The Mass Transfer Rate through the Liquid-Liquid Interface. I. Potential Barriers near the Interface

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In the treatment of mass-transfer through phases, the two concentrations immediately next to the interface have been assumed to be in distribution-equilibrium. In recent years, however, efforts have been made to obtain the true relation between these concentrations,[1-13] and some workers reported that there is a resistance in mass-transfer through the interface, so that the two concentrations are not in equilibrium.[1,3,8,13] Sinfelt and Drickamer[8] observed a high interfacial resistance by a static experiment on the diffusion of molecular sulfur across liquid-liquid interfaces; they associated this with the hydrogen bonding of liquids. On the other hand, Ward and Brooks[4] studied the diffusion of carboxylic acids statically across the water-toluene interface by the Lamm scale method; no distinct interfacial resistance was observed, but they carefully stated that this type of experiment does not detect an activation barrier to the crossing of the interface unless it is very high. Quinn and Jeannin[13] more recently studied the diffusion of isobutanol into the laminar aqueous isobutanol-water jet and found an interfacial resistance of approximately 80 cm./sec.

One of the factors that fix the rate of mass-transfer may be the amount of adsorption as well as the two concentrations immediately next to the interface at a constant temperature, although this aspect has been rather neglected. The present work is concerned with some relations between these three quantities.

Both phases, one of which is a pure solvent and the other a solution of a surface-active transfer-material in a different solvent, and the two solvents are mutually-immiscible, are brought into contact with each other. The adsorption of the transfer-material from the solution onto the interface takes place after the contact, and, consequently, the amount of adsorption increases quickly; the concentrations immediately next to the interface vary at the same time, so that the initial uniformity is destroyed and a new distribution of concentration appears at every moment until equilibrium. This variation in local concentration is originated only by the chemical potential gap obtained by comparing the zero amount of adsorption on the interface with the concentration of the solution immediately next to the interface at the beginning, and so it spreads out from the interface to the interiors of both bulks. That is, this variation in a sufficiently small lapse of time is practically limited to the vicinity of the interface, because the diffusion in liquid is rather slow. Consequently, it can be considered to be nearly independent of the thickness and shape of the layers.

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[1] J. T. Davies, *J. Phys. and Colloid. Chem.*, **54**, 185 (1950).
[2] E. J. Scott, L. H. Tung and H. G. Drickamer, *J. Chem. Phys.*, **19**, 1075 (1951).
[3] L. H. Tung and H. G. Drickamer, ibid., **20**, 6, 10 (1952).
[4] A. F. H. Ward and L. H. Brooks, *Trans. Faraday Soc.*, **48**, 1124 (1952).
[5] F. H. Garner and A. H. P. Skelland, *Ind. Eng. Chem.*, **46**, 1255 (1954).
[6] P. L. Auer and E. W. Murbach, *J. Chem. Phys.*, **22**, 1054 (1954).
[7] J. B. Lewis, *Chem. Eng. Sci.*, **3**, 248, 260 (1954).
[8] J. H. Sinfelt and H. G. Drickamer, *J. Chem. Phys.*, **23**, 1095 (1955).
[9] J. B. Lewis, *Chem. Eng. Sci.*, **8**, 295 (1958).
[10] P. Raimondi and H. L. Toor, *A. I. Ch. E. Journal*, **5**, 86 (1959).
[11] S. H. Chiang and H. L. Toor, ibid., **5**, 165 (1959).
[12] J. T. Davies and J. B. Wiggill, *Proc. Roy. Soc.*, **A255**, 277 (1960).
[13] J. A. Quinn and P. G. Jeannin, *Chem. Eng. Sci.*, **15**, 243 (1961).

The net rate of adsorption generally decreases, and so the amount of adsorption becomes nearly constant with an increase in the time of contact. This state is usually reached in a very short time when the molecule of the transfer-material is sufficiently small. The first stage, where the net rate of adsorption is high enough, is called the " adsorption stage," while the second, where the rate is nearly zero and the amout of adsorption is nearly constant, is called the " transfer stage " hereafter. The " transfer stage " will be discussed in this work.

A curve of the time dependence of the transfer-amount extrapolated to zero time does not necessarily coincide with that of the real process when all the observations are in the " transfer stage." The imaginary process obtained from this extrapolation, which has no " adsorption stage," is now called the " ideal process " in contrast with the real one. In other words, a curve of the time dependence of the transfer-amount in the " ideal process " does not necessarily start from the point of origin, and the amount of transfer in the initial state of the " ideal process " is not necessarily zero, but rather may apparently have a finite value in contrast with that in the real process, which is undoubtedly zero. It is assumed that the initial state of the " ideal process " holds a relation in the " transfer stage " and that it is independent of the thickness and the shape of the layers. This assumption is quite valid if the " adsorption stage " ceases in a short enough time, as has been described above. We will concentrate on the initial state of the " ideal process," because we can thus not only obtain the amount of adsorption, the two concentrations immediately next to the interface, and the transfer rate in this state, as will be described later, but also it is the most appropriate method for detecting the deviation from the equilibrium relation of the concentrations because of the high transfer rate.

Experimental

An aqueous solution of *n*-butyric acid of a certain volume and concentration was placed in a glass vessel (I), shown in Fig. 1; at the same time, carbon tetrachloride was placed in another vessel (II), which had the same shape as vessel I. The temperature of vessels I and II was kept constant at 30°C by circulating jacket-water supplied from a thermostat. After the vessels had stood for 1 hr., carbon tetrachloride equal in volume to the aqueous *n*-butyric acid solution in vessel I was quickly taken out with a syringe from vessel II and introduced into vessel I, beneath the aqueous layer, much care being taken not to disturb the upper layer. Vessel I had been mounted on a stand to which a foam-rubber cushion was attached in order to insulate it from outside vibrations. *n*-Butyric acid was allowed to transfer from its aqueous solution into the carbon tetrachloride layer. After a certain lapse of time, the carbon tetrachloride layer was thoroughly taken out with a syringe, and the amount of *n*-butyric acid transferred into the carbon tetrachloride layer was determined by titration. This operation, now referred to as the " layer absorption method," was repeated with various volumes and concentrations of the aqueous *n*-butyric acid solution at definite periods of elapsed time after the contact of the two layers.

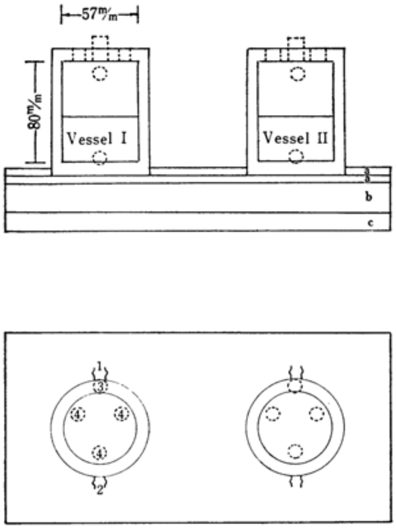

Fig. 1. Apparatus for the " layer absorption method."

a : Rubber sheet   b : Iron plate
c : Rubber cushion
1 : Inlet of water-jacket
2 : Outlet of water-jacket
3 : Thermometer hole
4 : Sample-inlets and beaker-supporter

When benzene was used in place of carbon tetrachloride, benzene was placed in vessel I and the aqueous solution of *n*-butyric acid, in vessel II, and then the latter was introduced beneath the benzene layer in vessel I. After a definite period of time, the aqueous layer was separated from the benzene layer and the titration was made on the latter.

The amount of *n*-butyric acid adsorbed at the interface was determined by the pendant drop method.[14] A drop of the denser phase was hung from a capillary tip (0.1 mm. I. D. and 3 mm. O. D.) which was attached to a syringe, and the silhouette of the drop was obtained by parallel-ray photography. This procedure was repeated with various concentrations of *n*-butyric acid at definite time intervals.

In order to recognize whether observations have

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[14] J. M. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

been made in the "transfer stage" or not, the variation in the amount of adsorption in very early stages must be determined, strictly, but, conventionally, recognized as follows. The "adsorption stage" takes place, but the "transfer stage" does not, when a new interface is made in the pendant drop method if the two phases have been previously brought into transfer-equilibrium. Consequently, this means that the observation has been made in the "adsorption stage" when the interfacial tension in the above experiment varies with time; on the contrary, the "adsorption stage" has ceased when no variation occurs, though only an approximate relation is obtained if the result is applied in the non-equilibrium system as it is.

The partition-equilibria of *n*-butyric acid in the water - carbon tetrachloride and water - benzene systems were determined by titrating equilibrated solutions.

Results

Examples of the amounts of *n*-butyric acid in organic solvents transferred from the aqueous phase in the "layer absorption method" are plotted against the time in Figs. 2a and 2b. All the observations were made in the "transfer stage," because its "adsorption stage" ended within 1 min., as was established by determining the variation of interfacial tension in the equilibrated system, as has been described above. Consequently, the curves in Figs. 2a and 2b indicate the "ideal process," though these are probably deformed by a disturbance.

The initial transfer rates at the extrapolated points or the initial state of the "ideal process," are plotted against the thickness of both layers in Figs. 3a and 3b. All the points in each concentration before contact nearly lie on a straight line; the straight lines in the case of carbon tetrachloride are inclined to the horizontal axis, but those in the case of benzene are parallel to the horizontal axis. According to the assumption that the initial state of the

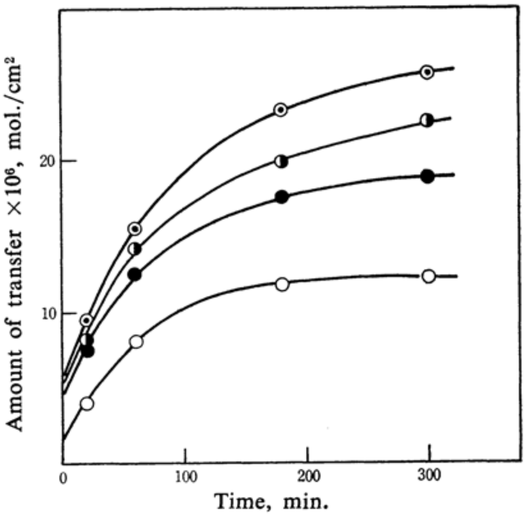

Fig. 2b. Time dependences of the amount of *n*-butyric acid transferred from the aqueous to the benzene phase at 30°C.
Concn. in the aq. soln. = 0.0503 N
Thickness of the layers: ○, 0.78 cm.; ●, 1.56 cm.; ◑, 2.34 cm.; ⊙, 3.12 cm.

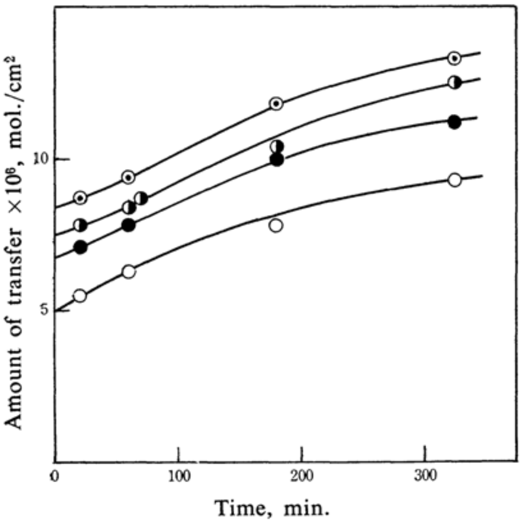

Fig. 2a. Time dependences of the amount of *n*-butyric acid transferred from the aqueous to the carbon tetrachloride phase at 30°C.
Concn. in the aq. soln. ≒ 0.0566 N
Thickness of the layers ○, 0.78 cm.; ●, 1.56 cm.; ◑, 2.34 cm.; ⊙, 3.12 cm.

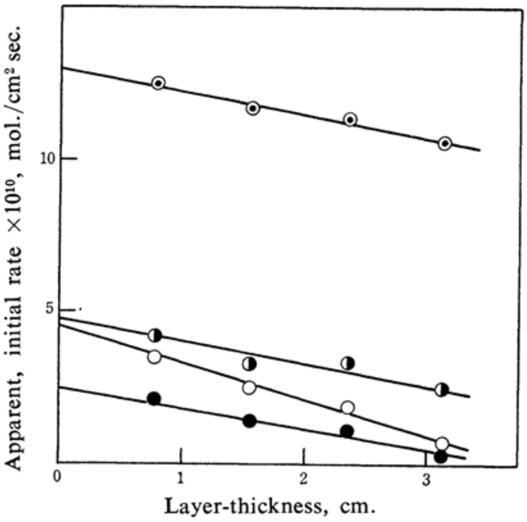

Fig. 3a. Layer-thickness dependence of the apparent, intial transfer-rate of *n*-butyric acid from the aqueous to the carbon tetrachloride phase at 30°C, determined by extrapolation.
Concn. in the aq. soln.: ○, 0.0115 N; ●, 0.0228 N; ◑, 0.0566 N; ⊙, 0.1137 N

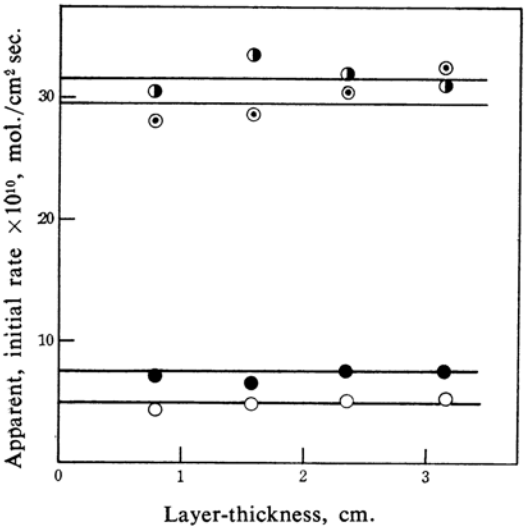

Fig. 3b. Layer-thickness dependences of the apparent, initial transfer-rate of *n*-butyric acid from the aqueous to the benzene phase at 30°C, determined by extrapolation.
Concn. in the aq. soln.: ○, 0.0100 N; ●, 0.0216 N; ◑, 0.0503 N; ⊙, 0.1038 N

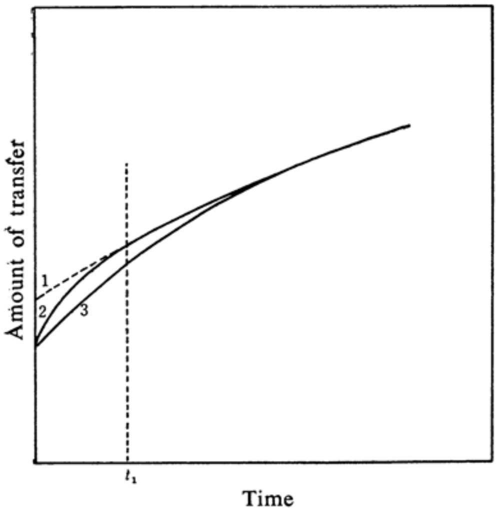

Fig. 4. Scheme of the deformation by the disturbance effect in the "ideal process."
1, Indicating extrapolation; 2, With the disturbance effect; 3, The "ideal process" without the disturbance effect

"ideal process" is independent of the thickness of the layer, all the straight lines in Figs. 3a and 3b should be parallel to the horizontal axis. The present authors attribute the cause of this discrepancy in the case of carbon tetrachloride to a disturbance at the beginning by the injection of carbon tetrachloride beneath the aqueous solution. The larger the thickness of the layer, the longer the time of injection, and therefore the stronger the disturbance. The disturbance deforms the intrinsic curve of the time dependence of the amount of *n*-butyric acid in the carbon tetrachloride phase transferred through the interface, as is shown schematically in Fig. 4. If the determinations are done after t_1 in Fig. 4, the initial rate of transfer on the extrapolated line should be less than the intrinsic one, and therefore the

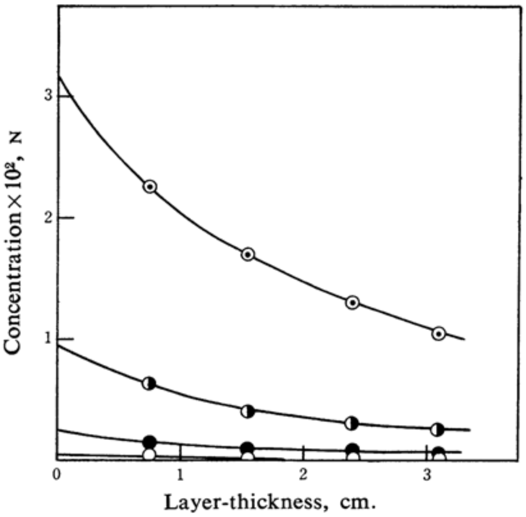

Fig. 5a. Layer-thickness dependences of the initial, average concentration of *n*-butyric acid in the carbon tetrachloride phase, determined by extrapolation, at 30°C.
Concn. in the aq. soln.: ○, 0.0114 N; ●, 0.0228 N; ◑, 0.0566 N; ⊙, 0.1137 N

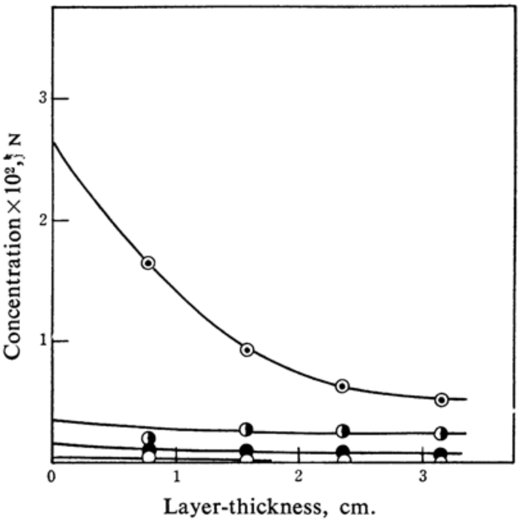

Fig. 5b. Layer-thickness dependences of the initial, average concentration of *n*-butyric acid in the benzene phase, determined by extrapolation, at 30°C.
Concn. in the aq. soln.: ○, 0.0100 N; ●, 0.0216 N; ◑, 0.0503 N; ⊙, 0.1038 N

straight lines should incline to the horizontal axis. Consequently, the correct values of the rate are given by extrapolating the straight lines to zero layer-thickness. On the contrary, the disturbance in the case of benzene is considered to be negligible, since the injection of the aqueous solution of *n*-butyric acid beneath the benzene layer causes much disturbance in the aqueous layer, but scarcely any in the benzene layer, which is sensitive to disturbance because of its low concentration.

The layer-thickness dependence of the average concentrations of *n*-butyric acid transferred into organic solvents at zero time in the apparent "ideal process," which means that it may include the disturbance effect, is shown in Figs. 5a and 5b, which were obtained from the amount of transfer extrapolated to zero time, as in Figs. 2a and 2b, divided by the volume of the layer. However, the values at the points extrapolated to zero thickness of the layer should show no disturbance, as has been described above, while at the same time they indicate the concentrations immediately next to the interface in the organic solvent at zero time in the "ideal process," according to the assumption that the initial state of the "ideal process" is independent of the thickness of the layer.

On the other hand, those for the aqueous phase are given from the following equation:

$$m = c_{10}v - c_{1a}v$$

$$c_{1a} = (c_{10}v - m)/v = c_{10} - c_{2a}$$

where m is the amount of solute transferred at time t; c_{10} is the concentration of *n*-butyric acid in the aqueous phase before contact; c_{1a} and c_{2a} are the average concentrations of *n*-butyric acid in an aqueous and an organic solvent respectively at time t, and v is volume of the phase.

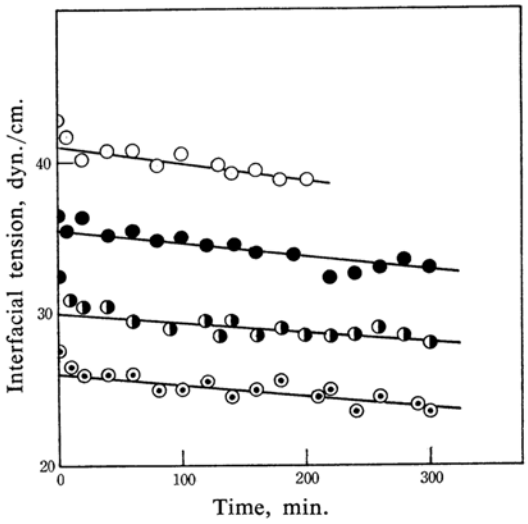

Fig. 6a. Time dependences of the interfacial tension of the pendant drop, when an aqueous solution of *n*-butyric acid and carbon tetrachloride were brought into contact with each other at 30°C.
Concn. in the aq. soln.: ○, zero; ●, 0.0227 N; ◑, 0.0566 N; ⊙, 0.1137 N

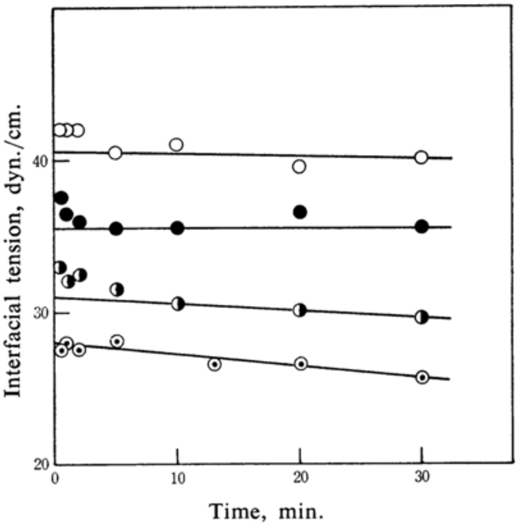

Fig. 6b. Particulars of the variation of the interfacial tension in the early stage of Fig. 6a.

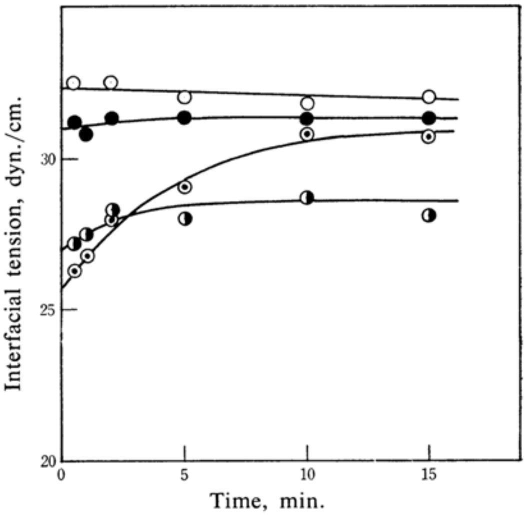

Fig. 6c. Time dependences of the interfacial tension of the pendant drop, when an aqueous solution of *n*-butyric acid and benzene were brought into contact with each other at 30°C.
Concn. in the aq. soln.: ○, zero; ●, 0.0206 N; ◑, 0.0514 N; ⊙, 0.1041 N

The results of the pendant drop experiment are shown in Figs. 6a, 6b and 6c. In the case of carbon tetrachloride, all points after about 30 min. are nearly on a straight line in every run, and the straight lines are nearly parallel with each other. It may be seen that a rapid change of interfacial tension sets in within about 5 min. The first period, within 5 min., is considered to include the "adsorption stage," and the second period, from 5 to 30 min., the "transfer stage," while in the third period, after 30 min., a process is dominant in which carbon tetrachloride in the pendant drop dissolves in the aqueous phase outside the drop.

Therefore, the value obtained by extrapolating the interfacial tensions along the second process to zero time gives an interfacial tension of the "ideal process" at zero time nearly equal to that in the "layer absorption method," because the initial state in the "ideal process" is independent of the thickness and the shape of the layer according to the above assumption, provided that the curvature effect of the drop-surface is assumed to be negligible.

On the other hand, the value by extrapolating it along the third process to zero time gives the interfacial tension at an equilibrium state in the transfer of *n*-butyric acid and water eliminated the effect of transfer for carbon tetrachloride. The concentration in the aqueous phase outside the drop in transfer-equilibrium is approximated as equal to that before contact for a large volume ratio (1000 times) of the aqueous to the carbon tetrachloride phase.

In the case of benzene, the technique to obtain initial interfacial tensions is almost same, but those in transfer-equilibrium at various concentrations in the aqueous phase were obtained with systems previously brought into transfer-equilibrium.

Since the interfacial phases are composed of a mono-layer of *n*-butyric acid,[15] no distribution of the concentration of *n*-butyric acid in the interfacial phases along the transfer coordinate can be defined; therefore, the transfer of *n*-butyric acid in the interfacial phases in the transfer direction is regarded as in equilibrium at every moment, even in the transfer process. Therefore, the equations of state for the interfaces, which exist as a rule in equilibrium systems, must hold even in the rate process. In other words, the amount of adsorption in the rate process is determined by the surface pressure, the difference between the interfacial tension of a certain solution-system and that of the pure solvent-system, at every moment.

Table I shows the results of this experiment. In Table I the fractions of area covered by *n*-butyric acid molecules, θ, are nearly equal to the corresponding fractions, θ_1, calculated by assuming an equilibrium with the concentrations immediately next to the interfaces in the aqueous phase (c_{1i}), but the corresponding fractions, θ_2, calculated by assuming an equilibrium with those in the organic phases (c_{2i}), are very different from θ or θ_1 in some cases. (θ_1 and θ_2 are, so to speak, reduced concentrations of c_{1i} and c_{2i} respectively, calculated for comparison with θ.) This indicates that a distinct resistance occurs in the process of desorption into the organic phase required in order to transfer through the interfaces.

TABLE I. THE RESULTS OF EXPERIMENT (30°C)

A) Aq. soln. of *n*-butyric acid - CCl_4

$r_0\times10^{10}$ g. mol./cm^2 sec.	$c_{1i}\times10^2$ N	$c_{2i}\times10^2$ N	θ	θ_1	θ_2
4.50	1.10	0.04	0.30	0.26	0.05
2.67	2.07	0.21	0.72	0.64	0.33
4.84	4.72	0.94	0.99	0.99	0.84
13.00	8.20	3.20	1.00	1.00	1.00

B) Aq. soln. of *n*-butyric acid - benzene

$r_0\times10^{10}$ g. mol./cm^2 sec.	$c_{1i}\times10^2$ N	$c_{2i}\times10^2$ N	θ	θ_1	θ_2
4.86	0.96	0.04	0.01	0.06	0.00
7.23	2.02	0.14	0.10	0.11	0.02
31.80	4.72	0.31	0.24	0.23	0.04
30.20	7.68	2.70	0.28	0.30	0.22

In comparison with other formula, the following semi-empirical one was fond the best to represent the relation of factors in a simple form:

$$r=k(a_{1i}-K_0a_{2i})A/(1+b\theta) \qquad (1)$$

where r is transfer rate through the interface; k is the apparent rate constant transferring through the interface; K_0 is the distribution coefficient for an infinite dilution; b is a constant determined by means of the materials and temperature; a_{1i} and a_{2i} are the activities of the solute immediately next to the interface for bulks 1 and 2 respectively; θ is the fraction of area covered by adsorbed molecules, and A is the area of the interface. As a process of transferring through the interfaces, an adsorption-desorption mechanism is considered according to the method of Langmuir;[16] when the amount of adsorption is in equilibrium with the concentration in bulk 1 (the aqueous layer) immediately next to the interface, as is indicated in our experiments, and the interaction among adsorbed molecules is negligible, it would seem that an equation replaceing θ with the a_{1i} in Eq. 1 should be derived.[17] However, a comparison applying

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[15] R. K. Schofield and E. K. Rideal, *Proc., Roy. Soc.*, **A109**, 57 (1925).

[16] I. Langmuir, *J. Am. Chem. Soc.*, **39**, 1858 (1917).

[17] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), p. 367.

the experimental data prefers Eq. 1. This might be due to interaction among adsorbed molecules.

From Eq. 1:

$$A(a_{1i}-K_0 a_{2i})/r=1/k+b\theta/k$$

As in our experiments, $a_{1i}=c_{1i}$ ($f_1=1.000-0.985$); therefore,

$$A(c_{1i}-Kc_{2i})/r=1/k+b\theta/k \qquad (2)$$

where c_{1i} and c_{2i} are the concentrations immediately next to the interface for bulks 1 and 2 respectively; f_1 is the activity coefficient in bulk 1, and K is the distribution coefficient. If Eq. 2 holds good, the value on the left-hand side of the equation must be in linear relation to θ, as is shown in Figs. 7a and 7b. The point at $\theta=1.0$ in Fig. 7a is far away from the straight line which indicates the linear relation; the reason for this not distinct. Figures 7a and 7b indicate plainly that the two concentrations immediately next to the respective interfaces, c_{1i} and c_{2i}, are not in equilibrium with each other in these cases, because if $c_{1i}=Kc_{2i}$, $A(c_{1i}-Kc_{2i})/r=0$ and all the points should fall on the horizontal axis; the facts are otherwise.

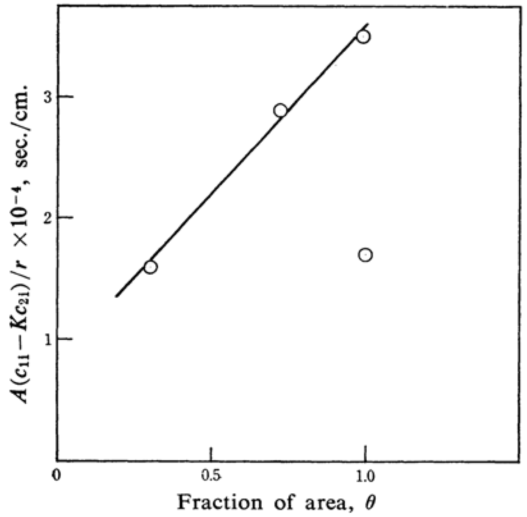

Fig. 7a. Plot of Eq. 2 for the system of an aqueous solution of *n*-butyric acid and carbon tetrachloride at 30°C.

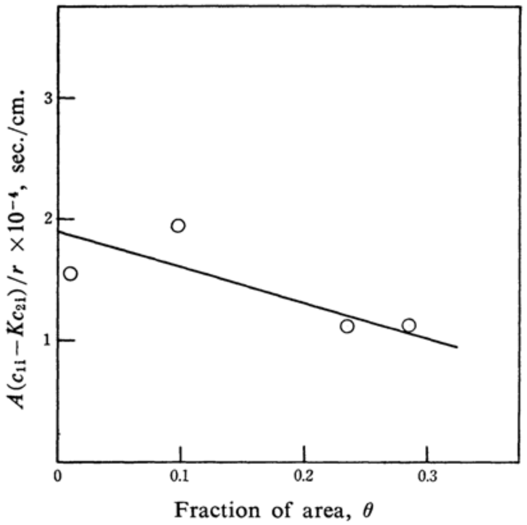

Fig. 7b. Plot of Eq. 2 for the system of an aqueous solution of *n*-butyric acid and benzene at 30°C.

Discussion

In order to compare it with the theory, Eq. 1 is transformed as follows. If $c_{1i}=\tau'\theta$, $\tau'=\boldsymbol{F}(c_{1i}, T)$, and

$$r_0=r/A=k(\tau'\theta-Kc_{2i})/(1+b\theta)$$
$$=k\tau'\theta/(1+b\theta)-kKc_{2i}/(1+b\theta) \qquad (3)$$

where τ' is the coefficient representing the equilibrium-relation between c_{1i} and θ; T is the absolute temperature, and r_0 is the transfer rate through the interface per unit of area.

A theoretical formula of the adsorption rate,[18] which has exponential factors representing the interaction among adsorbed molecules, is:

$$-r_0=k_{a2}a_{2i}(1-\theta)e^{x\theta}-k_{d2}\theta e^{-y\theta} \qquad (4)$$

where k_{a2} is the rate constant of absorption from bulk 2 to the interface; k_{d2} is the rate constant of desorption from the interface to bulk 2, and x and y are constants representing the effect of interaction among adsorbed molecules.

For an infinite dilution, $\theta\to 0$, and $a_{2i}\to c_{2i}$; Eq. 4 then becomes:

$$-r_0=k_{a2}c_{2i}-k_{d2}\theta$$

At the same time, Eq. 3 becomes:

$$r_0=k\tau'_0\theta-kK_0c_{2i}$$

where τ'_0 is the critical value of τ' for an infinite dilution.

θ and c_{2i} are mutually independent variables, and therefore

$$k_{a2}=kK_0, \qquad k_{d2}=k\tau'_0 \qquad (5)$$

and

$$-r_0=kK_0a_{2i}/(1+b\theta)-k\tau'\theta/(1+b\theta)$$
$$=kK_0a_{2i}(1-\theta)e^{x\theta}-k\tau'_0\theta e^{-y\theta}$$

Accordingly,

$$\left.\begin{aligned} x&=-(1/\theta)\ln(1+b\theta)-(1/\theta)\ln(1-\theta)\\ y&=(1/\theta)\ln(1+b\theta)-(1/\theta)\ln(\tau'/\tau'_0)\end{aligned}\right\} \quad (6)$$

The numerical values of x and y obtained from

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[18] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), p. 365.

TABLE II. VALUES OF x AND y (30°C)

A) Aq. soln. of *n*-butyric acid - CCl_4

θ	$\tau' \times 10^2$ N	x	y
0.30	3.67	−1.0	5.4
0.72	2.87	0.1	3.3
0.99	4.76	3.8	2.1
1.00	8.20	—	1.6
average		1	3

B) Aq. soln. of *n*-butyric acid - benzene

θ	$\tau' \times 10^2$ N	x	y
0.20	4.95	−1.26	6.1
0.40	3.35	−0.72	4.8
0.60	3.12	−0.20	3.8
0.80	3.30	0.41	3.0
average		−0.4	4.4

Eq. 6 are shown in Table II, but actually x and y are rather affected by θ or τ'.

The free energy of attractive interaction between one adsorbed molecule and its neighbors in a saturated state is calculated as follows:[19]

$$x = psV/\boldsymbol{R}T, \qquad y = (1-p)sV/\boldsymbol{R}T$$

$$\therefore \quad sV = (x+y)\boldsymbol{R}T \tag{7}$$

where p is the fraction of free energy; s is the coordination number of absorbed molecules in a saturated state; V is the free energy of attractive interaction between two adjacent adsorbed molecules; $\boldsymbol{R}$ is the gas constant, and $\boldsymbol{T}$ is the absolute temperature.

According to the activated-complex theory, specific rate constants are given by:

$$k'_{a2} = \kappa_{a2}(\boldsymbol{kT/h})e^{-\Delta F^{\ddagger}_{a2}/\boldsymbol{R}T}$$

$$k'_{d2} = \kappa_{d2}(\boldsymbol{kT/h})e^{-\Delta F^{\ddagger}_{d2}/\boldsymbol{R}T}$$

where k'_{a2} is the specific rate constant of adsorption from bulk 2 to the interface; k'_{d2} is the specific rate constant of desorption from the interface to bulk 2; κ_{a2} and κ_{d2} are the transmission coefficients; $\boldsymbol{k}$ is the Boltzmann constant; $\boldsymbol{h}$ is the Planck constant; $\Delta F^{\ddagger}_{a2}$ is the free energy of activation to adsorb from bulk 2 to the interface, and $\Delta F^{\ddagger}_{d2}$ is the free energy of activation to desorb from the interface to bulk 2.

From the definitions,

$$k_{a2} = k'_{a2}\lambda \quad \text{or} \quad \lambda = k_{a2}/k'_{a2} \tag{8}$$

$$k_{d2}\theta = (k_{d2}/\Gamma_\infty)\Gamma = k'_{d2}\Gamma \quad \text{or} \quad k'_{d2} = k_{d2}/\Gamma_\infty \tag{9}$$

where λ is the length of the adsorption path from the boundary site of bulk 2 to the interface; Γ is the amount of adsorption, and Γ_∞ is the value of Γ in a saturated state.

If both κ_{a2} and κ_{d2} are assumed to be unity:

$$k'_{a2} = (\boldsymbol{kT/h})e^{-\cdot F^{\ddagger}_{a2}/\boldsymbol{R}T} \tag{10}$$

$$\Delta F^{\ddagger}_{d2} = \boldsymbol{R}T \ln (\boldsymbol{k}T/\boldsymbol{h}k'_{d2})$$

$$= \boldsymbol{R}T \ln (\boldsymbol{k}T\Gamma_\infty/\boldsymbol{h}k_{d2}) \tag{11}$$

$$\Delta F^{\ddagger}_{a2} = \Delta F^{\ddagger}_{d2} + \Delta F_1 - \Delta\chi \tag{12}$$

where ΔF_1 is the standard free energy of adsorption from bulk 1 to the interface, and $\Delta\chi$ is the standard free energy of transference from bulk 1 to 2.

According to Ward and Tordai,[20]

$$\tau = \delta\boldsymbol{k}T e^{-\Delta F_1/\boldsymbol{R}T}, \text{ or } \Delta F_1 = \boldsymbol{R}T \ln (\delta\boldsymbol{R}T/\tau) \tag{13}$$

where τ is Traube's constant, and δ is the thickness of the interfacial phase. Thermodynamically, $\Delta\chi$ is given by:

$$\Delta\chi = \boldsymbol{R}T \ln (a_1/a_2)_e = \boldsymbol{R}T \ln K_0 \tag{14}$$

where a_1 and a_2 are activities, and e indicates equilibrium.

The values of $\Delta F^{\ddagger}_{d2}$, ΔF_1 and $\Delta\chi$ are calculated according to Eqs. 11, 13 and 14 respectively, with the experimental values, k_{d2}, Γ_∞, τ and K_0, and δ, which is given as equal to the statistical length of a *n*-butyric acid molecule (9.86 Å[20]), because the adsorbed molecules in these cases have been known to form monolayers.[15] Therefore, $\Delta F^{\ddagger}_{a2}$ is given by Eq. 12, considering the continuity of the standard free energy in the transfer process. Then k'_{a2} is calculated by Eq. 10, and finally λ is given by Eq. 8.

The results of calculations from the experimental data are given in Table III. The values of both k_{a2} and k_{d2} in one system are very different from those in the other system; nevertheless, the values of $\Delta F^{\ddagger}_{d2}$, the free energy of activation to desorb from the interface into the bulk of organic solvent, in the

TABLE III. RESULTS OF CALCULATION FROM EXPERIMENTAL DATA (30°C)

System: Aq. soln. of *n*-butyric acid - CCl_4

Constants	Unit	$S=CCl_4$	$S=C_6H_6$
$k \times 10^4$	cm./sec.	1.14	0.44
b	—	3.04	−1.57
K_0	—	11.50	3.24
$\tau'_0 \times 10^4$	g. mol./cm³	1.05	1.56
$k_{a2} \times 10^3$	cm./sec.	1.31	0.14
$k_{d2} \times 10^8$	g. mol./cm² sec.	1.20	0.69
sV	kcal./mol.	2.40	0.49
$\Delta F^{\ddagger}_{d2}$	kcal./mol.	15.50	16.30
ΔF_1	kcal./mol.	−2.72	−2.39
$\Delta\chi$	kcal./mol.	1.47	0.71
λ	Å	7.58	7.99

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[19] Ibid., pp. 363—366. In the original, sV means the free energy of the repulsive interaction instead of that of the attractive interaction.

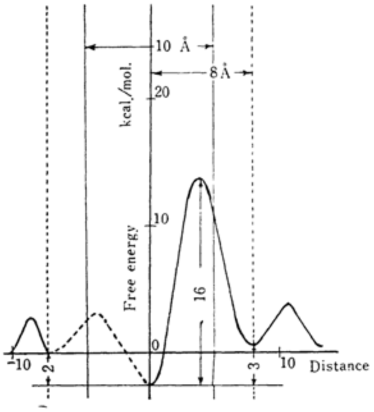
[20] A. F. H. Ward and L. Tordai, *Trans. Faraday Soc.*, **42**, 415 (1946).

two systems are nearly equal (16 kcal./mol.), so it may be supposed that the desorptions in the two systems proceed via the same mechanism.

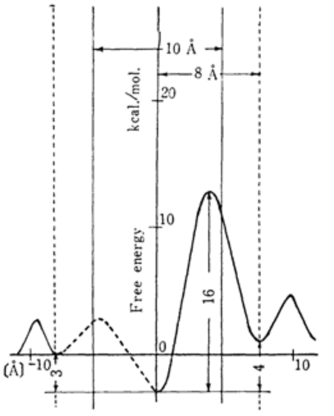
The values of λ, the length of the adsorption path from the boundary site in an organic bulk to the interface, for the two systems are also nearly equal, 8 Å, and are reasonable when compared with the statistical length of an *n*-butyric acid molecule, 9.86 Å.

The value of sV, the free energy of attraction between an adsorbed molecule and the adjacent one in a saturated state, for the water-benzene system is very small compared with the value for the other system, and both values are positive, indicating that the interactions are both attractive. These results are considered to agree with those given by Schofield and Rideal in a study of surface film.[15]

Figure 8 shows the standard free energy change for our systems in the course of mass transfer through the interface. To interpret the origin of such a potential barrier, the following hypothesis is introduced. As Fig. 9 shows, it is known that two hydrogen bonds exist between two water molecules and a carboxyl radical of the *n*-butyric acid molecule in the state of adsorption at the interface;[21,22] the bonds must be split off when the molecule transfers from the interface into the organic solvent bulk. Therefore, the molecule should have a free energy higher than that required to cut off the hydrogen bonds for the desorption into the organic phase. This may be considered to be the origin of such a high potential barrier, because the energy of that



System: Water - *n*-butyric acid - benzene



System: Water - *n*-butyric acid - CCl_4

Fig. 8. Potential barriers near the interfaces.

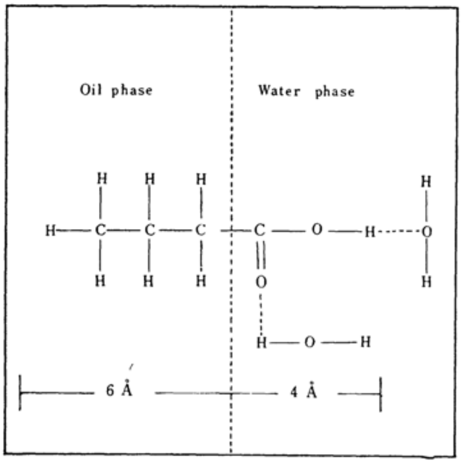


Fig. 9. Model of the adsorption state of a *n*-butyric acid molecule at the oil-water interface.

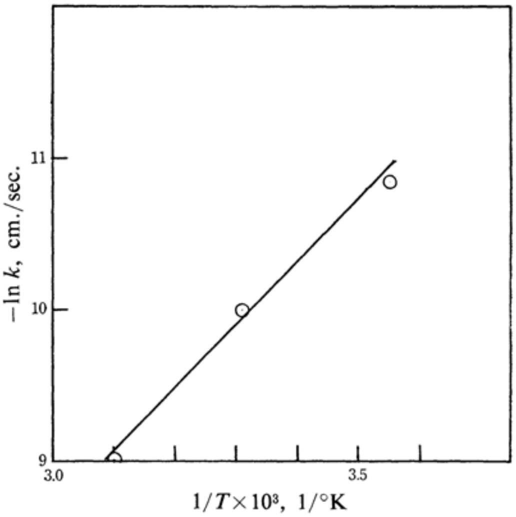


Fig. 10. Arrhenius plot for *n*-butyric acid transfer from the aqueous to the benzene phase.

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[21] W. J. Moore and H. Eyring, *J. Chem. Phys.*, 6, 391 (1938).

[22] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco (1960), p. 352.

sort of hydrogen bond, O–H–O, is usally about 5—8 kcal./bond.

In order to separate the energy term from the free energy of activation, experiments similar to those which had been made at 30°C were made in the systems of aqueous solutions of *n*-butyric acid and benzene at the temperatures of 10°C and 50°C respectively. The activation energy of mass transfer through the interface from the aqueous to the benzene phase, $\Delta E^{\ne}_{12}$, for *n*-butyric acid was determined to be 8.15 kcal./mol. by the Arrhenius plot, as is shown in Fig. 10.

The standard free energy of adsorption from the aqueous phase to the interface, ΔF_1, is determined to be -2.39 kcal./mol., as is shown in Table III; if the entropy term is negligible, as in the case of the system composed of an aqueous solution of *n*-butyric acid and air ($\Delta E_1 = -2.83$ kcal./mol., $\Delta F_1 = -2.54$kcal./mol.), the energy of activation for the desorption of *n*-butyric acid from the interface into the benzene bulk, $\Delta E^{\ne}_{d2}$, becomes 10.5 kcal./mol. (obtained by subtraction, $\Delta E^{\ne}_{12} - \Delta F_1$). If this value is given by the sum of energies for the two hydrogen bonds, the average bond-energy is 5.2 kcal./bond, which agrees well with the literature, 5.1 kcal./bond.[22]

The entropy of activation associated with this process, $\Delta S^{\ne}_{d2}$, is calculated as follows:

$$\Delta S^{\ne}_{d2} = (\Delta E^{\ne}_{d2} - \Delta F^{\ne}_{d2})/T = -19.2 \text{ e. u.}$$

Davies observed a large negative entropy of activation (-20 e. u.) in the diffusion of potassium iodide from the nitrobenzene phase into the aqueous phase.[1] It is interesting that the present result of the entropy of activation in the desorption of *n*-butyric acid from the water-benzene interface into the benzene phase has the same sign and magnitude as the above datum of Davies.

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