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Diffusion Through the Liquid-Liquid Interface: Part II. Interfacial Resistance in Three-Component Systems

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In an investigation of the transfer of solute molecules across the liquid-liquid interface, the transfer of acetic acid, benzoic acid, oleic acid, and cholesterol between benzene and water was measured. Experiments were carried out with a laminar jet apparatus wherein the organic phase was spread as a thin film on the surface of an aqueous jet. The results indicate that any interfacial resistance in these systems is negligibly small.

In an earlier publication (*23*) we considered some basic features of interphase mass transfer in binary systems. From experimental results for benzene and for toluene diffusing into water at contact times as small as 0.01 sec., it appears that in two-component systems chemical equilibrium is established rapidly at a freshly formed liquid-liquid interface and any interfacial resistance is vanishingly small. The present investigation is an extension of the previous study to the more significant case of transfer in three-component systems.

Most of the experimental work reported on diffusion of a solute through the liquid-liquid interface has been carried out with stationary systems (with or without mechanical stirring in the bulk phases) or transfer from droplets. [Pertinent literature has been summarized elsewhere (*7*, *16*, *23*).] The difficulties encountered in using stationary systems are (1) contact times are relatively long and therefore bulk resistances mask any interfacial resistances smaller than approximately 1,000 sec./cm. and (2) at long times attendant interfacial phenomena, such as the Marangoni effect, and contamination of the interface by ever-present surface-active impurities may further obscure the diffusion process. In studying transfer from droplets one must analyze the circulation within and around the droplet—a formidable problem involving flow in the bulk phases coupled with the rheological behavior of the interface.

To overcome the difficulties listed above it would appear that a suitable technique for studying diffusion across the liquid-liquid interface is a dynamic experiment, so that small contact times can be attained, with a well-defined flow field. Three such experiments have been reported recently (*15* to *17*), but none are applicable to three-component systems. In the present investigation a dynamic method has been developed for studying a wide range of three-component systems. The technique was previously tested by the authors on two binary systems (*23*). In the work reported here measurements have been made on four ternary systems.

THE EXPERIMENT

The two phases were contacted with a laminar jet apparatus with the organic phase spread as a thin film on the surface of an aqueous jet issuing from a circular nozzle. After falling some distance in contact, the phases were separated at a specially designed receiver. The resulting average concentration of solute in either of the phases could then be measured. In one system studied (benzene–acetic acid–water) there was a *net transfer* of solute between the phases. All other studies were carried out with a radioactive solute which exchanged between chemically equilibrated phases so that there was no net transfer.

The apparatus and the operation of the jet were described previously (*23*); only minor changes were made for the three-component experiments. All the experiments were performed in a constant temperature room maintained at 25°C. To collect the organic solution flowing off the jet a small Teflon reservoir was mounted on the outside of the receiver, 0.5 cm. below the point at which the phases separated. A

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1-cc. pipette could be inserted through the top of the jet chamber into the reservoir. In this way organic samples were removed for analysis. For drainage of the reservoir a small hole was drilled at the bottom and connected to a vacuum line.

Benzene-Water-Acetic Acid

In the first set of experiments on this system there was a net transfer of acetic acid from benzene to an aqueous phase. In this case 2 liters of benzene and 40 liters of water were mutually saturated. The phases were separated and 1.04 g. acetic acid/liter of solution was added to the benzene. The amount of acetic acid transferred in the jet experiment was determined by titration of water samples from the jet. Samples of exactly 100 cc. were titrated with 0.01 N sodium hydroxide solution, bromthymol blue being used as indicator. The base solution was standardized against benzene-saturated water containing a known amount of acetic acid. The precision and accuracy of the titrations were approximately 0.5%.

In the second set of experiments on this system, no net transfer of acetic acid occurred; rather there was an exchange of radioactive and nonradioactive acetic acid. For these experiments 38 liters of water, 5 liters of benzene, and 1,200 g. of acetic acid were thoroughly mixed to form a benzene solution of 0.960 g. acetic acid/liter of solution and an aqueous solution of 31.6 g. acetic acid/liter. Two liters of the benzene phase were withdrawn and mixed with 50 μc. of carbon-14 labeled acetic acid (as 1.4 mg. of acid). The aqueous phase and the tagged benzene phase were then transferred to the appropriate constant-head reservoirs of the jet apparatus.

The amount of tagged acetic acid transferred in the jet experiment was measured with a liquid scintillation spectrometer. A 1-cc. jet sample was added to 15 cc. of Kinard (22) scintillation fluid. This fluid gave a counting efficiency of approximately 50% on a Tri-Carb Liquid Scintillation Spectrometer, Series 314E. The concentration of tagged acetic acid originally present in the benzene phase was determined by contacting and equilibrating measured volumes of the benzene and water solutions. Virtually all of the tagged acid transferred to the aqueous phase, which was then sampled and counted.

Benzene-Water-Benzoic Acid

For the study of this system 41.7 liters of water, 4 liters of benzene, and 16.1 g. of benzoic acid were thoroughly mixed to form a benzene solution of 0.943 g. of benzoic acid/liter of solution and an aqueous solution of 0.295 g. of acid/liter. The phases were separated and 20 μc. of carbon-14 labeled benzoic acid (less than 1 mg. of acid) was added to the aqueous phase.

The benzene solution flowing off the jet was collected in the Teflon cup described above. One-cc. samples were withdrawn from the cup and diluted in 15 cc. of a toluene-base scintillation fluid (22) suitable for counting carbon-14 in benzene solution. The concentration of tagged benzoic acid originally present in the water was determined by contacting and equilibrating measured volumes of the benzene and water solutions. Benzene samples were counted and the original concentration in the water phase was calculated, as the distribution coefficient for benzoic acid was known. The measurement of the distribution coefficient is described elsewhere (22).

Benzene-Water-Oleic Acid

In this system the benzene and water phases were not equilibrated with respect to oleic acid as was done with the solutes mentioned above, because of the difficulty of dissolving oleic acid in water. The solubility of the carbon-14 labeled oleic acid was apparently less than 0.1 p.p.m. in water. The aqueous solution was prepared by adding 50 μc. (1 mg. of oleic acid in 0.2 g. pentane) to 40 liters of benzene-saturated water. The solution was stirred vigorously for several days. Analysis showed that from a third to a half of the oleic acid found its way to the bulk of the solution. A G.M. tube (1 in. diameter) held near the surface displayed counting rates of the order of 10^5 counts/min. indicating that some of the oleic acid was on the water surface. This matter is further discussed with the results.

The water containing tagged oleic acid was transferred to the jet feed reservoir, taking care to avoid transferring the undissolved acid on the water surface. The distribution coefficient of oleic acid between benzene and water was found to be of the order of 10^3 favoring the benzene. Thus a benzene solution containing 0.02 g. oleic acid/liter was prepared for use in the jet.

The benzene flowing off the jet was sampled and counted exactly as was done with benzoic acid. The original concentration of tagged oleic acid in the water was determined by counting 1-cc. samples of water from the reservoir in Kinard scintillation fluid.

Benzene-Water-Cholesterol

The procedure for preparing the cholesterol solutions was similar to that for the benzoic acid solutions. Four liters of benzene, 41.7 liters of water, and 4.00 g. of cholesterol were thoroughly mixed. The phases were separated and 50 μc. of cholesterol (1 mg. of cholesterol) were added to the water. The benzene solution flowing off the jet was sampled and counted as was done in the study of benzoic acid.

ANALYSIS AND DIFFUSION CALCULATIONS FOR THE LAMINAR LIQUID JET

The flow system to be analyzed comprised two concentric jets issuing from a circular nozzle and falling under the influence of gravity. It was assumed throughout, and confirmed by the results, that the fluid dynamics of the central, aqueous jet was virtually unaffected by the presence of the outer phase, the thin (20 μ) skin of organic fluid flowing concurrently with the inner jet. As the jet accelerated, the original parabolic velocity profile within the jet changed to a uniform profile, and the two-dimensional character of the flow must be considered when one solves for the mass flux into the jet.

The diffusion problem for a binary mixture was treated in a previous work (23). For two components, with unidirectional transfer from the outer film to the inner jet, the total mass transfer rate is independent of film thickness and, with suitable assumptions, the experimental results can be interpreted quantitatively. The final result of the binary analysis was the prediction of the slope (S) of a plot of $(\overline{C} - C_o)/(C^* - C_o)$ vs. $\sqrt{x/Q_w}$ at the point x_1 where the velocity in the jet becomes uniform,

$$\frac{S}{S_i} = \left\{1 + \frac{gx}{\overline{u}^2_o}\left(\frac{R}{R_o}\right)^4\right\}^{1/2}_{x_1}, \quad S_i = 4\sqrt{D} \tag{1}$$

S_i is the slope of such a plot for an "ideal" jet, that is, one in which the velocity is everywhere constant and equal to the average velocity at the nozzle. Experimental results were presented for the diffusion of benzene and toluene into water at 25°C. The slope S was predicted to be $4.36\sqrt{D}$ and the range of experimental conditions was such that the data could be fitted to a linear equation with constant slope. As a check on the analysis, diffusivities were calculated from the data and were found to agree well with literature values.

A linear extrapolation of the data gave an intercept on the abscissa which was approximately the same (0.25 sec.$^{1/2}$/cm.) for both systems. Thus the binary data can be reduced to a single equation

$$\left\{\frac{\overline{C} - C_o}{C^* - C_o}\right\}\frac{1}{\sqrt{D}} = \left[\alpha\sqrt{\frac{x}{Q_w}} - \beta\right] \tag{2}$$

with $\alpha = 4.36$ and $\beta = 1.09$ sec.$^{1/2}$/cm. (as opposed to $\alpha = 4$ and $\beta = 0$ for an ideal jet). Equation (2) may be viewed as a semiempirical relation which can be used to translate from jet length and flow rate to average concentration for the apparatus and conditions used in the experiments reported here. Moreover, as shown below, Equation (2) can be used to interpret the ternary data.

As a highly simplified model for the three-component system, first consider the problem of transient diffusion in a semi-infinite composite medium. For the case of an ideal jet the system can be imagined to be a static one in which diffusion across the interface begins at $t = 0$, the instant at which the two phases are brought into contact. In the coordinates below, the film extends from $y = 0$, the outer surface, to $y = a$, the liquid-liquid interface; the region $y > a$, presumed semi-infinite, corresponds to the aqueous jet. Assume that the concentration of solute is everywhere small and that the two solvents are completely immiscible; then the diffusion equations are

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial y^2}, \quad 0 < y < a \tag{3}$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial y^2} \quad y > a \tag{4}$$

With initial and boundary conditions

$$C_1(y, 0) = C_{10}, \; C_2(y, 0) = C_{20} \tag{5}$$

$$\frac{\partial C_1}{\partial y}(0, t) = 0, \; C_2(\infty, t) = C_{20} \tag{6}$$

$$C_1(a, t) = m\, C_2(a, t); \; D_1 \frac{\partial C_1}{\partial y}(a, t) = D_2 \frac{\partial C_2}{\partial y}(a, t) \tag{7}$$

These equations can readily be solved (22) and the resulting mass flux at the interface can be determined. Thus

$$N_1 = -D_1 \frac{\partial C_1}{\partial y}(a, t) = A \frac{(1-\lambda)}{2} \sqrt{\frac{D_1}{\pi t}} \sum_{n=0}^{\infty} \lambda^n \{\exp[-n^2 Z^2] - \exp[-(n+1)^2 Z^2]\} \tag{8}$$

with

$$A = C_{10} - m\, C_{20}, \; \lambda = \frac{m\,\mu - 1}{m\,\mu + 1}$$

$$\mu = \sqrt{\frac{D_1}{D_2}}, \text{ and } Z = \frac{a}{\sqrt{D_1 t}}$$

and the integrated flux is, therefore

$$\phi = \int_0^t N_1 dt = A \frac{(1-\lambda)}{Z}\, a \sum_{n=0}^{\infty} \lambda^n \{\text{ierfc}\,[nZ] - \text{ierfc}\,[(n+1)Z]\} \tag{9}$$

[ierfc x is the first integral of the complementary error function (4).] Experimentally, the quantity of importance is the average concentration. Expressed as the fractional approach to saturation, the average concentration is given by

$$\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}} = \frac{\overline{C_2} - C_{20}}{C_2^* - C_{20}} = \frac{(1-\lambda)}{Z} \sum_{n=0}^{\infty} \lambda^n \{\text{ierfc}\,[nZ] - \text{ierfc}\,[(n+1)Z]\} \tag{10}$$

where

$$C_1^* = \lim_{t \to \infty} \overline{C_1} = m\, C_{20}$$

In subsequent discussion four limiting forms of Equation (10) are of importance. These are

1. Film thickness becomes large, or contact time approaches zero

$$\left\{\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}}\right\}_o \simeq \frac{(1-\lambda)}{a} \sqrt{\frac{D_1 t}{\pi}} \tag{11}$$

2. The distribution coefficient m becomes small

$$\frac{\overline{C_1}}{C_{10}} \simeq 1 - \frac{2}{Z} \sum_{n=0}^{\infty} (-1)^n \{\text{ierfc}\,[nZ] - \text{ierfc}\,[(n+1)Z]\} \tag{12}$$

3. $m >> 1$ and $C_{10} = 0$

$$\frac{\overline{C_1}}{C_{20}} = \frac{2}{a} \sqrt{\frac{D_2 t}{\pi}} \tag{13}$$

4. The film is perfectly mixed at all times; that is, D_1 becomes infinite

$$\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}} = 1 - \exp\left[\frac{D_2 t}{(am)^2}\right] \text{erfc}\left[\frac{\sqrt{D_2 t}}{am}\right] \tag{14}$$

If the jet is assumed to be ideal then the above equations for the static, composite medium can be applied to the moving jet simply by replacing t and a by their steady state counterparts in the flow problem, namely

$$t = \int_0^x \frac{dx}{u} = \frac{x}{u} = \frac{\pi x d^2}{4 Q_w} \tag{15}$$

and

$$a = \frac{Q_B}{\pi u d} = \frac{d}{4} \frac{Q_B}{Q_w} \tag{16}$$

However, the jet is not ideal. The experimental results for the two-component systems show the deviation from ideality and, moreover, the results may be used to improve the three-component calculations. Consider the expansion of the series in Equation (10). The first term of the series is identical to Equation (11) and therefore represents the average concentration at small times, that is, at times sufficiently small so that the film is virtually semi-infinite as far as the diffusing species is concerned. Equation (10) can be rewritten as

$$\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}} = \left\{\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}}\right\}_o - \frac{(1-\lambda)}{Z} \left[\text{ierfc}\,[Z] - \sum_{n=1}^{\infty} \lambda^n \{\text{ierfc}\,[nZ] - \text{ierfc}\,[(n+1)Z]\}\right] \tag{17}$$

If the films were semi-infinite, the solutions for the fractional approach to equilibrium in the binary and the ternary cases would be analogous, differing only in a constant coefficient. Thus, substituting Equations (15) and (16) into Equation (11) and rearranging we obtain

$$\left\{\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}}\right\}_o \left(\frac{2}{(1-\lambda)\sqrt{D_1}}\right) \left(\frac{Q_B}{Q_w}\right) = 4 \sqrt{\frac{x}{Q_w}} \tag{18}$$

This equation is the analog of Equation (2) which was deduced from the binary data. In correcting the ternary calculations for acceleration in the jet we replace the right-hand side of Equation (18) with the semiempirical form of Equation (2) to give the following approximate form

$$\left\{\frac{\overline{C_1} - C_{10}}{C_1^* - C_{10}}\right\}_{o,\,(\text{corr.})} = \frac{(1-\lambda)}{2} \sqrt{D_1} \left(\frac{Q_w}{Q_B}\right) \left[\alpha \sqrt{\frac{x}{Q_w}} - \beta\right] \tag{19}$$

Since the experimental conditions (flow rates, nozzle, etc.) for the ternary and binary results are similar, the values of α and β listed following Equation (2) are used throughout.

The first term on the right-hand side of Equation (17) is by far the dominant term in most of the present calculations. In applying this equation to the jet problem, one substitutes Equation (19) into (17), yielding

$$\left\{\frac{\overline{C}_1 - C_{10}}{C_1^* - C_{10}}\right\}_{(\text{corr.})} = \left\{\frac{\overline{C}_1 - C_{10}}{C_1^* - C_{10}}\right\}_{o,\,(\text{corr.})} - \frac{(1-\lambda)}{Z}\Bigg[\operatorname{ierfc}[Z] - \sum_{n=1}^{\infty}\lambda^n \{\operatorname{ierfc}[nZ] - \operatorname{ierfc}[(n+1)Z]\}\Bigg] \qquad (20)$$

with

$$Z = \frac{Q_B}{2\sqrt{\pi D_1 Q_w x}}$$

For terms higher than the first, Z is calculated from Equations (15) and (16). Equation (20) is compared with experimental data in the discussion.

RESULTS AND DISCUSSION

Acetic Acid

Experimental Results. The measured transfer rates for acetic acid diffusing from benzene to water are shown in Figures 1 and 2. Figure 1 shows the fractional approach to equilibrium $\overline{C}_2/C_2^*$ as a function of $\sqrt{x/Q_w}$, the abscissa being proportional to the square root of the nominal contact time. Data have been plotted for the two cases of a net transfer and no net transfer. Experiments were carried out at Q_w = 1.00 cc./sec., Q_B = 2.055 cc./min., and jet lengths from 2 to 7 cm. The solid line has been calculated from Equation (20) using the physical constants indicated. The distribution coefficient was extrapolated from literature values (3, 9) and the diffusion coefficients are those reported by Davies and Wiggill (7). The diffusion coefficients are concentration dependent, and the concentration range here is considerably more dilute than that used by Davies and Wiggill. However, their values are more likely to be correct than those calculated from empirical formulas.

A plot of $\overline{C}_2/C_2^*$ vs. Q_B is shown in Figure 2. These runs were conducted at a constant water flow rate (Q_w = 1.67 cc./sec.) and jet length (L = 3 cm.) with benzene flow rates varying from 0.46 to 9.25 cc./min. The average film thickness is proportional to the benzene flow rate, and here, the film thickness ranged from approximately 2 to 30 μ. The full line through the lower points has been calculated with Equation (20). Equation (19), the semi-empirical relation derived from the binary data, does not hold as the film thickness, or benzene flow rate, approaches zero. For this reason the calculated curve of Figure 2 at low values of Q_B (for Q_B less than 2 cc./min.) is shown as a broken line. The broken line is an extrapolation from the region in which Equation (19) is valid (Q_B greater than 2 cc./min.) to the known intercept of $\overline{C}_2/C_2^*$ = 1 for Q_B = 0. The open circles of Figures 1 and 2 represent the results with no net transfer and each point is the average of five samples. The agreement of samples within runs and the reproducibility between runs was of the order of ± 3%. For the case of net transfer, each point represents the average of two samples, with the reproducibility within and between runs approximately ± 2%.

Zero Net Transfer. First consider the results in which there was zero net transfer of acetic acid. In this case $\overline{C}_2/C_2^*$ is a measure of the fractional approach to equilibrium for the carbon-14 labeled acetic acid exchanging between the film and the aqueous phase. The principal observation to be made is that these data are in excellent agreement with Equation (20), in which interfacial equilibrium has been assumed. A significant departure of the data from Equation (20) would be approximately 20%. Such a departure would be readily observable experimentally; also it would be out of the range which could reasonably be accounted for by arbitrarily adjusting the physical constants which enter into the calculation. At the smallest contact time at which data were taken this departure corresponds to an interfacial resistance of less than 15 sec./cm. [This value is calculated from Equation (5) in reference 8.] By comparison, a resistance of 100 sec./cm. would lower the predicted concentration by a factor of five (at the smallest contact time attained in the experiments); a resistance of 400 sec./cm. would yield a predicted value an order of magnitude lower than Equation (20).

These results contradict those of Lewis (*12*) and Vignes (*20*), who reported interfacial resistances of 1,000 and 400 sec./cm., respectively, for acetic acid diffusing between toluene and water. It is highly unlikely that the benzene-water and toluene-water interfaces would behave much differently toward the transfer of a third component. Our results indicate that the resistance at a clean benzene-water interface cannot be greater than 15 sec./cm. and, most probably, it is considerably smaller. It should be added that Ward and Brooks (*21*), studying the diffusion

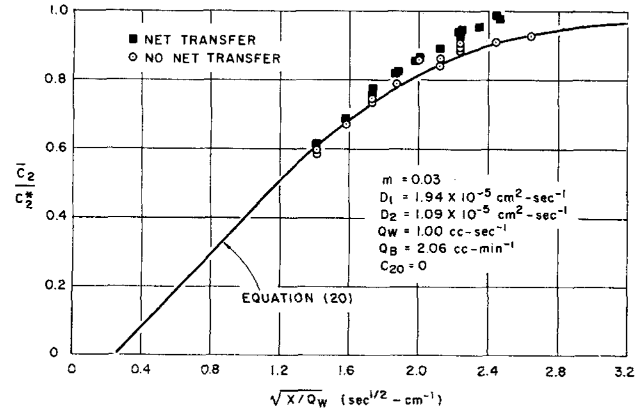

Fig. 1. Experimental results compared with Equation (20) for the diffusion of acetic acid across the water-benzene interface. Constant film thickness, variable contact time.

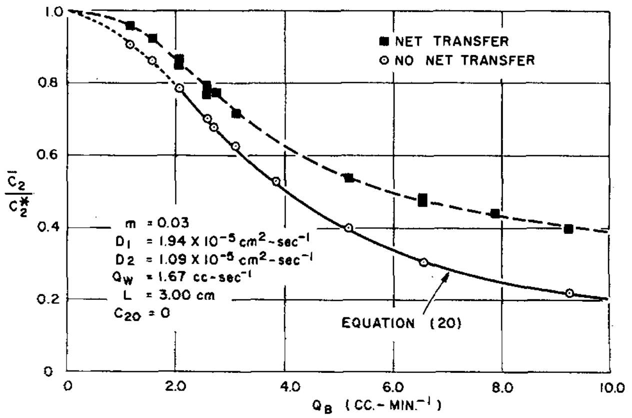

Fig. 2. Effect of net transfer on the diffusion of acetic acid from benzene to water. Fixed contact time, variable film thickness.

of acetic acid between water and toluene, and Davies and Wiggill (7), who measured diffusion rates for acetic acid transferring between water and both toluene and benzene, detected no interfacial resistance. However, they could not detect resistances smaller than 1,000 sec./cm. Several other investigators have also studied the diffusion of acetic acid between benzene or toluene and water. The findings cited above are typical of the conflicting results which have been reported.

Net Transfer. In contrast to the data obtained for the case of no net transfer, it is clear from Figure 1 that with a net transfer of acetic acid the data are higher than values predicted from Equation (20). This small but distinct difference might be thought to be due to a systematic experimental error. That this is not the case is seen in Figure 2 where an extension of the two sets of data shows the two cases differing by as much as a factor of two at the greatest film thickness. The explanation for the higher results with a net transfer is seemingly, interfacial turbulence; this turbulence or agitation being brought about by axial variations in interfacial tension (*19*). Interfacial turbulence and/or spontaneous emulsification has been noted in this and similar systems by many authors (*7*). The significance of the present data is that if indeed interfacial turbulence is responsible for the enhanced rate of transfer, the effect is quantitatively reproducible and it is manifest at so small a contact time (nominally 0.04 sec.).

In the limit, interfacial turbulence could lead to complete radial mixing in the film. In this case Equation (14) obtains and an approximate calculation indicates that at a benzene flow rate of 10 cc./min., $\overline{C_2}/C_2^*$ is of the order of 0.9. Thus, turbulence in the film resulting in a state somewhere between the completely mixed and the unmixed film is well capable of causing the observed effect. Turbulence may also be present on the water side of the interface. If so, it would have a minor effect on the transfer rate since $m << 1$ for this system [see Equation (12)]. In this connection it is interesting to note that in the system acetic acid–water–toluene, Davies and Wiggill (7) found that spontaneous emulsification occurred principally on the toluene side of the interface, an observation also made by other authors (*6, 13*).

Interfacial turbulence appears to be the only plausible explanation for the anomalous results with net transfer. One might suspect that the high results are due to a change in the fluid dynamics of the jet brought about by increasing the film thickness, that is, the benzene flow rate. This is disproven by the zero net transfer results which agree with predicted values over the entire range of film thicknesses. The close agreement of the zero net transfer results also lends credence to the assumption made in the calculations that the film has little effect on the fluid dynamics of the jet. A still further explanation might be that D_1 is strongly concentration dependent and its average value greatly different for the two cases. This appears unlikely, since the solutions were at all times highly dilute. Also, since D_1 enters the calculation only to the square root, it would have to vary over a wide range to account for the difference.

Benzoic Acid

Figures 3 and 4 show the results for tagged benzoic acid transferring from the aqueous to the benzene phase. The data are shown as $\overline{C_1}/C_1^*$ vs. $1/Q_B$ for two jet lengths and water flow rates: $L = 5$ cm. with $Q_w = 1.00$ cc./sec. and $L = 3$ cm. with $Q_w = 1.67$ cc./min. The solid line drawn on each figure has been calculated with Equation (20). Each experimental point represents the average of three to five samples with precision and reproducibility comparable to the acetic acid data. At the concentrations used the distribution coefficient was measured to be 3.20 ± 0.10. The diffusion coefficients of benzoic acid in benzene and in water were calculated from an empirical correlation (*18*). Benzoic acid is known to exist in the form of dimers in benzene (*1*); therefore, D_1 was calculated for a dimer of benzoic acid.

In general, the data of Figures 3 and 4 fall below the predicted values, in some cases as much as 5 to 10% below. This difference is not considered significant, since the physical constants used in calculating the predicted values can be adjusted within their range of variance to give adequate agreement. For example, increasing the value of m by 2% and decreasing D_2 by 10% would cause the predicted line to pass through the data. And, indeed, the values for m and D_2 are not known more precisely than ± 2% and ± 10%, respectively. The diffusion coefficient in the film D_1, has relatively little effect on the predicted line, because here $m > 1$. For example, increasing D_1 by 50% increases the calculated values for C_1/C_1^* by only 5% at $Q_B = 3$ cc./ min. and virtually not at all at $Q_B = 1$ cc./ min.

As with acetic acid, a significant departure of the data from predicted values would be approximately 20% and this corresponds to a maximum value for an interfacial resistance of 20 sec./cm. Thus these results contradict those of Lewis (*12*) and Blokker (*2*), who both reported resistances of the order of 1,000 sec./cm. for benzoic acid diffusing between toluene and water. It is possible that the experiments of Lewis and of Blokker were influenced

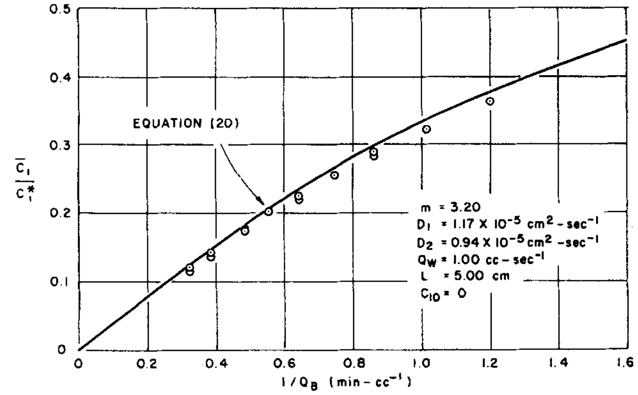

Fig. 3. Experimental results for the diffusion of tagged benzoic acid across the water-benzene interface. No net transfer, variable film thickness.

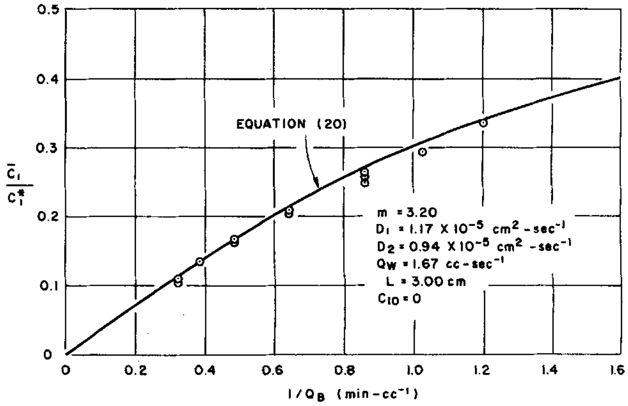

Fig. 4. Transfer of tagged benzoic acid from water to benzene. Figures 3 and 4 show results at two different contact times.

by inadvertent contamination of the interface with surface-active impurities. However, the present data confirm the results obtained with acetic acid: at a fresh liquid-liquid interface equilibrium is rapidly established and any interfacial resistance is negligibly small.

Net transfer of benzoic acid was not studied. Unlike the acetic acid system, $\overline{C_1}/C_1^*$ is sensitive to the value of *m* in the transfer of benzoic acid and with a net transfer the value of *m* would have varied significantly over the length of the jet. Results with *m* variable would not be readily comparable with the zero net transfer data.

Oleic Acid

To accent the role of the interface, the transfer of oleic acid was studied. Oleic acid is highly surface-active and one would expect that any interfacial resistances of a physicochemical nature would be emphasized in this system. The experimental results are somewhat tentative, inasmuch as certain features of the data could not be reproduced quantitatively. This lack of precision in the data was due to the extremely small solubility of oleic acid in water—considerably less than 1 p.p.m.

Typical results are shown in Figures 5 and 6 with $\overline{C_1}$ as a function of contact time at constant film thickness and $\overline{C_1}$ as a function of film thickness at fixed contact time. The dotted line drawn through the experimental points of Figure 5 was fitted to the data by a least squares analysis. The equation of this line is

$$\overline{C_1} = 82.9\sqrt{x/Q_w} - 18.5 \tag{21}$$

with $\overline{C_1}$ expressed as counts per minute (counts/min.) per cc. of benzene. The intercept on the abscissa is 0.22 $\sqrt{\text{sec.}}$/cm.

An approximate measurement of *m* indicated that *m* was sufficiently large (of the order of 10^3) to justify the use of Equation (13). [Actually, Equation (13) was not used, but rather the "corrected" form of the equation, that is, the equation was corrected with the binary data as was Equation (19).] The solid lines of Figures 5 and 6 were calculated from the corrected form of Equation (13); the dotted line of Figure 6 was calculated from the equation fitted to the data of Figure 5, assuming that the constants of Equation (21) were proportional to Q_B in the same manner as in the corrected form of Equation (13). The diffusion coefficient for oleic acid in water was calculated from the correlation of Wilke and Chang (*18*).

As shown in Figures 5 and 6, the experimental data are approximately 30% below the values predicted for interfacial equilibrium. A deviation such as this might be attributed to an interfacial resistance, but there are several reasons to reject this explanation, the principle one being that the predicted and experimental results give essentially identical intercepts on the abscissa of Figure 5. Any predicted curve with a nonzero resistance would necessarily extrapolate to an intercept different from the zero-resistance value (*20*).

There is evidence to suggest that some of the oleic acid in the water fed to the jet was not in solution but was present in the form of an extremely fine emulsion. As discussed in the experimental section, it proved to be quite difficult to dissolve oleic acid in water, even with prolonged, vigorous stirring. If an emulsion existed, then the effective value of C_{20} based on the amount of dissolved oleic acid would be less than the measured value, because in counting a feed sample containing extremely fine suspended droplets the acid in the droplets would also be counted. Lowering C_{20} would, of course, decrease the slope of the predicted curve but it would not change the value of the intercept.

In studying this system, several acid solutions were prepared and run. Results obtained with a given solution were reproducible; however, the data from different solutions were not consistent. The features common to all the data were: identical intercept and a slope smaller than predicted. Repeated filtering of the feed solution improved the agreement between predicted and measured results. Apparently, the effect of the filtration was to adsorb some acid on the filter paper as well as filtering out some of the emulsion. Each filtration removed some tagged acid and reduced C_{20}. Before complete agreement was reached the overall concentration had been reduced to a value too small for meaningful counting.

A value for the solubility of oleic acid in water could not be found in the literature. The solubility of stearic acid has been reported as 0.7 p.p.m. (*10*). It seems doubtful that oleic acid would be considerably less soluble than stearic acid, as suggested by the present data. Possibly, in our experiments the oleic acid reacted with trace impurities in the water to form a highly insoluble material. In spite of these uncertainties it can be concluded that oleic, or a less soluble derivative of oleic acid, encounters no significant resistance at the benzene-water interface.

Cholesterol

As a further example of a surface-active solute, cholesterol was examined. If steric factors impede the penetration of the interfacial layer, then a high molecular weight solute such as cholesterol with its sterol structure might be expected to exhibit a reduced transfer rate. Results

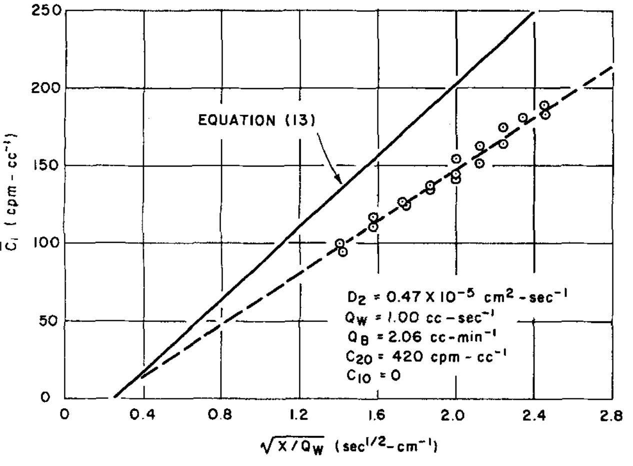

Fig. 5. Experimental results for the transfer of oleic acid from water to benzene. Constant film thickness, variable contact time.

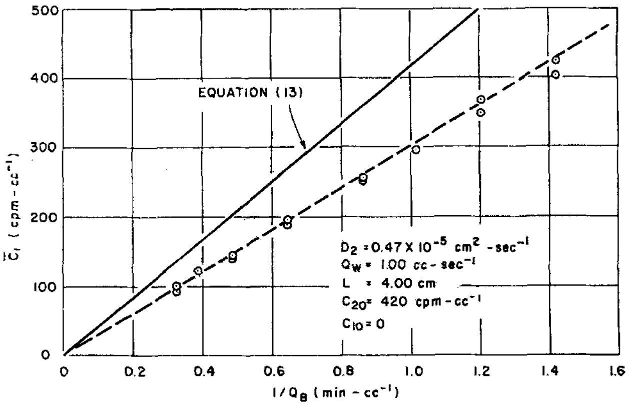

Fig. 6. Benzene-water-oleic acid system. The effect of film thickness at fixed contact time.

with this system were similar to the oleic acid data. Measured concentrations were consistently below (in one case an order of magnitude below) the predicted values. Data obtained from a given feed solution were consistent, but from batch to batch the data were not reproducible. All the data when plotted as $\overline{C_1}$ vs. $\sqrt{x/Q_w}$ at a fixed benzene flow rate gave an intercept on the abscissa within the interval 0.1 to 0.4 $\sqrt{\text{sec.}}$/cm. This would indicate that the very low results for this system are not caused by an interfacial resistance.

Two factors complicated the investigation of this system and they are probably the cause of the anomalous results. The first is that cholesterol is highly insoluble in water. The reported solubility is 2.6 g. cholesterol per 1,000 g. solution at 25°C. (*14*). We found, however, that the solubility is at least two orders of magnitude smaller than this value (*22*). Therefore, it is possible that some cholesterol in the water feed was not dissolved, just as in the experiments with oleic acid. It should be emphasized that the predicted results are not dependent on the absolute solubility, but rather on the initial concentration, C_{20}. Here again, as with oleic acid, m is very much larger than unity and the simplifications of Equation (13) result.

The second complicating factor was that while cholesterol is stable under ordinary conditions (*11*), radioactive cholesterol is unstable (*5*). In the presence of air the tagged material undergoes oxidation about the 5, 6 double bond. It is possible that some of the cholesterol was oxidized in the process of dissolving it in the water. Whatever the cause of the irregular results, there is no evidence that the interfacial resistance in this system is appreciably different from the other three systems studied.

CONCLUSIONS

Studies of the liquid-liquid interface parallel those of the gas-liquid interface. Because of additional experimental difficulties encountered with liquid-liquid studies, liquid results have lagged somewhat behind comparable ones for gases. As techniques improve anomalies are resolved and the upper limit for measurable interfacial resistances becomes smaller. Our results indicate that any resistance to the transfer of acetic acid or benzoic acid through a freshly formed benzene-water interface is less than 20 sec./cm. There is also strong evidence to suggest that the same result obtains for the transfer of oleic acid and cholesterol (or close derivatives of these compounds). These results on acetic acid and benzoic acid are in disagreement with earlier published results wherein resistances of the order of 400 to 1,000 sec./cm. were reported. The results also make questionable the large resistances which have been reported for a variety of three-component liquid-liquid systems.

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NOTATION

a = film thickness, cm.
A = $C_{10} - m\,C_{20}$, g.-moles/cc.
C = concentration, g.-moles/cc.
$\overline{C}$ = average concentration, g.-moles/cc.
C_o = initial concentration, g.-moles/cc.
C^* = saturation concentration, g.-moles/cc.
d = jet diameter, cm.
D = diffusion coefficient, sq. cm./sec.
g = acceleration of gravity, cm./sec.^{2}
L = jet length, cm.
m = distribution coefficient, defined by Equation (7)
N = local mass flux, g.-moles/(sq. cm.)(sec.)
Q = volumetric flow rate, cc./sec.
R = radius of the jet, cm.
R_o = initial radius of the jet, cm.
S = slope of the plot, $\overline{C}/C^*$ vs. $\sqrt{x/Q_w}$, cm./sec.$^{1/2}$
S_i = slope of the plot, $\overline{C}/C^*$ vs. $\sqrt{x/Q_w}$, for an ideal jet, cm./sec.$^{1/2}$
t = contact time, sec.
u = axial velocity, cm./sec.
$\overline{u}_o$ = average axial velocity at the nozzle, cm./sec.
x = axial distance measured from nozzle, cm.
x_1 = axial distance at which jet velocity becomes uniform, cm.
y = coordinate normal to interface, cm.
Z = $a/\sqrt{D_1 t}$, dimensionless variable, Equation (8)

Greek Letters

α = constant defined by Equation (2), dimensionless
β = constant defined by Equation (2), sec.$^{1/2}$/cm.
λ = $(m\,\mu - 1)/(m\,\mu + 1)$, dimensionless
μ = $\sqrt{D_1/D_2}$, dimensionless
ϕ = total mass transfer rate, g.-moles/sec.

Subscripts

0 = semi-infinite film, Equation (11)
1 = film properties, $0 < y < a$
2 = bulk properties, $y > a$
(corr.) = corrected, see Equation (19)

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