The Effect of Surface Active Agents on Liquid-Liquid Mass Transfer Rates

LYLE K. MUDGE and WILLIAM J. HEIDEGER

University of Washington, Seattle, Washington

An interferometric investigation of the transfer of *n*- and iso-butyl alcohols from water to carbon tetrachloride revealed the existence of large interfacial resistances (500 to 2,500 sec./cm.) attributable to the presence of surface active agents. Evidence of a solute-surfactant interaction has been obtained with sodium dodecyl sulfate and sodium tetradecyl sulfate, but the effect appears to be much less pronounced with the shorter chain length surfactant or with the branched chain alcohol.

The influence which surface active agents exert on the transfer rate of a solute between immiscible phases may be either beneficial or deleterious. Since there are several competing mechanisms by which this effect may be generated, any attempt at understanding must begin by separating the hydrodynamic from the physico-chemical factors. The important hydrodynamic effects may include variation in stable drop size for dispersed systems, changes in circulation velocities, interface immobilization, and the restriction of interface movement because of interfacial tension gradients (*11, 12, 20, 21, 31*). Physico-chemical factors, on the other hand, are such effects as surface blocking (sieve effect) or solute-surfactant interactions (energy barrier) and will lead to a departure from interfacial concentration equilibrium when mass interchange occurs between phases.

The physico-chemical effect, usually referred to as an *interfacial resistance* or *barrier*, has been demonstrated in studies of the effect of monolayers on water evaporation rates (*1, 18, 19, 27, 29*) and gas absorption-desorption rates (*2, 13, 15, 28*). However, studies in liquid-liquid systems have not been conclusive in identifying the existence of a true interfacial barrier with surface active agents present. Hutchinson (*17*) observed the effect of surface active agents on the transfer of various solutes through a plane interface from water to benzene and found a significant transfer rate reduction which varied in magnitude depending upon the solute transferring. Although Hutchinson hypothesized a solute-surfactant interaction, Blokker (*3*) and Lewis (*20*) explained observed reductions in transfer rates between independently stirred phases in terms of changes in hydrodynamic factors caused by surface active agents. Terjesen and co-workers (*4, 16, 22, 23*) and Garner and co-workers (*11, 12*) investigated the effect of surfactants on the transfer to or from drops and reported a significant reduction in the transfer rate. Since it is well known that hydrodynamic effects may be very pronounced in dispersed systems, no resolution of mechanism can be made from the above results.

Davies and Wiggill (*9*), employing a Lamm scale technique capable of detecting only resistances greater than 1,000 sec./cm., reported that various monolayers introduced no measurable resistance in the transfer of acetic acid between water and oils. They did observe, however, interfacial instabilities in the clean systems which were eliminated by the surfactants. Vignes (*33*), utilizing the less selective technique of measuring total transfer in a specified time, reported an apparent resistance of 1,200 sec./cm. for the same system. He could not detect, however, the hydrodynamic instabilities observed by Davies, so that it is impossible to determine what fraction of his reported resistance may correspond to the damping of interfacial motions by the surfactant.

Very large resistances, on the order of 25,000 to 400,000 sec./cm., were reported by Drickamer and co-workers (*30, 32*) for the transfer of tagged sulfur compounds across various liquid-liquid interfaces. No effect of adding surface active agent, Tween 20, was observed; however, Davies and Rideal (*8*) have suggested that the measured resistances might have resulted from interfacial contamination from rubber cell gaskets.

The present work is concerned with the determination of any interfacial resistance which is caused by the addition of surface active agents to a liquid-liquid mass transfer system. The resistance is evaluated from direct measurement of concentrations in the vicinity of the interface during mass transfer. The concentrations at the interface determine the degree of any departure from equilibrium which is a direct measurement of the barrier mechanism. The nature of the interfacial resistance is discussed on the basis of the effect of changes in concentration of two surfactants and two solutes.

THE EXPERIMENTAL METHOD

Equipment

A Mach-Zehnder interferometer with a helium-neon laser light source was used to measure local concentrations during interfacial mass transfer. The distortion of initially straight fringes in photographs taken with a 16 mm. cine' camera, for example, Figure 1, is a measure of concentration variation.

The laser proved to be a convenient light source providing light of sufficient intensity to photograph the fringe pattern on Plus X negative film as speeds up to 24 frames/sec. The tedious interferometer adjustment necessary with mercury light sources (*7*) was eliminated because of the long coherence length of laser light. For the same reason, it was possible to observe fringes in both phases simultaneously without resorting to the use of unsatisfactory split reference cells.

The use of the interferometer requires a cell with two opposing sides transparent to allow passage of the light through the cell and the cell contents. A schematic of the cell as viewed along the light beam is shown in Figure 2. The cell body was made of 1 in. stainless steel with the faces surface ground to be parallel to within 7 sec. of arc. Teflon gaskets were used between the ½ in. thick plate glass windows and stainless steel cell body. All the lines were stainless steel, and the valves were stainless steel with Teflon packing. Glass reservoirs were used to store both phases.

Preliminary Procedure

The cell components were cleaned in a sodium dichromate-sulfuric acid cleaning solution prior to each run, with the exception of the stainless lines which were rinsed thoroughly with distilled water and reagent grade methanol and dried with filtered air. The glass windows were treated such that the surface that was to contact the organic phase in the assembled cell was hydrophobic and oleophilic, while the surface in con-

---

Lyle K. Mudge is with the Battelle Northwest Laboratories, Richland, Washington.

tact with the aqueous phase was hydrophilic. With the glass surfaces treated in this manner, the interface would adhere to the boundary between the two types of surfaces. Proper alignment of the glass windows greatly aided the flattening of the interface.

The glass treatment procedure involved the vapor deposition of trimethylchlorosilane on a heated glass surface (100°C.) that had been cleaned in hot (120°C.) sulfuric acid-sodium dichromate cleaning solution, rinsed with distilled water and reagent grade methanol, and vapor cleaned with boiling *n*-butanol. The silane coating was then removed from the portion of the surface that was to contact the aqueous phase by immersion of that portion of the surface in a hot sulfuric acid-sodium dichromate cleaning solution (70°C.). The entire glass surface was then rinsed wth distilled water and methanol and polished with lens paper. The wetting characteristics of the two surface regions are illustrated in Figure 3.

After the cell components were cleaned and prepared, assembly was undertaken, with great care exercised to assure alignment of the glass windows. The assembled cell was placed in a constant temperature water bath which was maintained at 25°C. and, along with the solutions, was given 2 hr to reach thermal equilibrium.

Operating Procedure

The major step in preparing for a run was the filling of the cell. The procedure can be described with reference to the flow diagram in Figure 4. The flow of the carbon tetrachloride phase into the cell and out the lower slit filled the cell up to the slits. The aqueous phase was then admitted to the cell in order to fill the line from the aqueous phase reservoir to the cell. Air was purged from the upper half of the cell by injecting the aqueous phase with a syringe through the aqueous phase outlet line into the cell and out the vent line on the aqueous phase inlet. About 10 ml. of fresh aqueous solution was pulled through the vent line from the reservoir with a syringe, while the aqueous phase was flowing through the cell. In this manner it was assured that the vent line contained no solution that might have a concentration different from that of the aqueous phase reservoir. Capping of the vent line with a serum stopper completed the filling of the cell.

Approximately 50 to 75 ml. of both the aqueous and the organic phases, which was more than the volume necessary to give uniform concentrations in both phases, were run through the cell simultaneously before the flow rates were adjusted for boundary sharpening. The aqueous and organic phase flow rates were set at about ½ ml./min., and then both were adjusted slightly to give as flat an interface as possible with uniform concentrations in both phases. If a flat interface could not be obtained, it was necessary to disassemble the equipment and repeat the above cleaning and assembly procedure.

When the interface was flat to within less than 0.3 mm. in thickness, the flow through the cell was stopped, which determined the experimental zero time. The cine′ camera was started within 10 sec. and ran continuously for about the first 65 sec. At 10-sec. intervals the reference beam of the interferometer was blocked to mark the time on the film and to give a shadow graph which showed the thickness and position of the interfacial region. Shadow graphs and interferograms were taken in short bursts at various times up to about 30 min. After 400 sec. the curvature of the fringes extended to the edge of the frame, so the fringe shifts in each phase after that time had to be photographed separately. For example, the camera was moved upward on the tripod, and the fringe shift in the organic phase was photographed at 1,200 sec. The camera was then quickly moved downward to photograph the organic phase shift at 1,225 sec., essentially the same time. The interface was visible in both interferograms (Figure 1).

Frequently, after about 40 or 50 sec. into the run, a convective disturbance commenced in the aqueous phase only. The disturbance started at one side of the cell next to the aqueous phase exit slit and gradually progressed across the cell to the other side. An exchange of liquid between the slit and the cell presumably caused this disturbance, but evaluation of interfacial concentrations was not prevented by the resulting distortion. The penetration depth, calculated from the diffusion equation integrated with the usual assumptions and with a diffusivity of 10^{-5} sq.cm./sec., is about 0.8 mm. after 40 sec. The slit width is 0.5 mm, and, since the solution in the slit has contacted the organic phase for only a short time and is lighter than the solution next to the interface in the penetration region, the solution in the slit may be displaced by the heavy layer at the interface. No disturbance was noted in the organic phase, a fact which always made interpretation of the results possible.

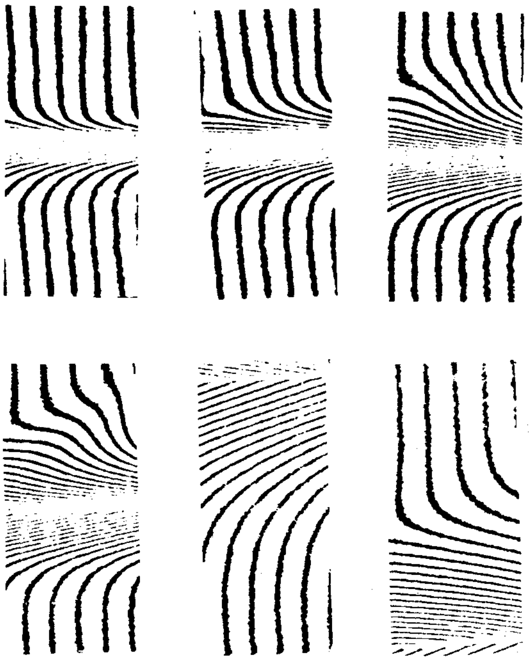

Fig. 1. Interference fringe patterns: 30, 60, 144, 225, 1,200 sec. Organic phase 1,225 sec. Aqueous phase 7 mm. height shown.

Systems Investigated

The requirements for the study of mass transfer in a stagnant system by an optical technique include transfer of a solute such that no density inversions occur and transfer of a solute which produces detectable changes in the optical properties of the system. The transfers of *n*-butyl alcohol and of isobutyl alcohol from water to carbon tetrachloride fulfill both of these requirements. The decrease in the alcohol concentration in the aqueous phase in juxtaposition to the interface results in an increased density, while the increase in alcohol concentration in the carbon tetrachloride phase adjacent to the interface decreases the density of that region. Therefore, the transfer of *n*-butyl alcohol and isobutyl alcohol from water to carbon tetrachloride is convectively stable with respect to density gradients. Moreover, the refractive indexes of the components are amenable to an optical study.

The transfer of both *n*-butyl alcohol and isobutyl alcohol from water to carbon tetrachloride is accompanied by violent interfacial eruptions. Both sodium dodecyl sulfate and sodium tetradecyl sulfate, the surfactants used in the study, completely damped all such interfacial turbulence at all the concentrations of surfactant investigated. The systems were chosen because of reports in the literature of a resistance to mass transfer caused by surface active agents during the transfer of *n*-butyl alcohol (*3, 17*) and because of reports of resistances caused by the sodium alkyl sulfates (*5*). The nature of the above resistances was not evident, however, from the reported results.

The solutes *n*-butyl alcohol and isobutyl alcohol were selected in order to study the effect of a change in the chain structure of the solute on the interfacial resistance. Sodium dodecyl sulfate and sodium tetradecyl sulfate were chosen as surfactants to evaluate the effect of a change in the surfactant chain length. Two different concentrations of *n*-butyl alcohol and sodium tetradecyl sulfate were used in the experimental runs. Simply distilled water and reagent grades of carbon tetrachloride, *n*-butyl alcohol, and isobutyl alcohol were employed. The surfactants were originally prepared by methods

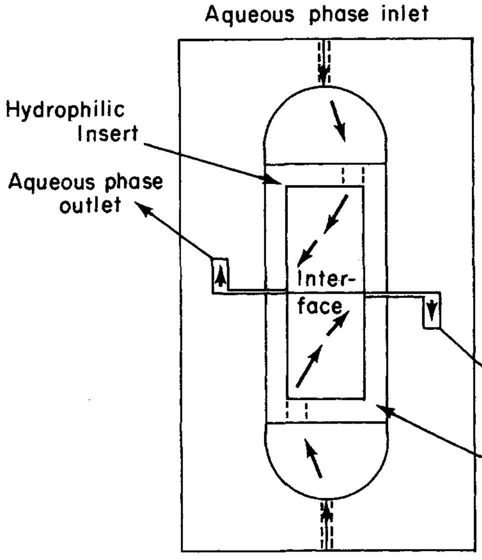

Fig. 2. Cell schematic.

outlined by Dreger et al. (*10*) for use in the determination of micellar molecular weights. The pure-water-alcohol-carbon tetrachloride system that was prepared with the materials described above showed considerable interfacial instability, indicating that no significant amounts of surface active impurities were present.

METHOD OF ANALYSIS

Time dependent concentration profiles in the vicinity of the interface may be obtained for both phases from an evaluation of the interferograms. Measurements may be made as close to a planar surface as the optical resolution of the system permits; however, the presence of any meniscus at the liquid-liquid interface will result in a narrow interfacial band in which concentrations are not observable. Even with great pains taken to eliminate the meniscus, a region of thickness up to 0.1 or even 0.2 mm. sometimes existed, in which the concentrations of the two phases could not be obtained experimentally. Extrapolation to the interface was then done either graphically or by means of the flux equation obtained by integration of the diffusion equation with the usual boundary conditions of no interfacial resistance and infinite phases:

$$D_i \frac{\partial C_i(x, t)}{\partial x} = \frac{mC_o}{1 + m\sqrt{D_2/D_1}} \sqrt{\frac{D_2}{\pi t}}\, e^{-\frac{x^2}{4D_i t}} \qquad (1)$$

where $i = 1$ or 2.

The flux at some point $x = a$ near the interface is obtained from the experimental data. The flux at $x = 0$ is obtained by multiplying the observed flux at $x = a$ by the ratio of the calculated fluxes given by

$$\frac{\partial C_i(0, t)/\partial x}{\partial C_i(a, t)/\partial x} = e^{\frac{a^2}{4D_i t}} \qquad (2)$$

The concentrations may then be extended through the interfacial region at the arithmetic average of the observed slope at $x = a$ and the extrapolated slope at $x = 0$.

The resistances are calculated by using the following boundary condition at $x = 0$ for an interfacial resistance R_s:

$$D_i \frac{\partial C_i(0, t)}{\partial x} + \frac{1}{R_s}(C_{2i} - mC_{1i}) = 0 \qquad (3)$$

where C_{2i} and C_{1i} are the interfacial concentrations in the two phases. The fluxes and interfacial concentrations are obtained directly from the experimental data.

An alternative method of calculating the interfacial resistance verifies, in some cases, the results obtained from Equation (3). Equation (3) is used with the usual initial condition and the boundary condition for no accumulation at the interface to obtain the following expressions for the concentration profiles in a two-phase system infinite in extent (9):

$$C_1(x, t) = \frac{C_o}{1 + m\sqrt{D_2/D_1}} \left[1 + m\sqrt{\frac{D_2}{D_1}} \left\{ \operatorname{erf} \frac{x}{2\sqrt{D_1 t}} + \exp(h_1 x + h_1^2 D_1 t) \operatorname{erfc}\left(\frac{x}{2\sqrt{D_1 t}} + h_1\sqrt{D_1 t} \right) \right\} \right] \qquad (4)$$

$$C_2(x, t) = \frac{mC_o}{1 + m\sqrt{D_2/D_1}} \left[\operatorname{erfc} \frac{|x|}{2\sqrt{D_2 t}} - \exp(h_2 |x| + h_2^2 D_2 t) \operatorname{erfc}\left(\frac{|x|}{2\sqrt{D_2 t}} + h_2\sqrt{D_2 t} \right) \right] \qquad (5)$$

where h_1 and h_2 are given by

$$h_1 = \frac{m + \sqrt{D_1/D_2}}{D_1 R_s} \qquad (6)$$

$$h_2 = \frac{1 + m\sqrt{D_2/D_1}}{D_2 R_s} \qquad (7)$$

The interfacial concentrations are determined from Equations (4) and (5) to be

$$C_1(0, t) = \frac{C_o}{1 + m\sqrt{D_2/D_1}} \left[1 + m\sqrt{\frac{D_2}{D_1}} \{\exp(h_1^2 D_1 t) \operatorname{erfc}(h_1\sqrt{D_1 t})\} \right] \qquad (8)$$

$$C_2(0, t) = \frac{mC_o}{1 + m\sqrt{D_2/D_1}} [1 - \exp(h_2^2 D_2 t) \operatorname{erfc}(h_2\sqrt{D_2 t})] \qquad (9)$$

An approximation to the interfacial concentrations is obtained from the expansion of $e^{x^2} \operatorname{erfc}(x)$ given by

$$e^{x^2} \operatorname{erfc} x = \frac{1}{x\sqrt{\pi}} \left[1 - \frac{1}{2x^2} + \frac{1\cdot 3}{(2x^2)^2} - \frac{1\cdot 3\cdot 5}{(2x^2)^3} + \dots \right] \qquad (10)$$

Equations (8) and (9) become the following with all but the first term in the expansion neglected:

$$C_1(0, t) = \frac{C_o}{1 + m\sqrt{D_2/D_1}} \left[1 + \frac{m\sqrt{D_2/D_1}}{h_1\sqrt{\pi D_2 t}} \right] \qquad (11)$$

$$C_2(0, t) = \frac{mC_o}{1 + m\sqrt{D_2/D_1}} \left[1 - \frac{1}{h_2\sqrt{\pi D_2 t}} \right] \qquad (12)$$

The interferometric technique (7) that is used to obtain the data yields a record of the fringe shift as a function of x and t. The fringe shift is the number of fringes a vertical fringe is displaced laterally by a gradient in refractive index. The fringes are adjusted initially to be vertical, parallel, and evenly spaced. Changes in concentration that occur during mass transfer result in commensurate changes in the refractive index. If the change in refractive index is linear with the concentration change, the relation between the fringe shift S and the concentra-

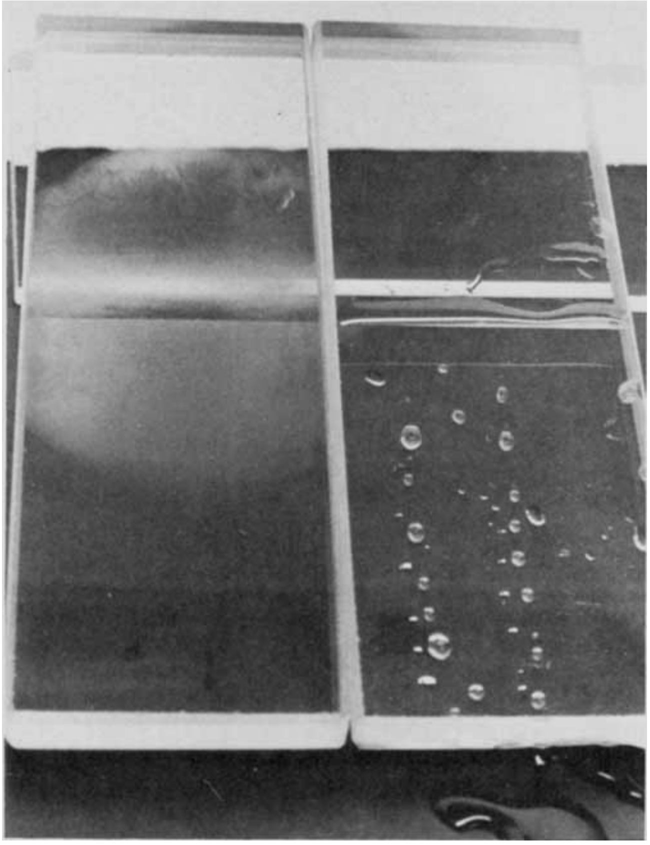

Fig. 3. Wetting characteristics of glass plates: upper section hydrophilic, lower section hydrophobic.

tion change ΔC is

$$\Delta C = \frac{\lambda}{d} \beta S \tag{13}$$

The ratio of the fringe shift S observed in a system exhibiting an interfacial resistance to the fringe shift S^* in that same system at equilibrium distribution is given by

$$\frac{S}{S^*} = \frac{\Delta C}{\Delta C^*} \tag{14}$$

Substitution of Equations (11) and (12) into (14), with $\Delta C_1 = C_o - C_1(0, t)$, $\Delta C^*_1 = C_o - C_1(0, \infty)$, $\Delta C_2 = C_2(0, t)$, and $\Delta C^*_2 = C_2(0, \infty)$, yields for phases 1 and 2, respectively

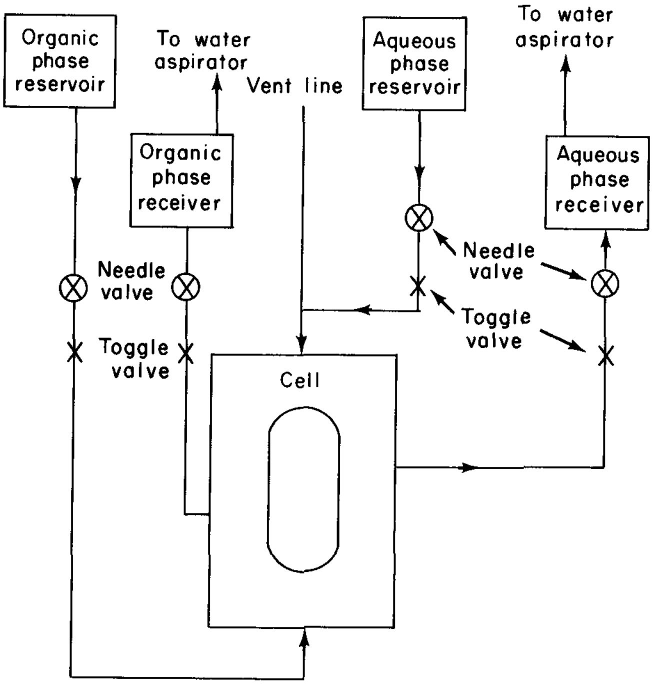

Fig. 4. Flow diagram.

$$S_1 = S^*_1 \left[1 - \frac{1}{h_1 \sqrt{\pi D_1 t}} \right] \tag{15}$$

$$S_2 = S^*_2 \left[1 - \frac{1}{h_2 \sqrt{\pi D_2 t}} \right] \tag{16}$$

Equations (15) and (16) predict a linear variation of the fringe shift with $1/\sqrt{t}$ for times long enough to give a value of about 3 for $h\sqrt{Dt}$. It should be possible to calculate the resistance from the slope of such a plot, and indeed, Harvey and Smith (*15*) used such a relationship in the evaluation of gas absorption data. However, it is extremely difficult to design an experiment to satisfy all the conditions necessary for the application of Equations (15) and (16).

TABLE 1. RESISTANCES FOR RUN 887, EXTRAPOLATION COMPARISON
Concentration of sodium tetradecyl sulfate, 2.5 p.p.m.
Concentration of *n*-butanol, 0.106M
Equilibrium distribution, 0.520

		Resistance, sec./cm.			
		Flux extrapolation		Graphical extrapolation	
Time, sec.	Thickness of blind zone, mm.	Flux equalization	Extension of organic phase profile	Extension of aqueous phase profile	Extension of organic phase profile
10	0.226	500	10	1,410	940
20	0.205	1,130	440	—	—
30	0.237	570	160	1,980	740
40	0.224	460	270	1,180	980
50	0.208	1,010	450	1,480	720
60	0.153	1,050	890	1,440	1,150
100	0.159	850	880	—	—
144	0.162	1,060	610	1,600	610
169	0.205	1,220	510	1,830	240
225	0.179	1,450	690	1,680	840
324	0.172	900	900	—	—
400	0.188	1,270	1,270	1,660	1,410
625-645	0.164	1,970	1,970	1,700	2,240
1,225-1,245	0.161	1,260	1,260	1,330	1,440
1,849-1,865	0.166	1,420	1,420	2,240	1,580

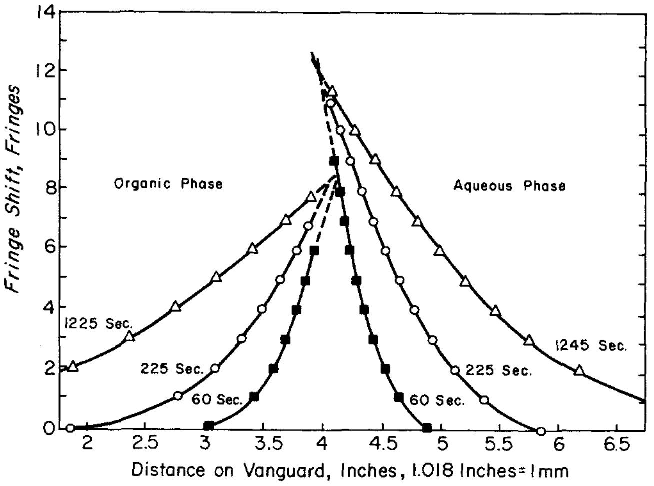

Fig. 5. Fringe profiles, Run 887.

RESULTS

In order that an artificially large value of the resistance would not be measured, it was decided to bias deliberately the data reduction to give low values wherever any uncertainty existed. Thus, all faint fringes, even those which might have resulted from reflection at the interface, were included in the determination of the fringe shift.

Since any uncertainty in the location of the interfacial plane within the narrow band obscured by the meniscus introduced problems in the extrapolation of concentrations to the interface, a conservative method of extrapolation was selected. The interferometric data were converted to concentration profiles as shown in Figure 5. The resistances calculated from these concentration profiles are recorded in Table 1 for two methods of extrapolation through the interfacial region to an interfacial plane located at two positions for each extrapolation method.

The two positions of the interfacial plane for flux extrapolation were selected by determining the point at which the calculated fluxes in the two phases were equal, inasmuch as possible, and by arbitrarily locating the plane next to the aqueous phase (which always resulted in small values of the resistance). A separate analysis based on the concentration profile predicted by integration of the diffusion equation with the usual conditions and zero resistance indicated that extrapolation to a line plane would result in too great a concentration change (*24*). Therefore, low experimental values of the resistance will result from such extrapolations.

As can be seen in Table 1, graphical extrapolation of the profiles in Figure 5 gave more consistent values of the resistance than the method of flux extrapolation. The two positions of the interface for the graphical extrapolation were located on either side of the interfacial region, which means that the actual value of the resistance is somewhere between the values shown. It is immediately apparent that the method of extrapolation will strongly affect the calculated resistances when the blind zone at the interface is as large as that in Table 1. Flux extrapolation gives especially low values for the resistance at early times, since the actual concentration profiles are more linear than predicted by the integrated diffusion equation. The flux extrapolation technique was used to evaluate all the data, however, since it would give conservatively low values of the resistance. In two of the runs the interfacial region was less than 0.1 mm. thick, which made the extrapolation method less critical. It is important to note that when the blind zone at the interface was very thin (for example, 0.003 mm.) and little extrapolation was necessary, large resistances were always calculated. The technique of biasing the data reduction to give small values of the resistance when any uncertainty existed also resulted in considerable scatter in the results. However, this procedure was deemed necessary in order that the existence of a resistance might be confirmed. In spite of the conservatively low values thus obtained, an interfacial resistance of considerable magnitude was detected in all experiments with *n*-butanol as solute. For transfer from an aqueous solution at two concentrations (0.108 and 0.156M) to carbon tetrachloride, the resistance calculated from Equation (3) fell in the range of 1,800 to 2,400 sec./cm., with 60 to 65 p.p.m. of sodium tetradecyl sulfate initially in the aqueous phase. However, a subjective evaluation of the data reduction permits an estimate of the best value for the resistance in this system as a number near the upper end of this range. Similarly, with a 0.106M aqueous solution of *n*-butanol containing 2.5 p.p.m. sodium tetradecyl sulfate, the resistance measured was in the range of 800 to 1,400 sec./cm., while it was between 600 and 1,200 sec./cm. when the aqueous solution contained initially 65 p.p.m. sodium dodecyl sulfate. In the transfer to carbon tetrachloride of isobutanol from a 0.114M aqueous solution containing initially 65 p.p.m. sodium tetradecyl sulfate, the measured resistance was less than 700 sec./cm.

TABLE 2. ESTIMATES OF RESISTANCE

Solute	Initial solute concentration, (g.)(moles)/liter	Surfactant	Surfactant concentration, p.p.m.	Resistance, sec./cm.
n-C_4H_9OH	0.108	$NaC_{14}H_{29}SO_4$	61	2,300
n-C_4H_9OH	0.156	$NaC_{14}H_{29}SO_4$	65	2,100
n-C_4H_9OH	0.106	$NaC_{14}H_{29}SO_4$	2.5	1,050
n-C_4H_9OH	0.106	$NaC_{12}H_{25}SO_4$	65	850
i-C_4H_9OH	0.114	$NaC_{14}H_{29}SO_4$	65	<500

Our best estimates of the magnitudes of the above resistances, weighted in favor of those measurements which required the least extrapolation, are given in Table 2.

The coefficients of diffusion for *n*-butanol and isobutanol in water required in the calculation of resistances were determined from the literature to be 0.88×10^{-5} (*26*) and 0.72×10^{-5} sq.cm./sec. (*14*), respectively. The diffusivities of the solutes in carbon tetrachloride were evaluated from the data to be 1.08×10^{-5} sq.cm./sec. for *n*-butanol and 0.88×10^{-5} sq.cm./sec. for isobutanol. The value of the change in concentration of *n*-butanol per unit change in refractive index was determined to be 132 and 150 (g.)(moles)/liter in water and carbon tetrachloride, respectively. The same values for isobutyl alcohol were respectively 132 and 144 (g.)(moles)/liter. This calibration was made by analysis of standard solutions on a Brice-Phoenix differential refractometer (*6*).

The equilibrium distribution values were determined with the use of the differential refractometer and were also estimated from the experimental data extrapolated to infinite time. The values that were used for initial concentrations of 0.108M *n*-butanol and 0.156M *n*-butanol were 0.52 and 0.58, respectively. For the run with isobutyl alcohol, a value of 0.49 was used.

DISCUSSION OF RESULTS

The ability to detect small interfacial resistances with high precision by utilizing the interferometer technique depends heavily on the quality of the interface attained. A realistic estimate for the present equipment would be

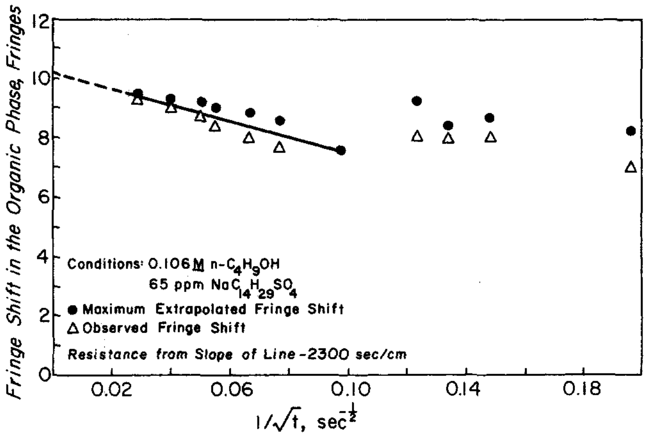

Fig. 6. Time dependence of interfacial fringe shift, Run 657A.

a minimum detectable resistance of about 100 sec./cm., assuming the interfacial blind zone can be maintained at 0.1 mm. or less. At this low level, however, the measurement would be expected to be precise only to within a factor of 2. For the resistance levels reported here, again assuming a blind zone of less than 0.1 mm., a precision of about 20% is considered reasonable. Not all the runs made in the present study had an interface of this quality, although, for a few, the blind zone was substantially narrower. Again, it is worth noting that where the precision was expected to be low, the data reductions were biased to generate low measures of the resistance. Thus, although the scatter evidenced by the results is somewhat disappointing, it is nevertheless very clear from these measurements that substantial resistances to mass transfer were encountered at the interface.

Any uncertainty in the value of the equilibrium distribution is especially pronounced at long times when the system approaches equilibrium. The values of the resistance at long times would increase markedly if too high a value of m were used, and the opposite would occur if too low an m value were used.

The method of locating the interfacial plane at a position within the interfacial region such that the fluxes in the two phases are equal was hampered by a convective disturbance in the aqueous phase as can be noted in Figure 1. No similar disturbance was observed in the organic phase. The convection made the aqueous phase flux determination unreliable, but the overall concentration change in the aqueous phase could still be determined.

Figures 6 and 7 show plots of the observed and extrapolated fringe shifts in the organic phase vs. $1/\sqrt{t}$ for runs where the interfacial region was less than 0.1 mm. The actual fringe shift lies between the observed and extrapolated values. The resistances calculated from the slopes of best fit lines, and Equation (16) would be consistent with the values obtained from Equation (3). However, the lines in Figures 6 and 7 have been drawn to show the slope necessary to give the associated resistances.

Comparison of the results with literature values is difficult, since no similar values for liquid-liquid systems are to be found. The magnitude of the resistances is much larger than anything reported for gas-liquid systems. In liquid-liquid systems, Davies and Wiggill (9) reported that any resistance caused by sodium dodecyl sulfate in the transfer of acetic acid from water to benzene was less than 1,000 sec./cm., the lower limit they could detect. The lack of precision in their method stems from two complications. First, they analyzed their results with an equation for the total amount of solute transferred based on the integration of the diffusion equation with the usual conditions. However, the initial condition employed is not valid, since at the experimental zero time a significant amount has already transferred and is included in the experimental quantity. Second, their data were taken with the first experimental point at about 1,000 sec., for which time the bulk phase diffusional resistances are already about 18,000 sec./cm.

It is significant that Blokker (3) noted a resistance caused by surfactant (sodium cetyl sulfate) only for the transfer of n-butanol from water to benzene. Hutchinson (*17*) also reported a considerable resistance for the same system. The results of the present study confirm Hutchinson's observations and his hypothesis that the resistance is caused by a solute-surfactant interaction.

Vignes (33) reported resistances of 1,200 and 1,150 sec./cm. at 20° and 25°C., respectively, for the transfer of acetic acid from water to toluene in the presence of Teepol. He attributed the resistance to a purely physicochemical action, but his results are somewhat questionable, since he apparently did not consider any effects of the surfactants on the spontaneous emulsification reported for this system by Davies and Wiggill (9). Further, he apparently neglected the effect of the surfactant on the interfacial instability that the pure system exhibits. Nevertheless, he compared the value of the apparent resistance with Teepol to the apparent resistance in the pure system, reported as 400 sec./cm., which gave a ratio of 3. The analysis which he developed predicted a ratio of 2.9, which is remarkably good agreement.

The analysis of Vignes was used to calculate the ratio of the resistance with surfactant to the resistance of the pure system for the systems studied in the present work. Values of 2.6, 1.1, and 1.4 were determined for systems with 65 p.p.m. sodium tetradecyl sulfate, 2.5 p.p.m. sodium tetradecyl sulfate, and 65 p.p.m. sodium dodecyl sulfate, respectively. Although the range of resistances determined in this study is consistent with these ratios, the resistance for the transfer of n-butanol in a pure system would have to be unbelievably high, 700 sec./cm.

The results of the runs with n-butanol and isobutanol indicate that the resistance depends on the type of solute that is being transferred and rule out steric hindrance as a controlling factor. The fact that the resistance decreases with concentration of the surfactant indicates that the surfactant is blocking the passage of solute in some manner and could be interacting with the solute. No change in the resistance with solute concentration suggests that a large excess of n-butanol already exists at the interface at the lower bulk concentration, and an increase in bulk concentration would not affect any interaction of solute and surfactant, which is the favored explanation of the results.

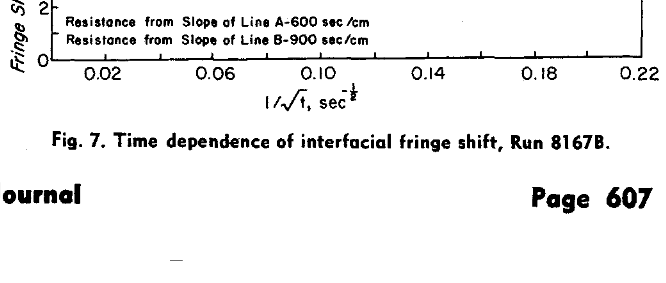

Fig. 7. Time dependence of interfacial fringe shift, Run 8167B.

Another indication of solute-surfactant interaction is found in the literature dealing with the study of micelles, in which the presence of sulfate surfactant micelles results in increased alcohol solubility (*34*). Also, in the study of the adsorption of tritiated sodium dodecyl sulfate from water, Nilsson (*25*) reports that the amount of sodium dodecyl sulfate adsorbed at the surface is unchanged by the addition of *n*-dodecanol, although the surface tension is drastically reduced. A study of the adsorption of tritiated *n*-dodecanol showed that the *n*-dodecanol penetrated into the film of long chain sulfate ions, indicating again an interaction between alkyl sulfate ions and alcohols.

The results of this study show a large barrier type of resistance caused by surfactants. Many factors contribute to the scatter in results, but conclusions can still be made on the nature of the resistance which can be explained in terms of a solute-surfactant interaction.

CONCLUSIONS

1. An interfacial resistance of considerable magnitude exists for the experimental systems with *n*-butanol as the transferring species in the presence of the surfactants used. Thus, the action of surfactants as a barrier to interfacial mass transfer was confirmed.
2. The interfacial resistance for the transfer of isobutanol, if it exists at all, is very considerably less than for the transfer of *n*-butanol under identical conditions.
3. The resistance to the transfer of *n*-butanol from water to carbon tetrachloride decreases markedly with a decrease in the initial bulk concentration of sodium tetradecyl sulfate in the aqueous phase.
4. A drastic reduction in the interfacial resistance occurs when the sodium tetradecyl sulfate is replaced with an equal bulk concentration of sodium dodecyl sulfate. (Note: the ratio of the amount of interfacial adsorption of sodium tetradecyl sulfate to sodium dodecyl sulfate was calculated to be 2.3, assuming no interaction with the *n*-butanol; consequently, the reduced resistance could result from the diminished interfacial concentration with the use of sodium dodecyl sulfate.)
5. No significant change in the interfacial resistance with changing solute concentration was observed.
6. The relative order of magnitude of the resistances that were observed in the experimental runs was consistent with the hypothesis of Hutchinson (*16*) that a solute-surfactant interaction exists.
7. The results with isobutyl alcohol suggest that a barrier resistance may not exist with all surface active agents. At least, the resistance could be considerably less in magnitude.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the Engineering Division of the National Science Foundation, which made the work reported here possible.

NOTATION

a = arbitrary distance from interface, Equation (2), cm.
C = solute concentration, (g.)(moles)/cc.; ΔC^* = change in concentration at infinite time
d = length of light path through cell, cm.
D = solute diffusion coefficient, sq.cm./sec.
h = interfacial resistance parameter, defined by Equations (6) and (7)
m = phase equilibrium distribution coefficient, concentration in phase 2 at $x = 0$/concentration in phase 1 at $x = 0$
R_s = interfacial resistance, sec./cm.
S = fringe shift, fringes; S^* = fringe shift at equilibrium distribution
t = time, sec.
x = coordinate normal to interface, cm.
β = concentration coefficient of refractive index change, (g.)(mole)/cc.
λ = wavelength of light, cm.

Subscripts

i = interfacial condition or phase designation
o = initial condition
1 = aqueous phase
2 = organic phase

LITERATURE CITED

1. Archer, R. J., and V. K. LaMer, *J. Phys. Chem.*, **59**, 200 (1955).
2. Blank, M., and F. J. W. Roughton, *Trans. Faraday Soc.*, **56**, 1832 (1960).
3. Blokker, P. C., *Proc. 2nd Intern. Congress of Surface Activity*, **1**, 503 (1957).
4. Boye-Christensen, G., and S. G. Terjesen, *Chem. Eng. Sci.*, **7**, 222 (1958).
5. *Ibid.*, **9**, 225 (1959).
6. Brice, B. A., and R. Speiser, *J. Opt. Soc. Am.*, **36**, 363 (1946).
7. Caldwell, C. S., J. R. Hall, and A. L. Babb, *Rev. Sci. Instr.*, **28**, 816 (1957).
8. Davies, J. T., and E. K. Rideal, "Interfacial Phenomena," 2 ed., Academic Press, London, England (1963).
9. Davies, J. T., and J. B. Wiggill, *Proc. Royal Soc.*, **A255**, 277 (1960).
10. Dreger, E. E., G. I. Klein, G. D. Miles, Leo Shedlovsky, and John Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).
11. Garner, F. H., and A. R. Hale, *Chem. Eng. Sci.*, **2**, 157 (1953).
12. Garner, F. H. and A. H. P. Skelland, *ibid.*, **4**, 149 (1955)
13. Goodridge, F., and I. D. Robb, *Ind. Eng. Chem. Fundamentals*, **4**, 49 (1965).
14. Griffith, R. M., *Chem. Eng. Sci.*, **12**, 198 (1960).
15. Harvey, E. A., and W. Smith, *ibid.*, **10**, 274 (1959).
16. Holm, A., and S. G. Terjesen, *ibid.*, **4**, 265 (1954).
17. Hutchinson, E., *J. Phys. Colloid Chem.*, **52**, 897 (1948).
18. LaMer, V. K., T. W. Healy, and L. A. G. Aylmore, *J. Coll. Sci.*, **19**, 673 (1964).
19. Langmuir, I., and D. B. Langmuir, *J. Phys. Chem.*, **31**, 1719 (1927).
20. Lewis, J. B., *Chem. Eng. Sci.*, **3**, 248 (1954).
21. ———, and H. R. C. Pratt, *Nature*, **171**, 1155 (1953).
22. Lindland, K. P., and S. G. Terjesen, *Chem. Eng. Sci.*, **5**, 1 (1956).
23. Melhus, B. J., and S. G. Terjesen, *ibid.*, **7**, 83 (1957).
24. Mudge, L. K., Ph.D. dissertation, Univ. Wash., Seattle (1968).
25. Nilsson, G., *J. Phys. Chem.*, **61**, 1125 (1957).
26. Olander, D. R., *AIChE J.*, **7**, 175 (1961).
27. Rideal, E. K., *J. Phys. Chem.*, **29**, 1585 (1925).
28. Sada, Eizo, and D. M. Himmelblau, *AIChE J.*, **13**, 860 (1967).
29. Sebba, F., and H. V. A. Briscoe, *J. Chem. Soc.*, 106 (1940).
30. Sinfelt, J. H., and H. G. Drickamer, *J. Chem. Phys.*, **23**, 1095 (1955).
31. Thorsen, G., and S. G. Terjesen, *Chem. Eng. Sci.*, **17**, 137 (1962).
32. Tung, L. H., and H. G. Drickamer, *J. Chem. Phys.*, **20**, 6, 10 (1952).
33. Vignes, A., *ibid.*, **57**, 999 (1960).
34. Ward, A. F. H., and A. G. Chitale, *Proc. 2nd Intern. Congress Surface Activity*, **1**, 405 (1957).

Manuscript received June 4, 1968; revision received January 13, 1969; paper accepted January 16, 1969. Paper presented at AIChE Tampa meeting.