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**THE EFFECT OF DETERGENTS ON
GAS ABSORPTION PROCESSES**

Jerry A. Caskey

Ralph F. Herbert

Yan Pui To

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Jerry A. Caskey
Assistant Professor
Department of Chemical Engineering
Virginia Polytechnic Institute
and State University

Ralph F. Herbert
Graduate Student
Department of Chemical Engineering

Yan Pui To
Graduate Student
Department of Chemical Engineering

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Water Resources Research Center
Virginia Polytechnic Institute
and State University
Blacksburg, Va.
April 1971

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Dr. A. G. ...
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University of ...
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Dr. ...
Department of ...
University of ...
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Dr. ...
Department of ...
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Dr. ...
Department of ...
University of ...
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PREFACE

During the past ten years there has been an increasing public awareness of the effect of detergents on our waters. Such phenomena as foaming and biodegradability have become well-known topics of concern. Each of these problems has been dealt with by tailoring the detergent molecule.

There is another problem with detergents in that they lower the efficiency of secondary waste treatment plants by reducing oxygenation rates. This report looks at several different types of surfactant molecules and discusses their effects on gas absorption rates.

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I. INTRODUCTION

Within the past two decades the effect of surfactants on mass transfer rates has received increasing attention in the chemical and chemical engineering literature. In the early 1920's, evaporation control by monolayers of insoluble surfactants was studied to conserve water supplies in lakes and reservoirs. It was found that monolayers do fulfill the requirement as an effective barrier to evaporation, and that they also should not be harmful to aquatic life or to subsequent users of the water. It was then that many investigations were conducted to study the effect of surfactants on absorption using gases essential to aquatic life.

The results of most of these experiments have been inconclusive for two main reasons: one, the techniques were not reliable enough to measure the transport of small quantities of gas, and two, the surfactants used were a mixture of several compounds. Therefore, it was not possible to determine whether the observed effect was due to a single compound or several compounds present at the interface.

During the past few years, there has been an increasing public awareness of ecology. Chemical and Sanitary Engineers have been especially aware of the problems presented to water pollution by various detergents which contain many surfactants. As the concern for the effect of the surfactants becomes important, engineers want to know the contribution of the sizes and interfacial orientation of the surfactant molecules to the interfacial resistance. Also a suitable model is necessary to describe the mass transfer. Much has been learned, but much remains unknown.

II. ABSTRACT

The purpose of this investigation was to determine the effect of the position and the molecular weight of the hydrophilic group on the rate of gas absorption.

A quiescent-state absorption apparatus was used with carbon dioxide and water as the absorption system. Six surfactants were selected for study, namely, n-octanol, 4-octanol, lauryl diglycol amide, lauryl diethanol amide, sodium lauryl sulfate, and sodium lauryl benzene sulfonate.

Preliminary absorption tests were made using pure deionized water to determine the diffusion coefficient for the system. A value of $1.93 \pm 0.05 \times 10^{-5}$ square centimeters per second was obtained. The absorption tests were repeated with the six surfactant solutions at different concentrations. Then the interfacial resistance for each solution was calculated.

The octanol with the hydroxyl group at a branched position was found to cause a higher interfacial resistance than those with hydroxyl groups at the end of the hydrophobic chain. It was also concluded that increasing the molecular weight of the hydrophilic group decreased the interfacial resistance.

III. LITERATURE REVIEW

Theory for Gas Absorption

In order to determine quantitatively the effect of surfactants on gas absorption rates, a mathematical model which can describe the system is needed. Several models have been developed with the assumption that the gas concentration at the liquid surface is in equilibrium with the gas phase due to a lack of knowledge about the interface.

Description of the System. Davis and Rideal¹² present a simple description of mass transfer across an interface. If a molecule of gas passes across the gas-liquid interface, it encounters a total resistance which is the sum of three separate resistances, (1) resistance through the gas phase, (2) resistance across the region constituting the interface, and (3) resistance through the liquid below the interface. Figure 1 diagrams these resistances.

Development of Model for Interfacial Resistance for Quiescent State Systems. Since it would be lengthy to present the development for all the models in the literature, only one will be reviewed here.

If a gas such as carbon dioxide is being absorbed into a liquid the resulting unsteady state is described by

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad [1]$$

where

C = concentration of the solute gas, gm mole/cm³

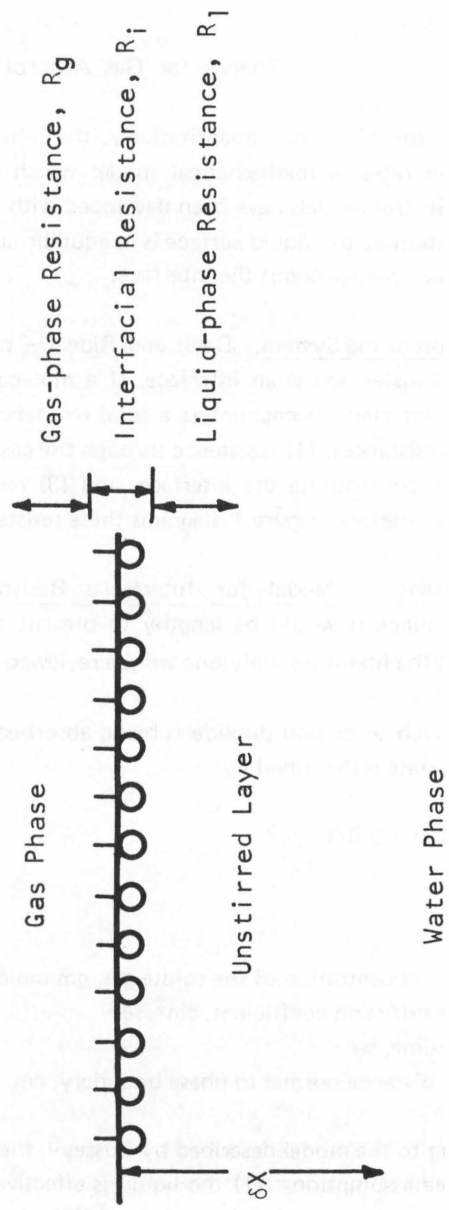
D = diffusion coefficient, cm²/sec

t = time, sec

x = distance normal to phase boundary, cm.

According to the model described by Bussey⁵, the boundary conditions come from three assumptions: (1) the liquid is effectively infinite in depth, (2) the absorption process is isothermal, and (3) the absolute pressure in the absorption vessel does not change significantly during the absorption period of interest.

FIGURE 1
TOTAL RESISTANCE AT GAS-WATER INTERFACE¹²



$$C(x, 0) = C_0 \quad [2]$$

$$C(\infty, t) = C_0 \quad [3]$$

$$C(0, t) = C_i(t) \quad [4]$$

The functional form of $C_i(t)$ indicates that Bussey⁵ does not assume equilibrium at the interface. Also, he assumes that the rate of gas absorption for surfactant solutions is proportional to the square root of time as for a pure water system. In terms of changes in pressure, a time dependent interfacial resistance was derived. Herbert²¹ gives a similar development in terms of a change in volume, thus adapting Bussey's development to the apparatus used in this investigation. The interfacial resistance is given by

$$R_i / \sqrt{t} = 1 / k_i \sqrt{t} = \left(\frac{\sigma_E - \sigma_R}{\sigma_E} \right) \sqrt{\frac{\pi}{D}} \quad [5]$$

where

R_i = interfacial resistance, sec/cm

k_i = interfacial mass transfer coefficient, cm/sec

σ_E = slope of gas uptake versus \sqrt{t} plot for pure carbon dioxide-water system, $\text{cm}^3/\text{cm}^2 \text{ sec}^{1/2}$

σ_R = slope of gas uptake versus \sqrt{t} plot for aqueous surfactant solution system, $\text{cm}^3/\text{cm}^2 \text{ sec}^{1/2}$.

Experimental Measurement of Interfacial Resistance

The interfacial resistance can be found by measuring the rate of gas absorption. Many experimental techniques have been devised, and Himmelblau²² has reviewed some of the methods used. The techniques fall into two categories: unsteady-state and steady-state. The unsteady-state quiescent systems will be reviewed here. The gases commonly used have been carbon dioxide, oxygen, sulphur dioxide, and ammonia.

Unsteady-State Quiescent Systems. This category has been used in many forms. Common to all of them, the major problems have been eliminating

convection currents caused by density differences, and isolating the system from vibrations which would upset the quiescent nature of the liquid.

One of the earlier workers to use this method was Carlson⁹ in 1911. To reduce convection, he added 1% potassium chloride to increase the density of the solution and assumed that the electrolyte has little effect on the diffusion coefficient. Very lengthy contact time was required. The whole apparatus was set on a firm base to prevent vibration.

Some workers attempted to eliminate convection by adding colloids to the liquid. Hagenbach¹⁶ used a 20% gelatin solution. He stated that the gelatin used offered greater resistance to the diffusing gas. Similarly, Tamman and Jessen³⁵ added agar to water with the assumption that agar has little effect on the rate of diffusion. Davidson and Cullen¹¹ suggested there is some evidence this assumption is true in specific cases, but it is unlikely that it is generally true.

Another way of eliminating convection is to enclose the liquid in a capillary thereby decreasing the size of the cylinder. The apparatus used by Ringbom³³ consisted of a gas-saturated and a gas-free water column (introduced from either end into a capillary tube) separated by a pure gas phase. The rate at which the gas-saturated water column was moving into the displaced gas phase gave a measure of the diffusion coefficient of the gas in water.

Blank¹ noticed when the gas uptake was plotted versus the square root of time, the curve was a straight line up to a certain time, about a few minutes, and then the slope began to change. He suggested that it was due to the onset of convection. Bussey⁷ noticed the same thing, and the same reason was given. Only this initial linear portion of the curve was used in their calculations. Blank¹ put a mercury substrate in the cell; no specific reason was given. McCutchen³⁰ recommended that the layer of mercury should be less sensitive to convection currents either from external motion or from the absorption process. This would increase the amount of data applicable to non-convective absorption represented by the initial portion of the absorption curves.

Many techniques of measuring the amount of gas absorption have been used. Carlson⁹ in 1911 analyzed the liquid. Gouy²² first considered the use of interferometric techniques in which the progress of diffusion of the gas into the liquid is followed and recorded by the change of the refractive index of

the liquid as a function of distance and time. Blank¹ used a Barcroft temperature-compensated differential manometer and recorded the height of the column as a function of time.

Later on, more sophisticated techniques were devised. Plevan and Quinn³² used a pressure transducer to measure the pressure difference. Bussey⁶ used a Decker differential pressure sensor and the output signal was amplified and then recorded continuously on a strip chart. However, he noticed the inability to measure short contact times and that the frequency response technique developed by Lamb²⁴ can overcome this problem.

Steady-State Laminar Flow System. This category includes the use of liquid jets and flow apparatus of different geometry²² such as wetted spheres, wetted wall columns, stirred flasks, flow in rectangular ducts, and rotating drums. However, only laminar jets will be reviewed here since they have been the most widely used.

Himmelblau²² gives a summary of the advantages of jets. "Jets are simple in design, have freedom from ripples, have small end effects, are stable and have such short time that surface active agents do not have time to adsorb to the surface. Above all they are rapid." Also, jets are very suitable for obtaining values for industrial work ($\pm 5\%$), and with more care, data of $\pm 1\%$ precision can be obtained.

Duda and Vrentas¹³ have done a rigorous analysis of jet hydrodynamics. They noted that laminar liquid jets possess several advantages over other methods. Yet there are still two uncertainties associated with jet absorption studies which must be resolved before this experimental technique can gain wide acceptance as an accurate method of measuring diffusion coefficients. The first is the possible existence of a significant resistance to mass transfer at the phase interface. If this is large, then short contact time equipment can be of little use. The second uncertainty is the influence of the jet hydrodynamics on the rate of mass transfer.

The Effect of Surfactants on Mass Transfer Rates

This section deals mainly with gas absorption, but other types of mass transfer will be mentioned if gas absorption literature is not available.

There have been many experiments reported on this topic. Most reports agree that surfactants do cause interfacial resistance and decrease the rate of gas

absorption. However, there are a few workers^{4,8,36} that have reported that some or all soluble surfactant monolayers do not produce an interfacial resistance. The retardation of water evaporation by surfactant monolayers has been much studied, but the permeability of monolayers to gases other than water vapor has not been examined as much.

Variables Investigated. The variables investigated in the existing literature are bulk concentration, surface concentration, temperature, structure of the surfactant molecules, and rate of agitation.

Most of the literature agrees that the rate of absorption decreases with increasing surfactant surface concentration. However, some investigators reported bulk concentration instead of surface concentration. Boyadzhiev³ and O'Connor³¹ noticed that for some surfactants the rate of absorption decreased with increasing surface concentration up to a limiting value.

Burnett,⁴ who studied straight-chained surfactants with four to twenty-four carbon atoms, observed that most insoluble surfactants decreased the rate of gas absorption while most soluble surfactants increased the absorption rates. He also concluded that the interfacial movements during gas absorption with soluble surfactants were caused by the Marangoni effect which is the generation of movement in an interface by longitudinal variations of interfacial tension.

Goodridge and Robb¹⁵ reported that the resistance due to surfactants decreased with rising temperature. However, nothing was found for the effect of pressure.

Several investigators^{1,2,10,20} have reported that interfacial resistance increases with increasing hydrophobic chain length. In addition to that, Caskey¹⁰ observed that the surface orientation of surfactant molecules changes the magnitude of gas absorption rates. Blank and Rougton² found that for the same hydrocarbon chain length the interfacial resistance varies with polar groups, the hydroxyl group being a more effective retarder than the carboxyl group; and that other factors besides molecular diameter are involved in the passage of small molecules through condensed monolayers. Herbert²⁰ observed that different surfactant hydrophilic functional groups cause different values of interfacial resistance, but no reason was found for the variation. As for the effect of agitation of the liquid phase, Goodridge and Robb¹⁶ found that the conductance of gas increases with higher rate of agitation.

On the whole, with the exception of chain length and concentration, not much has been done to determine the contribution of each of these variables to the interfacial resistance.

Causes of Interfacial Resistance. Goodridge and Robb¹⁵ suggest that the presence of surfactants in the interfacial region could have four effects which, working either singly or in conjunction, would account for the considerable reduction in absorption rates. They are the energy barrier effect, sieve effect, hydrodynamic effect, and interfacial turbulence effect. The energy barrier effect is caused by the potential energy barrier gas molecules must overcome in order to penetrate the surfactant film and enter the liquid. The sieve effect is caused by the film reflecting a fraction of the incoming gas molecules. The hydrodynamic effect is due to a boundary layer.

Goodridge and Robb¹⁵ mentioned that the carbon dioxide-water system does not exhibit any interfacial turbulence. They concluded that interfacial phenomena can be explained, in both a quantitative and qualitative manner, by postulating an energy barrier and a hydrodynamic effect operating at the same time.

IV. EXPERIMENTAL

This section includes the plan of experimentation, procedure, and results.

Plan of Experimentation

Literature Review. A survey of the literature shows that many studies have been made to determine the gross effect of surfactants on gas absorption. In spite of a number of studies concerning the hydrophobic chain length, no investigations have been made to study the effect of the hydrophilic functional group. The property selected for study in this investigation was the effect of the position and type of the hydrophilic functional group on gas absorption.

Selection of Apparatus. The unsteady-state quiescent absorption apparatus constructed by McCutchen²⁶ was used in this investigation. The apparatus is similar to the one used by Blank and Rougton² with a Barcroft differential manometer. It has a dummy cell on one side of the manometer to reduce the effect of temperature variation and a reaction cell on the other side of the manometer. The amount of gas absorbed is determined by the change in the height of the manometer fluid. Meriam D-3166 was chosen as the manometer fluid because of its low vapor pressure and low density.

Selection of System. Carbon dioxide was used as the absorbing gas throughout the investigation. N-octanol, 4-octanol, lauryl diglycol amide, lauryl diethanol amide, sodium lauryl sulfate, and sodium lauryl benzene sulfonate were used to study the effect of the position and type of hydrophilic functional groups. Octanols were used instead of decanols because the solubility of the decanols was too low.

Treatment of Data. The gas absorbed for deionized water was calculated and plotted versus the square root of time. The slope of the initial linear portion of the plot was used to calculate the diffusion coefficient. The average value of the diffusion coefficients was taken as the standard for this investigation. This provided a standard slope whereby the interfacial resistances for surfactant tests were calculated. A range could be seen from the tests made with pure deionized water, and a similar range was expected for the runs with surfactants.

The surface tension of the surfactant solutions at different concentrations was measured at 25°C. The surface tension data were plotted on semi-log

paper from which the surface concentration was calculated using Gibbs' adsorption isotherm. The surface concentration was required in order to correlate the interfacial resistances. Gas absorption tests were repeated for each surfactant at different bulk concentrations. The results for each surfactant were plotted as the interfacial resistance versus surface concentration.

Improvement of the Model. Originally, the uptake of carbon dioxide in surfactant solutions was considered to be a function of the square root of time, the same as for pure water. This assumption led to an interfacial resistance which was a function of time. In order to develop an interfacial resistance independent of time, another model was developed as outlined in the Appendix.

Procedure

Preparation of Surfactant Solution. The deionized water for both testing and making surfactant solutions was prepared by passing distilled water through a Bantam demineralizer. A flow rate of about ten gallons per hour was induced by pressurizing a metal tank containing the distilled water.

Surfactant solutions with specific concentrations were prepared by adding the correct amount of surfactant to the corresponding amount of deionized water in a volumetric flask. A double-pan analytical balance was used to weigh the surfactant. If the surfactant was a sparingly soluble liquid, a glass petri dish was used to weigh the surfactant as this eased washing the liquid into the volumetric flask. Lower concentrations were prepared by diluting the initial solution with deionized water using a pipette.

Constant Temperature Preparation. The room temperature was maintained at $25.0^{\circ} \pm 0.5^{\circ}\text{C}$. The room was cooled continuously with an air conditioner and the temperature was maintained by intermittently overriding the cooling with a warm air fan. A constant temperature bath was used to control the apparatus temperature. The temperature of the bath was maintained at $25.0^{\circ} \pm 0.05^{\circ}\text{C}$.

Equilibrium Surface Tension Measurement. Three separate samples were drawn from each surfactant solution of a specified concentration and were placed in covered petri dishes (to retard evaporation). The samples were allowed to sit for at least an hour to ensure that equilibrium conditions were reached. An apparent surface tension for each sample was measured with a

Fisher interfacial tensiometer. The average value of the three samples gave the apparent surface tension of the surfactant solution at a particular concentration. The actual equilibrium surface tension was obtained by applying a correction factor¹⁴ to the apparent surface tension.

Presaturation of a Solution for Absorption. The solution was placed in a side-arm flask which was connected to a vacuum pump, mercury manometer, and carbon dioxide gas source. The arrangement is shown in Figure 2. The supply valve A was closed and a vacuum was applied through valve B until the desired evacuation pressure was attained. Usually this evacuation pressure was at the bubble point, and the solution was allowed to degas for a short time. Valve B was then closed and carbon dioxide was allowed to enter through valve A until the system returned to atmospheric pressure. The procedure was repeated two times. The system was then closed and the magnetic stirrer turned on. As absorption took place, carbon dioxide was added to maintain a pressure near the atmospheric pressure. The solution became saturated in about twenty minutes when no further changes in the manometer height were seen. This pressure was the presaturation pressure of the solution.

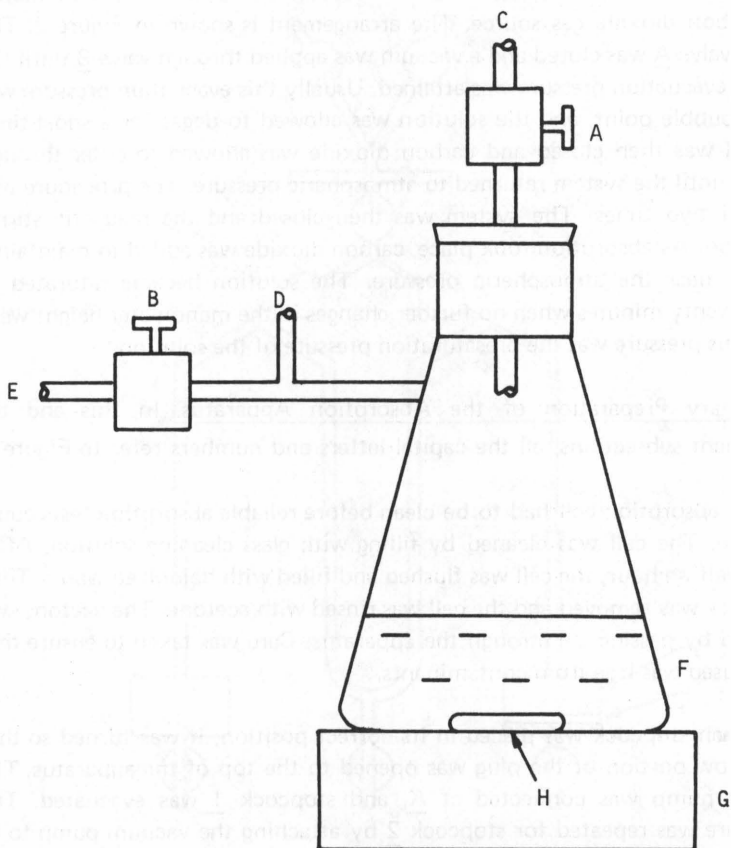
Preliminary Preparation of the Absorption Apparatus. In this and the subsequent subsections, all the capital letters and numbers refer to Figure 3.

The gas absorption cell had to be clean before reliable absorption tests could be made. The cell was cleaned by filling with glass cleaning solution. After about half an hour, the cell was flushed and filled with deionized water. Then the water was removed and the cell was rinsed with acetone. The acetone was removed by passing air through the apparatus. Care was taken to ensure that the air used was free from contaminants.

After each stopcock was placed in its correct position, it was turned so that the hollow portion of the plug was opened to the top of the apparatus. The vacuum pump was connected at A, and stopcock 1 was evacuated. The procedure was repeated for stopcock 2 by attaching the vacuum pump to B. Connections at A, C, and D were then closed and stopcock 2 was turned to allow the evacuation of stopcock 3. Stopcock 3 was turned to allow the evacuation of stopcocks 4 and 5. The remaining stopcocks were evacuated in a similar manner.

Introduction of Manometer Fluid. Meriam D-3166, the manometer fluid, was introduced into the Barcroft manometer through stopcock 8. A soft plastic tubing was fitted with a funnel at one end and attached to the glass tube below stopcock 8 at the other end. The Meriam D-3166 fluid was allowed to

FIGURE 2
APPARATUS USED TO PREPARE SURFACTANT SOLUTIONS FOR ABSORPTION

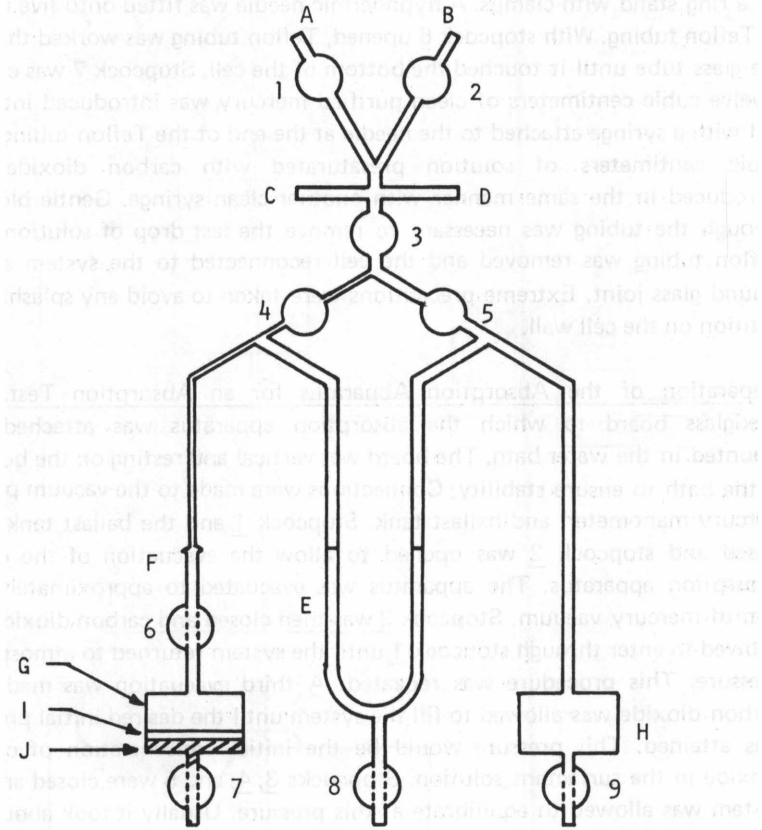


Legend

- | | |
|--------------------|----------------------|
| A, B - Valves | F - Solution Sample |
| C - Gas Inlet | G - Magnetic Stirrer |
| D - Manometer Line | H - Stirring Bar |
| E - Vacuum Line | |

FIGURE 3

**SCHEMATIC DIAGRAM OF UNSTEADY-STATE
ABSORPTION SYSTEM**



Legend

- | | |
|-------------------------|------------------------|
| A - Gas Source | F - Ground Glass Joint |
| B - Vacuum Source | G - Absorption Cell |
| C - Ballast Tank | H - Dummy Cell |
| D - Mercurial Manometer | I - Solution Sample |
| E - System Manometer | J - Mercury Substrate |
| 1-9 - Vacuum Stopcocks | |

flow into both arms of the manometer. The plastic tubing was raised until the desired height of fluid was obtained. Stopcock 8 was then closed and excess fluid and tubing removed.

Introduction of Mercury Substrate and Solution. The absorption cell was detached from the system at the ground glass joint and mounted vertically on a ring stand with clamps. A hypodermic needle was fitted onto five inches of Teflon tubing. With stopcock 6 opened, Teflon tubing was worked through the glass tube until it touched the bottom of the cell. Stopcock 7 was closed. Twelve cubic centimeters of clean purified mercury was introduced into the cell with a syringe attached to the needle at the end of the Teflon tubing. Ten cubic centimeters of solution presaturated with carbon dioxide was introduced in the same manner with another clean syringe. Gentle blowing through the tubing was necessary to remove the last drop of solution. The Teflon tubing was removed and the cell reconnected to the system at the ground glass joint. Extreme precautions were taken to avoid any splashing of solution on the cell wall.

Preparation of the Absorption Apparatus for an Absorption Test. The plexiglass board to which the absorption apparatus was attached was mounted in the water bath. The board was vertical and resting on the bottom of the bath to ensure stability. Connections were made to the vacuum pump, mercury manometer, and ballast tank. Stopcock 1 and the ballast tank were closed and stopcock 2 was opened to allow the evacuation of the entire absorption apparatus. The apparatus was evacuated to approximately 450 mm of mercury vacuum. Stopcock 2 was then closed and carbon dioxide was allowed to enter through stopcock 1 until the system returned to atmospheric pressure. This procedure was repeated. A third evacuation was made and carbon dioxide was allowed to fill the system until the desired initial pressure was attained. This pressure would be the initial concentration of carbon dioxide in the surfactant solution. Stopcocks 3, 4, and 5 were closed and the system was allowed to equilibrate at this pressure. Usually it took about one and a half to two hours to equilibrate as shown by no further change in the height of the manometer fluid. The pressure in the system after equilibration is called the saturation pressure.

With stopcock 3 closed, the ballast tank was evacuated to almost the highest vacuum that could be obtained with the vacuum pump by opening stopcock 3. Then, stopcock 2 was closed and carbon dioxide was allowed to enter through stopcock 1 until the ballast tank returned to atmospheric pressure. This procedure was repeated and the ballast tank was filled to a slight positive pressure.

Absorption Test. After equilibration, the system was ready for an absorption test. The cooling water and agitators were turned off to avoid upsetting the quiescent system. Stopcocks 4 and 5 were opened to allow the manometer fluid to flow back to its original level. Then stopcock 3 was opened for about six seconds to allow carbon dioxide to fill the absorption and dummy cells. The increase in pressure was referred to as the step increase in pressure. The resultant pressure after the step increase was called the operating pressure. After closing stopcocks 4 and 5 simultaneously, the timer was started immediately and the reading on the mercury manometer was recorded. Then, the change in height of the fluid in the Barcroft manometer was recorded as a function of time.

The change in height of the manometer fluid was measured with a cathetometer for some runs. The meniscus of the manometer fluid was brought into focus and aligned with respect to a cross hair in the eyepiece. The position of the telescope on the scale was then read to the nearest 0.1 millimeter using the vernier scale. The telescope was made to travel downward with the meniscus of the manometer fluid.

Conclusion of Absorption Test. At the conclusion of the test, the tubing at A, B, C, and D was disconnected and the apparatus was removed from the water bath. Stopcock 3 was opened. Stopcocks 4 and 5 were opened simultaneously to avoid the loss of fluid from the Barcroft manometer. The absorption cell was then removed and cleaned.

Results

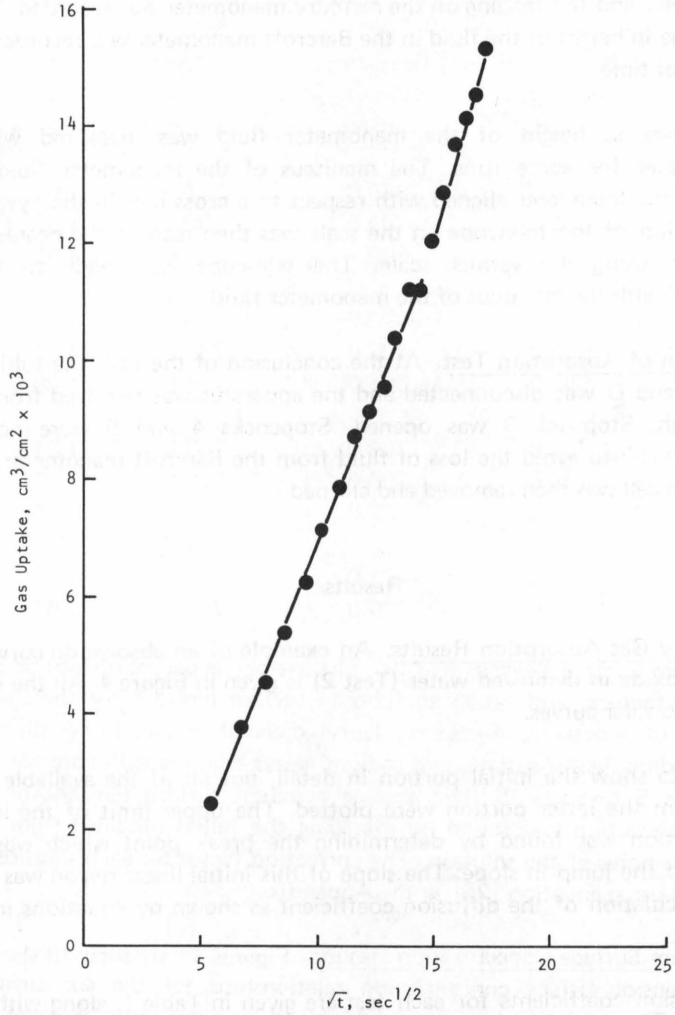
Preliminary Gas Absorption Results. An example of an absorption curve for carbon dioxide in deionized water (Test 2) is given in Figure 4. All the other tests gave similar curves.

In order to show the initial portion in detail, not all of the available data points from the latter portion were plotted. The upper limit of the initial linear portion was found by determining the break point which was the location of the jump in slope. The slope of this initial linear region was used in the calculation of the diffusion coefficient as shown by equations in the Appendix.

The diffusion coefficients for each test are given in Table I, along with the corresponding parameter values: saturation pressure, operating pressure, and the pressure increment. Saturation pressure is the pressure at which a

FIGURE 4

CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT
25°C and 700.0 mm Hg (TEST NUMBER 2)



deionized water sample was given a specific initial concentration of carbon dioxide. Operating pressure is the pressure at which the absorption process took place. The pressure increment is the difference between the operating pressure and the saturation pressure.

TABLE I

DIFFUSION COEFFICIENTS FOR ABSORPTION OF CARBON DIOXIDE INTO DEIONIZED WATER AT 25°C

<u>Test Number</u>	<u>Saturation Pressure mm Hg</u>	<u>Operating Pressure mm Hg</u>	<u>Pressure Increment mm Hg</u>	<u>Diffusion Coefficient cm²/sec x 10⁵</u>
1	498.5	690.0	191.5	1.98
2	500.0	700.0	200.0	1.97
3	498.0	699.0	201.0	1.95
4	500.0	700.0	200.0	1.97
5	500.0	702.0	202.0	1.93
6	500.0	704.0	204.0	1.89
7	500.0	703.0	203.0	1.91
8	500.0	700.0	200.0	1.92
9	500.0	702.0	202.0	1.91
10	500.0	701.0	201.0	1.94
11	500.0	700.0	200.0	1.91

Equilibrium Surface Tension Results. The average apparent surface tensions, correction factors, and actual equilibrium surface tensions for the aqueous solutions of n-octanol, 4-octanol, lauryl diglycol amide, lauryl diethanol amide, sodium lauryl sulfate, and sodium lauryl benzene sulfonate are given in Figures 5 through 10. The average apparent surface tension for each surfactant solution was found by averaging the values obtained from three separate samples of the solution. The correction factor for each solution was calculated using equation [26] in the Appendix.

Equilibrium Surface Concentration Results. Figures 11 through 16 show the surface tension-surface concentration relationships for the six surfactant solutions. These relationships were determined by a computer program using equation [29] in the Appendix.

FIGURE 5

EQUILIBRIUM SURFACE TENSION: N-OCTANOL

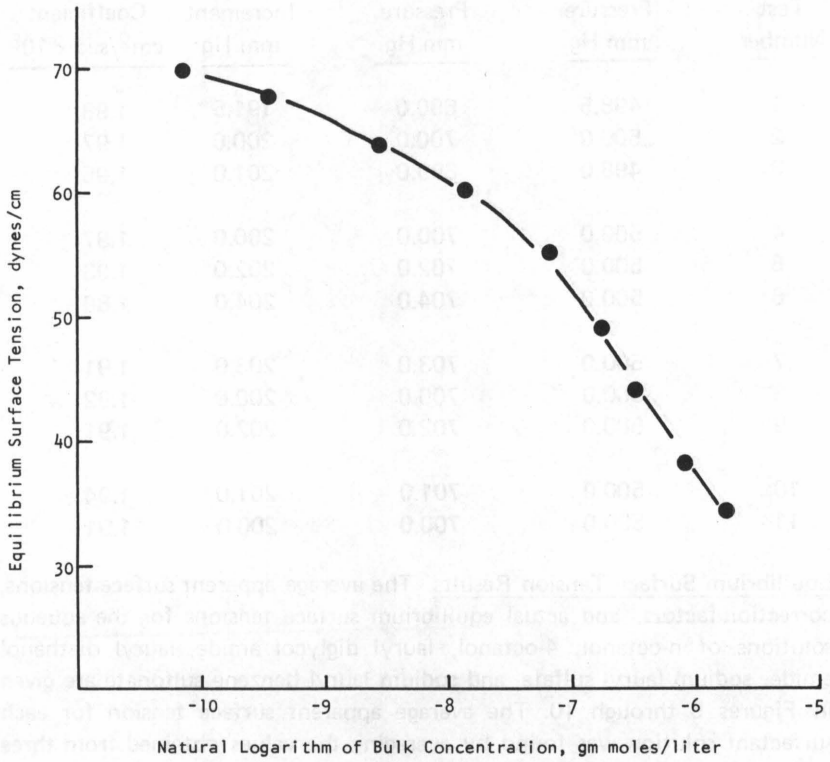


FIGURE 6

EQUILIBRIUM SURFACE TENSION: 4-OCTANOL

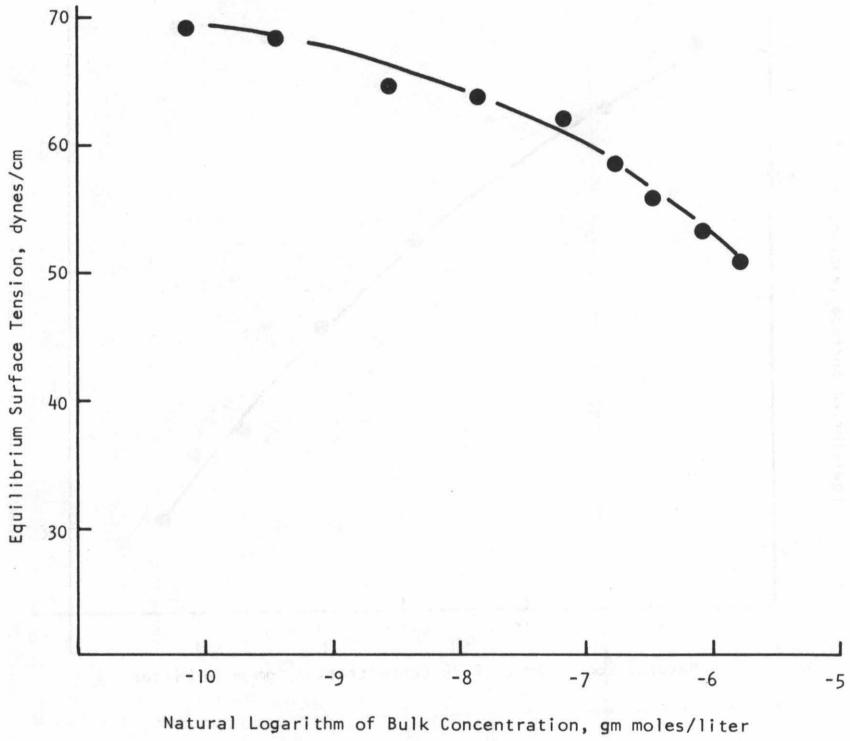


FIGURE 7

EQUILIBRIUM SURFACE TENSION: LAURYL DIGLYCOL AMIDE

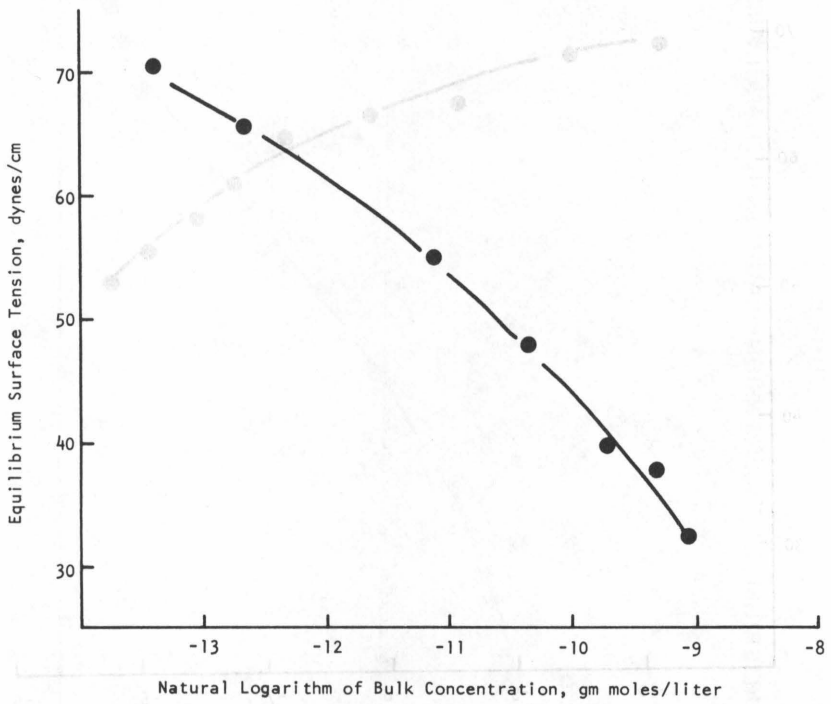


FIGURE 8

EQUILIBRIUM SURFACE TENSION: LAURYL DIETHANOL AMIDE

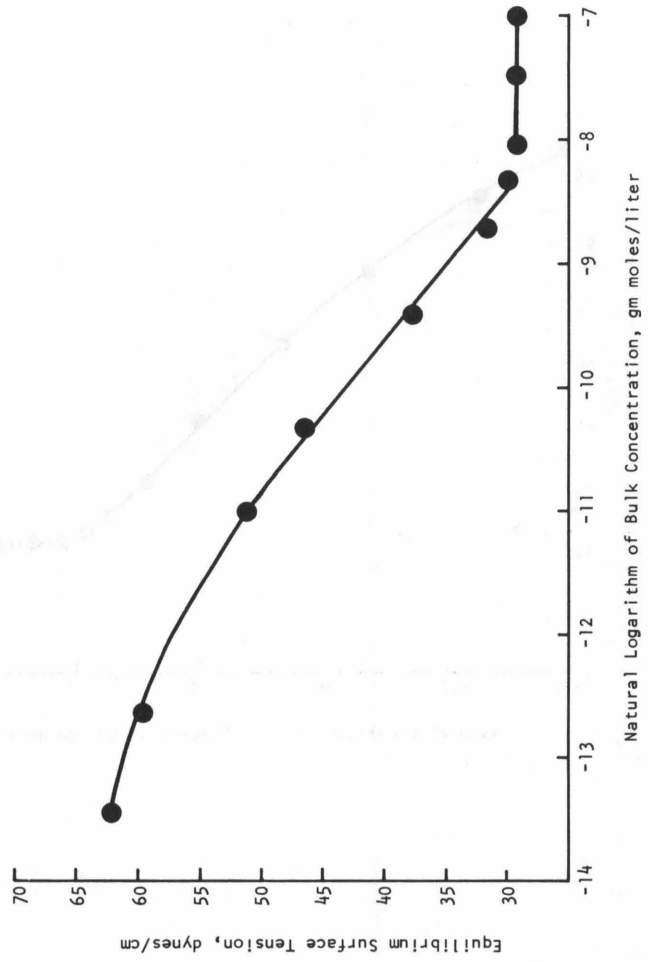


FIGURE 9

EQUILIBRIUM SURFACE TENSION: SODIUM LAURYL SULFATE

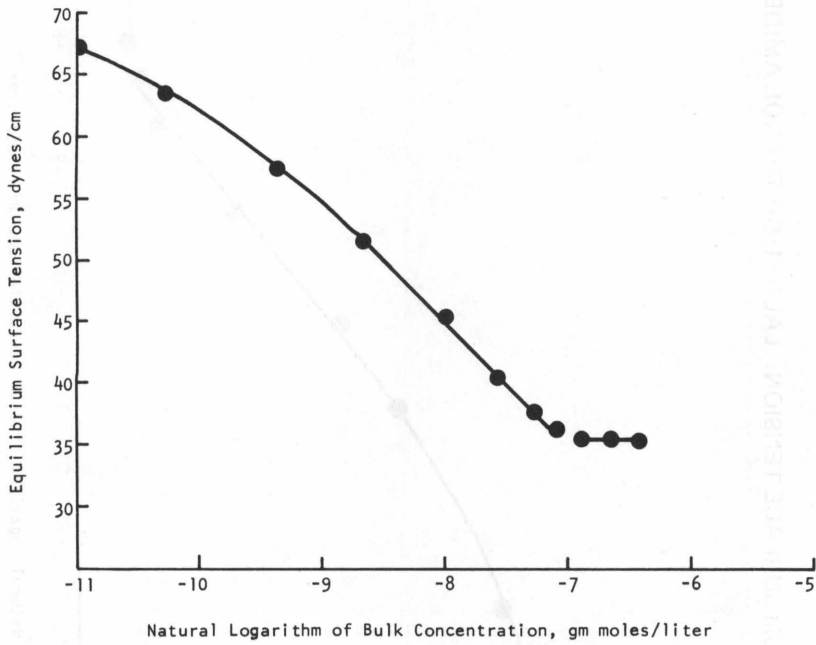


FIGURE 10

EQUILIBRIUM SURFACE TENSION:
SODIUM LAURYL BENZENE SULFONATE

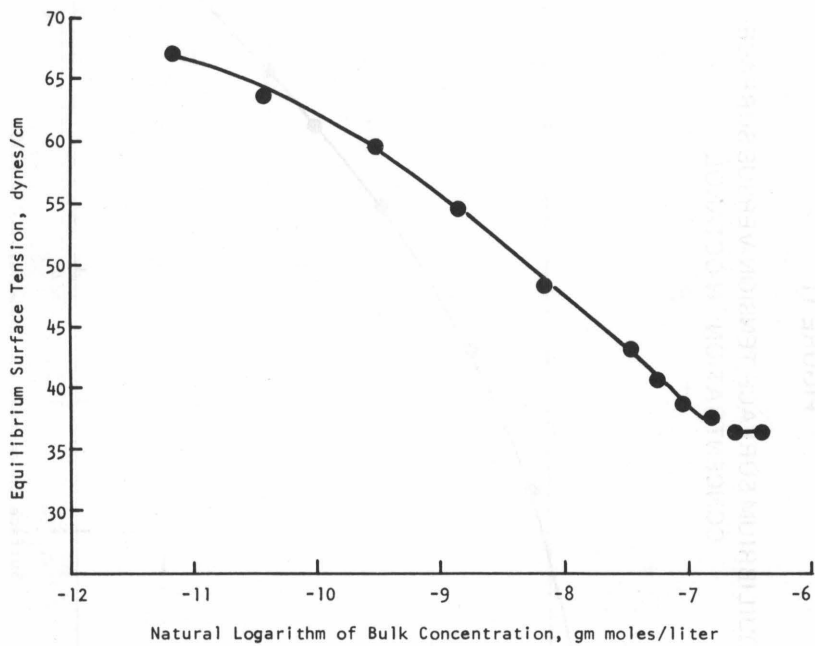


FIGURE 11
EQUILIBRIUM SURFACE TENSION VERSUS SURFACE
CONCENTRATION: N-OCTANOL

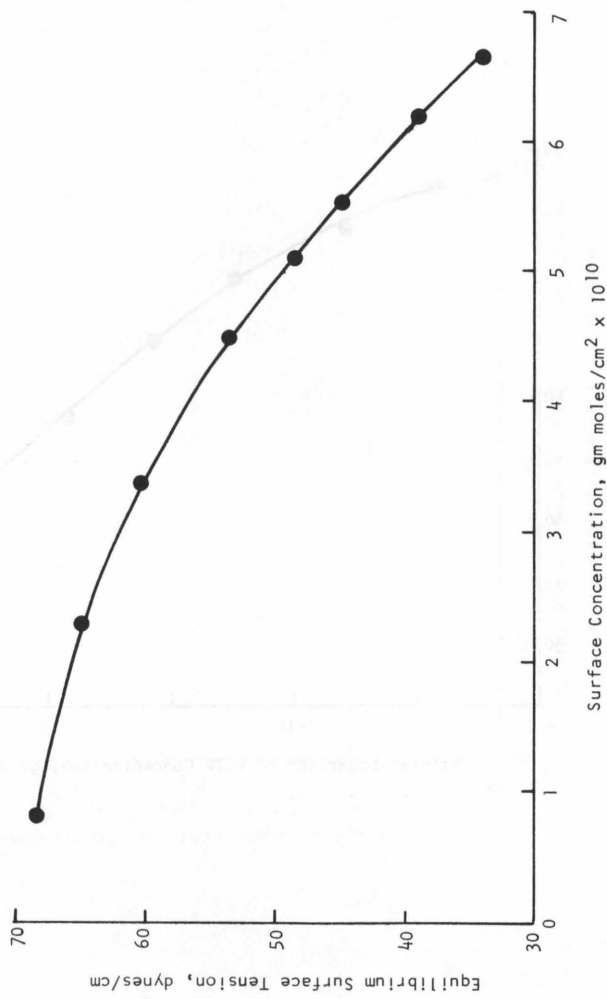


FIGURE 12

EQUILIBRIUM SURFACE TENSION VERSUS SURFACE
CONCENTRATION: 4-OCTANOL

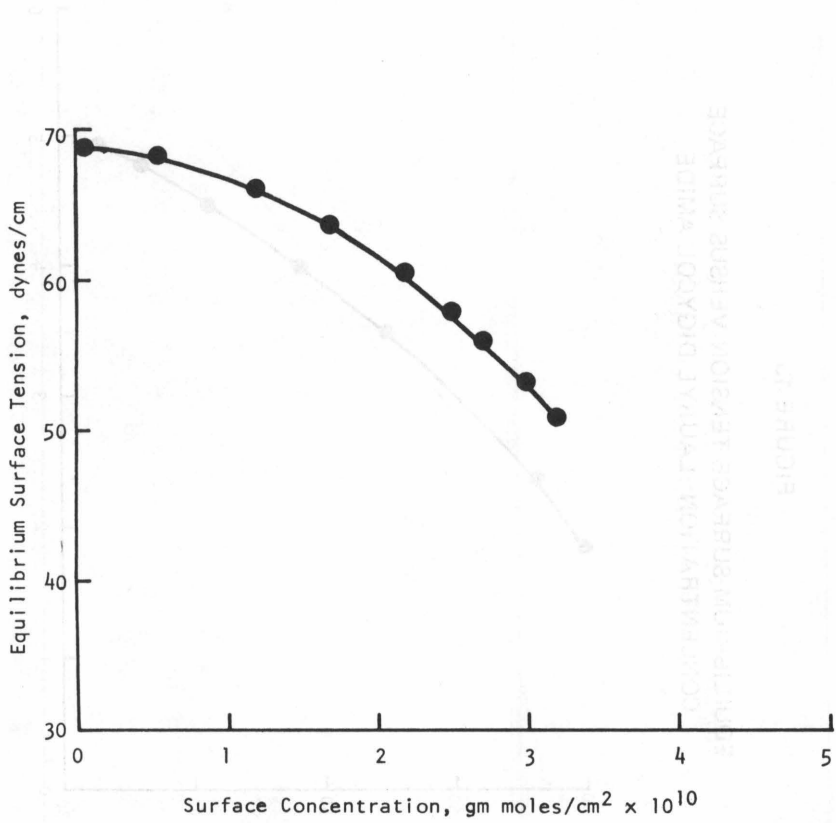


FIGURE 13

EQUILIBRIUM SURFACE TENSION VERSUS SURFACE CONCENTRATION: LAURYL DIGLYCOL AMIDE

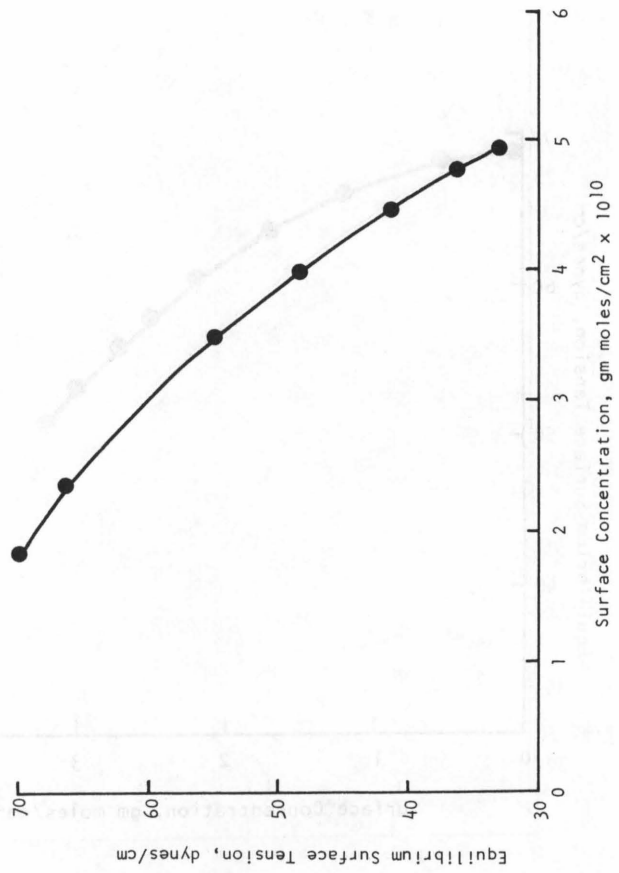


FIGURE 14

EQUILIBRIUM SURFACE TENSION VERSUS SURFACE
CONCENTRATION: LAURYL DIETHANOL AMIDE

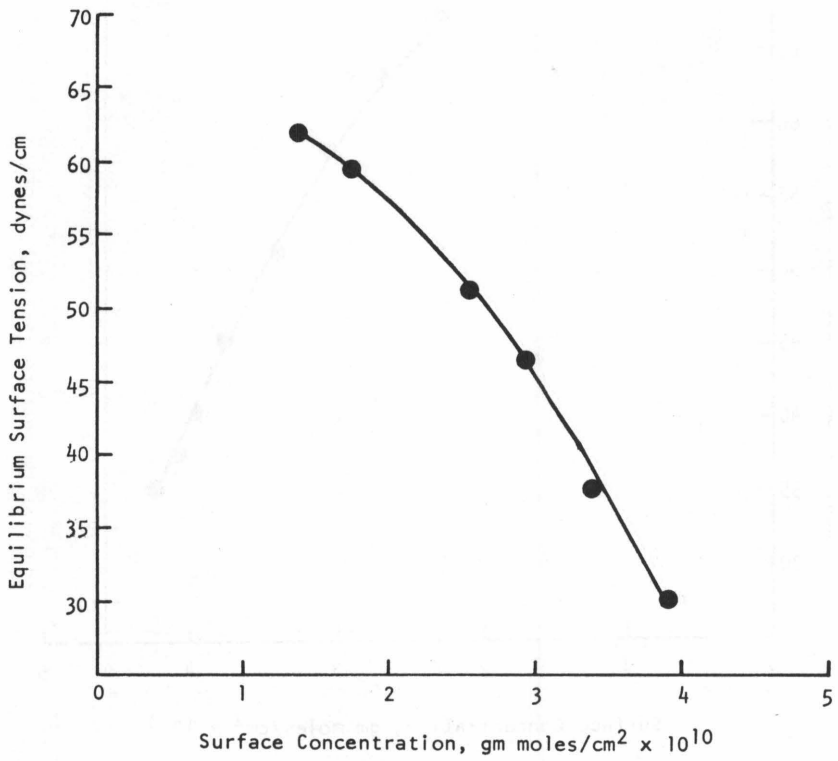


FIGURE 15

EQUILIBRIUM SURFACE TENSION VERSUS SURFACE
CONCENTRATION: SODIUM LAURYL SULFATE

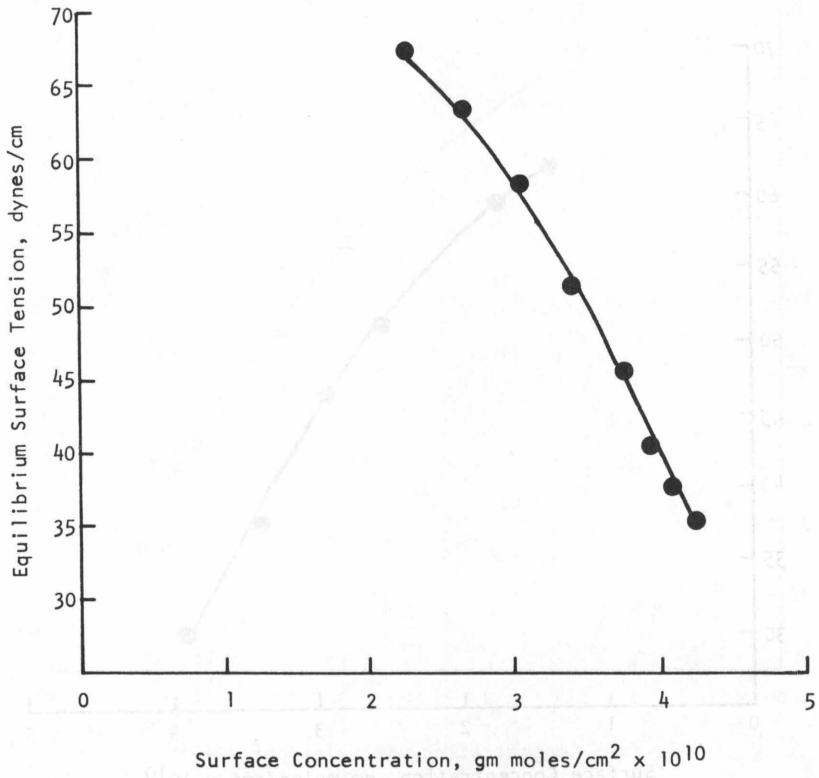
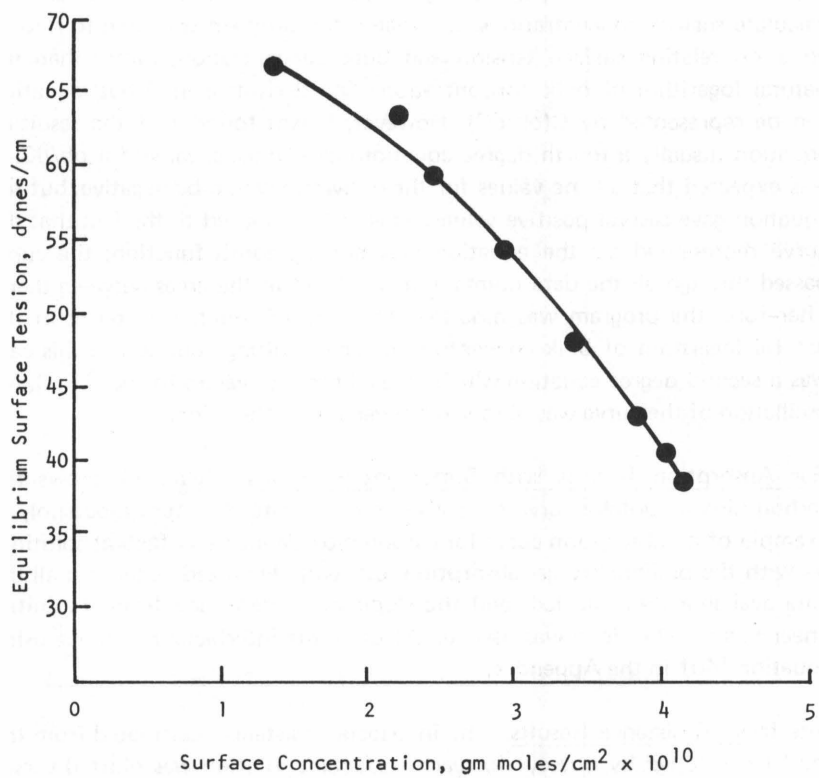


FIGURE 16

EQUILIBRIUM SURFACE TENSION VERSUS SURFACE
CONCENTRATION: SODIUM LAURYL BENZENE SULFONATE



The computer program was a polynomial regression program and was identical, except for several changes in format statements and the addition of an execution statement, to that given in the IBM Scientific Data Package.³¹ The program will fit a polynomial curve to experimentally determined data points (surface tension values) and calculate the regression coefficients of the curve. Improvement of the fit of the curve is based on the improvement of the sum of squares of the residuals and the value obtained from a statistical "F" test.

The polynomial equation obtained from the program was used to calculate the derivative, $\partial b / \partial \ln C$, appearing in Gibbs' equation which was used to calculate surface concentrations. Originally, the program was used to find an equation relating surface tension and bulk concentration, rather than the natural logarithm of bulk concentration. The derivative in Gibbs' equation can be represented by $C(\partial b / \partial C)$. However, it was found that the resulting equation (usually a fourth degree equation) gave unusual values for $\partial b / \partial C$. It was expected that all the values for the derivative would be negative, but the equation gave several positive values. This was attributed to the fact that the curve represented by the equation was not a smooth function; the curve passed through all the data points, but oscillated in the areas between them. Therefore, the program was modified to give an equation in terms of the natural logarithm of bulk concentration. The resulting equation in this case was a second degree equation which gave all negative values for $\partial b / \partial \ln C$. No oscillation of the curve was observed between the data points.

Gas Absorption Results with Surfactant Solutions. Figure 17 shows the carbon dioxide uptake curve for carbon dioxide into 300 ppm n-octanol, an example of an absorption curve for carbon dioxide into a surfactant solution. As with the preliminary gas absorption tests with deionized water, not all the data available were plotted, and the slope was determined from the initial linear region. The slope was used to calculate the interfacial resistance using equation [40] in the Appendix.

Interfacial Resistance Results. The interfacial resistance (calculated from the model developed by Bussey) for each surfactant solution was plotted versus the corresponding surface concentration. The results for the 6 surfactants are shown in Figures 18 and 19.

A new time independent model for interfacial resistance was developed and is shown in the Appendix. The results for n-octanol and 4-octanol are shown in Figure 20.

FIGURE 17

CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION
(300 PPM) AT 25°C AND 700 mm Hg

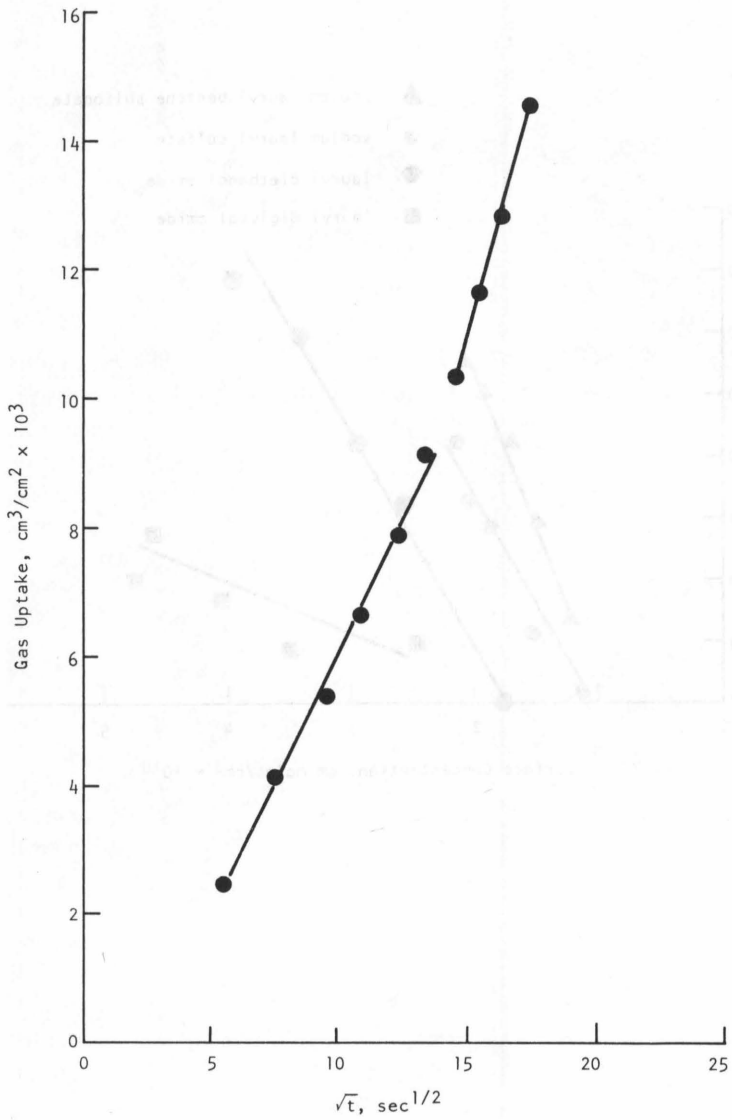


FIGURE 18

INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION

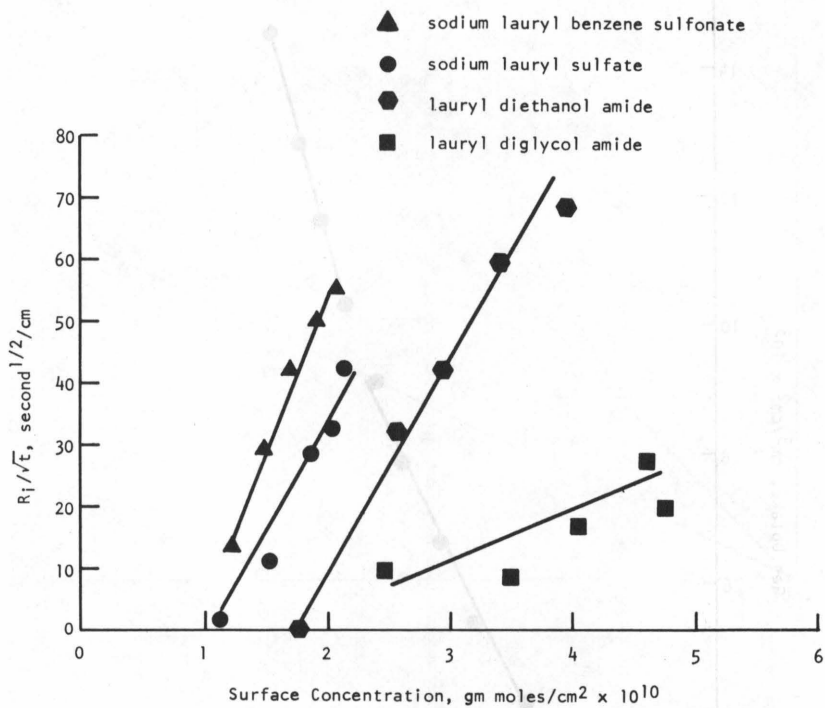


FIGURE 19

INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION

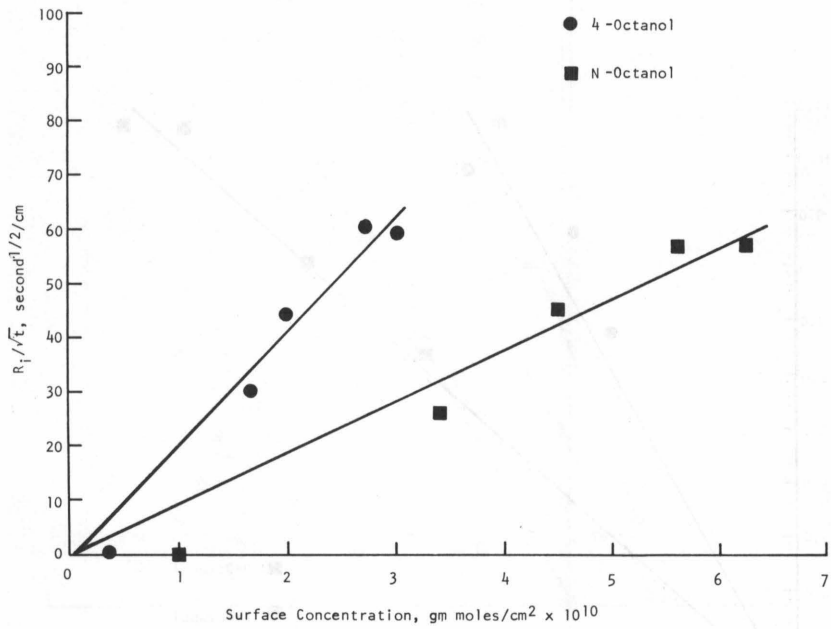
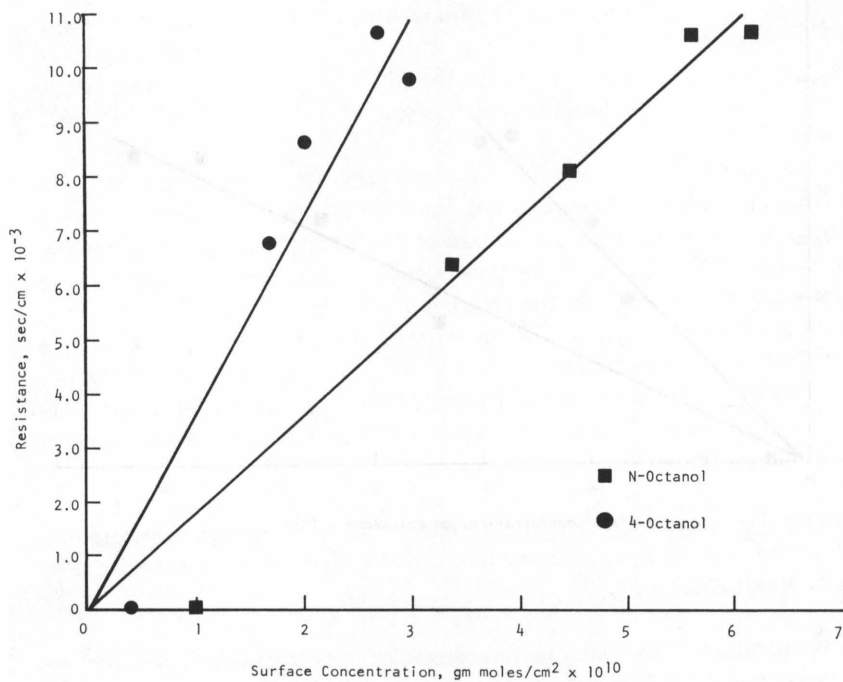


FIGURE 20

INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION USING THE TIME INDEPENDENT MODEL



V. DISCUSSION

Discussion of Procedure

Stability of the System. Any disturbance of the solution in the absorption cell upsets the quiescent nature of the system which was the basic assumption in this investigation. In order to avoid this, the apparatus was firmly mounted on aluminum rods and the agitators were turned off during the gas absorption data taking period. Resting the plexiglass board on the bottom also helped to prevent the apparatus from vibrating. However, the possibility of occasional vibration of the building affecting the system raised some questions.

Cleanliness of the Absorption Cell. The cleanliness of the absorption cell was very important. If the cell was dirty, water droplets would stick to the cell wall and the meniscus of water with the wall was not regular. These effects would increase the interfacial area used in the calculation.

Many precautions were taken to avoid any impurities entering the cell. The cell was cleaned with glass cleaning solution, rinsed with water, and then acetone. Compressed air in the laboratory was used to evaporate the acetone. The compressed air used to remove acetone vapor was suspected to be a major cause of impurities in the cell, therefore, other means of drying or the use of an air filter should be considered. The mercury used was cleaned by a physical chemistry technique³⁴, filtering through a filter paper with a pin hole. The scum left behind was collected for later purification. This technique was sufficient for this study as there was no opportunity for the mercury to amalgamate with metals.

Constant Temperature Arrangement. The temperature of the room did not stay at 25°C constantly. During hot summer days, the temperature was usually about $25.5^{\circ} \pm 0.5^{\circ}\text{C}$.

The temperature of the water bath was relatively constant with a deviation of not more than $\pm 0.1^{\circ}\text{C}$. However, on hot days, the temperature of the cooling water went as high as 24.6°C. The cooling water could cause an unequal distribution of temperature after the agitators were turned off.

Surface Tension Measurement. To ensure accuracy of the surface tension measurements using the Fisher interfacial tensiometer, the platinum ring was cleaned by rinsing in benzene and again in acetone. The ring was then heated in the oxidizing portion of a gas flame. The Fisher tensiometer was calibrated

with deionized water at 25°C to a surface tension of 71.9 dynes per centimeter (apparent surface tension was 76.9).

Presaturation of Samples with Carbon Dioxide. The water containing the surfactant solutions was placed in a side-arm flask. The flask was evacuated and refilled with carbon dioxide three times. Evacuations were carried out to 700 millimeters of mercury to ensure sufficient removal of air in the flask, and the sample was allowed to degas so that any previously dissolved gas would be desorbed.

McCutchen²⁷ and Herbert¹⁷ presaturated the samples with carbon dioxide to the saturation pressure of the absorption test. They suggested that very little desorption occurred while transferring the solutions to the absorption cell. This conclusion was based on tests of exposing the presaturated solutions to the atmosphere for ten minutes. However, it was found that carbon dioxide desorbed while the air was being evacuated from the absorption apparatus. Based on five tests, the extent to which the samples were presaturated had little bearing on the final results. Yet, it was preferable to presaturate the samples to a pressure higher than the saturation pressure so that a larger amount of carbon dioxide would be retained in the solution after evacuation in the absorption cell had taken place. The samples were then resaturated to establish an initial concentration in the sample solution.

Preparation of the Absorption Apparatus for the Absorption Tests. In evacuating the absorption apparatus, the vacuum should not be drawn over 500 millimeters of mercury to avoid excessive desorbing of carbon dioxide from the solution, making the pre-saturation step useless.

The value for the operating pressure was not important in the experimental determination of the diffusion coefficient for the pure carbon dioxide-water system. As for the tests with surfactant solutions, the slope of gas uptake plot versus the square root of time had to be corrected for different step pressure increases before interfacial resistance could be calculated. Therefore, the operating pressure was left at around 700 millimeters of mercury.

After allowing carbon dioxide to refill the system to the operating pressure, the time taken to turn valves 4 and 5 off was quite critical. The reason is that if the timer was not started immediately, the concentration of the sample at time zero would not correspond to the recorded initial concentration which is the saturation pressure. According to Blank and Rougton², six seconds was necessary for the pressure to settle down to a steady level. Yet if the valves were not closed and the timer was not turned on fast enough, the readings

obtained would be undesirable, i.e. absorption would have taken place before the timer was started.

Discussion of Results

Diffusion Coefficient Results. Referring to Table I, the values obtained for the diffusion coefficient of the pure carbon dioxide-water system ranged from 1.89 to 1.98×10^{-5} square centimeters per second. All of these values fell between 1.85 to 2.00×10^{-5} , the acceptable range for this investigation. The average of the values determined from Tests 1 through 11 was 1.93×10^{-5} square centimeters per second with a reproducibility of $\pm 0.05 \times 10^{-5}$.

All tests were taken under almost the same saturation pressure and operating pressure, around 500 millimeters and 700 millimeters of mercury, respectively. Tests 1 through 4 were taken under the same conditions except for the difference in presaturation pressure. The results showed that the presaturation pressure had little bearing on the diffusion coefficient.

Attempts were made to improve the precision of the measurements in the tests. The manometer change for tests 1 through 6 was recorded in intervals of 15 seconds while the others were recorded in intervals of 30 seconds. No significant difference was observed. In tests 7 through 11, the change was recorded with a cathetometer. The advantages will be discussed in a later subsection. Even though the tests all gave diffusion coefficients within the acceptable range, the improvement in precision using the cathetometer did narrow the range. However, no conclusion can be drawn unless more tests were taken using the cathetometer or some other high precision recording instrument.

About ten gas absorption tests were taken without turning off the agitators in the water bath. The diffusion coefficient values of these results were found to be much higher than the acceptable range. Also there was no range to which they were distributed, showing that the results obtained were useless and therefore were not recorded.

Equilibrium Surface Tension Results. The surface tension for each surfactant at each concentration was the average of three samples. Many troubles were encountered in getting satisfactory surface tension data, especially with the octanols. It was found that the surface tension data obtained for samples from the same solution could differ as much as three dynes per centimeter. Even the surface tension for the same sample could be different at different

times. Any set of samples having values close to each other (within one dyne per centimeter) was considered acceptable. Any set of samples that had a wider distribution of values was discarded and the surface tension was measured again with new samples.

There were many factors that could have contributed to the deviation. First was the time taken to achieve the equilibrium state. It was not known how long was required, or whether the equilibrium state was disturbed when the sample was transferred and the ring dropped into the sample solution. Second was the effect of evaporation. Condensation was sometimes observed on the petri dish cover. The amount evaporated might either reduce or increase the concentration of the surfactant solution. Third was the effect of temperature variation in the room which could cause condensation on the petri dish cover and could also change the surface tension as a function of temperature.

No critical micelle concentration was observed for the aqueous solution of the two octanols and for lauryl diglycol amide. Probably these surfactants were not soluble enough to get to the critical micelle concentration, and they were all non-ionic. It should be noted that some non-ionic surfactants have critical micelle concentration and others do not.

Gas Absorption Results. It has been assumed by many workers that no convection occurs in the initial range. When the gas uptake curve was examined, it was found that the initial portion was quite linear, thus suggesting that the assumption of no convection in this range is valid. However, the initial portion was not exactly linear even for tests using the cathetometer. This may be caused by some minute convection currents or some other effects that were not accounted for.

The upper boundary of the initial linear region was determined by the location of the point from which the slope abruptly changed. It was found that the second part of the curve stayed quite linear with very little scatter in the data points. Therefore, it was easier to locate the lower boundary of this line. The points below this point were used to calculate the slope of the initial linear region by a least squares fit.

It was found that the slope of the initial linear portion increased moderately as an extra point was taken into consideration. The number of points considered was crucial to the value of the slope. The interpretation of the plot depends on the method used to find the break point. This is especially true when the data points scatter. In some of the plots the first point scattered quite badly from the line. The reason might be the delay in turning valves 4 and 5 off and starting the timer when the absorption test started.

The original computer program was developed with a gas volume space of 136.25 cubic centimeters and a manometer fluid density of 1.043 grams per cubic centimeter. These values should be adjusted if the volume of mercury substrate and solute changes, and if the manometer fluid is changed. In an effort to increase precision of the measurements, a cathetometer was used to measure the height changes in the manometer. Tests 7 through 11 for water and all tests for lauryl diglycol amide were measured with a cathetometer.

By comparing the gas absorption plots, many advantages could be seen with the increased precision. All the points fit quite well to two straight lines, the initial linear portion and the latter portion. Therefore, there was no trouble in locating the break point which was the intersection of the two straight lines. Also, the first point was always on the line and so would not affect the slope to a misleading value.

Interfacial Resistance. The slope of the initial linear portion of the uptake versus square root of time curves for each test with surfactants was used to calculate interfacial resistances using equation [40]. The values tabulated should be considered as a point in a range rather than an exact value. As discussed earlier, the tests with a pure water system showed a range in the diffusion coefficient which is equivalent to a difference of $0.02 \times 10^{-3} \text{ sec}^{1/2}/\text{cm}$ in the slope. This difference in the slope could cause a difference of as much as $15 \text{ sec}^{1/2}/\text{cm}$ in the interfacial resistance.

The interfacial resistances were plotted as a function of surface concentration. From Figure 20, the two octanols are seen to have different interfacial resistances. At high surface concentrations, 4-octanol has the higher interfacial resistance. However, at lower surface concentrations, they are almost the same. N-octanol and 4-octanol are isomers, similar in having an eight carbon chain and having the same molecular weight, but the position of the hydroxyl group is different. Therefore, the position of the hydrophilic group affects the interfacial resistance. The branched chain in 4-octanol may be the cause for the greater resistance than the straight chain in n-octanol, as explained by the sieve effect.

The results for lauryl diglycol amide can be compared to the results for lauryl diethanol amide. Lauryl diethanol amide caused a higher interfacial resistance than lauryl diglycol amide. The structure of the two compounds are similar in that the hydrophobic portions are the same. Yet lauryl diglycol amide has two extra hydroxyl groups and a higher molecular weight for the hydrophilic portion. This suggests that a larger hydrophilic group causes a lower interfacial resistance. Also, the lower interfacial resistance may be caused by

the extra hydroxyl groups. It may also suggest that the higher the number of hydroxyl groups in the hydrophilic portion of the surfactant, the lower the interfacial resistance.

Lauryl diethanol amide and lauryl diglycol amide can be compared with sodium lauryl sulfate because all three of these surfactants have 12-carbon-chain hydrophobic groups. For any given surface concentration, sodium lauryl sulfate caused a higher resistance to gas absorption than either of the alkanol amides. This further suggests that the higher the molecular weight of the hydrophilic functional group the lower the interfacial resistance, since sodium lauryl sulfate has a lower molecular weight than either of the alkanol amides. Finally, sodium lauryl benzene sulfonate fits the same pattern as the other three surfactants shown in Figure 19. It has the highest resistance of the four surfactants, yet the hydrophilic portion of the molecule has the lowest molecular weight. However, it could also be suggested that sodium lauryl benzene sulfonate should have the highest resistance since it has an additional component to the hydrophobic portion of the molecule, namely a benzene ring.

Interfacial Resistance Using A New Model. According to the original model, the interfacial resistance for a surfactant solution was a function of the square root of time. It was suspected that an interfacial resistance independent of time could better describe the gas absorption into surfactant solutions. Under this assumption a new model was developed. Comparing Figures 20 and 21, the same type of correlation is seen except in the magnitude of the interfacial resistance which has different units. Therefore, the new model serves the same purpose as Bussey's model correlating the interfacial resistance with surface concentration.

VI. CONCLUSIONS

The investigation of the effect of the position and molecular weight of the surfactant hydrophilic function group on the rate of absorption of carbon dioxide in water led to the following conclusions:

1. Using the unsteady-state absorption apparatus, the diffusion coefficient for the carbon dioxide-water system at 25°C was found to be $1.93 \pm 0.05 \times 10^{-5}$ square centimeters per second.
2. The higher the surface concentration of surfactants, the higher the interfacial resistance to gas absorption.
3. The location of the hydroxyl group at different positions on the hydrophobic chain causes different magnitudes of interfacial resistance, with the location of the hydroxyl group at a branched position causing a higher resistance than at the end of the hydrophobic chain.
4. The molecular weight of the hydrophilic functional group causes different magnitudes of interfacial resistance, with the higher molecular weight causing a lower resistance.

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VIII. APPENDIX

Derivation of Interfacial Resistance Model

The time dependent model for interfacial resistance is described in detail by Bussey⁵ and Herbert²¹. Presented here is a development of the time independent interfacial resistance. Although it is similar to the former model, it is in a more generalized form.

Starting with a form of the Fick's Second Law as in equation [1],

$$\partial\phi/\partial t = D \partial^2\phi/\partial x^2 \quad [6]$$

where

$$\phi = C - C_0. \quad [7]$$

The boundary conditions are

$$\phi(x, 0) = C(x, 0) - C_0 = 0 \quad [8]$$

$$\phi(\infty, t) = C(\infty, t) - C_0 = 0$$

$$\phi(0, t) = \phi_i \quad [10]$$

$$N(0, t) = -D\partial\phi(0, t)/\partial x \quad [11]$$

where

$$N = \text{gas absorption rate, gm mole}/(\text{sec})(\text{cm}^2).$$

A Laplace transform solution yields

$$C(x, t) = \frac{1}{\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t-\tau}} \exp \left[-\frac{x^2}{4D(t-\tau)} \right] N(0, \tau) d\tau \quad [12]$$

at $t = 0$,

$$C(x, 0) = \frac{1}{\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t-\tau}} N(0, \tau) d\tau. \quad [13]$$

Up to this point, the development is the same as Bussey.⁵ After this, the following assumption is made:

$$\phi = K + At^B \quad [14]$$

where K, A, and B are parameters.

It should be noted that this is a more generalized form than Bussey⁵ where B = ½ and K = 0. From [14]

$$N(0, t) = \partial\phi/\partial t = ABt^{B-1}. \quad [15]$$

Substituting [15] into [13]

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} \int_0^t (t - \tau)^{1/2 - 1} \tau^{B-1} d\tau. \quad [16]$$

From the MacLaurin series,

$$(t - \tau)^{-1/2} = \frac{1}{t^{0.5}} + \sum_{n=1}^{\infty} \frac{(2n-1)(2n-3)(2n-5)\dots(1)(-1)^n}{(2^n)(n!)} \frac{\tau^n}{t^{n+0.5}} \quad [17]$$

Substituting [17] into [16], and integrating yields

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} t^{B-1/2} \left[\frac{1}{B} + \sum_{n=1}^{\infty} \frac{(2n-1)(2n-3)\dots(1)(-1)^n}{2^n (n!) (B+n)} \right] \quad [18]$$

Substituting gamma function for the series and simplifying yields

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} t^{B-1/2} \frac{\Gamma(B) \Gamma(1/2)}{\Gamma(B+1/2)}. \quad [19]$$

Equating [19] with [7]

$$C(0, t) = C_0 + \frac{AB}{\sqrt{D}} t^{B-1/2} \frac{\Gamma(B)}{\Gamma(B+1/2)} \quad [20]$$

The driving force in concentration is

$$\Delta C = C_e - C_i = C_e - C(0, t) \quad [21]$$

where

C_e = equilibrium concentration, gm mole/cm³
 C_i = concentration at interface, gm mole/cm³.

Substituting [20] into [21],

$$\Delta C = C_e - C_0 - \frac{AB}{\sqrt{D}} t^{B - 1/2} \frac{\Gamma(B)}{\Gamma(B + 1/2)} \quad [22]$$

Expressing the concentration in terms of pressure using Henry's law

$$\Delta C = (PP - P_s) \frac{V_g}{H} - \frac{AB}{\sqrt{D}} t^{B - 1/2} \frac{\Gamma(B)}{\Gamma(B + 1/2)} \quad [23]$$

where

V_g = volume of gas space, cm³
 PP = operating pressure in system, mm mercury
 P_s = saturation pressure in system, mm mercury
 H = Henry's law constant, 2.245×10^7 (mm Hg)(cm³)/gm mole.

The time independent interfacial resistance is given by

$$R_i = \frac{\Delta C}{N} \quad [24]$$

where

R_i = interfacial resistance, sec/cm.

Sample Calculations

The following section gives examples of the calculations used to obtain the results from the experimental data.

Calculation of Equilibrium Surface Tension. Readings of the surface tensiometer give apparent surface tension. In order to obtain the true surface tension the following relationship was used

$$S_t = S_a \times F \quad [25]$$

where

S_t = true surface tension, dyne/cm
 S_a = apparent surface tension, dyne/cm
 F = correction factor.

The correction factor¹⁴ can be read off from a chart, and is defined in the following form

$$F = 0.7250 + \left(\frac{0.0145S_a}{C_r^2(D-d)} + 0.04534 - \frac{1.679r}{R} \right)^{1/2} \quad [26]$$

where

C_r = circumference of the ring, 6.015 cm
 D = density of the lower liquid phase, gm moles/cm³
 d = density of the upper air phase, gm moles/cm³
 r = radius of the wire of the ring, 0.01778 cm
 R = radius of the ring, 0.9578 cm.

The average apparent surface tension, S_a , of a 400 ppm aqueous n-octanol solution was 38.3 dynes/cm. Using equation [26] the correction factor is

$$F = 0.725 + \left(\frac{0.0145(38.3)}{6.015^2 (1)} + 0.04534 - \frac{1.679 \times 0.01778}{0.9578} \right)^{1/2}$$

$$= 0.8968 \quad [27]$$

$$S_t = 34.5 \text{ dynes/cm.} \quad [28]$$

Calculation of Equilibrium Surface Concentration. Equilibrium surface concentration for non-ionic surfactants was calculated from Gibbs' adsorption equation

$$\eta = - \frac{1}{RT} \left(\partial S_t / \partial \ln C_b \right)_T \quad [29]$$

where

η = surface concentration, gm moles/cm²
 C_b = bulk liquid concentration, gm moles/liter
 R = gas constant, 8.314×10^7 ergs/(gm moles)(°K).

The derivative in this equation is calculated from a polynomial regression equation of the form

$$S_t = A_1 + A_2 \ln C_b + A_3 (\ln C_b)^2 \quad [30]$$

where A_1 , A_2 , and A_3 are constants.

Equation [30] is differentiated with respect to $\ln C$ to obtain

$$\frac{\partial S_t}{\partial \ln C_b} = A_2 + 2 A_3 \ln C_b. \quad [31]$$

Using a computer program, the regression coefficients were calculated by fitting the experimental data points to equation [30]. For n-octanol, the polynomial regression obtained was

$$S_t = -126.2336 - 39.00351 \ln C_b - 1.946333(\ln C_b)^2. \quad [32]$$

Equation [31] becomes

$$\frac{\partial S_t}{\partial \ln C_b} = -39.00351 - 2 (1.946333) (\ln C_b). \quad [33]$$

The surface concentration was calculated by substituting the above equation into Gibbs' equation. For a surface tension of 34.27 dynes/cm and $\ln C_b = -5.7855$

$$\begin{aligned} \eta &= \frac{-2 (1.946333) (-5.7855) - 39.00351}{(8.314 \times 10^7) (298.16)} \\ &= 3.190208 \times 10^{-10} \text{ gm moles / cm}^2. \end{aligned} \quad [34]$$

Calculation of Diffusion Coefficient. The following equations were used in the calculation of gas uptake.

$$\Delta p' = \frac{-A h P P}{(A h + 20 V_g)} \quad [35]$$

$$\Delta p = \Delta p' - h \quad [36]$$

$$x = \frac{273.16}{T_{p_0}} \times \Delta p \times \frac{A h}{20} \times \frac{P P - P_w + \Delta p}{\Delta p} - V_g \quad [37]$$

where

h = difference in height of the fluid in the manometer arms, mm

A = area of manometer bore, cm^2

PP = operating pressure in system, mm fluid (Meriam D-3166)

V_g = volume of gas space, cm^3

$\Delta p'$ = pressure change in dummy vessel, mm fluid (Meriam D-3166)

Δp = pressure change in reaction cell, mm fluid (Meriam D-3166)

X = amount of gas absorbed at standard conditions, cm^3

T = temperature of absorption test, $^\circ\text{K}$

p_w = vapor pressure of water, mm fluid (Meriam D-3166)

p_0 = standard pressure, mm fluid (Meriam D-3166).

The operating pressure of all the absorption tests originally expressed in mm mercury was converted to mm of Meriam D-3166 fluid in the calculation in this section. The density of mercury was taken as 13.534 gm/cm^3 and that of Meriam D-3166 was taken as 1.043 gm/cm^3 at 25°C .

Test number 11 in Table I was taken to show the sample calculation. The results were analyzed to locate the break point of the data from the initial linear region.

The diffusion coefficient was calculated from the following equation

$$D = \left[\frac{(dQ / Ad t) \times \sqrt{\pi}}{2 (C_e - C_0)} \right]^2 \quad [38]$$

where

Q = amount of gas absorbed, gm moles

A = interfacial area, cm^2

C_e = equilibrium concentration of dissolved gas in the bulk liquid phase, gm moles / cm^3

C_0 = initial concentration of dissolved gas in the bulk liquid phase, gm moles / cm^3

D = diffusion coefficient, cm^2 / sec

t = contact time, sec.

In calculating C_e and C_0 , Henry's law was assumed to be valid over the range of the concentration of carbon dioxide concerned. Expressing in terms of operating pressure and saturation pressure,

$$D = \left[\frac{(dQ / Ad t) \times \sqrt{\pi}}{2 (PP - Ps) / H} \right]^2 \quad [39]$$

where

$dQ/Ad t$ = slope of the gas uptake curve, $\text{cm}^3/(\text{cm}^2) (\text{sec}^{1/2})$

PP = operating pressure, mm Hg

Ps = saturation pressure, mm Hg

H = Henry's law constant, $2.245 \times 10^7 (\text{mm Hg})(\text{cm}^3)/\text{gm mole}$.

Then

$$PP - Ps = 700.0 - 500.0 = 200 \text{ mm Hg}$$

$$\text{slope} = 0.9827 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{1/2}).$$

From equation [39]

$$D = 1.905 \times 10^{-5} \text{ cm}^2/\text{sec}.$$

Calculation of Interfacial Resistance. The interfacial resistance to gas uptake caused by a surfactant solution is given by

$$\frac{R_i}{\sqrt{t}} = \frac{1}{k_i \sqrt{t}} = \frac{\sigma_E - \sigma_R}{\sigma_R} \sqrt{\frac{\pi}{D}} \quad [40]$$

where

R_i = interfacial resistance, sec/cm

k_i = interfacial mass transfer coefficient, cm/sec

σ_E = slope of gas uptake versus \sqrt{t} plot for pure carbon dioxide-water system, $\text{cm}^3 / (\text{cm}^2) (\text{sec}^{1/2})$

σ_R = slope of gas uptake versus \sqrt{t} plot for carbon dioxide-surfactant solution system, $\text{cm}^3 / (\text{cm}^2) (\text{sec}^{1/2})$

From all the tests with pure water systems, the average for diffusion coefficient is $1.934 \times 10^{-5} \text{ cm}^2/\text{sec}$, with $\sigma_E = 0.99 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{1/2})$. From Figure 17, $\sigma_R = 0.867 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{1/2})$ for the absorption of carbon dioxide into a 300 ppm aqueous n-octanol solution

$$R_i / \sqrt{t} = \left(\frac{0.99 - 0.867}{0.867} \right) \sqrt{\frac{3.1426}{1.934 \times 10^{-5}}} = 57.14 (\text{sec}^{1/2}) / \text{cm}. \quad [41]$$

Calculation of Time Independent Interfacial Resistance Model

The gas absorption is a function of time as expressed in question [15]. At different times, the absorption rate is different, but the parameters A, B, and K are almost the same for a surfactant solution. A computer program was used to fit the parameters to equation [14], and equations [23] and [24] were used to calculate the interfacial resistance. For 300 ppm n-octanol solutions,

$$N = (0.9144 \times 10^{-3})(0.512)t^{0.003578} - 1. \quad [42]$$

At $t = 30$ sec

$$N = 0.6861 \times 10^{-4} \text{ gm moles}/(\text{sec})(\text{cm}^2)$$

$$R_i = 1007 \text{ sec}/\text{cm}.$$

And since seven points were used according to Figure 17

$$R_i = 1007, 1086, 1103, 1096, 1076, 1048, 1016$$

at $t = 30, 60, 90, 120, 150, 180, 210$, respectively.

The average of these seven points is

$$R_i = 1061.7 \text{ cm}/\text{sec}.$$

This value was taken as the interfacial resistance for 300 ppm n-octanol solution.

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