

The Mass Transfer Rate through the Liquid-Liquid Interface. II. The Boundary Condition of the Diffusion Equation at the Interface

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When dealing with mass transfer through an interface which consists of either a gas phase and a liquid phase, or two liquid phases, it has been assumed that the concentration for the phase immediately next to the interface is in distribution-equilibrium with that for the other phase. However, this is only an assumption and no distinct theoretical or experimental verification has been given. Therefore, it may be equally probable *a priori* that the equilibrium relation does not hold in the process. In order to verify that the equilibrium relation does exist in the process, it is insufficient to indicate only that the experimental values are in accord with the theoretical values calculated on the basis of this equilibrium; it is also necessary to indicate that the experimental values are not in accord with the theoretical values calculated on the non-

equilibrium basis. In other words, when the difference between the experimental and the theoretical values calculated on the basis of this equilibrium is smaller than the experimental error, the experimental values are apparently in accord with the theoretical values, even if the true equilibrium relation does not exist in these concentrations, as has also been described by Ward and Brooks.¹⁾

The authors have previously studied a mass transfer through liquid-liquid interface; the results have been described in the preceding paper. In that study the transfer rate of *n*-butyric acid through the water-carbon tetrachloride or the water-benzene interface, both concentrations of *n*-butyric acid immediately next to the respective interfaces, and the

1) A. F. H. Ward and L. H. Brooks, *Trans. Faraday Soc.*, **48**, 1124 (1952).

amounts of adsorption at the respective interfaces were determined under particular conditions; the results of analysis indicate that Nernst's law of distribution, which exists as a rule in equilibrium systems, does not hold in the mass-transfer process between these concentrations immediately next to the interface. This paper will deal with the experimental data as has been described in the first paper, but in the method of analysis these papers differ from each other. This paper will also deal with Fick's differential equation of diffusion.

Some authors have reported mass transfer through liquid-liquid interfaces with Fick's equation of diffusion.¹⁻⁸⁾ Crank gave the solution of the one-dimensional semi-infinite composite medium with no interfacial resistance.⁹⁾ Scott, Tung, and Drickamer gave a solution of a finite composite medium with finite interfacial resistance phenomenologically in terms of an interfacial transfer coefficient.³⁾ Auer and Murbach gave some solutions with or without interfacial resistance by means of a three-region model.⁵⁾ It seems to us, the present authors, that the boundary and initial conditions have been decided rather conventionally. The properties of the interface have been studied, however, by Gibbs, Langmuir, and others theoretically or experimentally.^{10,11)} Consequently, the present authors are now concentrating on the interfacial phase, so that a reasonable boundary condition can be derived.

Theoretical

The nature of a surface, or an interface in general, is very different from a bulk phase, because the state of the aggregation of molecules is converted discontinuously at the interface. Adsorption and desorption, accordingly, are characteristic of the interface. Therefore, in treating a process of mass transfer through an interface, it is rational to distinguish the interfacial phase, in which adsorption and desorption govern mass transfer, from the bulk

phases, in which Fick's law of diffusion governs mass transfer.

A model of the neighborhood of the interface is shown in Fig. 1. The positions of the two boundaries of the interfacial phase are appointed on the distance axis as minus-zero and plus-zero, where the activities of the solute in the bulk phase are a_{1i} and a_{2i} respectively; the relation between the two activities, namely, the boundary condition for Fick's law of diffusion at the zero-position, will be derived, so that we can solve the equation of diffusion in the usual manner. The distance between $x = -0$ and $x = +0$, where x is the distance from the interface, has a finite value, about 16 \AA , according to our experimental results, as has been indicated in the first paper, but this is to be regarded as zero compared with the thickness of the bulk phase.

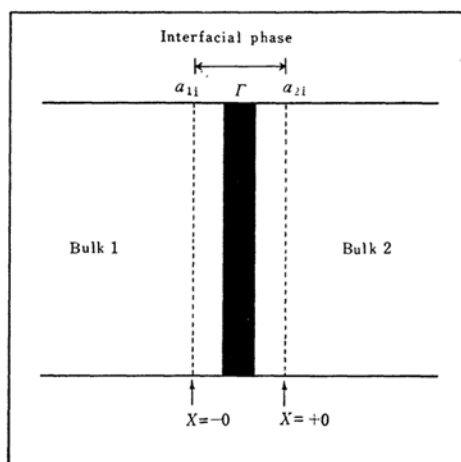


Fig. 1. A model of the neighborhood of the liquid-liquid interface.

Adsorption rate equations, taking the effect of interaction among adsorbed molecules into account,¹²⁾ are represented as:

$$\left. \begin{aligned} d\Gamma_1/dt &= k_{a1}a_{1i}(1-\theta)e^{x_1\theta} - k_{d1}\theta e^{-y_1\theta} \\ d\Gamma_2/dt &= k_{a2}a_{2i}(1-\theta)e^{x_2\theta} - k_{d2}\theta e^{-y_2\theta} \end{aligned} \right\} \quad (1)$$

where Γ_1 and Γ_2 are the net amounts of the solute adsorbed by the interface per unit of area from bulks 1 and 2 respectively; t is the time; k_{a1} and k_{a2} are the rate constants of the adsorption to the interface from bulks 1 and 2 respectively; k_{d1} and k_{d2} are the rate constants of the desorption from the interface into bulks 1 and 2 respectively; a_{1i} and a_{2i} are the activities of the solute in bulks 1 and

2) J. T. Davies, *J. Phys. and Colloid. Chem.*, **54**, 185 (1950).

3) E. J. Scott, L. H. Tung and H. G. Drickamer, *J. Chem. Phys.*, **19**, 1075 (1951).

4) L. H. Tung and H. G. Drickamer, *ibid.*, **20**, 6, 10 (1952).

5) P. L. Auer and E. W. Murbach, *ibid.*, **22**, 1054 (1954).

6) J. H. Sinfelt and H. G. Drickamer, *ibid.*, **23**, 1095 (1955).

7) J. T. Davies and J. B. Wiggill, *Proc. Roy. Soc.*, **A255**, 277 (1960).

8) J. A. Quinn and P. G. Jeannin, *Chem. Eng. Sci.*, **15**, 243 (1961).

9) J. Crank, "The Mathematics of Diffusion," Oxford University Press, London (1956).

10) J. W. Gibbs, *Scientific Papers*, **1**, 219 (1878).

11) I. Langmuir, *Z. physik. Chem.*, **64**, 385 (1908).

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

2 respectively immediately next to the interface; θ is the fraction of area covered by adsorbed molecules, and x_1, y_1, x_2 , and y_2 are constants representing the effect of interaction among adsorbed molecules.

It is assumed that the amount of adsorption, Γ , is constant with the lapse of time, as

$$d\Gamma/dt = d\Gamma_1/dt + d\Gamma_2/dt = 0 \quad (2)$$

From Eqs. 1 and 2,

$$a_{2i} = \alpha a_{1i} + \beta \quad (3)$$

$$\alpha \equiv -\left(\frac{k_{a1}}{k_{a2}}\right)e^{(x_1 - x_2)\theta}$$

$$\beta \equiv \left(\frac{k_{d1}e^{-y_1\theta} + k_{d2}e^{-y_2\theta}}{k_{a2}e^{x_2\theta}}\right)\frac{\theta}{1-\theta}$$

where k_{a1}, k_{d1}, k_{a2} and k_{d2} are positive constants determined by the material system and the temperature, and θ is a positive constant less than unity due to the definition and the assumption; consequently, in the rate process α is always a negative constant and β is always a positive constant.

When a distribution-equilibrium is attained, the net amount of solute adsorbed by the interface from each bulk becomes constant:

$$d\Gamma_1/dt = k_{a1}a_{1i}(1-\theta)e^{x_1\theta} - k_{d1}\theta e^{-y_1\theta} = 0$$

$$\therefore \theta/(1-\theta) = k_{a1}e^{x_1\theta}a_{1i}/k_{d1}e^{-y_1\theta} \quad (4)$$

From Eqs. 3 and 4 the distribution coefficient, K , is derived, since $x_1 + y_1 = x_2 + y_2 = sV/RT$:¹²⁾

$$\frac{a_{2i}}{a_{1i}} = \left(\frac{k_{a1}}{k_{d1}}\right)e^{(x_1 + y_1)\theta} \left/\left(\frac{k_{a2}}{k_{d2}}\right)e^{(x_2 + y_2)\theta}\right.$$

$$= \frac{k_{a1}/k_{d1}}{k_{a2}/k_{d2}} = K$$

where s is the coordination number of adsorbed molecules in the saturated state; V is the free energy of attractive interaction between two adjacent adsorbed molecules; R is the gas constant, and T is the absolute temperature.

When α and β are defined as only unfixed constants, it becomes possible for the boundary condition derived in the rate process, $a_{2i} = \alpha a_{1i} + \beta$, to represent also the relation in the distribution-equilibrium, for the equilibrium relation is represented by specifying $\alpha = K$, and $\beta = 0$. Consequently, it is possible to distinguish whether or not the equilibrium relation holds between a_{1i} and a_{2i} in the rate process, because α should have a negative and β , a positive finite value in the case of non-equilibrium on the one hand, and on the other hand, α should be positive, equal to the distribution coefficient, and β , zero in the case of equilibrium.

As has been described in the first paper, the condition $\theta = \text{const.}$ does not necessarily hold

in the initial state of the real process, but it can be assumed that this condition holds even in the initial state of the so-termed "ideal process" obtained by extrapolating the part of the real process where this condition actually holds. The analytical results in the preceding paper, which have been obtained on the basis of this assumption, have not indicated any serious conflict. Consequently, as far as we take the boundary condition to be $a_{2i} = \alpha a_{1i} + \beta$, derived by assuming $\theta = \text{const.}$, the "ideal process" should be studied. The concept of the "ideal process" has been described in detail in the first paper.

Now let us solve the differential equations of diffusion with a suitable initial condition and with the boundary condition obtained for the semi-infinite composite medium in one-dimensional diffusion.

Fick's second law of diffusion is represented by:

$$\left. \begin{aligned} \frac{\partial c_1}{\partial t} &= D_1 \frac{\partial^2 c_1}{\partial x^2}, & x < 0 \\ \frac{\partial c_2}{\partial t} &= D_2 \frac{\partial^2 c_2}{\partial x^2}, & x > 0 \end{aligned} \right\} \quad (5)$$

where c_1 and c_2 are the concentrations of the solute in bulks 1 and 2 respectively, while D_1 and D_2 are the diffusion coefficients in bulks 1 and 2 respectively.

The initial conditions are, as will be described later, assumed to be:

$$\left. \begin{aligned} c_1 &= c_{10}, & x < 0, & t = 0 \\ c_2 &= \xi e^{-\eta x}, & x > 0, & t = 0 \end{aligned} \right\} \quad (6)$$

where c_{10} is the initial value of c_1 , and ξ and η are constants independent of x .

The boundary conditions are given by:

$$\left. \begin{aligned} c_2 &= \alpha c_1 + \beta, & x = 0 \\ D_1 \frac{\partial c_1}{\partial x} &= D_2 \frac{\partial c_2}{\partial x}, & x = 0 \end{aligned} \right\} \quad (7)$$

where α and β are defined as unfixed constants independent of time; the second equation represents the mass balance between the positions for the two sides immediately next to the interface, involving that the amount of adsorption is constant.

As the solution of Eqs. 5, 6, and 7, we have

$$c_1 = c_{10} - \left[\frac{\alpha c_{10} + \beta}{\alpha + (D_1/D_2)^{1/2}} \right] \text{erfc} \left\{ \frac{|x|}{2(D_1 t)^{1/2}} \right\}$$

$$+ \left[\frac{\xi}{\alpha + (D_1/D_2)^{1/2}} \right] \exp \left\{ \eta (D_2/D_1)^{1/2} |x| \right.$$

$$\left. + D_2 \eta^2 t \right\} \text{erfc} \left\{ \frac{|x|}{2(D_1 t)^{1/2}} + \eta (D_2 t)^{1/2} \right\}$$

$$\begin{aligned}
c_2 = & \left[\frac{(D_1/D_2)^{1/2}(\alpha c_{10} + \beta)}{\alpha + (D_1/D_2)^{1/2}} \right] \operatorname{erfc} \left\{ \frac{x}{2(D_2 t)^{1/2}} \right\} \\
& - \left(\frac{\xi}{2} \right) e^{D_2 \eta^2 t} \left\{ e^{-\eta x} \cdot \operatorname{erfc} \left[\frac{x}{2(D_2 t)^{1/2}} \right] \right. \\
& \left. - \eta (D_2 t)^{1/2} \right\} + e^{\eta x} \cdot \operatorname{erfc} \left[\frac{x}{2(D_2 t)^{1/2}} \right] \\
& + \eta (D_2 t)^{1/2} \left\{ \right\} + \xi \cdot \exp \left\{ D_2 \eta^2 t - \eta x \right\} \\
& + \left[\frac{\alpha \xi}{\alpha + (D_1/D_2)^{1/2}} \right] \exp \left\{ \eta x \right. \\
& \left. + D_2 \eta^2 t \right\} \operatorname{erfc} \left\{ \frac{x}{2(D_2 t)^{1/2}} + \eta (D_2 t)^{1/2} \right\} \quad (8)
\end{aligned}$$

If we assume that $\alpha = K$, $\beta = 0$, $\xi = 0$, and η = finite, we obtain:

$$\begin{aligned}
c_1 = & \frac{c_{10}}{1 + (K(D_2/D_1)^{1/2})} \left[1 + \right. \\
& \left. K(D_2/D_1)^{1/2} \operatorname{erfc} \left\{ \frac{|x|}{2(D_1 t)^{1/2}} \right\} \right] \\
c_2 = & \left[\frac{K c_{10}}{1 + K(D_2/D_1)^{1/2}} \right] \operatorname{erfc} \left\{ \frac{x}{2(D_2 t)^{1/2}} \right\}
\end{aligned}$$

which is identical with the solution by Crank.⁹⁾

The diffusion rate immediately next to the interface in bulk 1, r_{1i} , is given by:

$$\begin{aligned}
r_{1i} = & -D_1 \left(\frac{\partial c_1}{\partial x} \right)_{x=0} = (D_1/\pi t)^{1/2} [\alpha c_{10} + \beta - \xi \\
& + \xi \eta (\pi D_2 t)^{1/2} e^{D_2 \eta^2 t} \operatorname{erfc} \{ \eta (D_2 t)^{1/2} \}] / \\
& [\alpha + (D_1/D_2)^{1/2}]
\end{aligned}$$

or

$$\begin{aligned}
\alpha + F_1(t) \beta &= F_2(t) \quad (9) \\
F_1(t) &\equiv 1/[c_{10} - r_{1i}(\pi t/D_1)^{1/2}] \\
F_2(t) &\equiv \{ r_{1i}(\pi t/D_2)^{1/2} + \xi [1 - \eta (\pi D_2 t)^{1/2}] \cdot \\
& e^{D_2 \eta^2 t} \operatorname{erfc} \{ \eta (D_2 t)^{1/2} \} \} F_1(t)
\end{aligned}$$

Consequently, it becomes possible to give α and β numerically from D_1 , D_2 , c_{10} , ξ , η , and $r_{1i}(t)$ by means of Eq. 9.

Results and Discussion

The experimental procedures and the basis of analysis have been described in the first paper. Examples of time dependences of the transfer rate through the interface for *n*-butyric acid from aqueous solutions to carbon tetrachloride layers are shown in Figs. 2a and 2b. The inversion on the early stages in Figs. 2a and 2b is interpreted in terms of a disturbance effect, as has been described in the first paper, resulting from the injection of carbon tetrachloride beneath the aqueous layers of an *n*-butyric acid solution, provided that the initial values are given by extrapola-

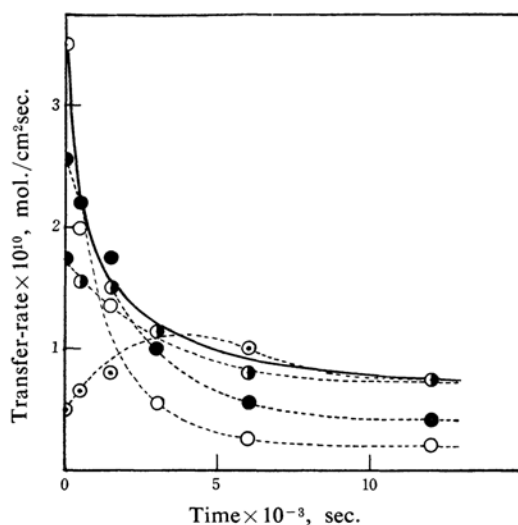


Fig. 2a. Time dependences of the apparent transfer-rate of *n*-butyric acid from the aqueous phase ($c_{10}=0.0115$ N) to the carbon tetrachloride phase in natural, one-dimensional diffusion at 30°C.

Layer-thickness: ○, 0.78 cm.; ●, 1.56 cm.; ○●, 2.34 cm.; ●●, 3.12 cm.

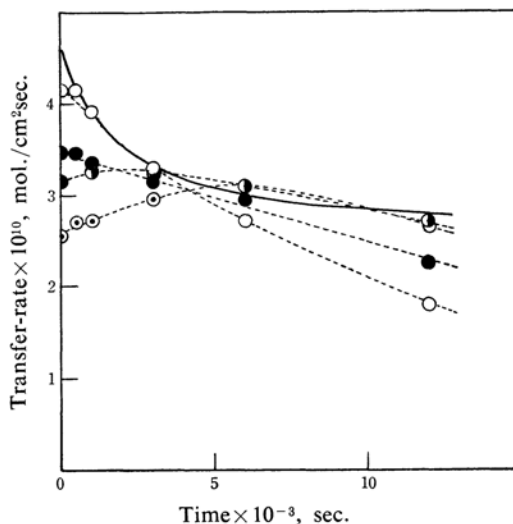


Fig. 2b. Time dependences of the apparent transfer-rate of *n*-butyric acid from the aqueous phase ($c_{10}=0.566$ N) to the carbon tetrachloride phase in natural, one-dimensional diffusion at 30°C.

Layer-thickness: ○, 0.78 cm.; ●, 1.56 cm.; ○●, 2.34 cm.; ●●, 3.12 cm.

tion. Because the two curves representing the time dependences of the transfer rate in 2.34 and 3.12 cm. layer-thicknesses coincide approximately except for the part indicating the inversion by disturbance, they are taken to approximate the case of an infinite layer-thickness. Therefore, the full curve of the

envelope in the group of dotted lines is regarded as indicating the case of a semi-infinite composite medium, including no disturbance effect of injection, provided that the initial transfer rates (in the "ideal processes") are obtained by the way described in the first paper.

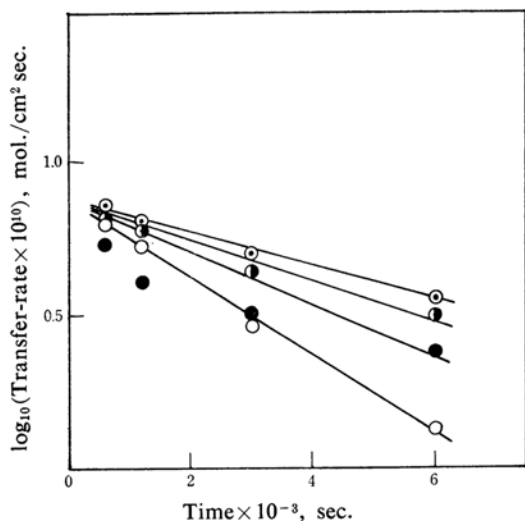


Fig. 3a. Time dependences of the apparent transfer-rate of *n*-butyric acid from the aqueous phase ($c_{10}=0.0216$ N) to the benzene phase in natural, one-dimensional diffusion at 30°C .

Layer-thickness: \circ , 0.78 cm.; \bullet , 1.56 cm.; \circ , 2.34 cm.; \odot , 3.12 cm.

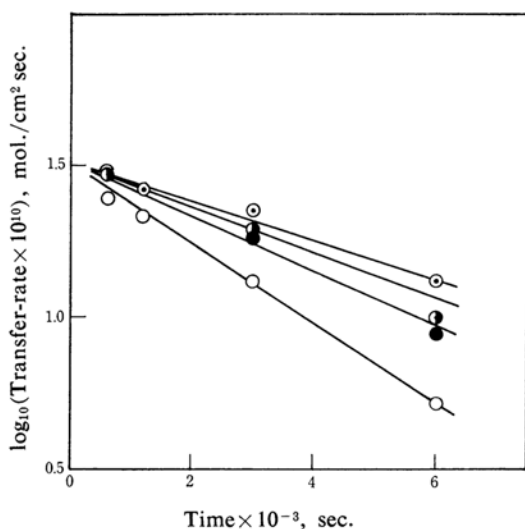


Fig. 3b. Time dependences of the apparent transfer-rate of *n*-butyric acid from the aqueous phase ($c_{10}=0.0503$ N) to the benzene phase in natural, one-dimensional diffusion at 30°C .

Layer-thickness: \circ , 0.78 cm.; \bullet , 1.56 cm.; \circ , 2.34 cm.; \odot , 3.12 cm.

Examples of the time dependences of the apparent transfer rate through the interface for *n*-butyric acid from aqueous solutions to benzene layers are shown in Figs. 3a and 3b. Unlike the case of carbon tetrachloride, Figs.

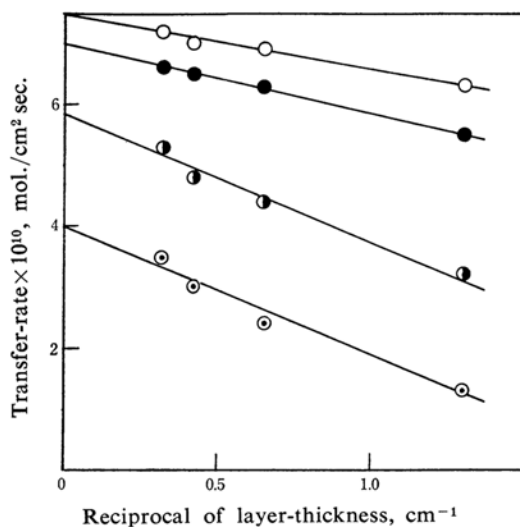


Fig. 4a. Relations between the corrected transfer-rates of *n*-butyric acid and the reciprocals of layer-thickness with the time as a parameter.

System: 0.0216 N aqueous soln. of *n*-butyric acid and benzene (30°C)

Time: \circ , 0.60×10^3 sec.; \bullet , 1.20×10^3 sec.; \circ , 3.00×10^3 sec.; \odot , 6.00×10^3 sec.

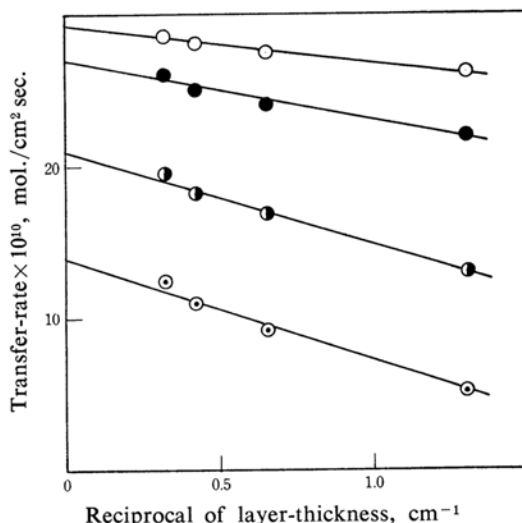


Fig. 4b. Relations between the corrected transfer-rates of *n*-butyric acid and the reciprocals of layer-thickness with the time as a parameter.

System: 0.0503 N aqueous soln. of *n*-butyric acid and benzene (30°C)

Time: \circ , 0.60×10^3 sec.; \bullet , 1.20×10^3 sec.; \circ , 3.00×10^3 sec.; \odot , 6.00×10^3 sec.

3a and 3b show no appreciable inversion in the time dependences of the transfer rate, indicating that the disturbance effect is negligible in this case. This agrees with the interpretation of the disturbance effect in this system described in the first paper. Figures 4a and 4b show examples of the relations between the transfer rates and the reciprocals of layer-thickness; the rates extrapolated to zero of the reciprocal of layer-thickness are regarded as indicating one in a semi-infinite composite medium.

The diffusion coefficients of *n*-butyric acid were estimated from the data in the literature.^{1,13)} They are shown in Table I.

TABLE I. DIFFUSION COEFFICIENTS OF *n*-BUTYRIC ACID AT 30°C

Solvent	Diffusion coefficient $\times 10^5$, cm ² /sec.
Water	1.21
Carbon tetrachloride	1.60
Benzene	1.71

The initial distributions of concentration in the "ideal process" required in order to obtain ξ and η in Eq. 9 were estimated as follows. The time dependences of the amount of solute transferred through the interface in the "ideal process" were obtained from the apparent dependences, correcting the parts deviated by the disturbance, which were easily distinguished in Figs. 2a and 2b, by graphical integration on the curve of the time dependence of transfer rate in the "ideal process," shown as the full curves in these figures. The layer-thickness dependence of the initial amount of solute transferred in the "ideal process," as defined

in the first paper, was obtained from this. The initial distributions of the concentration in an organic solvent in the "ideal process" were finally given from the layer-thickness dependences by graphical differentiation of the initial amount of solute transferred in the "ideal process," assuming that the initial state of the "ideal process" is independent of the layer-thickness. These are approximately represented by the second equation of Eq. 6 in the cases of both carbon tetrachloride and benzene.

The initial condition in the real process is undoubtedly represented as $c_1=c_{10}$, $x<0$ and $t=0$, and $c_2=0$, $x>0$ and $t=0$ instead of Eq. 6. However, the amount of adsorption increases relatively quickly in the early stages after these two bulks are brought into contact with each other if the solute is surface-active; then the boundary condition of Eq. 7 becomes unsuitable, because Eq. 7 holds only when $\theta = \text{const.}$ Consequently, if the solute is surface-active and the second equation of Eq. 7 is adopted, the initial condition in the real process, mentioned above, should not be adopted.

The initial distributions of the concentration in the aqueous phase in the "ideal process" could also be obtained in the same way, but the concentrations were estimated to be constant throughout the layer, because the deviation from the values before contact was kept relatively small, even near the interface, for the sake of simplification. This is considered to be the reason why the disturbance effect was negligible in the case of benzene, since the benzene layer was little disturbed, in this case, by the injection of an aqueous solution beneath the benzene layer at the

TABLE II. CONSTANTS SPECIFYING THE INITIAL DISTRIBUTIONS OF CONCENTRATION AND THE TRANSFER RATES AS A FUNCTION OF TIME (30°C)

A) Aqueous solution of *n*-butyric acid - carbon tetrachloride

$c_{10} \times 10^5$ g. mol./cm ³	$\xi \times 10^6$ g. mol./cm ³	η cm ⁻¹	$r_{11} \times 10^{10}$		g. mol./cm ² sec.	
			$t=20$ min.	$t=1$ hr.	$t=3$ hr.	$t=5$ hr.
1.14	0.19 \pm 0.13*	1.27 \pm 0.14*	1.95	1.16	0.85	0.72
5.66	3.10 \pm 0.19*	0.74 \pm 0.23*	4.12	3.35	2.75	2.28

B) Aqueous solution of *n*-butyric acid - benzene

$c_{10} \times 10^5$ g. mol./cm ³	$\xi \times 10^6$ g. mol./cm ³	η cm ⁻¹	$r_{11} \times 10^{10}$		g. mol./cm ² sec.	
			$t=10$ min.	$t=20$ min.	$t=50$ min.	$t=100$ min.
1.00	1.22 \pm 0.11*	1.07 \pm 0.11*	4.30	4.04	3.19	2.01
2.16	1.22 \pm 0.08*	1.07 \pm 0.08*	7.50	7.04	5.85	4.06
5.03	4.30 \pm 0.13*	1.07 \pm 0.13*	29.30	27.00	21.20	14.00
10.38	12.20 \pm 0.36*	1.07 \pm 0.36*	30.00	29.60	27.70	23.50

* Estimated standard error

13) C. R. Wilke, *Chem. Eng. Progress*, 45, 218 (1949).

beginning (actually the benzene layer must be more or less disturbed by the so-called "Marangoni effect,"^{1,7,14-17}) though this effect might be small compared with the disturbance effect of the injection), whereas the aqueous layer was disturbed very much.

The constants specifying the initial distribution of concentration and the transfer rate in the "ideal process" as a function of time are shown in Table II, while the values of α and β calculated statistically by the method of least squares from the data in Tables I and II by Eq. 9 are shown in Table III.

TABLE III. VALUES OF α AND β CALCULATED FROM THE EXPERIMENTAL DATA (30°C)

Org. solvent	$c_{10} \times 10^5$ g. mol./cm ³	α —	$\beta \times 10^5$ g. mol./cm ³
CCl ₄	1.14	-0.807 ± 0.020*	0.964 ± 0.014*
CCl ₄	5.66	-0.708 ± 0.042*	4.384 ± 0.183*
C ₆ H ₆	1.00	-0.940 ± 0.080*	0.899 ± 0.015*
C ₆ H ₆	2.16	-0.775 ± 0.029*	1.836 ± 0.022*
C ₆ H ₆	5.03	-0.799 ± 0.004*	4.504 ± 0.001*
C ₆ H ₆	10.38	-0.764 ± 0.008*	9.229 ± 0.019*

* Estimated standard error

Fairly large errors are estimated in some cases of ξ and η parameters of the initial distribution of the concentration in the "ideal process." However, the contribution of such errors in both ξ and η to that in α and β factors specifying the boundary condition is not very serious. For example, the estimated contributions of the errors in the case of a $c_{10} = 1.14 \times 10^{-5}$ g. mol./cm³ aqueous solution of *n*-butyric acid and carbon tetrachloride, are $\alpha \pm 0.073$ and $\beta \pm 0.053 \times 10^{-5}$ g. mol./cm³ (about 9 and 5% α and β respectively, against 69 and 11% ξ and η respectively).

Moreover, $\alpha < 0$ and $\beta > 0$ do not come from adopting the initial condition of the "ideal process," since the results of adopting that of the real process, $c_1 = c_{10}$ ($x < 0$, $t = 0$) and $c_2 = 0$ ($x > 0$, $t = 0$), are, for example, $\alpha = -0.84$ and $\beta = 0.97 \times 10^{-5}$ g. mol./cm³ and $\alpha = -0.78$ and $\beta = 4.51 \times 10^{-5}$ g. mol./cm³ in $c_{10} = 1.14$ and 5.66×10^{-5} g. mol./cm³ aqueous solutions of *n*-butyric acid and carbon tetrachloride respectively.

Table IV shows what the values of α and β in Eq. 9 should be when Nernst's law of distribution holds in the two concentrations immediately next to the interface. In order to obtain the theoretical values of α and β in Eq. 3 when Nernst's law does not exist

generally, it is assumed for the sake of simplification that $k_{a1} = k_{a2}$, $k_{d1} = k_{d2}$, $x_1 = x_2$ and $y_1 = y_2$; then Eq. 3 becomes

$$\alpha = -(k_{a1}/k_{a2})e^{(x_1-x_2)\theta} = -1$$

$$\beta = [(k_{d1}e^{-y_1\theta} + k_{d2}e^{-y_2\theta})/k_{a2}e^{x_2\theta}]\theta/(1-\theta)$$

$$= 2(k_{d2}/k_{a2})e^{-sV\theta/RT} \cdot \theta/(1-\theta) \quad (10)$$

Approximate values of α and β obtained by Eq. 10 from the data in the first paper are shown in Table V. It may be clearly seen by comparing Tables III, IV and V with one another that Nernst's law of distribution does not hold in these two concentrations immediately next to the interface in the mass-transfer process for our experimental series.

TABLE IV. VALUES OF α AND β IN CASE NERNST'S LAW HOLDS (30°C)

Org. solvent	α	β
CCl ₄	0.087	0
C ₆ H ₆	0.309	0

TABLE V. APPROXIMATE VALUES OF α AND β BY EQ. 10 (30°C)

Org. solvent	$c_{10} \times 10^5$ g. mol./cm ³	α —	$\beta \times 10^5$ g. mol./cm ³
CCl ₄	1.14	-1	0.24
CCl ₄	5.66	-1	3.60
C ₆ H ₆	1.00	-1	0.61
C ₆ H ₆	2.16	-1	1.29
C ₆ H ₆	5.03	-1	2.82
C ₆ H ₆	10.38	-1	3.70

The convection effect resulting from the dependence of the local density on the concentration is, in general, considered to increase the diffusion coefficients obviously. The experiments, however, were made with samples as dilute as possible for the sake of analysis (0.01–0.10 N), so that this effect might be negligible. No such convection effect should take place in the system of an aqueous solution of *n*-butyric acid and benzene, considering the variation in density with the concentration. In the case of carbon tetrachloride, however, a little such effect should take place in the aqueous phase. This may be negligible, though, because the convection in the aqueous phase should have little effect on the mass-transfer through the interface, as has been indicated above in discussing the disturbance effect.

Besides the convection arising from the difference in local density, a spontaneous interfacial turbulence resulting from the Marangoni effect, referred to above, must more or less affect the mass transfer. However, the evaluation of this effect is considered to be difficult.

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