The Mass Transfer Rate through the Liquid-Liquid Interface. III. Factors Specifying Boundary Conditions

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In the previous papers of this series, it was found that the resistance to the transfer of *n*-butyric acid through the interfaces of water-benzen and water - carbon tetrachloride systems were appreciably high. In these systems, no equilibrium was established during the transference process for the solute in the two concentrations immediately next to the interface. A rate-determining potential barrier was found on the interfaces of the non-aqueous side, a barrier which was attributed to the breaking of the hydrogen bonds between the carboxyl radicals and water.

In the present paper, the results of studies of carboxylic acids and amines will be summarized. These substances form hydrogen bonds with water and show similar transference resistances. The second paper of this series gave an equation, $c_{1i}=\alpha c_{2i}+\beta$, which holds when the amount of adsorption on the interface, Γ, is constant with respect to the time, when, that is, the fraction of coverage, θ, is constant. In this equation, c_{1i} and c_{2i} are the concentrations (or, more precisely, the activities) of the solute in phases 1 and 2 respectively, next to the interface, and α and β are functions of θ, independent of the time at a constant temperature. When the interfacial resistance is not zero, $\alpha<0$ and $\beta>0$; $\alpha=K>0$ and $\beta=0$ otherwise, as has been described in the preceding paper. Here K is Nernst's partition coefficient. It is possible to determine whether the interfacial resistance is zero or not by solving this equation numerically for α and β. The boundary condition of Fick's diffusion equation is specified by determining the values of α and β and the problem of transference through the interface is solved by solving Fick's equation. The numerical evaluation of α and β is an important problem from both theoretical and practical points of view.

Experimental

The apparatus used is shown in Fig. 1. The experimental procedure was given in detail in the first

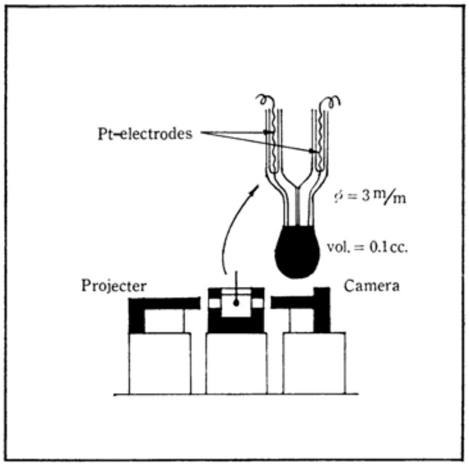

Fig. 1. Apparatus.

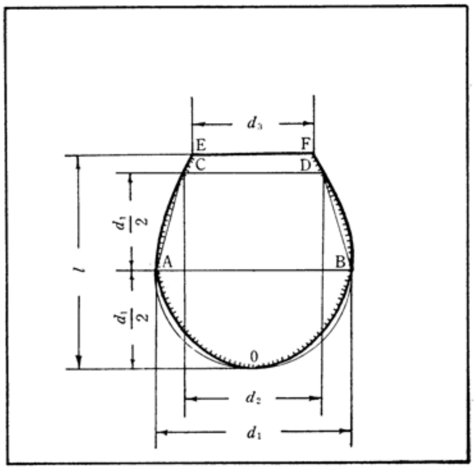

Fig. 2. Scheme of the pendant drop.

paper. As in the pendant-drop method of measuring interfacial tension, a water drop was suspended in an organic solution of a solute, and the change in the average concentration of the solute in the drop was traced conductometrically, with a pair of platinum electrodes coated with platinum black. Every result was recorded automatically. The use of the platinum black increased the sensitivity and improved the response. The average concentration was obtained approximately from the relationship between the equilibrium concentration and the conductivity calibrated beforehand. The actual concentration-distributions in the drop were, however, not uniform, and only approximate values could be estimated by this method. The interfacial tension was determined by the pendant-drop method,[1] in the same time, using photographs of the drop.

The final concentration in the drop was about 0.01—0.10 N. In the calculation of the interfacial tension, the densities of the first and second phases were given to be approximately equal to those of the pure solvents. In order to prevent the communication of the solute from the internal part of the syringe, the tip was made from a capillary tube. No transfer of the solute from the syringe to the drop of pure water hung at the tip of the capillary tube was detected by the conductometry, even when the syringe was filled with a concentrated solution.

The drop was estimated to be a sphere of the same volume. The volume and surface area of the drop were calculated from the OAB hemisphere and from the truncated cones, ABCD and CDEF, shown in Fig. 2, by using these equations:

$$V=\frac{\pi}{24}[2d_1^3+d_1(d_1^2+d_1d_2+d_2^2)+2(l-d_1)(d_2^2+d_2d_3+d_3^2)]$$

$$A=\frac{\pi}{4}[2d_1^2+(d_1+d_2)\{d_1^2+(d_1-d_2)^2\}^{1/2}+(d_2+d_3)\{4(l-d_1)^2+(d_2-d_3)^2\}^{1/2}]$$

where V is the volume of liquid drop, and A is the surface area of the liquid drop. The values obtained by this method were in agreement with those determined by Simpson's method of graphical integration, in which the height was divided into ten sections, with an accuracy of 5%. The radii of spheres with both the same volume and the same interfacial area show a good agreement (within 2%).

All disturbance effects, for example, the disturbance of making the pendant drop, the convection resulting from the difference in local density, and the spontaneous interfacial turbulence, due to the so-called "Marangoni effect," were disregarded.

Theoretical

Consider a sphere of the first phase suspended in a second phase of infinite dimensions. The three-dimensional diffusion equations[2] are represented as:

$$\frac{\partial U_1}{\partial t}=D_1\frac{\partial^2 U_1}{\partial r^2},\quad 0\leqslant r<R,\ t>0 \tag{1}$$

$$\frac{\partial U_2}{\partial t}=D_2\frac{\partial^2 U_2}{\partial r^2},\quad R<r,\ t>0 \tag{2}$$

$$U_1=\alpha U_2+\beta,\quad r=R,\ t>0 \tag{3}$$

$$D_1\left(\frac{1}{r}\cdot\frac{\partial U_1}{\partial r}-\frac{U_1}{r^2}\right)=D_2\left(\frac{1}{r}\cdot\frac{\partial U_2}{\partial r}-\frac{U_2}{r^2}\right),\quad r=R,\ t>0 \tag{4}$$

$$\left.\begin{array}{l} U_1=rC_{10},\quad 0\leqslant r<R,\ t=0 \\ U_2=rC_{20},\quad R<r,\ t=0 \end{array}\right\} \tag{5}$$

$$C_1:\ \text{finite},\ r=0 \tag{6}$$

where U_1 and $U_2=rC_1$ and rC_2 respectively; r is the distance from the center of the sphere; C_1 and C_2 are the local concentrations of the solute in phases 1 and 2 respectively; R is the radius of the sphere; D_1 and D_2 are the diffusion coefficients of the solute in both phases; t is the time, and C_{10} and C_{20} are the initial concentrations of the solute in the two phases respectively. Equation 4 expresses the condition of continuity, indicating that the amount of solute flowing into the interface from the first phase in the unit of time is equal to that from the interface into the second.

The initial concentration in the drop of pure water, C_{10}, is zero, while C_{20} is the concentration in the solution before their contact. As has been shown in the first paper, however, the amount of adsorption on the interface may be increased very rapidly in the early stage, the "adsorption stage." According to the second paper, Eq. 3 holds only when there is no time-change in the amount of adsorption. In the "adsorption stage," neither Eq. 3 nor 4 is applicable.

As may be seen in Fig. 3, the process in the early stage (in 5 min.) is quite different from that in the later stage. As was described in the second paper, the interfaces of water-benzene and water - carbon tetrachloride systems show a high resistance to the passage of *n*-butyric acid. Putting other resistances in the bulk diffusion of zero as the limiting case, we have:

$$\frac{\mathrm{d}m}{\mathrm{d}t}=V\frac{\mathrm{d}C_1}{\mathrm{d}t}=-k(C_1-KC_2)A \tag{7}$$

where m is the amount of solute transferred, and k is the rate constant of transferring through the interface.

Since the concentration-distribution is to be assumed even in each phase, and since the second phase is infinite in volume, we have $C_2=C_{20}$, and

$$\frac{\mathrm{d}C_1}{\mathrm{d}t}=-k\left(\frac{A}{V}\right)(C_1-KC_{20}) \tag{8}$$

Assuming that the radius of the sphere is

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

[2] J. Crank, "Mathematics of Diffusion," Clarendon Press, Oxford (1956).

independent of the time, we integrate Eq. 8 as:

$$\ln\left[(KC_{20}-C_{10})/(KC_{20}-C_1)\right]=ktA/V \qquad (9)$$

An example of the plots of Eq. 9 is shown in Fig 3, where the measured values after about 3 min. fall on a straight line. In some cases no such liner plot was observed. This is probably due to the facts that the interfacial phase is not taken account in Eq. 7, and that the actual situation is not strictly represented by such a limiting equation as Eq. 7.

All the plots obtained consist of two sections, one for the early stage (in 5 min.) and the other for the later stage. The extrapolation of the later section meets the ordinate. The values of C_{10} obtained by this extrapolation are all positive. This result is not contrary to the following interpretation. Let us denote the starting time of the later stage as t_0 and then shift the origin to t_0. When t is sufficiently large, this transformation produces no error. This situation corresponds to the case where no "adsorption stage" occurs, and $C_{10}>0$. As for C_{20}, the values preceding the contact were used. As the magnitude of C_{20} is sufficiently large, the error due to the use of this initial value is considered to be negligible.

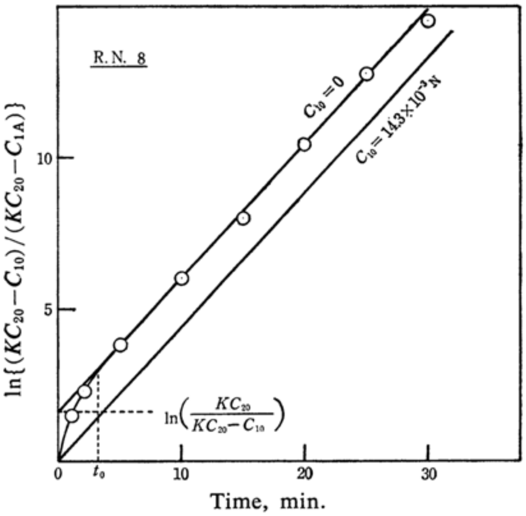

Fig. 3. An example of time dependences of the average concentration in the drop.

Solving Eqs. 1—6 (see Appendix I), we have

$$\begin{aligned}C_1 \doteqdot C_{10}&+\frac{1}{r}\sum_{n=0}^{\infty}\Bigl\{K_1\Bigl[\operatorname{erfc}\Bigl\{\frac{(2n+1)R-r}{2(D_1t)^{1/2}}\Bigr\}\\&-\operatorname{erfc}\Bigl\{\frac{(2n+1)R+r}{2(D_1t)^{1/2}}\Bigr\}\Bigr]\\&+\frac{K_2}{h}\Bigl[\operatorname{erfc}\Bigl\{\frac{(2n+1)R-r}{2(D_1t)^{1/2}}\Bigr\}\\&-e^{h\{(2n+1)R-r\}+D_1th^2}\operatorname{erfc}\Bigl\{\frac{(2n+1)R-r}{2(D_1t)^{1/2}}\\&+h(D_1t)^{1/2}\Bigr\}-\operatorname{erfc}\Bigl\{\frac{(2n+1)R+r}{2(D_1t)^{1/2}}\Bigr\}\\&+e^{h\{(2n+1)R+r\}+D_1th^2}\operatorname{erfc}\Bigl\{\frac{(2n+1)R+r}{2(D_1t)^{1/2}}\\&+h(D_1t)^{1/2}\Bigr\}\Bigr]\Bigr\}\end{aligned} \qquad (10)$$

$$\begin{aligned}C_2 \doteqdot C_{20}&+\frac{1}{r}\Bigl\{K'_1\Bigl[\operatorname{erfc}\Bigl\{\frac{r-R}{2(D_2t)^{1/2}}\Bigr\}\\&-2\sum_{n=0}^{\infty}\operatorname{erfc}\Bigl\{\frac{2(n+1)(D_2/D_1)^{1/2}R+(r-R)}{2(D_2t)^{1/2}}\Bigr\}\\&+\frac{K'_2}{h'}\Bigl[\operatorname{erfc}\Bigl\{\frac{r-R}{2(D_2t)^{1/2}}\Bigr\}\\&-e^{h'(r-R)+D_2th'^2}\operatorname{erfc}\Bigl\{\frac{r-R}{2(D_2t)^{1/2}}\\&+h'(D_2t)^{1/2}\Bigr\}\Bigr]+\frac{K'_3}{h'}\sum_{n=0}^{\infty}\\&\Bigl[\operatorname{erfc}\Bigl\{\frac{2(n+1)(D_2/D_1)^{1/2}R+(r-R)}{2(D_2t)^{1/2}}\Bigr\}\\&-e^{h'\{2(n+1)(D_2/D_1)^{1/2}R+(r-R)+D_2th'^2\}}\operatorname{erfc}\\&\Bigl\{\frac{2(n+1)(D_2/D_1)^{1/2}R+(r-R)}{2(D_2t)^{1/2}}\\&+h'(D_2t)^{1/2}\Bigr\}\Bigr]\Bigr\}\end{aligned} \qquad (11)$$

$$K_1\equiv\frac{R(\alpha C_{20}-C_{10})+\beta}{1+\alpha(D_1/D_2)^{1/2}}$$

$$K_2\equiv\frac{\alpha\{1+(D_1/D_2)^{1/2}\}\{R(\alpha C_{20}-C_{10})+\beta\}}{R\{1+\alpha(D_1/D_2)^{1/2}\}^2}$$

$$h\equiv\frac{1-\alpha D_1/D_2}{R(D_1/D_2)^{1/2}\{1+\alpha(D_1/D_2)^{1/2}\}}$$

$$K'_1\equiv\frac{-(D_1/D_2)^{1/2}\{R(\alpha C_{20}-C_{10})+\beta\}}{1+\alpha(D_1/D_2)^{1/2}}$$

$$K'_2\equiv\frac{(D_1/D_2)^{1/2}\{1+(D_1/D_2)^{1/2}\}\{R(\alpha C_{20}-C_{10})+\beta\}}{R\{1+\alpha(D_1/D_2)^{1/2}\}^2}$$

$$K'_3\equiv\frac{2(D_1/D_2)^{1/2}(1-\alpha D_1/D_2)\{R(\alpha C_{20}-C_{10})+\beta\}}{R\{1+\alpha(D_1/D_2)^{1/2}\}^2}$$

$$h'\equiv\frac{1-\alpha D_1/D_2}{R\{1+\alpha(D_1/D_2)^{1/2}\}}$$

The Concentrations immediately next to the interface, C_{1i} and C_{2i}, are given from Eqs. 10 and 11, putting $r=R$, as:

$$\begin{aligned}C_{1i}\doteqdot C_{10}&+K_1/R+(K_2/Rh)\\&\times\left[1-e^{D_1th^2}\operatorname{erfc}\{h(D_1t)^{1/2}\}\right]\end{aligned} \qquad (12)$$

$$C_{2i}\doteqdot C_{20}+K'_1/R\Bigl[1-2\sum_{n=0}^{\infty}\operatorname{erfc}\Bigl\{\frac{(n+1)R}{(D_1t)^{1/2}}\Bigr\}\Bigr]$$

$$+(K'_2/Rh')\,[1-\mathrm{e}^{D_2th'^2}\,\mathrm{erfc}\{h'(D_2t)^{1/2}\}]$$
$$+\frac{K'_3}{Rh'}\sum_{n=0}^{\infty}\Big[\mathrm{erfc}\Big\{\frac{(n+1)R}{(D_1t)^{1/2}}\Big\}$$
$$-\mathrm{e}^{2(n+1)(D_2/D_1)^{1/2}Rh'+D_2th'^2}\,\mathrm{erfc}$$
$$\Big\{\frac{(n+1)R}{(D_1t)^{1/2}}+h'(D_2t)^{1/2}\Big\}\Big] \qquad (13)$$

Equations 10 and 11 exist strictly at $t\to0$ (see Appendix I) : $\lim\limits_{t\to0}C_{1\mathrm{i}}=C_{10}+K_1/R$, $\lim\limits_{t\to0}C_{2\mathrm{i}}=C_{20}+K'_1/R$, and $\lim\limits_{t\to0}C_{1\mathrm{i}}=\alpha(\lim\limits_{t\to0}C_{2\mathrm{i}})+\beta/R$, that is in accord with Eq. 3.

The average concentration in the drop is represented as:

$$\overline{C}_{1\mathrm{A}}=\frac{\iiint_v \overline{C}_1r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi}{\iiint_v r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi}=\frac{3}{R^3}\int_0^R\overline{U}_1r\mathrm{d}r \qquad (14)$$

where θ and φ are the angles in the solid polar coordinates.

By calculating Eq. 14 by applying Eq. 27 in Appendix I, and by inversion to the original function, we have:

$$C_{1\mathrm{A}}\fallingdotseq C_{10}+[R(\alpha C_{20}-C_{10})+\beta]$$
$$\times\Big\{\frac{6(D_1t/\pi)^{1/2}}{R^2}\Big[\frac{1+\alpha(D_1/D_2)^{3/2}}{(1-\alpha D_1/D_2)^2}\Big]$$
$$-\frac{3D_1t}{R^3(1-\alpha D_1/D_2)}+3\alpha(D_1/D_2)$$
$$\times[1+(D_1/D_2)^{1/2}]^2\,[\mathrm{e}^{D_1th^2}\,\mathrm{erfc}\{h(D_1t)^{1/2}\}$$
$$-1]/R(1-\alpha D_1/D_2)^3+S_1+S_2\Big\} \qquad (15)$$

$$S_1\equiv\frac{12}{R^2(1+\alpha(D_1/D_2)^{1/2})}\sum_{n=1}^{\infty}[(D_1t/\pi)^{1/2}\mathrm{e}^{-n^2R^2/D_1t}$$
$$-nR\,\mathrm{erfc}\{nR/(D_1t)^{1/2}\}]$$
$$S_2\equiv\frac{6\alpha\{1+(D_1/D_2)^{1/2}\}(1-\alpha D_1/D_2)^2}{(D_1/D_2)R^5\{1+\alpha(D_1/D_2)^{1/2}\}^4}$$
$$\times\sum_{n=1}^{\infty}\Big[2h\Big(\frac{D_1t}{\pi}\Big)^{1/2}\mathrm{e}^{-n^2R^2/D_1t}$$
$$-(1+2nRh)\,\mathrm{erfc}\Big\{\frac{nR}{(D_1t)^{1/2}}\Big\}$$
$$+\mathrm{e}^{2nRh+D_1th^2}\,\mathrm{erfc}\{nR/(D_1t)^{1/2}+h(D_1t)^{1/2}\}\Big]$$

Therefore, our purpose is to determine the numerical values of α and β suitable for Eq. 15 from the expermental data, R, C_{10}, C_{20}, $C_{1\mathrm{A}}$, D_1 and D$_2$. Equation 15 is deformed as:

$$\beta=(C_{1\mathrm{A}}-C_{10})/\boldsymbol{F}(\alpha,t)-R(\alpha C_{20}-C_{10}) \qquad (16)$$
$$\boldsymbol{F}(\alpha,t)\equiv\frac{6(D_1t/\pi)^{1/2}}{R^2}\Big[\frac{1+\alpha(D_1/D_2)^{3/2}}{(1-\alpha D_1/D_2)^2}$$
$$-\frac{3D_1t}{R^3(1-\alpha D_1D_2)}$$
$$+\frac{3\alpha(D_1/D_2)\,[1+(D_1/D_2)^{1/2}]^2}{R(1-\alpha D_1/D_2)^3}$$
$$\times\mathrm{e}^{D_1th^2}\,\mathrm{erfc}\{h(D_1t)^{1/2}\}-1]+S_1+S_2 \qquad (17)$$

As β is an explicit function of the time, t, it can be evaluated as the function of t by specifying α. We denote the values of β at $t=t_1, t_2,\cdots\cdots,t_n$ as $\beta=\beta_1, \beta_2,\cdots\cdots,\beta_n$, and define $\tilde{\beta}=(\beta_1+\beta_n)/2$ and $\varDelta\beta=|\beta_1-\beta_n|$ (see Appendix II). Therefore, the requisite condition of α and β being the solution of Eq. 16 is $\varDelta\beta=0$ in a definite value of α, because α and β are constant with the time-lapse.

An example of plots of $\tilde{\beta}$ and $\varDelta\beta$ against α is shown in Fig. 4. In Fig. 4, points A and B satisfy the condition, $\varDelta\beta=0$. Point A is, however, physically meaningless, since $C_1<0$ when α and $\beta<0$ and $C_2>0$ in Eq. 3. Point B has no definite value, because at B, $\alpha=D_2/D_1$, both denominater and numerator in the third term of Eq. 17 become zero; in the limiting value of the indefinite form, $\varDelta\beta=0$.

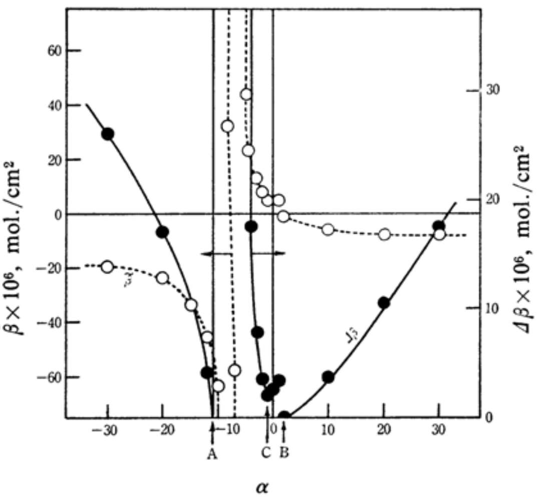

Fig. 4. An example of α-dependences of the $\varDelta\beta$ and $\tilde{\beta}$.
System: water- benzene solution of n-butyric acid ($C_{20}=10.41\times10^{-6}$ mol./cm^3) at 30°C.

From the physical point of view, one reasonable solution at least should be definitive. If we can assume that the value of point C, where $\varDelta\beta$ is at its minimum, must fall on the α axis in spite of its actually taking some finite value because of errors, we can estimate, from the position of the minimum, the approximate value of α, or α_0, and the corresponding value of $\tilde{\beta}$ (the most probable value of β), or β_0, as is shown in Fig. 4. All the experimental plots behave similarly.

$C_{1\mathrm{i}}$ and $C_{2\mathrm{i}}$ were estimated by putting the numerical values of α_0 and β_0 obtained by the above graphical method into Eqs. 12 and 13.

TABLE I. EXPERIMENTAL AND CALCULATED RESULTS (30°C)

No.	System	$C'_{20}\times 10^6$ g. mol./cm³	α_0 —	$\beta_0\times 10^6$ g. mol./cm²	$C_{1i}\times 10^6$ g. mol./cm³	$C'_{2i}\times 10^6$ g. mol./cm³	$C_S\times 10^6$ g. mol./cm³
1	PB	34.5	−0.6	5.0	19.0	−122.0	11.3
2	PB	94.5	−0.8	14.0	61.7	−623.0	47.0
3	PT	68.0	−1.0	9.6	44.7	−462.0	2.5
4	PT	112.5	−0.7	17.0	72.9	−685.0	25.5
5	PC	49.0	−0.6	1.8	8.7	−1330.0	6.3
6	PC	77.7	−0.2	3.5	13.8	−1730.0	2.5
7	BuB	8.7	−0.7	2.0	6.6	0.1	8.4
8	BuB	46.0	−1.0	11.0	35.9	−20.7	50.0
9	BuT	36.5	−0.5	12.0	44.6	−43.4	31.8
10	BuT	67.3	−1.2	18.0	58.5	3.9	57.5
11	BuC	41.5	−0.6	5.9	27.2	−231.0	29.9
12	BuC	57.3	−1.0	8.0	41.8	−574.0	39.2
13	P'B	6.2	−0.6	0.8	2.1	2.4	12.0
14	P'B	15.2	−0.5	2.3	5.5	11.5	13.1
15	P'C	68.5	−0.3	6.5	24.8	−40.2	30.5
16	P'C	135.1	−0.1	19.0	70.1	−171.0	71.0
17	Bu'B	8.2	−0.5	2.4	3.7	7.0	10.0
18	Bu'B	15.7	−0.6	4.6	4.6	15.7	17.0
19	Bu'C	3.8	−0.9	0.9	1.8	4.0	4.5
20	Bu'C	18.2	−1.0	3.7	6.1	11.8	18.5

P Propionic acid; B Benzene; Bu *n*-Butyric acid; T Toluene; P' *n*-Propyl amine; C Cyclohexane; Bu' *n*-Butyl amine

Results

The results obtained are shown in Table I. These were obtained by the aid of an electronic digital computer using Eqs. 12, 13 and 16, assuming that D_1 and D_2 in these equations can be estimated by Wilke's method.[3] In Table I, no description is given for water, which is a substance common to all the systems. C_{1i} is the concentration of the solute in the first (aqueous) phase immediately next to the interface. C'_{20} and C'_{2i} are the concentrations of the solute in the first phase in equilibrium with those in the second phase, initial (C_{20}) and immediately next to the interface (C_{2i}). C_S is the concentration of the solute in the first phase in equilibrium with the surface pressure (or the difference between the interfacial tension of the pure solvents and that of the solutions). C'_{20}, C'_{2i}, and C_S are, so to speak, the reduced concentrations of C_{20}, C_{2i} and Γ respectively, in comparison with C_{1i}. C_{1i}, C'_{2i} and C_S are the values at $t=2$ min. In all the results, $\alpha_0<0$ and $\beta_0>0$. No consistent relation is found between α_0 and C'_{20}, while β_0 increases with the increase in C'_{20}. According to the second report,

$$\alpha = -(k_{a2}/k_{a1})e^{(x_2-x_1)\theta}$$

$$\beta = [(k_{d1}e^{-y_1\theta}+k_{d2}e^{-y_2\theta})/k_{a1}e^{x_1\theta}]\,[\theta/(1-\theta)]\,R$$

where k_{a1} and k_{a2} are the rate constants of the adsorption onto the interface from the two phases respectively; k_{d1} and k_{d2} are the rate constants of desorption from the interface into the two phases respectively; x_1, x_2, y, and y_2 are factors defining the mutual interaction of adsorbed molecules, and θ is the relative amount of adsorption (the fraction of coverage). When k_{a1}, k_{a2}, k_{d1} and k_{d2} have finite values, $\alpha<0$ and $\beta>0$. If $\theta/(1-\theta)$ has a large effect upon the variation in β, θ generally increases with the increase in C'_{20}, while $\theta/(1-\theta)$ increases more rapidly, resulting in the increase in β. The experimental results are not inconsistent with these speculations; this is evidence that a finite interfacial resistance exists in these cases.

In the cases of fatty acids and also in the P'C system (though C'_{2i} shows unreasonable values in these cases), the value of C_S approach those of C_{1i}, while others approach those of C'_{2i}. These facts may be ascribed to the existence of a rate-determining potential barrier. That is to say, in the former cases the rate-determining stage may be the adsorption from the organic solvent onto the interface, while in the latter it may be the desorption from the interface into the aqueous phase. The reason for the appearance of unreasonable values of C'_{2i} in some cases is not certain, but it may be connected with the long time range, t_1-t_n, for the calculation of $\tilde{\beta}$ or $\Delta\beta$, because on a

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[3] C. R. Wilke, *Chem. Eng. Progress*, **45**, 218 (1949).

longer time range the applicability of the condition, that is, the base of Eqs. 3 and 4, $\theta=$ const., seems poor in these cases; as has been described above, when we put other resistances in a bulk diffusion of zero as a limiting case compared with the interfacial resistance, we have $C_{1i}=C_{1A}$ and $C'_{2i}=C'_{20}$. When $C_s=C_{1i}$, the condition in the cases of fatty acids and in the P'C system, $C_s=C_{1A}$ and $\theta\fallingdotseq$const.; on the other hand, when $C_s=C'_{2i}$, $C_s=C'_{20}$ and $\theta=$const.

The values of α and β recalculated from the data of the reverse, one-dimensional diffusion given in the second paper are as follows: $\alpha=-1.3$; $\beta=2.2\times10^{-6}$ (No. 7) and 13.0×10^{-6} (No. 8) g. mol./cm². These values are in good agreement with the present results for the Bu-B system shown in Table I, considering rough approximations are included in the present results. The values of the present results, if denoted as α' and β', are related to those (α and β) in the preceding paper as follows: $\alpha'=1/\alpha$, and $\beta'=-R\beta/\alpha$, provided that $R=0.294$ (No. 7), 0.317 (No. 8) cm.; $\alpha=0.779$, that is the average of α' sin $c_{10}=2.16\times10^{-5}$, 5.03×10^{-5} and 10.38×10^{-5} g. mol./cm³ (as shown in Table III of the second paper), and c_{1i}, which should fix the value of β, approximates c_{10}. The positions of the potential barriers have been taken to be the same for both sets of results.

The time dependence of the thickness of the diffusion layer in the aqueous drop has also been calculated. As may be seen in Fig. 5,

$$\mathrm{d}m/\mathrm{d}t=V(\mathrm{d}C_{1A}/\mathrm{d}t)=D_1(\Delta C_1/l)A$$

or

$$l=D_1\Delta C_1/(V/A)(\mathrm{d}C_{1A}/\mathrm{d}t) \qquad (18)$$

where l is the thickness of the diffusion layer of phase 1, and ΔC_1 is the difference in the boundary concentrations in the diffusion layer of phase 1.

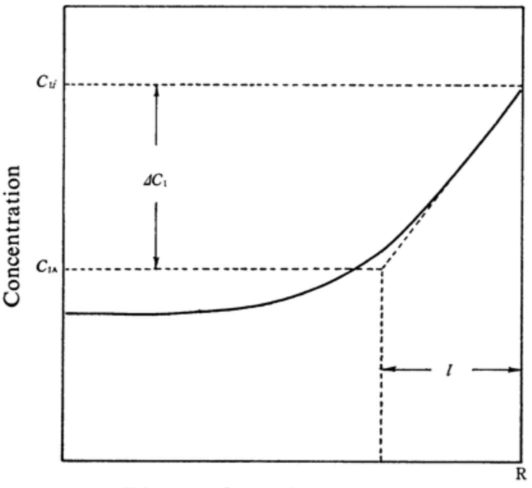

Fig. 5. Scheme of the distribution of concentration in the drop.

It is assumed that C_{1i}, on which the calculation of ΔC_1 is based, is in equilibrium with the surface pressure. As $C_{1i}=C_S$, we have

$$l=D_1(C_S-C_{1A})/(V/A)(\mathrm{d}C_{1A}/\mathrm{d}t) \qquad (19)$$

The values of the thicknesses of the diffusion layer, l, calculated according to Eq. 19

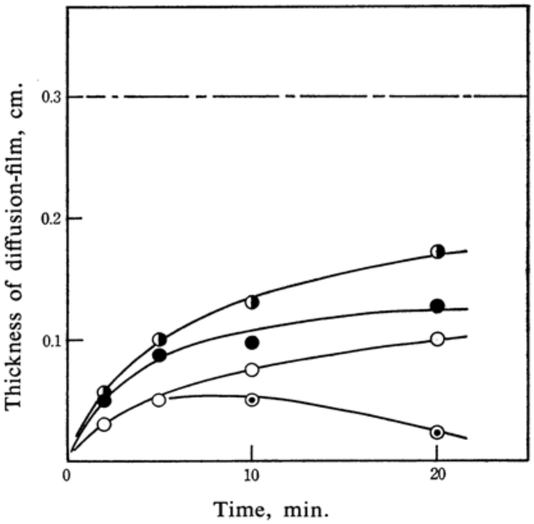

Fig. 6a. Time dependences of the thickness of the diffusion film in fatty acid series of solute (30°C).
System: ○, PB (0.0106 N); ●, BuB (0.0309 N); ◑, PC (0.0053 N); ⊙, BuC (0.0298 N)

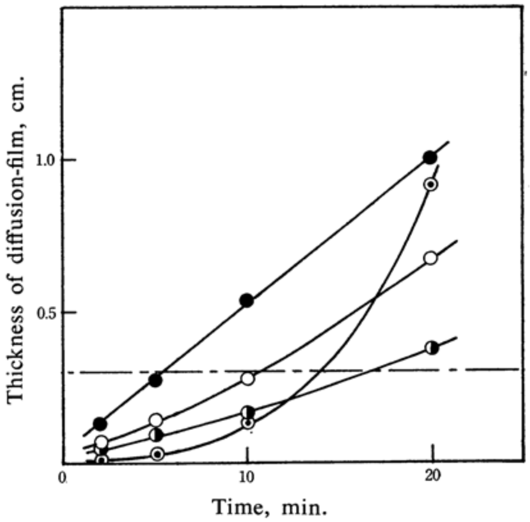

Fig. 6b. Time dependences of the thickness of the diffusion film in fatty amine series of solute (30°C).
System: ○, P'B (0.0201 N); ●, Bu'B (0.0214 N); ◑, P'C (0.0096 N); ⊙, BU'C (0.0200 N)

are shown in Figs. 6a and 6b. As may be seen in these figures, l is smaller than the radius of the aqueous drop for the fatty acids used as solutes, while it becomes much larger than the radius for the fatty amines. When the various theoretical errors included are taken into account, the plots of the fatty acids are quite reasonable, while those of the amines are ununderstandable.

In the cases of fatty acids, the condition, $C_{1i}=C_S$, is satisfied, while in the amine systems except P′C, this condition is not fulfilled in Table I. It should be noted here that Eq. 19 is based on this condition. We put $C_S-C_{1i}=\phi$. Then the error in l, Δl, is represented as $\Delta l=D_1\phi A/V(\mathrm{d}C_{1A}/\mathrm{d}t)$. For the amine systems except P′C, $\phi\gg 0$. Therefore, $\Delta l>0$, and positive deviations may be anticipated. The unreasonable behavior in the plots of fatty amines is to be ascribed to the error due to the assumption that $C_{1i}=C_S$. The curious results of P′C will be discussed later.

Discussion

In the first paper, the transference of n-butyric acid from the aqueous to the benzene phase was studied. The rate-determining potential barrier which the solute molecules encounter during the passage from the interface into the benzene phase was ascribed to the breaking of the two hydrogen bonds formed per solute molecule between the carboxyl radicals of n-butyric acid adsorbed on the interface and water molecules. The energy of the breaking of the hydrogen bonds was assumed to be equal to the activation energy of the desorption process. However, more data must be collected in order to prove the general applicability of this assumption.

In general, it may be assumed that the activation energy of the desorption of a solute from an interface made up of a polar and a non-polar medium to the non-poar sollvent is the sum of the association energies between the polar groups in the adsorbed molecule and the polar solvent (for example, the hydrogen bond), and that the activation energy of the reverse process is the sum of the interaction energies between the non-polar groups in the adsorbed molecule and the non-polar solvent. The entropy associated with the processes is taken to be constant in every case, as in the case of a gas-liquid transition, for which the law of constant entropy is known as Trouton's rule.

If the transfer of n-butyric acid from the interface to the benzene phase is the rate-determining step, it may be concluded from the above assumption that the activation energy of the transfer from the interface to the benzene phase is greater than that of the reverse process. Therefore, the association energy between a carboxyl radical and water may be greater than that of a n-propyl radical and benzene. The interaction of solute molecules among themselves can be disregarded, because the standard state of the rate process is that of infinite dilution. There is not much difference in the interacticn energies between solute and solvent for the solvents used (benzene, toluene, and cyclohexane), which have similar molecular configurations. Since the interaction energy between a non-polar solvent and the non-polar groups of the solute increases at a rate approximately equal to the increase in the carbon number in the non-polar group of a molecule, the association energy of a carboxyl radical with water may be far greater than the interaction energy between an ethyl radical and benzene. In the present results concerning the fatty acid systems, the assumption given above, on the basis of which the rate-determining step in all these systems is presumed to be the transfer of the solute from the interface into the non-polar solvent, is proved experimentally.

In the case of amine systems besides the system of n-propyl amine and cyclohexane, the rate-determining step, on the contrary, is taken to be the transfer from the interface into the aqueous phase. These facts may be explained by assuming that the interaction energy of an amino radical and water is slightly smaller than that of a n-propyl radical and benzene. In the n-propyl amine and cyclohexane system, if the interaction energy between a n-propyl radical and cyclohexane is sufficiently smaller than that with benzene, the situation may be reversed.

As has been shown above, the thickness of the diffusion layer has apparently been found by calculation to become greater than the radius of the water drop in this system. This fact may be explained as follows. The transfer of the solute from the interface into the cyclohexane phase might not be the rate-determining step because of the small difference in interaction energies between an amino radical - water and an n-propyl radical - cyclohexane ; therefore, no equilibrium may be established between the interfacial tension and the concentration in the aqueous phase immediately next to the interface, whereas the calculation of the thickness of the diffusion layer is based on this equilibrium.

The interaction energies between a non-polar radical and a non-polar solvent are calculated as follows : according to Benson,[4] the interaction energy per mole of a non-polar solvent is represented as :

$$(E_m)_{AA}=\phi_{AA}\boldsymbol{N}\sum_{i=1}^{\infty}n_i/r_i^6$$

were r_i is the distance between i-th and the center molecule; n_i is the coordinate number of the i-th molecules; $\boldsymbol{N}$ is Avogadro's number, and ϕ_{AA} is the force constant between solvent molecules.

Now one solvent molecule (A) is replaced by one solute molecule (B). Hereby it is assumed that the relative positions of the solvent molecules are unchanged. Then the interaction energy between A and B molecules made from the above exchange may be represented as:

$$(E_m)_{AB}=(\phi_{AB}/\phi_{AA})(E_m)_{AA} \tag{20}$$

Considering that $\phi_{AA}=(3/4)\boldsymbol{h}\nu_A\alpha_A^2$, $\phi_{AB}=(3/2)\alpha_A\alpha_B\boldsymbol{h}\nu_A\boldsymbol{h}\nu_B/(\boldsymbol{h}\nu_A+\boldsymbol{h}\nu_B)$, $\alpha=3[R]/4\pi\boldsymbol{N}$, and $\boldsymbol{h}\nu=\boldsymbol{P}$, the ϕ_{AB}/ϕ_{AA} factor is represented as:

$$\phi_{AB}/\phi_{AA}=([R]_B/[R]_A)2P_B/(P_A+P_B) \tag{21}$$

where α is the polarizability: $\boldsymbol{h}$ is Planck's constant; ν is the intrinsic oscillation number of the electron system; $[R]$ is the molar refraction, and $\boldsymbol{P}$ is the ionization potential. The interaction energy (the dispersion effect) between A and B molecules at an infinite dilution may then be easily calculated according to Eqs. 20 and 21 and the method of Benson.4)

According to this method, the interaction energies between a propane-molecule and benzene and cyclohexane solvents were calculated for 9.8 and 9.3 kcal./mol. respectively at 30°C, assuming that $(P)_{\text{benzene}}=9.6$ eV.,5) $(P)_{\text{cyclohexane}}=9.24$ eV.6) and $(P)_{\text{propane}}=11.3$ eV7). If a n-propyl radical can be assumed to approximate a propane-molecule (considering that the contribution of a hydrogen-atom is negligible), the interaction energy between an radical and benzene should become more or less higher than that between the radical and cyclohexane; this does not contradict the above discussion.

The relation between the interaction energy of a functional radical of a transfer material with a solvent and the activation energy of the transfer process through the liquid-liquid interface (or the activation free energy) is an important subject both theoretically and experimentally.

The present theory is based on the following crude approximations, and therefore, the conclusion is not precisely quantitative. 1) The pendant drop is taken to be a sphere. 2) The difference between the values of concentration obtained by the conductometric method and the true mean concentrations is neglected. 3) The entropy of activation associated with the desorption of the solute from the interface is assumed to be constant irrespective of the direction of movement and the materials used as solvent and solute. 4) All disturbance effects are disregarded.

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Appendix I

By the Laplace transformation, Eqs. 1—6 are reduced to the ordinary differential equations as:

$$\frac{\mathrm{d}^2\overline{U}_2}{\mathrm{d}r}-q_1^2\overline{U}_1=-\left(\frac{C_{10}}{D_1}\right)r,\ 0\leqslant r<R \tag{22}$$

$$\frac{\mathrm{d}^2\overline{U}_2}{\mathrm{d}r^2}-q_2^2\overline{U}_2=-\left(\frac{C_{20}}{D_2}\right)r,\ R<r \tag{23}$$

$$\overline{U}_1=\alpha\overline{U}_2+\beta/p \quad r=R \tag{24}$$

$$D_1\left(R\frac{\mathrm{d}\overline{U}_1}{\mathrm{d}r}-\overline{U}_1\right)=D_2\left(R\frac{\mathrm{d}\overline{U}_2}{\mathrm{d}r}-\overline{U}_2\right),\ r=R \tag{25}$$

$$\overline{C}_1:\ \text{finite},\ r=0 \tag{26}$$

where p is the conversion parameter in the Laplace transformation, and q_1 and $q_2=(p/D_1)^{1/2}$ and $(p/D_2)^{1/2}$ respectively.

Solving Eqs. 22, 23, and 26, we obtain:

$$\overline{U}_1=rC_{10}/D_1q_1^2+\boldsymbol{A}\sinh(rq_1) \tag{27}$$

$$\overline{U}_2=rC_{20}/D_2q_2^2+\boldsymbol{B}[\cosh(rq_2)-\sinh(rq_2)] \tag{28}$$

where $\boldsymbol{A}$ and $\boldsymbol{B}$ are integration constants.

Applying the boundary conditions, Eqs. 24 and 25, the constants, $\boldsymbol{A}$ and $\boldsymbol{B}$, in Eqs. 27 and 28 are given as Eqs. 29 and 30.

$$\boldsymbol{A}=\frac{R(\alpha C_{20}-C_{10})+\beta}{p\left[\left\{1-\frac{D_1}{D_2}\left(\frac{\alpha}{1+Rq_2}\right)\right\}\sinh(Rq_1)+\frac{D_1}{D_2}\left(\frac{\alpha Rq_1}{1+Rq_2}\right)\cosh(Rq_1)\right]} \tag{29}$$

$$\boldsymbol{B}=\boldsymbol{A}\left(\frac{D_1}{D_2}\right)\left\{\frac{Rq_1\cosh(Rq_1)-\sinh(Rq_1)}{(1+Rq_2)[\sinh(Rq_2)-\cosh(Rq_2)]}\right\} \tag{30}$$

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4) S. W. Benson, *J. Chem. Phys.*, **15**, 367 (1947).

5) *Int. Crit. Table*, **6**, p. 72.

6) J. D. Morrison, *J. Chem. Phys.*, **19**, 1305 (1951).

7) D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.*, **64**, 1588 (1942).

$$\boldsymbol{A}=\frac{2[(\alpha C_{20}-C_{10})R+\beta]}{pe^{Rq_1}\left[1-\alpha\left(\frac{D_1}{D_2}\right)\left(\frac{1-Rq_1}{1+Rq_2}\right)\right]\left[1-\left\{\frac{1-\alpha\left(\frac{D_1}{D_2}\right)\left(\frac{1+Rq_1}{1+Rq_2}\right)}{1-\alpha\left(\frac{D_1}{D_2}\right)\left(\frac{1-Rq_1}{1+Rq_2}\right)}\right\}e^{-2Rq_1}\right]} \tag{31}$$

$$\boldsymbol{A}\fallingdotseq\frac{2[(\alpha C_{20}-C_{10})R+\beta]}{pe^{Rq_1}[1-\alpha(D_1/D_2)(1-Rq_1)/(1-Rq_2)](1-e^{-2Rq_1})} \tag{32}$$

Converting Eq. 29 to an exponential function, we have Eq. 31.

If $0<Rq_1\ll 1$, we have Eq. 32.

Then, converted by the binomial theorem into a form in which the inversion is easy, we have:

$$\boldsymbol{A}\fallingdotseq 2\sum_{n=0}^{\infty}\left[K_1\left\{\frac{e^{-(2n+1)Rq_1}}{p}\right\}+K_2\left\{\frac{e^{-(2n+1)Rq_1}}{p(q_1+h)}\right\}\right] \tag{33}$$

$$\boldsymbol{B}\fallingdotseq K'_1\left[\frac{e^{Rq_2}}{p}-2\sum_{n=0}^{\infty}\frac{e^{-Rq_2\{2(n+1)(D_2/D_1)^{1/2}-1\}}}{p}\right]+K'_2\left\{\frac{e^{Rq_2}}{p(q_2+h')}\right\}+K'_3\sum_{n=0}^{\infty}\frac{e^{-Rq_2\{2(n+1)(D_2/D_1)^{1/2}-1\}}}{p(q_2+h')} \tag{34}$$

Even if Eq. 32 does not hold, Eqs. 33 and 34 are approximately true when the time, *t*, is sufficiently small.

Putting Eqs. 33 and 34 into Eqs. 27 and 28, and by inversion to the original functions,[8] we obtain Eqs. 10 and 11.

Appendix II

The time range, t_1-t_n, on the basis of which $\tilde{\beta}$ and $\Delta\beta$ were calculated, was determined to be as follows. As has been described above, Eqs. 3 and 4 do not hold in the "adsorption stage." Therefore, the authors took t_1 to be greater than the t_0 shown in Fig. 3. Equations 10, 11, 12, 13, and 15 are applicable, on the other hand, in a range where *t* is sufficiently small (see Apendix I). Precisely speaking, when the true exponential-type solution is composed of an infinite series, these equation hold only approximately in the range where the terms higher than the second of the true solution are negligible. The smaller the value of *t*, the better the approximation obtained generally in such an exponential-type solution. We assume that the terms higher than the second in the true solution and Eq. 17 become negligible at the same time, t_n, Therefore, the upper limit of t_n can be estimated from experimental values, specifying $\alpha=-0.01$, -0.10, -1.00, etc. S_1 and S_2 in Eq. 17 correspond to the terms higher than the second in the infinite series, and were neglected if their sum was less than 1% of the $\boldsymbol{F}(\alpha, t)$ in Eq. 17.

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[8] H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Clarendon Press, Oxford (1959).