, dynes/cm

k = rate constant, sec^{-1}

t = time, sec

Austin, Bright and Simpson [4], working with Manoxol OT, an anionic surfactant were also able to explain their data with Equation 6.

Posner and Alexander [27] using surface potential measurements found that their results for organic alcohols and two ionic soaps were also described by first-order kinetics, but in surface potential gradients. Addison and Litherland [2], however, have shown that surface potential and surface tension are not simply related, reducing somewhat the significance of their study.

III. EXPERIMENTAL

This section contains a brief outline of the plan of experimentation, procedural methods, and data and results.

Plan of Experimentation

The following paragraphs present an outline of the experimental plan followed during the course of this investigation.

Literature Review. A survey of the literature was carried out in three areas: (1) The general area of surface chemistry with specific emphasis on the physical chemistry of surfactants at the air-water interface; (2) the development of the oscillating jet technique for measuring dynamic surface tension; (3) proposed mechanisms and models which have been postulated for the kinetics of adsorption.

Selection of Surfactants. Three surfactants of commercial importance were chosen for this study, each containing a long chain segment of twelve carbon atoms. Cationic (dodecyl trimethyl ammonium bromide), anionic (sodium dodecyl sulfate), and nonionic (dodecyl diethanol amide) surfactants are all represented.

Equilibrium Surface Tensions. Static surface tensions as a function of concentration were measured for all surfactants to determine both the critical micelle concentration as well as surface excess.

Dynamic Surface Tensions. Four concentrations each were studied for the ionic surfactants and three for the nonionic. In addition, several duplicate tests were made to check for reproducibility. The

reliability of the apparatus along with conformation to the assumptions inherent in the Bohr equation were checked by measuring the dynamic surface tension of distilled and de-ionized water.

Treatment of Data. The jet dimensions and flow rate were reduced to dynamic surface tensions by applying Sutherland's modification of the Bohr equation, (Equation 1). Surface ages were calculated by assuming the jet to be a freely falling body under the influence of gravity. (Details are given in the Appendix)

An empirical model was developed to fit the dynamic surface tension data. This model was then used to smooth out the experimental results and test the diffusion model. First-order rate expressions were also examined.

Methods of Procedure

A detailed description of the procedures followed in determining equilibrium and dynamic surface tensions is contained in this section. All work was carried out in a constant temperature room at 25±1°C.

Equilibrium Surface Tensions. Glassware used in this portion of the experimentation was cleaned using a standard laboratory solution of sodium dichromate, sulfuric acid and water. This was followed by a thorough rinsing in tap water and then by rinsing in distilled and de-ionized water. Cleanliness can not be emphasized enough here, since even a small impurity can cause a significant change in surface tensions.

A concentrated one liter solution of surfactant was prepared. Distilled water which had been subsequently de-ionized in a Barnstead Still to less than 0.1 parts per million as NaCl was used. Surfactants were weighed on a double-pan analytical balance. Solutions of decreasing concentration were then obtained by dilution using 1, 10, and 15 milliliter pipettes and 100, 250 and 500 milliliter volumetric flasks.

The above solutions were placed in covered petri dishes to prevent evaporation, and left for one hour to equilibrate. Equilibrium surface tensions were then determined on a du Nüöy ring tensiometer. The ring was cleaned in methyl ethyl ketone and fired in a propane torch prior to each determination to eliminate contamination.

Because the tensiometer reads apparent surface tension it was necessary to apply the following correction factor [13]

$$F = 0.725 + \sqrt{\frac{0.01452\ P}{C^2(D - d)} + .04534 - \frac{1.679r}{R}} \qquad (7)$$

$$\gamma = F \times P \qquad (8)$$

where:

F = the correction factor

R = radius of the ring, cm

r = radius of the wire of the ring, cm

P = apparent surface tension, dynes/cm

D = density of the liquid, gm/cm^3

d = density of the air, gm/cm^3

C = circumference of ring, cm

γ = actual surface tension, dynes/cm

A minimum of three readings was taken for each sample, and a minimum of two samples for each concentration was used.

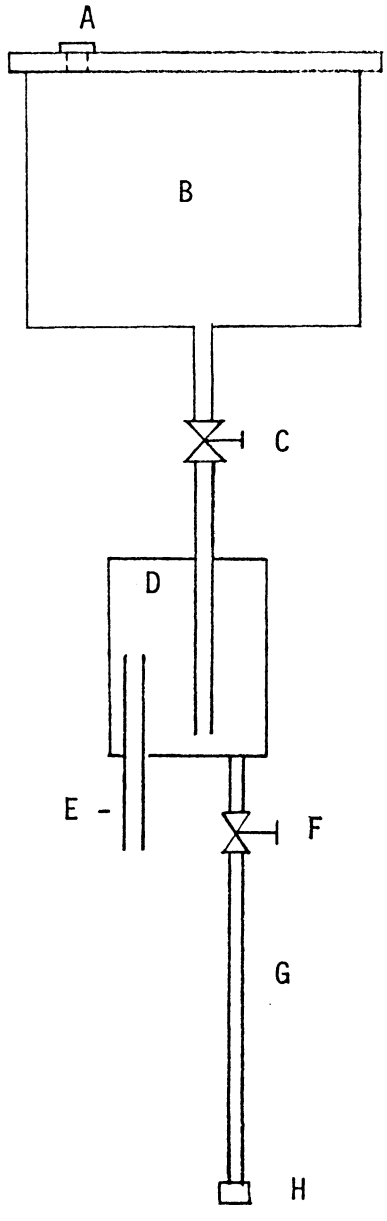
Dynamic Surface Tensions. Ten liters of surfactant solution of the desired concentration was prepared using distilled, de-ionized water. The surfactant was weighed on a double-pan analytical balance. the water was measured out in a one liter volumetric flask.

The remainder of this section will be clarified by reference to the apparatus shown in Figure 3.

The entire apparatus was first flushed out using tap water. Valves C and F were then closed and surfactant solution added to tank B. Valve C was then opened and tank D filled approximately two inches. Valve C was then closed, F opened, and tank D allowed to drain. Valve F was then closed, C opened, and tank D filled to the top of the overflow tube E.

Valve F was then adjusted to provide the desired flow rate. A smooth laminar stream of liquid from tube G was obtained with a flow rate of approximately two milliliters per second. This corresponded to a setting on the metering valve of 5.0 to 6.5.

The elliptical orifice, which was mounted on a 1/4 inch Swagelok tubing nut, was then filled with the surfactant solution by holding a finger over the opening. (A detailed description of the orifice and its fabrication is contained in the Appendix) The orifice was



A - PLUG
B - RESERVOIR TANK
C - NEEDLE VALVE
D - CONSTANT HEAD TANK
E - OVERFLOW TUBE
F - METERING VALVE
G - ENTRANCE TUBE
H - ORIFICE

FIGURE 3. APPARATUS USED TO MEASURE DYNAMIC SURFACE TENSION

then attached to a union on the bottom of tube G. The preceding procedure prevented bubbles from forming inside the orifice fitting, which would interfere with the flow pattern.

Valve C was adjusted to give a small overflow into tube E, thus providing a constant flow without excessive use of feed solution.

A small microscope illuminating lamp was placed behind the oscillating jet stream. A coordinate cathetometer was then used to measure the wavelengths and node diameters on the jet. Measurements were begun at the orifice and continued down the jet, eight to twelve nodes. At this point the jet was no longer sufficiently quiescent to take measurements, due to incipient turbulence.

Flow rates were determined by recording the time required to collect 250 milliliters of solution in a volumetric flask.

Between tests the apparatus was flushed out with tap water, followed by the surfactant to be used in that particular test, as described above.

Data and Results

The data and results obtained during this investigation are contained in this section.

Equilibrium Surface Tensions. Figures 4 through 6 present the graphical results of the equilibrium surface tension determinations of aqueous solutions of the surfactants studied. Critical micelle concentrations, CMC, where available from the literature, are shown. Figures 4 and 6 also present results obtained by other workers.

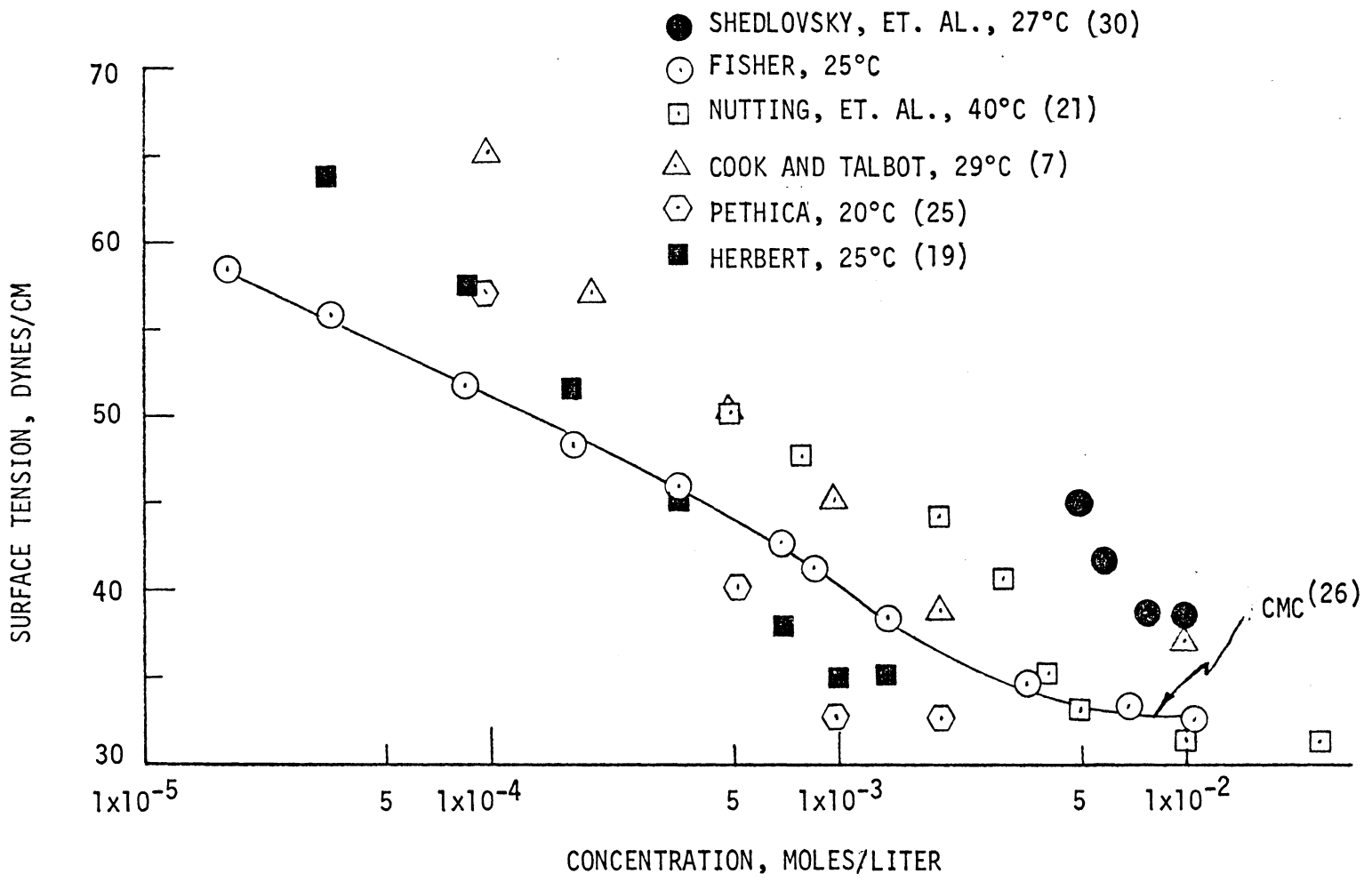


FIGURE 4. EQUILIBRIUM SURFACE TENSION OF SODIUM DODECYL SULFATE

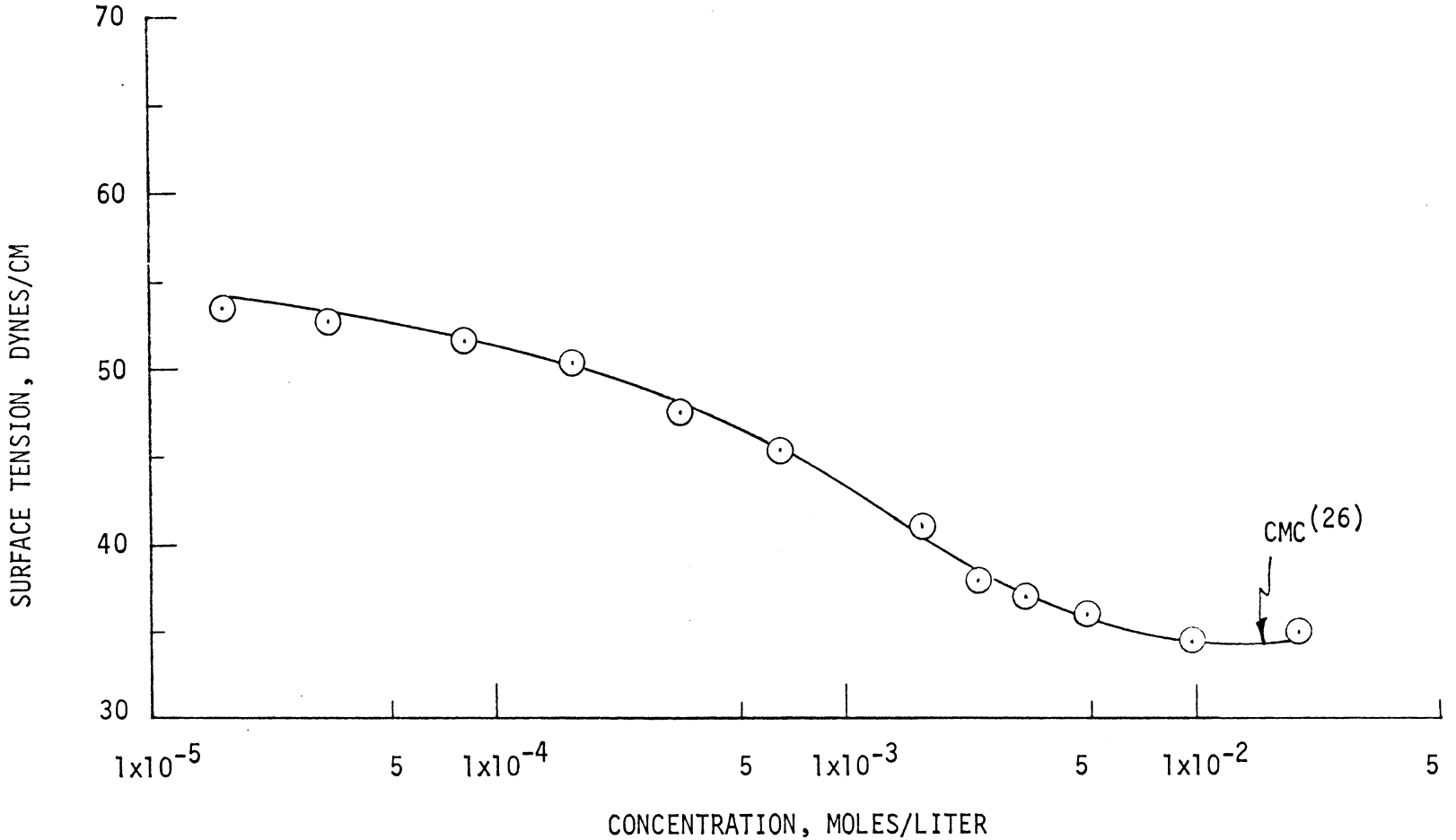


FIGURE 5. EQUILIBRIUM SURFACE TENSION OF DODECYL TRIMETHYL AMMONIUM BROMIDE

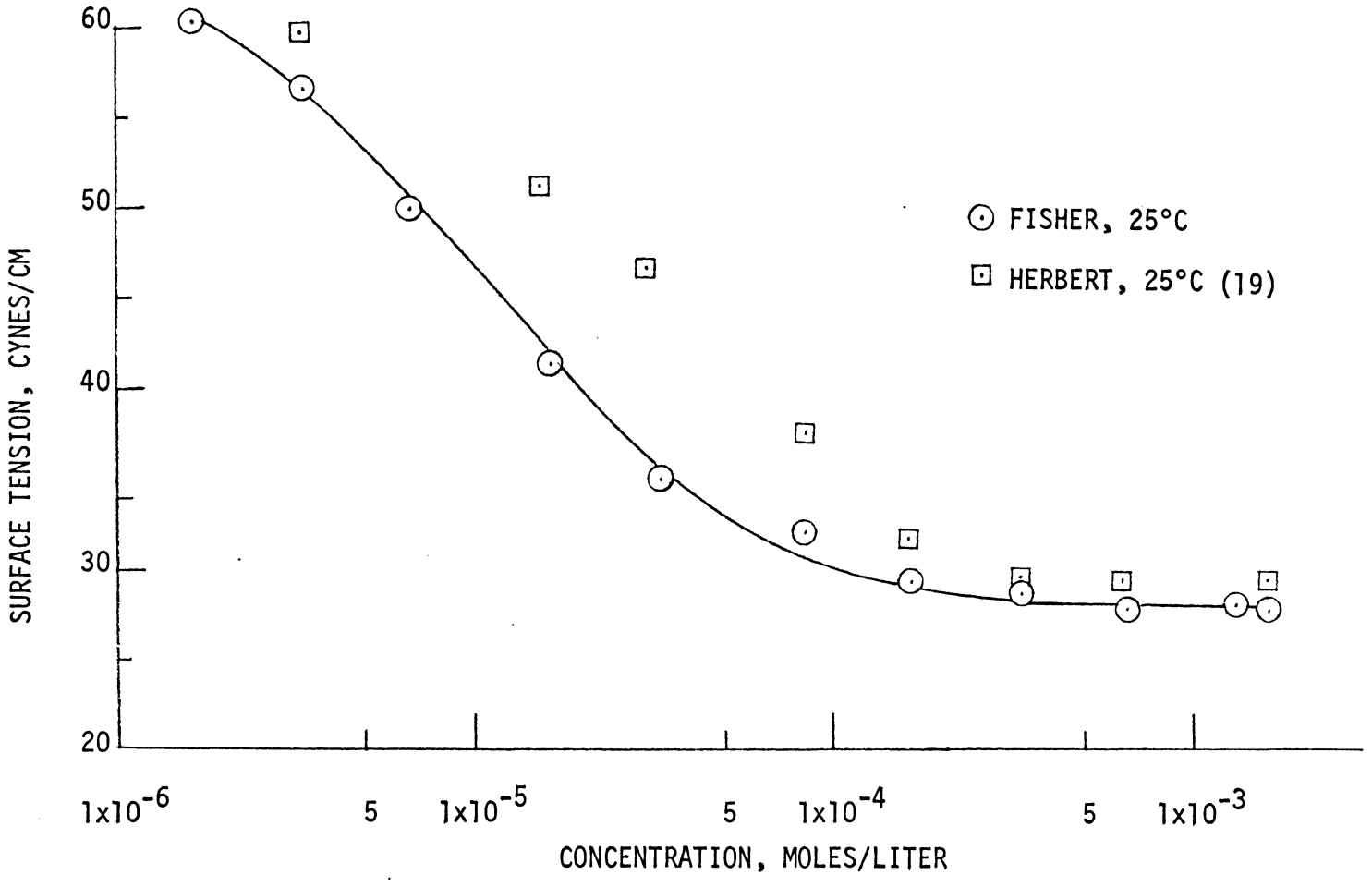


FIGURE 6. EQUILIBRIUM SURFACE TENSION OF DODECYL DIETHANOL AMIDE

Orifice Measurement. The dimensions of the orifice used for the dynamic surface tension determinations are shown in Figure 7. The circles were experimentally determined by direct measurement with the coordinate cathetometer. The solid line was plotted from the equation for an ellipse having the major and minor axes of the orifice. It can be seen that the orifice was, indeed, an ellipse.

Equipment Check. To verify that the apparatus did yield correct results, the dynamic surface tension of pure water was measured, at several flow rates. If the equipment conforms to the assumptions of the Bohr equation, then the dynamic surface tension should be constant with time, not significantly different from the static value, and invariant with respect to flow rate.

Graphical representation of the results of this test are shown in Figure 8. (See Appendix for data) The solid line in this figure was determined, by a least squares analysis, to be -0.152 dynes per centimeter per second. Statistically, however, one can not reject the null hypothesis that the slope is zero, at a 95 percent level of significance. The average value of the surface tension is 75.7 dynes per centimeter. The results of Caskey and Barlage [6] are also shown in this figure.

Dynamic Surface Tensions. Figures 9 through 11 display, in graphical form, the dynamic surface tensions, for varying concentrations, of the surfactants studied in this investigation. (See Appendix for data) The solid lines in these figures were drawn from the empirical model presented in the following section. For both sodium dodecyl sulfate

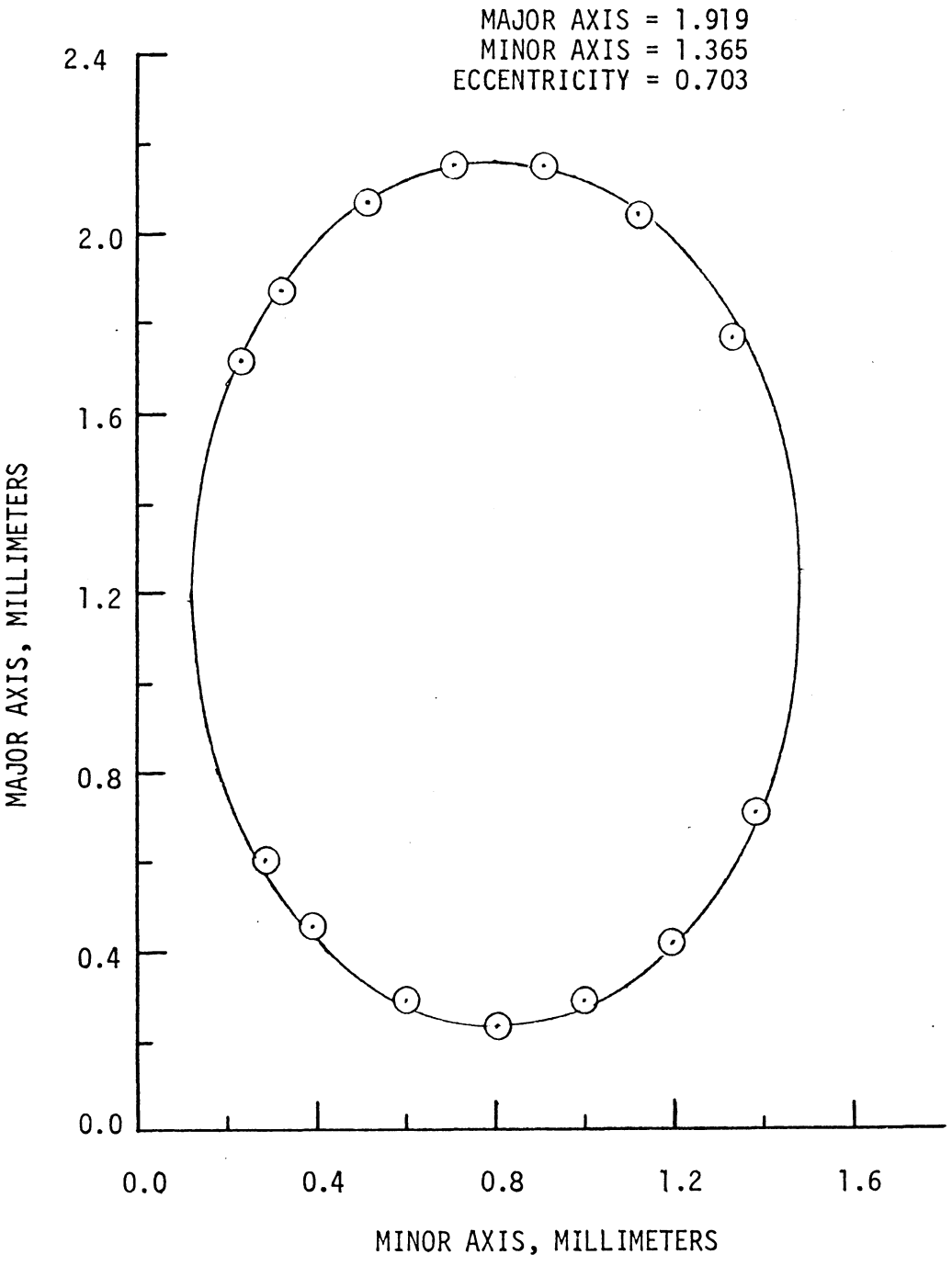


FIGURE 7. MEASUREMENT OF ELLIPTICAL ORIFICE

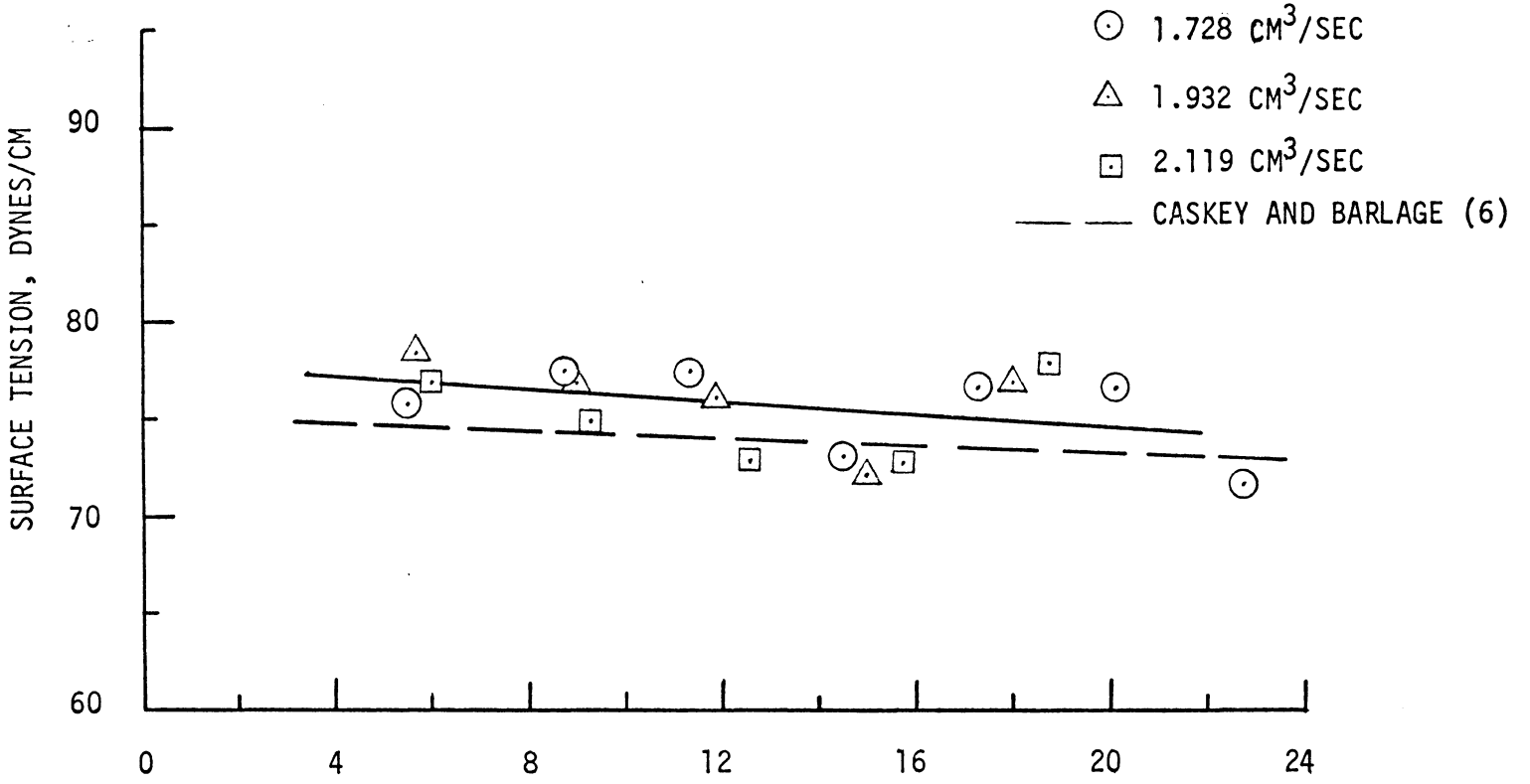


FIGURE 8. DYNAMIC SURFACE TENSION OF PURE WATER

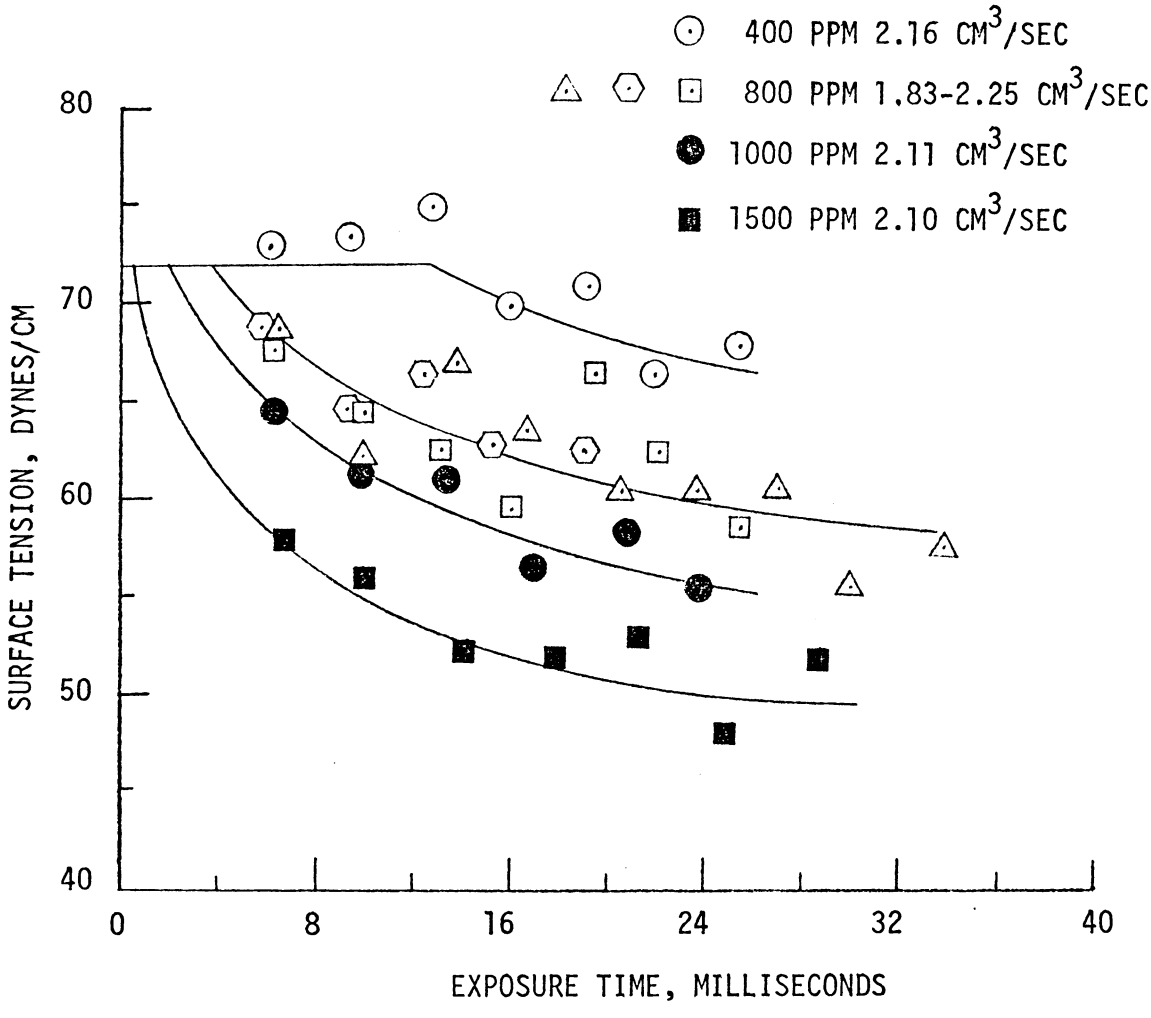


FIGURE 9. DYNAMIC SURFACE TENSION OF SODIUM DODECYL SULFATE

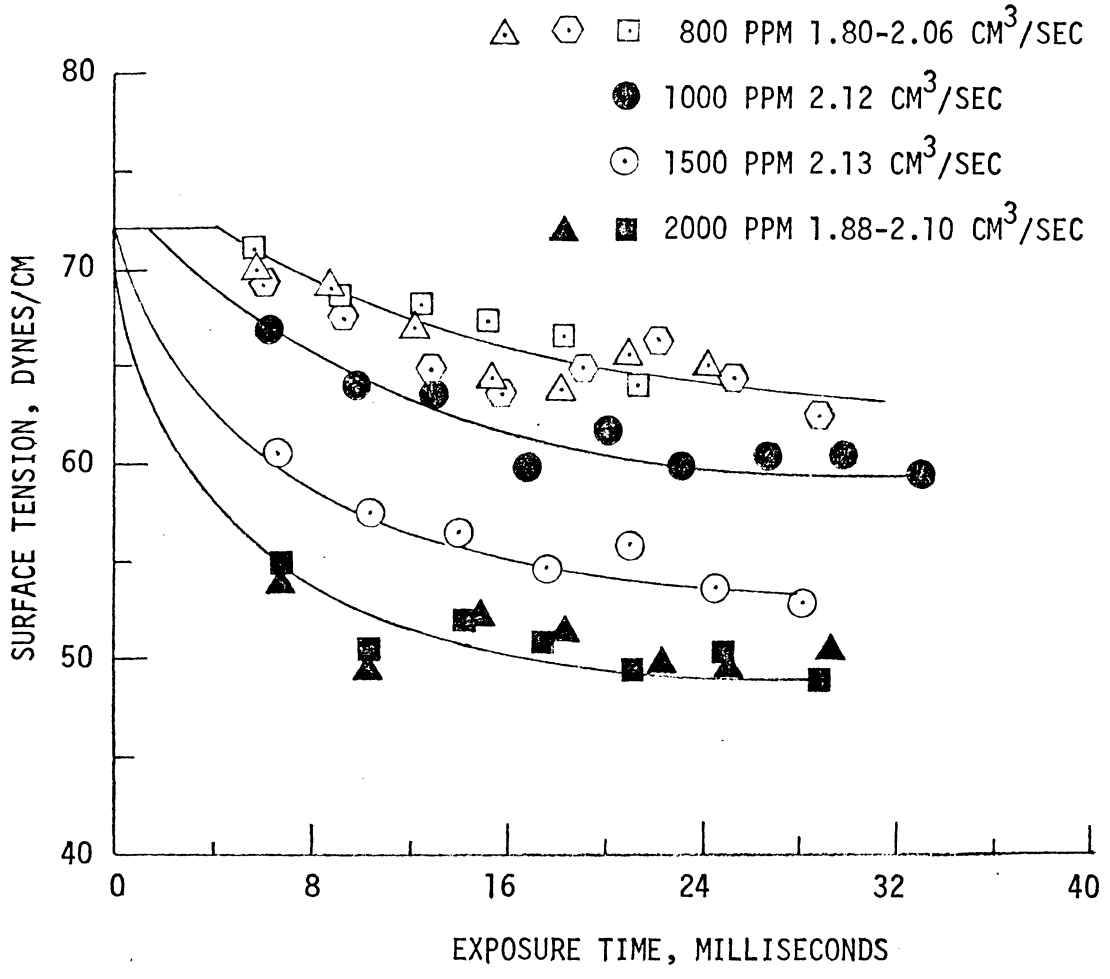


FIGURE 10. DYNAMIC SURFACE TENSION OF DODECYL TRIMETHYL AMMONIUM BROMIDE

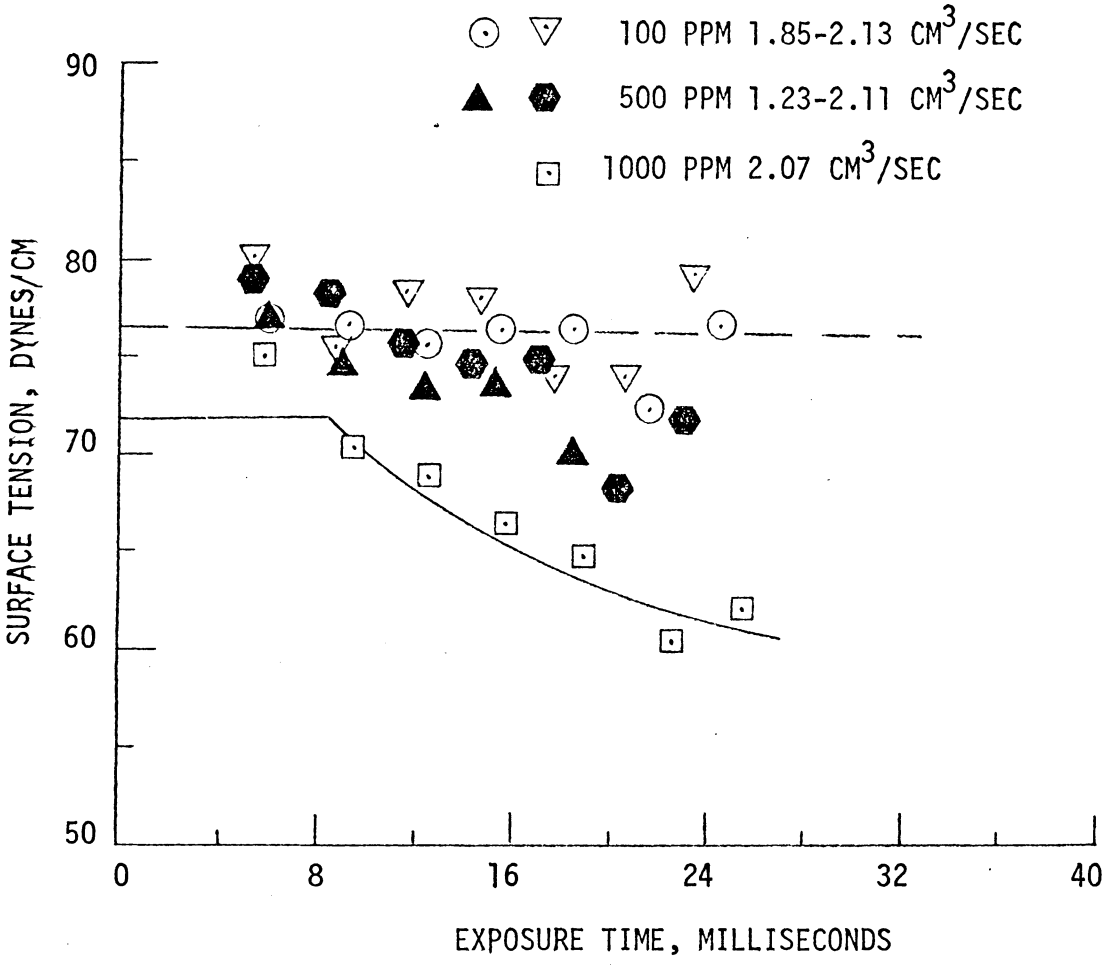


FIGURE 11. DYNAMIC SURFACE TENSION OF DODECYL DIETHANOL AMIDE

and dodecyl trimethyl ammonium bromide, concentrations below the CMC were used throughout. For dodecyl diethanol amide, however, it was necessary to exceed the CMC in order to obtain any surface tension depression within the first thirty milliseconds. The dotted line in Figure 11 is drawn for the average value of the surface tension, taken below the CMC, at 100 parts per million. This average value is 76.5 dynes per centimeter.

Empirical Model. An empirical correlation, relating the dynamic surface tension to time was found. The following equation expresses that correlation.

$$\gamma = kt^m \qquad (9)$$

$$\text{for } t > t^{72}$$

Or, in terms of logarithms,

$$\text{Logarithym } (\gamma) = m \text{ Logarithm } (t) + \text{Logarithm } (k) \qquad (10)$$

where:

γ = surface tension, dynes/cm

logarithm (k) = intercept

t = time, msec

m = slope of line

t^{72} = 72 dyne/cm intercept

A least squares analysis was done on Equation 10 to determine the intercept and slope. An average value of the slope was taken for each compound and the intercept recalculated. The value of the 72 dyne per centimeter intercept was also calculated, i.e. that time where the surface tension begins to decrease. Data prior to this time were not

included in the determination of the slope, since it was assumed that the surface tension remained constant up to this point.

The parameters obtained from the least squares fitting are displayed in Tables I through III. Figures 12 through 14 show the straight lines that resulted from this empirical fitting.

The coefficient k, as well as the 72 dyne per centimeter intercept, are concentration dependent. This dependence is shown in Figures 15 and 16 for sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide. Because only one of the curves for dodecyl diethanol amide showed any substantial decrease in surface tension, however, the determination of the concentration dependence of these two terms was precluded, for this compound.

Test of Previous Models. The diffusion theory of Ward and Tordai [33] was tested using two concentrations of sodium dodecyl sulfate. The empirical model of Equation 9 was used to smooth the equilibrium surface tension data. The diffusion coefficient was calculated at an exposure time of thirty milliseconds in both cases. The surface excess was found to be essentially constant over this range at 0.86×10^{-10} moles per square centimeter. The value of the integral in Equation 5 was calculated graphically from Simpson's rule. The results of this calculation are shown in Table IV.

Figure 17 is representative of results obtained from visually fitting a rate expression which is first-order in surface tension to the dynamic surface tension data. Figure 18 is also the result of a first-order model, but in the difference between dynamic surface tension and the equilibrium surface tension. (See Equation 6)

TABLE I

Least Squares Curve Fit of Empirical Model

for Sodium Dodecyl Sulfate[a]

Concentration	Slope	Intercept[b]	72 dyne/cm Intercept
ppm			milliseconds
400	-0.10005	1.96718	12.63
800	-0.09079	1.91628	3.90
1000	-0.10815	1.88861	2.06
1500	-0.09994	1.84460	0.73
	Average=-0.09973±0.0071		

[a] Logarithm(γ) = m Logarithm(t) + Logarithm(k), Equation 10

[b] Calculated from average slope

TABLE II

Least Squares Curve Fit of Empirical Model

for Dodecyl Trimethyl Ammonium Bromide[a]

Concentration	Slope	Intercept[b]	72 dyne/cm Intercept
ppm			milliseconds
800	-0.060515	1.89829	4.24
1000	-0.068468	1.87279	1.72
1500	-0.081331	1.82565	0.33
2000	-0.050755	1.78708	0.08

Average=-0.065267 ± 0.0129

[a] Logarithm(γ) = m Logarithm(t) + Logarithm(k), Equation 10

[b] Calculated from average slope

TABLE III

Least Squares Curve Fit of Empirical Model

for Dodecyl Diethanol Amide[a]

Concentration	Slope	Intercept[b]	72 dyne/cm Intercept
ppm			milliseconds
1000	-0.14626	1.9940	8.55

[a] Logarithm(γ) = m Logarithm(t) + Logarithm(k), Equation 10

[b] Calculated from average slope

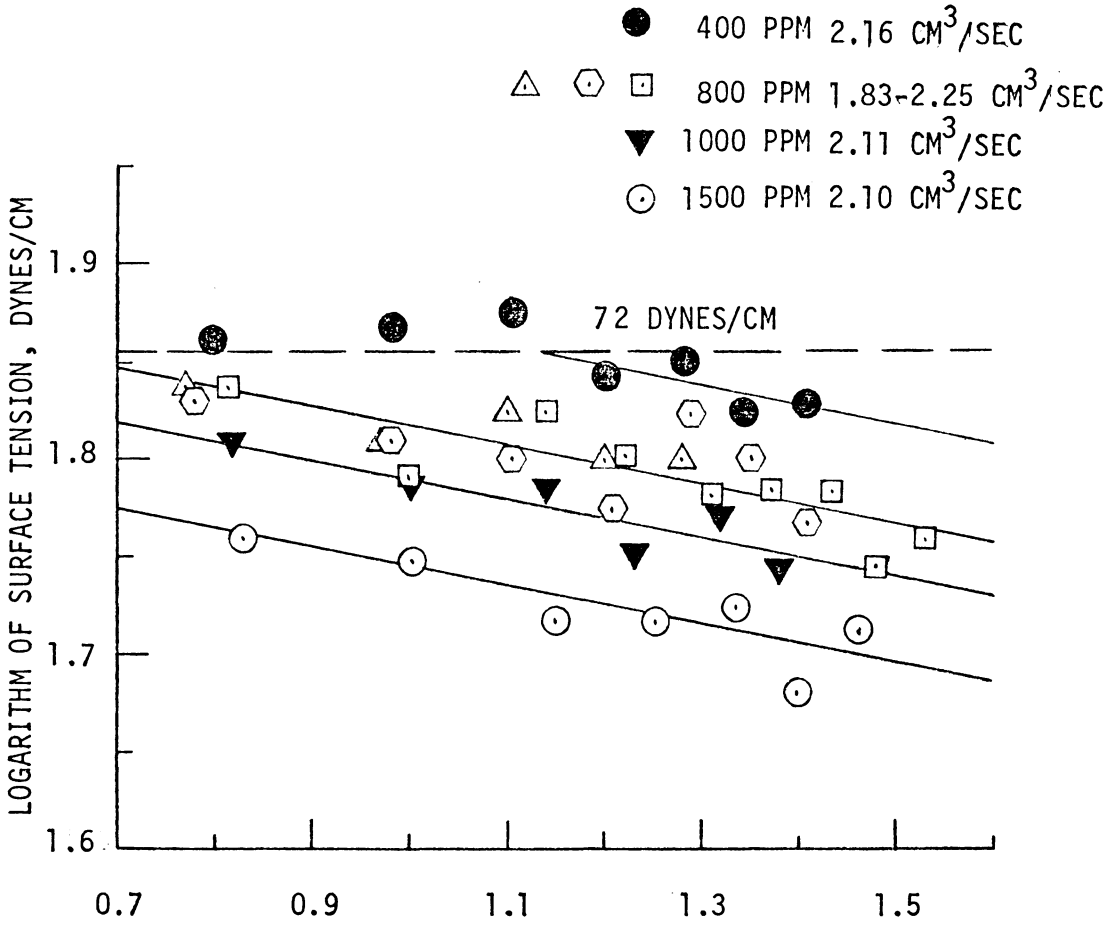


FIGURE 12. EMPIRICAL CORRELATION OF DYNAMIC SURFACE TENSION OF SODIUM DODECYL SULFATE

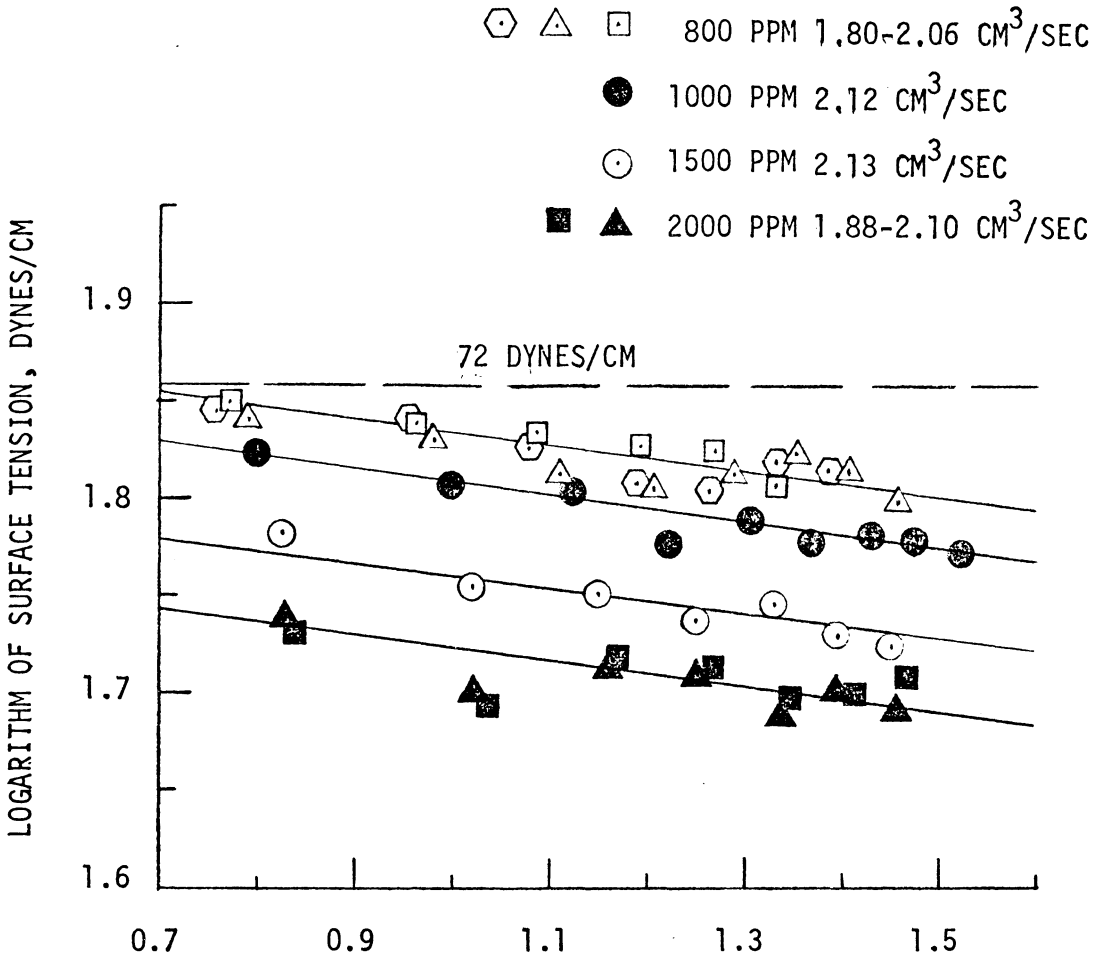


FIGURE 13. EMPIRICAL CORRELATION OF DYNAMIC SURFACE TENSION OF DODECYL TRIMETHYL AMMONIUM BROMIDE

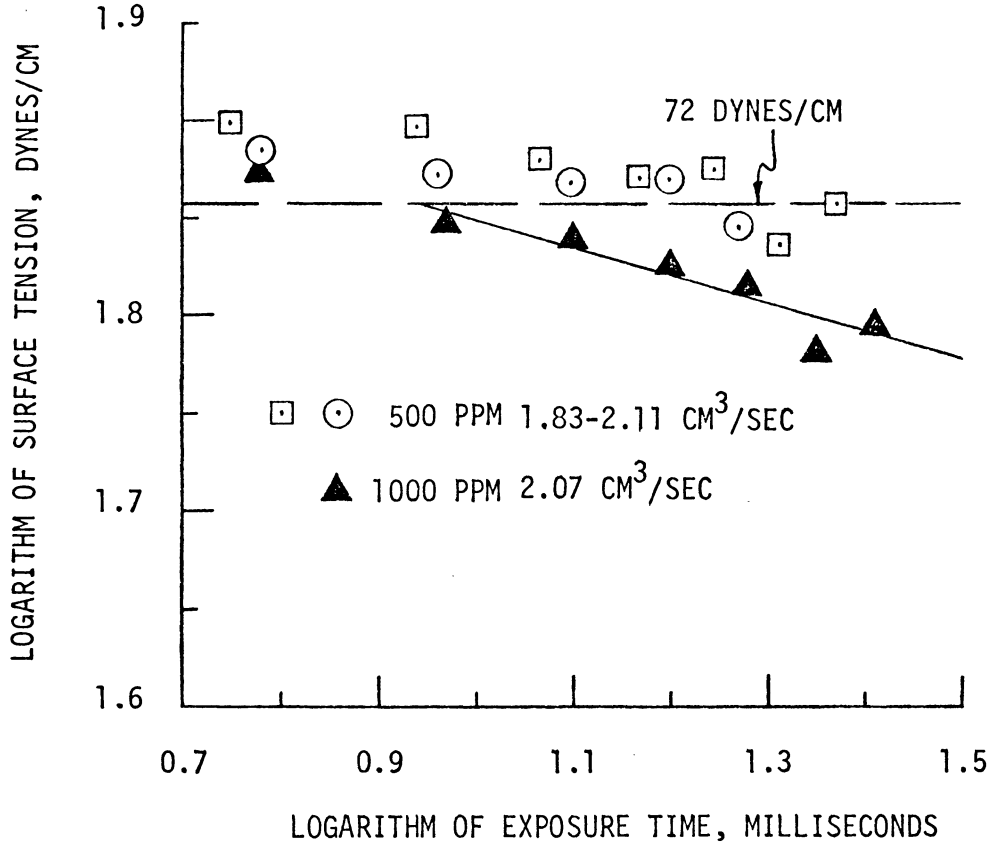


FIGURE 14. EMPIRICAL CORRELATION OF DYNAMIC SURFACE TENSION OF DODECYL DIETHANOL AMIDE

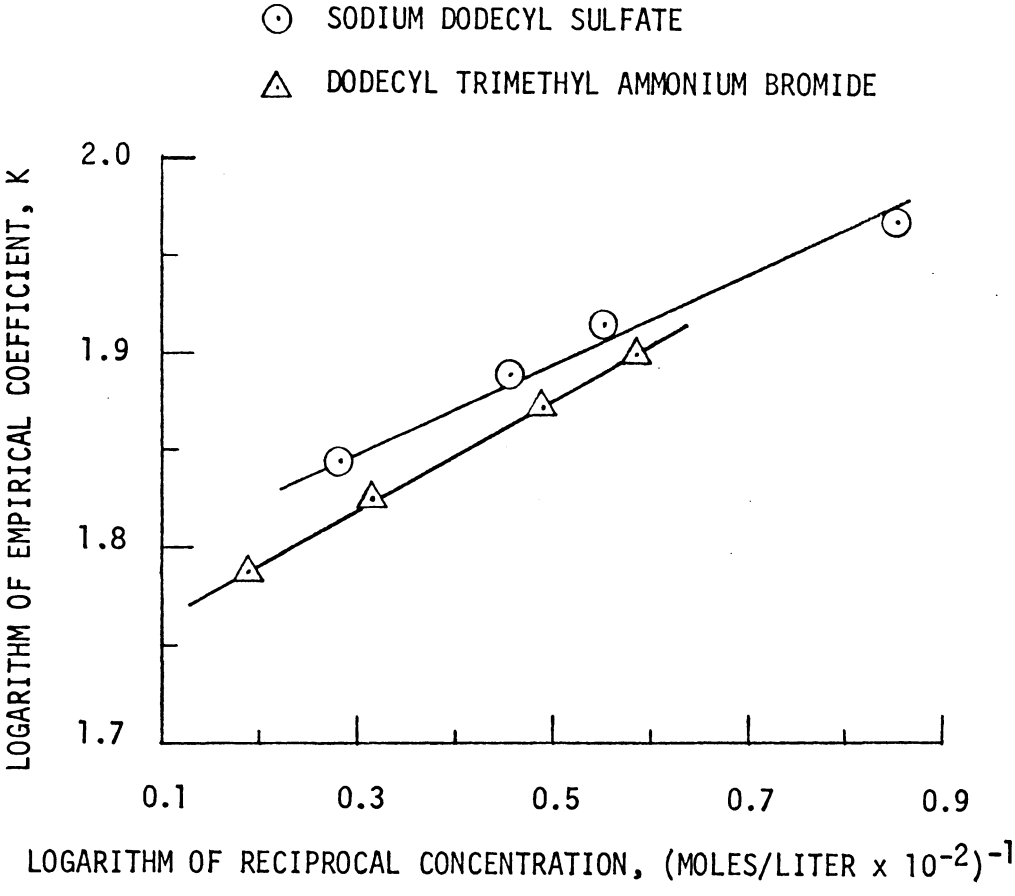


FIGURE 15. DEPENDENCE OF EMPIRICAL COEFFICIENT, K, ON CONCENTRATION

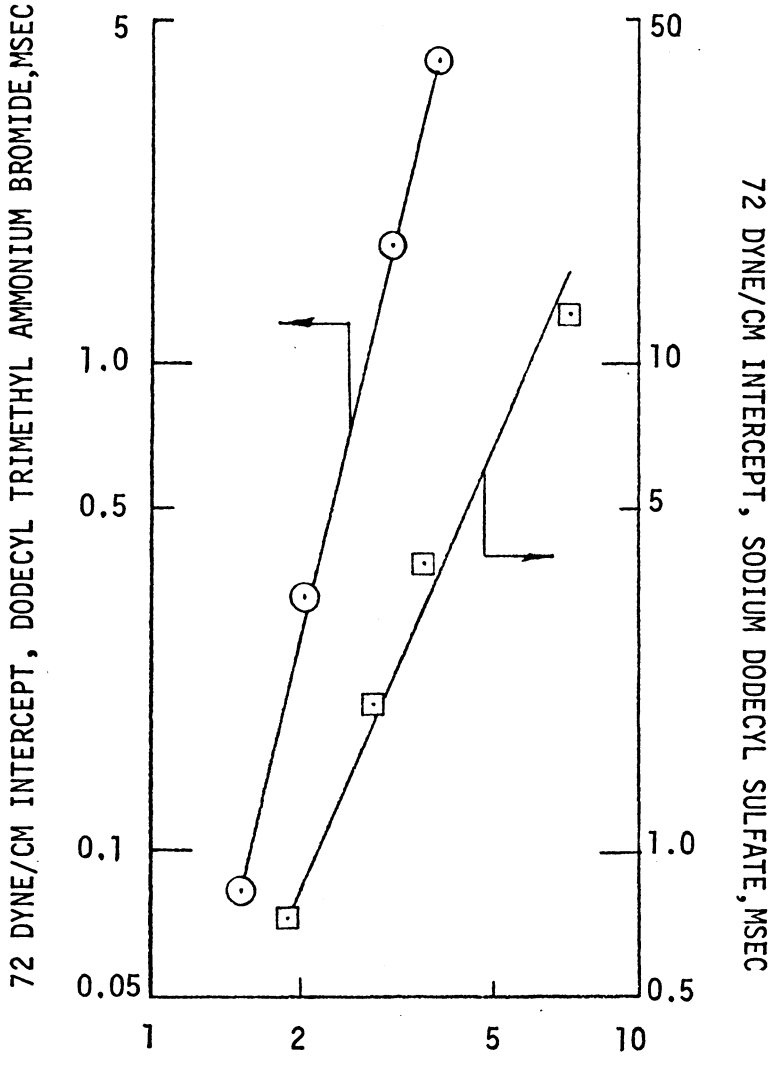


FIGURE 16. DEPENDENCE OF 72 DYNE/CM INTERCEPT ON CONCENTRATION

TABLE IV

Apparent Diffusion Coefficients for Sodium Dodecyl Sulfate

Concentration ppm	Diffusion Coefficient $cm^2/sec \times 10^8$	Back Diffusion[a] $\times 10^{10}$	Forward Diffusion[b] $\times 10^7$
800	2.50	1.02	4.82
1500	0.71	8.54	9.02

[a] $\int_0^{t^{1/2}} \phi(z)\, d[(t - z)^{1/2}]$, Equation 5

[b] $C_0 t^{1/2}$, Equation 5

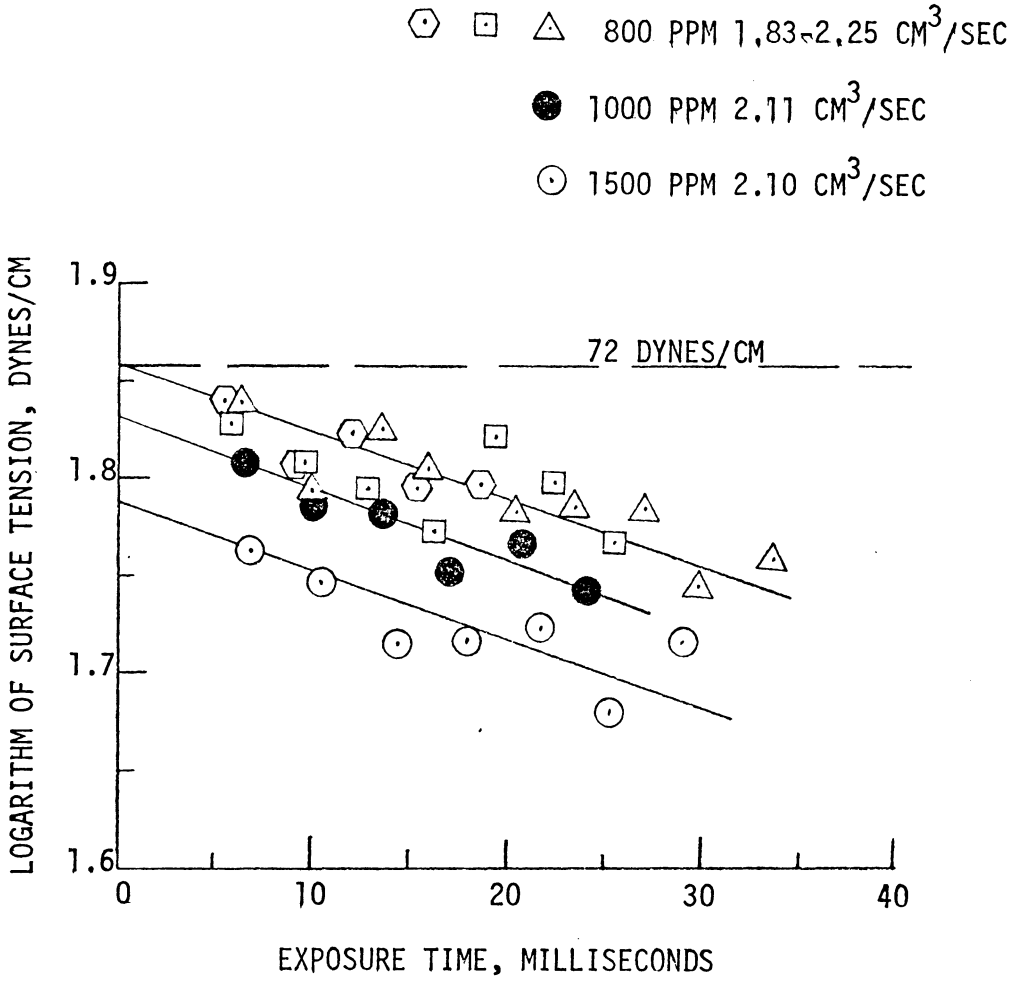


FIGURE 17. FIRST-ORDER RATE EXPRESSION IN SURFACE TENSION FOR SODIUM DODECYL SULFATE

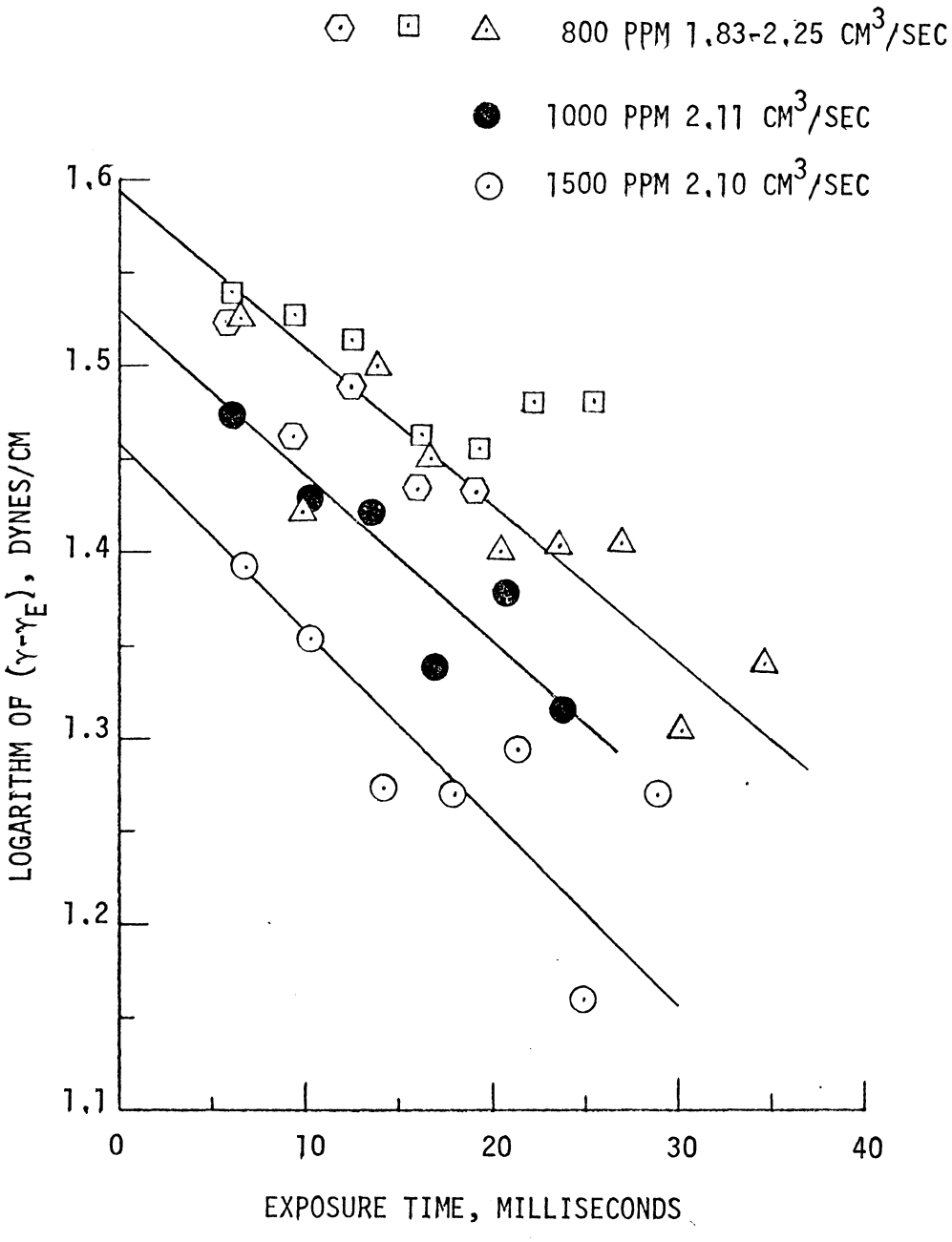


FIGURE 18. FIRST-ORDER RATE EXPRESSION IN $(\gamma-\gamma_E)$ FOR SODIUM DODECYL SULFATE

IV. DISCUSSION

This section contains a discussion of the results obtained in this, as well as previous investigations. An analysis of the procedure is also given. Finally, recommendations for further work and the limitations of the present study are given.

Discussion of the Literature

In the following paragraphs, results obtained in previous investigations, where available, are compared to those found in this study.

Equilibrium Surface Tensions. Figure 4 presents equilibrium surface tension results obtained by several workers, using a variety of methods. All used pure sodium dodecyl sulfate (SDS). The discordant results display, in striking fashion, the uncertainty involved in this data.

Phillips [26], in a study of micelle formation, reports a critical micelle concentration (CMC) of SDS in water of 0.008 moles per liter. Cook and Talbot [7], Nutting, Long and Harkins [21], as well as the present author are in agreement with this value. Pethica [25] and Herbert [19], however, both obtained static surface tension values that indicated a CMC of only 0.001 moles per liter, or almost a factor of ten different from the above authors. These results are even more staggering when one considers that the present author and Herbert [19] performed their measurements on the same instrument in the same laboratory.

Figure 6 indicates that discrepancies, similar to those above, exist for dodecyl diethanol amide (DDA). The values of the CMC for this compound, as well as dodecyl trimethyl ammonium bromide (DTAB), Figure 5, do however, agree fairly well.

In view of the above facts, it is impossible to deduce, with any degree of confidence, values of the surface excess. This follows directly, since surface concentrations are calculated from the slopes of the equilibrium surface tension curves. Critical micelle concentrations can, however, be determined with reasonable accuracy from the equilibrium values.

Discussion of Procedure

Difficulties encountered in measuring dynamic surface tensions and evidence to verify the technique used are presented in this section.

Experimental Problems. Several difficulties were met in determining the dynamic surface tensions. The first of these occurred in preparing the feed solution. All of the surfactants studied, foamed considerably. Because foam represents an area of highly concentrated solute, this was to be avoided. Therefore, the feed solution was added to the holding tank through a length of 1/2 inch tygon tubing, which extended to the bottom of the tank. This lessened, but did not eliminate, the foaming and it was therefore necessary to wait from one to two hours for the foam to settle. A uniformly concentrated solution was then available for testing.

In measuring the jet dimensions it was necessary to visually determine the distance between the nodes through the cathetometer. This proved to be the major experimental difficulty, since at the flow rates used the nodes were not sharply defined peaks, but rather smooth plateaus. Thus, the wavelengths are probably in error by no more than about 5 percent. For a dynamic surface tension of 76.7 dynes per centimeter this would give an error of 5.8 dynes per centimeter, which is a reasonable upper bound.

At flow rates below approximately 1.50 milliliters per second the nodes were quite sharp and easily located, however the surface tensions measured (for pure water) were found to be considerably higher than would be expected. In particular, at exposure times below eight milliseconds the dynamic surface tension was over 80 dynes per centimeter, these values decreasing until at 15 milliseconds the surface tension was only 75 dynes per centimeter. Flow rates in this study were therefore restricted to 1.7 to 2.2 milliliters per second. The reason for the anomalous behavior at low flow rates is given in the section below.

Verification of the Oscillating Jet Technique. In order to check the validity of the experimental results, the dynamic surface tension of pure water was first determined. The results, shown in Figure 8, indicate that the surface tension was essentially independent of both exposure time and flow rate. Moreover, the average value of 75.7 dynes per centimeter is not significantly different from the accepted value of 72 dynes per centimeter. Agreement between

this work and that of Caskey and Barlage [6], using the same technique, is also quite good.

The slightly negative slope of the line in Figure 8 can best be explained in terms of the assumptions inherent in the Bohr equation. Specifically, it was assumed that (1) the wavelength is large in comparison to the diameter of the jet and (2) no velocity profile exists across the jet. These assumptions will now be examined in detail.

Bohr [5] in determining the surface tension of water, maintained a wavelength to diameter (λ/D) ratio which always exceeded ten. In this investigation the ratio was between 3.5 and 5.0, being larger at longer exposure times. This explains the negative slope as well as the slightly high values obtained in Figure 8. As the exposure time increases the λ/D ratio increases and the assumption is better satisfied.

The above reasoning may also be applied to the results obtained at low flow rates, where the wavelengths were small and the amplitudes large. As a numerical example, during the first fifteen milliseconds, for a flow rate of 1.36 milliliters per second the λ/D ratio varied from 2.5 to 3.0. Over the same time range, with a flow rate of 1.73 milliliters per second, this ratio varied from 3.9 to 4.3. These are significant differences and could easily account for the observed behavior.

Regarding the second assumption, it is conceivable that a small velocity gradient existed across the jet as it discharged from the orifice. The liquid flowed through a length of 1/4 inch tubing in laminar flow. It then impinged on the diaphragm where the middle

portion went through the orifice. If the velocity profile in that portion of the jet which issued forth from the orifice were significant, it would have been slowly damped out at longer exposure times due to viscous forces. The values, however, would have been high as shown by Hansen, et. al. [17]. This again would account for the negative slope in Figure 8 and the high values obtained.

One may conclude that, although the technique used in this study is not an exact method for determining dynamic surface tension, it does yield correct results to within several percent.

Discussion of Results

This section contains a discussion of the results obtained in this investigation, along with an analysis of the several models which were fitted to the data.

Empirical Correlation. The empirical model, Equation 9, was found to represent well, all of the data obtained in this study, as shown in Figures 9 through 15. Tables I and II display the deviations in the slopes for this model. The standard deviation about the mean slope for SDS is 7.1 percent and for DTAB, 19.8 percent. These values are within the range of experimental error. The assumption of a constant slope for each compound does not, therefore, seem unreasonable.

This model, however, predicts a concentration dependent dead time which takes the form of an abrupt discontinuity in slope, something which is not often found in nature. This causes the model to be suspect, at least from a theoretical viewpoint.

Defay and Hommelen [11] noted this same lag time in their studies with aqueous solutions of organic acids and alcohols. They explained this effect by saying that the surface tension "....starts decreasing appreciably when diffusion has driven sufficient solute into the surface to form a compact layer." Hansen [16], however, refuted this reasoning by showing that diffusion theory predicts an infinite slope at the origin, not a zero slope.

In a subsequent paper, Hansen [15] conceded that the adsorption does appear to be "....diffusion-controlled except for an initial time lag...." He went on to postulate two possible theoretical explanations for this: (1) there is a small initial barrier to adsorption which dissipates after a small amount of solute has adsorbed at the surface; (2) surface tension does not depend on the surface solute concentration in the same way at equilibrium as it does in the dynamic case.

Thus, although the empirical model is not theoretically based, it does yield results which are qualitatively consistent with previous investigations. Extrapolation would probably be quite risky, however.

Diffusion Model. In order to test the theory of Ward and Tordai [33], two concentrations of SDS were chosen for calculations. For lack of any more reliable data, the equilibrium surface tensions obtained in this study were used to determine surface excesses. The Equilibrium surface tension curve was fit to a polynomial in the natural logarithm of concentration [19]. The surface excess was then found analytically from the derivative of this function (Equation 3).

The results, shown in Table IV, indicate that back diffusion is negligible over the range of exposure times considered. Apparent diffusion coefficients vary by a factor of more than three. The diffusion coefficient should be independent of concentration.

As previously noted, the surface excess values are only rough estimates, in terms of reliability. The above, therefore, does not really represent a rigorous test of diffusion theory. In addition, great care should be taken in extrapolating the interpretations of Hansen [15], Hansen and Wallace [18], and Defay and Hommelen [10,11] to this study. Each of these workers was involved with simple organic compounds, while the surfactants used in this investigation were structurally more complex.

The evidence from this investigation, therefore, would exclude diffusion as being the rate-controlling step. This follows both from the equation of Ward and Tordai, and the initial zero slope of the dynamic surface tension curve.

First-Order Processes. Several investigators [4,20,27] have reported that adsorption kinetics are well represented by a first-order rate equation. An attempt was made to fit the dynamic surface tension data of this study to two such expressions.

Typical results of using a rate equation, first-order in surface tension, are shown in Figure 16. Although the data appears to have been linearized by this model, the intercepts are clearly incorrect; they indicate an initial surface tension depression, whereas at the

origin the surface tension should be that of pure water. That is, all curves should intersect the y-axis at 72 dynes per centimeter.

The results of using a rate equation which is first-order in the $(\gamma-\gamma_e)$ gradient are presented in Figure 17. (See Equation 6) It should be noted that the more concentrated solutions have smaller intercepts. Now, if the surface tension at the origin is constant at 72 dynes per centimeter, then the equilibrium surface tension must increase with increasing concentration. On the other hand, if we consider the equilibrium surface tensions as known constants, then the surface tension at the origin decreases with increasing concentration. Neither of these results are reasonable; the first is not in accord with any of the equilibrium surface tension curves, and the second is not consistent with <u>any</u> of the data in the literature. Therefore, this model must not be applicable here.

It is not at all obvious why other workers were able to use first-order expressions, however several possible explanations will be put forth.

Netzel, et. al. [20], working with Triton X-100, encountered no inconsistencies in their intercepts. However, these workers did not use the surface tensions of the Bohr equation directly. Instead, they applied a correction factor to their results. This correction was time-dependent and was obtained by correcting their results for pure water to give the desired values. This assumes, however, that the same factor will apply over any range of dynamic surface tensions. This was not shown to be true and their results, therefore, may be in error.

If the results of Netzel, et. al. [20] are correct then they may have been able to use a first-order model because of the nature of the surfactant. Triton X-100 is a nonionic surfactant, derived from ethylene oxide. It would probably act most like the nonionic surfactant used in this study. Unfortunately, the data on DDA below the CMC was not sufficiently complete for comparison.

Austin, et. al. [4] studied solutions of Manoxol OT and reported that their results are explained by a first-order mechanism. On close examination of their data, however, a first-order dependence appears to hold only at lower concentrations. In salt solutions their data do indicate a first-order mechanism, but this would not apply to this investigation. It should also be mentioned that Manoxol OT is not a pure material. It is an ionic surfactant containing 0.2 percent sodium sulfate, and this may have affected the results.

Posner and Alexander [27] fitted their data to a model which was first-order in the surfact potential gradient. As was previously mentioned, Addison and Litherland [2] subsequently showed that surface potential is not simply related to surface tension. This is sufficient reason to doubt the applicability of the first-order model in their case.

Comparison of Surfactants. The results of applying the above models to both the SDS and DTAB are equally valid. This is not especially surprising, since both are monovalent ionic surfactants with a twelve carbon chain. Moreover, the data for both of these materials was taken below the CMC (as found in this work and reported

by Phillips [26]). The ionic charge on the hydrocarbon chains are opposite, however, and this might have made some difference.

The data from DDA was originally meant to complete the set of anionic, cationic, and nonionic surfactants. Unfortunately, it was necessary to exceed the CMC by a factor of greater than five to obtain any surface tension decrease within the exposure times studied. This is shown in Figure 11. The fact that the only meaningful tests that could be made with DDA were above the CMC, precluded any comparison with the other two surfactants.

It is worth noting, however, that the tests made at 100 and 500 parts per million DDA (Figure 11) were unusually high. In fact, the average value of the dynamic surface tensions at 100 parts per million was 76.5 dynes per centimeter as compared to only 75.7 dynes per centimeter for pure water. Data taken with SDS at low concentrations gave values that were more in line with pure water. At ten parts per million the average was 75.8 dynes per centimeter and at 200 parts per million the average was 74.6 dynes per centimeter.

The low concentration behavior of DDA suggests that it acts differently from the other surfactants studied. One possibility is that it sets up some type of hydrodynamic effect in the jet, which is not accounted for in the Bohr equation. For example, a superficial viscosity may exist.

Recommendations

This section contains suggestions for future work as well as possible improvements in the techniques used in this study.

Location of Nodes. In future studies with the oscillating jet technique a simple optical method for locating the nodes should be found. This is the major experimental difficulty with the technique and it would undoubtedly yield more accurate data.

Orifice. Another orifice with a smaller eccentricity should be constructed. This would increase the ratio of wavelength to jet diameter, in accord with the assumption inherent in the Bohr equation. With the incorporation of an optical method to locate the nodes this would cause no experimental difficulty.

Equilibrium Surface Tensions. These values should be accurately determined and the reasons for the discrepancies in the literature investigated. This would allow a rigorous test of the diffusion theory and possibly open the door for testing several other models.

Longer Exposure Times. Other methods of measuring dynamic surface tensions at greater exposure times should be investigated. One of these might be the falling meniscus method. Adsorption kinetics over a longer interval could then be found. In addition, the behavior of compounds such as dodecyl diethanol amide could be determined at low concentrations.

V. CONCLUSIONS

A study of the dynamic surface tensions of aqueous solutions of sodium dodecyl sulfate, dodecyl trimethyl ammonium bromide, and dodecyl diethanol amide, at 25°C, led to the following conclusions.

1. The technique used in this study is not exact, but does yield meaningful data which is correct to within five percent.

2. Data taken in this investigation was found to be well represented by the empirical equation, $\gamma = kt^m$. The coefficient, k, is concentration dependent, while the exponent, m, was found to depend only on the surfactant used. Both of these parameters were determined for sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide. Only m was determined for dodecyl diethanol amide.

3. The dynamic surface tension of dodecyl diethanol amide for solutions below the CMC did not decrease appreciably during the first thirty milliseconds.

4. Evidence from this investigation indicated that diffusion is not rate-controlling in the adsorption process.

5. A first-order rate expression does not describe the adsorption kinetics, since it introduces serious inconsistencies.

6. Sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide behave in a similar manner, from a kinetic viewpoint.

VI. SUMMARY

The purpose of this investigation was to study the adsorption rates of aqueous solutions of sodium dodecyl sulfate, dodecyl trimethyl ammonium bromide and dodecyl diethanol amide, at 25°C.

The oscillating jet method was used to obtain dynamic surface tensions at varying concentrations for each surfactant. A diaphragm type orifice was used. The apparatus was checked with distilled and de-ionized water, and was shown to yield reliable results to within 5 percent.

A diffusion model and two first-order rate expressions were tested using the dynamic surface tension data. Both models were found to be inadequate in describing the adsorption.

An empirical equation was developed which relates dynamic surface tension to time. This is a two parameter model, one of the parameters being concentration dependent and the other a constant, characteristic of the surfactant used.

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IX. APPENDIX

This section contains the data tables, lists of materials and apparatus, and sample calculations. In addition, details of the orifice construction and the calibration of the cathetometer are given.

Data Tables

The data taken during this investigation is given in this section.

Equilibrium Surface Tensions. Tables V through VII present the equilibrium surface tension results for the surfactants studied. The correction factor was calculated from Equations 7 and 8 and the data in the tensiometer manual. (13)

Surface Excess. Table VIII shows the variation of surface concentrations with bulk concentration for sodium dodecyl sulfate. These values were used to test the diffusion model.

Dynamic Surface Tensions. Tables IX through XXIX give the original, as well as the reduced dynamic surface tension data. The "Jet Height" is the vertical cathetometer reading, the first entry being at the orifice. The "Jet Diameter" is the diameter of the jet at the nodes and is expressed in revolutions of the vernier dial on the cathetometer. The conversion factor to centimeters is given at the bottom of each table.

TABLE V

Equilibrium Surface Tensions of Sodium Dodecyl Sulfate

Concentration	Apparent Surface Tension	Correction Factor	Actual Surface Tension
ppm	dynes/cm		dynes/cm
3000	36.7	0.894	32.8
2000	37.3	0.894	33.3
1000	38.7	0.896	34.7
400	42.5	0.901	38.3
250	45.6	0.904	41.2
200	47.3	0.906	42.8
100	50.5	0.910	46.0
50	53.0	0.912	48.3
25	56.5	0.916	51.8
10	60.1	0.920	55.3
5	63.1	0.923	58.2

TABLE VI

Equilibrium Surface Tensions of Dodecyl Trimethyl Ammonium Bromide

Concentration	Apparent Surface Tension	Correction Factor	Actual Surface Tension
ppm	dynes/cm		dynes/cm
6000	39.1	0.897	35.0
3000	38.5	0.896	34.5
1500	40.1	0.898	36.0
1000	41.2	0.899	37.0
750	42.1	0.900	37.9
500	45.4	0.904	41.0
200	49.8	0.909	45.2
100	52.2	0.911	47.6
50	55.3	0.915	50.6
25	56.6	0.916	51.8
10	57.5	0.917	52.7
5	58.4	0.918	53.6

TABLE VII

Equilibrium Surface Tensions of Dodecyl Diethanol Amide

Concentration	Apparent Surface Tension	Correction Factor	Actual Surface Tension
ppm	dynes/cm		dynes/cm
500	31.3	0.887	27.8
400	31.8	0.888	28.2
200	31.4	0.887	27.9
100	32.4	0.889	28.8
50	33.1	0.890	29.4
25	36.0	0.893	32.1
10	39.1	0.897	35.0
5	45.8	0.904	41.4
2.5	54.7	0.914	50.0
1	61.7	0.921	56.8
0.5	65.3	0.925	60.4

TABLE VIII

Surface Excess of Sodium Dodecyl Sulfate

Concentration ppm	Surface Excess moles/cm^2 x 10^{10}
2000	0.884
1000	0.881
400	0.878
250	0.876
200	0.875
100	0.872
50	0.870
25	0.867
10	0.864
5	0.861
1	0.855

TABLE IX

Dynamic Surface Tension of Water at a Flow Rate of 2.119 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.4735	---		
4.1850	17.15		
2.8365	24.94	76.9	5.96
3.4755	17.09	75.1	9.21
3.1135	24.31	73.0	12.37
2.7380	17.08	72.9	15.56
2.3730	23.84	78.0	18.60
2.0245	17.13		

[a] 0.00665 centimeters per revolution

TABLE X

Dynamic Surface Tension of Water at a Flow Rate of 1.932 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.3450	---		
4.0890	17.38		
3.7950	24.82	78.6	5.64
3.4660	17.48	77.0	8.87
3.1615	24.05	76.6	11.78
2.8265	17.38	72.1	14.88
2.4940	23.30	77.2	17.88
2.1815	17.28		

[a] 0.00665 centimeters per revolution

TABLE XI

Dynamic Surface Tension of Water at a Flow Rate of 1.728 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.9410	---		
4.7255	18.08		
4.4605	24.22	75.8	5.54
4.1760	17.96	77.5	8.67
3.9140	23.32	77.3	11.46
3.6225	17.74	73.2	14.48
3.3365	22.69	76.7	17.35
3.0575	17.60	76.7	20.08
2.7675	22.06	71.8	22.84
2.4600	17.35		

[a] 0.00665 centimeters per revolution

TABLE XII

Dynamic Surface Tension of a 400 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow Rate of 2.163 cm^3/sec

Jet Height cm	Jet Diameter revs[a]	Surface Tension dynes/cm	Exposure Time milliseconds
4.7320	---		
4.4295	17.28		
4.0560	24.84	73.0	6.25
3.6850	17.50	73.6	9.54
3.3120	23.79	75.1	12.75
2.9465	17.63	69.9	15.82
2.5395	22.87	70.9	19.15
2.1770	17.76	66.6	22.04
1.7395	22.09	67.6	25.45
1.3795	17.72		

[a] 0.00665 centimeters per revolution

TABLE XIII

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow Rate of 2.246 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7290	---		
4.4015	17.18		
3.9940	24.73	69.0	6.54
3.5950	17.39	62.0	9.94
3.1355	23.70	67.0	13.75
2.7690	17.50	63.6	16.70
2.2835	22.96	60.5	20.51
1.8890	17.50	60.9	23.53
1.4035	22.34	61.0	27.15
1.0080	17.66	55.6	30.03
0.4735	21.33	57.4	33.84
0.0895	17.81		

[a]0.00665 centimeters per revolution

TABLE XIV

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow Rate of 1.877 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7300	---		
4.4665	17.69		
4.1655	24.46	67.6	6.00
3.8115	18.02	64.6	9.58
3.4910	23.41	62.6	12.71
3.1205	18.16	59.6	16.23
2.7775	22.57	66.6	19.38
2.4475	18.11	62.7	22.34
2.0760	21.82	58.6	25.58
1.7125	17.86		

[a]0.00665 centimeters per revolution

TABLE XV

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow rate of 1.832 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7320	---		
4.4805	17.76		
4.1875	24.34	68.9	5.92
3.8525	18.10	64.5	9.39
3.5320	23.29	66.5	12.60
3.2045	18.15	62.7	15.79
2.8580	22.54	62.6	19.05
2.5260	18.13		

[a]0.00665 centimeters per revolution

TABLE XVI

Dynamic Surface Tension of a 1000 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow Rate of 2.111 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7370	---		
4.4265	17.31		
4.0360	24.66	64.4	6.62
3.6470	17.55	61.4	10.13
3.2330	23.62	61.0	13.75
2.8370	17.60	56.5	17.11
2.3840	22.80	58.6	20.85
1.9990	17.39	55.4	23.94
1.5125	21.83		

[a] 0.00665 centimeters per revolution

TABLE XVII

Dynamic Surface Tension of a 1500 ppm Aqueous Solution of Sodium Dodecyl Sulfate at a Flow Rate of 2.104 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7325	---		
4.4390	17.32		
4.0165	24.89	58.2	6.78
3.6185	17.50	56.1	10.38
3.1760	23.75	52.2	14.24
2.7375	17.42	52.2	17.96
2.2890	22.90	53.2	21.64
1.8565	17.46	47.9	25.10
1.3525	22.02	52.1	29.01
0.9580	17.52		

[a]0.00665 centimeters per revolution

TABLE XVIII

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 2.064 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7335	---		
4.4540	17.23		
4.0920	24.71	69.3	6.20
3.2760	17.59	67.8	9.59
3.3535	23.70	65.1	12.94
2.9670	17.73	63.9	16.31
2.5840	22.94	65.3	19.55
2.2035	17.74	66.7	22.70
1.8265	22.26	64.8	25.74
1.4305	17.76	62.6	28.85
1.0340	21.39		

[a]0.00665 centimeters per revolution

TABLE XIX

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 1.853 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Times
cm	revs[a]	dynes/cm	milliseconds
4.7365	---		
4.4840	17.61		
4.1830	24.53	71.2	5.95
3.8600	18.09	69.0	9.26
3.5455	23.39	68.6	12.39
3.2155	18.10	67.4	15.57
2.8900	22.55	66.8	18.61
2.5525	18.09	64.0	21.69
2.2065	21.85		

[a] 0.00665 centimeters per revolution

TABLE XX

Dynamic Surface Tension of an 800 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 1.805 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7315	---		
4.5035	17.74		
4.2090	24.34	70.1	5.77
3.8940	18.24	69.3	9.08
3.5945	23.30	67.2	12.14
3.2635	18.27	64.6	15.41
2.9440	22.30	64.0	18.47
2.6045	18.24	65.9	21.63
2.2920	21.48	65.4	24.46
1.9445	18.18		

[a]0.00665 centimeters per revolution

TABLE XXI

Dynamic Surface Tension of a 1000 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 2.120 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7360	---		
4.4285	17.20		
4.0625	24.73	67.0	6.34
3.6615	17.45	64.3	9.95
3.2755	23.71	63.8	13.33
2.8665	17.50	59.8	16.80
2.4475	22.76	61.8	20.25
2.0485	17.48	60.1	23.46
1.6130	22.08	60.6	26.87
1.2150	17.51	60.4	29.91
0.7750	21.56	59.5	33.20
0.3645	17.17		

[a]0.00665 centimeters per revolution

TABLE XXII

Dynamic Surface Tension of a 1500 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 2.131 cm^3/sec

Jet Height cm	Jet Diameter revs[a]	Surface Tension dynes/cm	Exposure Time milliseconds
4.7375	---		
4.4120	17.07		
4.0240	24.78	60.5	6.68
3.5920	17.30	57.1	10.53
3.1750	23.83	56.5	14.14
2.7345	17.35	54.7	17.83
2.2990	23.03	55.9	21.38
1.8660	17.45	53.7	24.81
1.4080	22.23	53.2	28.34
0.9640	17.25		

[a] 0.00665 centimeters per revolution

TABLE XXIII

Dynamic Surface Tension of a 2000 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 2.101 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7310	---		
4.4140	16.96		
3.9990	24.84	54.1	6.94
3.5535	17.19	49.5	10.96
3.0930	23.85	52.4	14.97
2.6710	17.21	51.6	18.53
2.1990	22.89	49.8	22.39
1.7560	17.30	50.1	25.91
1.2845	22.35	51.0	29.56
0.8460	17.15		

[a] 0.00665 centimeters per revolution

TABLE XXIV

Dynamic Surface Tension of a 2000 ppm Aqueous Solution of Dodecyl Trimethyl Ammonium Bromide at a Flow Rate of 1.877 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7315	---		
4.4530	17.26		
4.0860	24.74	55.1	6.82
3.7100	17.69	50.4	10.59
3.3035	23.60	52.0	14.52
2.9355	17.70	50.9	17.96
2.5155	22.68	48.8	21.75
2.1220	17.46	50.4	25.19
1.7095	21.77	49.1	28.70
1.3000	17.43		

[a] 0.00665 centimeters per revolution

TABLE XXV

Dynamic Surface Tension of a 100 ppm Aqueous Solution of Dodecyl Diethanol Amide at a Flow Rate of 2.126 cm^3/sec

Jet Height cm	Jet Diameter revs[a]	Surface Tension dynes/cm	Exposure Time milliseconds
4.7240	---		
4.4345	16.95		
4.0800	25.15	76.9	6.06
3.7190	16.80	76.4	9.31
3.3575	24.43	75.4	12.48
2.9875	16.75	76.5	15.64
2.6285	23.78	76.5	18.63
2.2550	16.64	72.1	21.67
1.8665	23,10	76.8	24.75
1.5175	16.70		

[a]0.00665 centimeters per revolution

TABLE XXVI

Dynamic Surface Tension of a 100 ppm Aqueous Solution of Dodecyl Diethanol Amide at a Flow Rate of 1.852 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.7255	---		
4.4850	17.30		
4.1990	24.90	80.0	5.67
3.8980	17.23	75.6	8.77
3.5870	24.12	78.6	11.88
3.2965	17.17	78.1	14.70
2.9800	23.45	73.8	17.69
2.6645	17.08	74.2	20.59
2.3460	22.72	79.5	23.44
2.0515	16.89		

[a] 0.00665 centimeters per revolution

TABLE XXVII

Dynamic Surface Tension of a 500 ppm Aqueous Solution of Dodecyl Diethanol Amide at a Flow Rate of 2.106 cm^3/sec

Jet Height cm	Jet Diameter revs[a]	Surface Tension dynes/cm	Exposure Time milliseconds
4.7315	---		
4.4580	17.05		
4.0955	25.09	76.9	6.04
3.7530	17.06	74.5	9.16
3.3740	24.28	73.6	12.51
3.0235	17.07	73.5	15.53
2.6400	23.35	70.1	18.75
2.2665	17.21		

[a] 0.00665 centimeters per revolution

TABLE XXVIII

Dynamic Surface Tension of a 500 ppm Aqueous Solution of Dodecyl Diethanol Amide at a Flow Rate of 1.830 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.9390	---		
4.7055	17.62		
4.4250	24.77	79.2	5.60
4.1290	17.68	78.3	8.69
3.8410	23.86	75.9	11.60
3.5295	17.71	74.3	14.66
3.2300	22.96	74.8	17.52
2.9175	17.79	68.4	20.43
2.5805	22.10	72.0	23.48
2.2840	17.83		

[a] 0.00665 centimeters per revolution

TABLE XXIX

Dynamic Surface Tension of a 1000 ppm Aqueous Solution of Dodecyl Diethanol Amide at a Flow Rate of 2.073 cm^3/sec

Jet Height	Jet Diameter	Surface Tension	Exposure Time
cm	revs[a]	dynes/cm	milliseconds
4.6575	---		
4.3785	17.11		
4.0320	24.85	75.1	6.03
3.6800	17.51	70.4	9.28
3.3050	23.72	69.0	12.64
2.9410	17.68	66.6	15.82
2.5495	23.04	64.8	19.14
2.1705	17.64	60.4	22.27
1.7440	22.35	62.3	25.70
1.3740	17.50		

[a] 0.00665 centimeters per revolution

Sample Calculations

This section contains examples of the calculations carried out while reducing the data.

Dynamic Surface Tensions. To reduce the jet dimensions and flow rate data to dynamic surface tensions, Equation 1 was used. Jet diameter was not measured at the orifice because of possible disturbances in the flow pattern there. Referring to the first entry in Table IX:

$$r_m = 24.94 \text{ revs} \times 0.00665 \frac{\text{cm}}{\text{rev}} \times \frac{1}{2}$$

$$r_i = \frac{17.15 + 17.09}{2} \text{ revs} \times 0.00665 \frac{\text{cm}}{\text{rev}} \times \frac{1}{2}$$

$$\rho = 1.00 \text{ gm/ml}$$

$$\gamma = 4.185 \text{ cm} - 3.4755 \text{ cm}$$

$$r = \frac{r_m + r_i}{2}$$

$$\frac{b}{a} = \frac{r_m - r_i}{r_m + r_i}$$

And γ is calculated to be 76.9 dynes/cm

Surface tensions were calculated at each successive node, using the average values of the end nodes.

Exposure times were calculated by assuming the jet to be a freely falling body. The center node of the wavelength was considered to be the distance from the orifice. The initial velocity was taken to be the volumetric flow rate divided by the area of the orifice. Thus,

$$t = \frac{-v_0 + \sqrt{v_0^2 + 2Lg}}{g \times 0.001}$$

where:

$v_0 = D/\pi ab$ = initial velocity at orifice, cm/sec

t = exposure time, msec

D = volumetric flow rate, cm^3/sec

a,b = semi-major and minor axes of orifice, cm

L = distance from orifice, cm

$g = 980\ cm/sec^2$

Again with reference to the first entry in Table IX:

$D = 2.119\ cm^3/sec$

$L = 1.6370$ cm

$a = 0.09595$ cm

$b = 0.06825$ cm

And the exposure time is calculated to be 5.96 msec.

Surface Excess. The equilibrium surface tension curve was fit, by least squares, to the following polynomial, (19)

$$\gamma = A + B_1 \ln c + B_2 \ln^2 c$$

where A, B_1 and B_2 are the regression coefficients. For sodium dodecyl sulfate these were found to be:

$A = 10.38$

$B_1 = -4.47$

$B_2 = -0.00929$

The surface excess now follows directly from Equation 3,

$$\Gamma = \frac{-(B_1 + 2B_2 \ln c)}{2RT}$$

Or, for SDS at 25°C and a concentration of 2000 ppm (6.94×10^{-6} moles/cm^3), the surface excess is 0.884×10^{-10} moles/cm^2.

Diffusion Model. To test the theory of Ward and Tordai [33], a rather extensive calculational procedure was required. The calculations are outlined below for SDS at a concentration of 800 ppm.

The data was first smoothed using the empirical model, Equation 9. From the smoothed dynamic surface tensions and the equilibrium surface tensions (Figure 4), the sub-surface concentrations, $\phi(z)$, were found for exposure times of five to thirty milliseconds, in five millisecond intervals. The quantity $(t - z)^{1/2}$ was also calculated at these times. These values follow:

z	$\phi(z)$	$(t - z)^{1/2}$
msec	moles/cm^3 x 10^6	sec$^{1/2}$
0	0.0	0.1732
5	1.0	0.1581
10	3.5	0.1414
15	6.1	0.1225
20	8.6	0.1000
25	12.5	0.0707
30	14.0	0.0000

The integral in Equation 5 was then solved numerically by Simpson's Rule. The results of these calculations are presented in Table IV, page 42.

Cathetometer Calibration

Because the coordinate cathetometer used in this study did not give direct readings in the horizontal direction, it was necessary for it to be calibrated.

An American-Optical Micrometer was used to calibrate the instrument. The micrometer was a microscope slide with a two millimeter scale, graduated in 0.01 millimeter divisions.

The cathetometer was found to move 0.00665 centimeters in the lateral direction, for every revolution of the vernier dial. This calibration was for the focal length used throughout this study.

Orifice Construction

The elliptical orifice used in determining dynamic surface tensions was fashioned by a trial and error procedure.

A short length of 1/8 inch stainless steel tubing was milled to a 1/16 inch circular cross-section at one end. This was placed between two aluminum blocks, which had been notched with curved grooves to fit the tubing. Pressure was then applied to the blocks in a mechanical press, elongating the circular hole to an oval cross-section.

This punch was now used to make several orifices in a sheet of two mil Mylar film. A nylon block was used as a base for punching. Those holes which were smoothly cut were measured with the cathetometer to determine whether or not they were ellipses.

If the punch did not produce an elliptical hole, it was gently worked to the desired cross-section with a thin piece of metal rod. After several trials, an orifice which conformed to the equation of an ellipse was made.

The orifice was then secured to the face of a 1/4 inch Swagelok tubing nut with silicone rubber bathtub caulk. It was subsequently coated with paraffin.

Materials

The following materials were used in the experimental phase of this study.

Cleaning Solution. A mixture of sodium dichromate, water and sulfuric acid, prepared from the laboratory stock of chemicals. Used to clean glassware.

Dodecyl Diethanol Amide. No. 4303. Obtained from K & K Laboratories, Inc., Plainview, New York. Used for determination of equilibrium and dynamic surface tensions.

Dodecyl Trimethyl Ammonium Bromide. No. 13370. Obtained from K & K Laboratories, Inc., Plainview, New York. Used for determination of equilibrium and dynamic surface tensions.

Methyl Ethyl Ketone. Technical Grade. Obtained from Fisher Scientific Co., Fair Lawn, New Jersey. Used to clean Tensiometer ring.

Mylar. Film, two mils thick. Donated by E. I. Dupont de Nemours, Inc., Wilmington, Delaware. Used to make orifice.

Sealant. Silicone rubber bathtub caulk, manufactured by Dow Corning Corp., Midland, Michigan. Used to seal tanks of dynamic surface tension apparatus.

Sodium Dodecyl Sulfate, U. S. P. No. 9625 . Obtained from K & K Laboratories, Inc., Plainview, New York. Used for determination of equilibrium and dynamic surface tensions.

Apparatus

The following laboratory equipment was used to determine the equilibrium and dynamic surface tensions.

Balance. Double-pan, analytical, Model No. 220-D, capacity 200 gm. Accurate to 0.0001 gm. Manufactured by Voland and Sons, Inc., New Rochelle, New York. Used to weigh surfactants.

Constant Head Tank Assembly. Constructed from plexiglass and stainless steel tubing by the Chemical Engineering Shop, from available materials. The constant head tank (E in Figure 3), provided a four inch head of water. Used to determine dynamic surface tensions.

Coordinate Cathetometer. Manufactured by Gaertner Scientific Co. Vertical range of five cm, horizontal range of approximately 0.2 cm, depending on focal length adjustment. Vertical graduations of 0.0005 cm. Horizontal graduations for focal length used in this study were 0.0000665 cm. Used for measuring jet dimensions and coordinates of orifice.

De-Ionizer. Bantam, Model BD-1, flow rate, ten gal/hr, 110v, 60 cycle. Manufactured by Barnstead Still and Sterilizer Co., Boston, Massachusetts. Used to de-ionize distilled water.

Dishes, Petri. Made of pyrex glass. Obtained from Fisher Scientific Co., Pittsburgh, Pennsylvania. Used as containers for surfactant solutions, during equilibrium surface tension measurements.

Flasks, Volumetric. 100, 250, 500 and 1000 ml. Obtained from Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to make up surfactant solutions.

Lamp. Microscope illuminating type, Catalog No. 31-33-93. Manufactured by Bausch and Lomb Optical Co., Rochester, New York. Used to illuminate jet for readings with cathetometer.

Pipettes. 1, 10 and 15 ml. Obtained from Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to make up surfactant solutions.

Tensiometer, du Nouy. Model 20, range 0 to 90 dynes/cm, graduated in increments of 0.1 dynes/cm. Manufactured by Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to determine equilibrium surface tensions.

Timer. Catalog No. 69230, 120v, 60 cycle, accurate to 0.1 seconds. Obtained from Precision Scientific Co., Pittsburgh, Pennsylvania. Used to measure flow rates.

THE KINETICS OF ADSORPTION AT THE AIR-WATER INTERFACE FOR A SERIES OF TWELVE CARBON SURFACTANTS

by

Stephen J. Fisher

ABSTRACT

The purpose of this investigation was to study the adsorption rates of aqueous solutions of sodium dodecyl sulfate, dodecyl trimethyl ammonium bromide and dodecyl diethanol amide, at 25°C.

The oscillating jet method was used to obtain dynamic surface tensions at varying concentrations for each surfactant. A diaphragm type orifice was used. The apparatus was checked with distilled and de-ionized water, and was shown to yield reliable results to within 5 percent.

A diffusion model and two first-order rate expressions were tested using the dynamic surface tension data. Both models were found to be inadequate in describing the adsorption.

An empirical equation was developed which relates dynamic surface tension to time. This is a two parameter model, one of the parameters being concentration dependent and the other a constant, characteristic of the surfactant used.