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Kinetics of the Transfer of Picrate Ion at the Water/Nitrobenzene Interface

Toshiyuki Osakai, Tadaaki Kakutani, and Mitsugi Senda*
Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University,
Sakyo-ku, Kyoto 606

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Kinetics of the transfer of picrate (Pic^-) ion at the interface between an aqueous solution of lithium chloride (LiCl) and a nitrobenzene solution of tetrabutylammonium tetraphenylborate (TBATPB) has been studied by phase-selective a.c. polarography with a two-electrode cell system. By assuming Butler-Volmer type equations for the rate constants, the kinetic parameters of the Pic^--ion transfer have been determined at various concentrations of LiCl (0.02—1.0 mol dm^{-3}) and TBATPB (0.05—0.17 mol dm^{-3}). The rate constants virtually do not change with the electrolyte concentrations. Frumkin correction for the double-layer effect of the rate constants has been examined. The result seems to indicate that the observed potential dependence of the rate constants obtained in moderately concentrated electrolyte solutions may reflect the real potential dependence of the rate constants.

In a previous paper[1)] we have shown that the phase-selective a.c. polarographic method is useful for accurate measurement of the rate of ion (tetramethylammonium ion) transfer at the interface between two immiscible electrolyte solutions (water/nitrobenzene interface). In this study, we have applied this technique to determine the rate constants of the transfer of picrate (Pic^-) ion at the interface between an aqueous solution of lithium chloride (LiCl) and a nitrobenzene solution of tetrabutylammonium tetraphenylborate (TBATPB).

Dependence of the rate constants of ion transfer on the potential difference across the interface between two immiscible electrolyte solutions has been a subject of theoretical[2,3)] and experimental[4—7)] studies; with tetraalkylammonium ions at water/nitrobenzene[4)] and water/1,2-dichloroethane[5)] interfaces, and with cesium ion[6)] and choline and acetylcholine ions[7)] at the water/nitrobenzene interface. According to Samec *et al.*,[6,7)] the observed potential dependence of the rate constants for the transfer of cesium, choline, and acetylcholine ions arises largely from the effect of the potential on the concentration of the transferred ions at the reaction planes, which are supposed to be located at the outer Helmholtz planes (OHP's) on each side of the interface. In this study we have determined the rate constants of the Pic^--ion transfer at the interface between aqueous and nitrobenzene solutions containing various concentrations of LiCl (0.02—1.0 mol dm^{-3}) and TBATPB (0.05—0.17 mol dm^{-3}), respectively. The observed rate constants were corrected for the double-layer effect (so called Frumkin correction) using the capacity data and the Gouy-Chapman theory. The results indicate that the formalism of Frumkin correction with the reaction planes being located at the OHP's to obtain the "true" rate constants is probably not valid for the Pic^--ion transfer across the water/nitrobenzene interface.

Experimental

The electrochemical cell employed in this study is represented by

$$\begin{array}{c|c|c|c|}
 & & \text{I} & \text{II} \\
\text{Ag} & \text{AgCl} & \begin{array}{c}0.1\ \text{mol dm}^{-3}\\ \text{TBACl}\\ \text{(W)}\end{array} & \begin{array}{c}x\ \text{mol dm}^{-3}\\ \text{TBATPB}\\ \text{(N)}\end{array}
\end{array}$$

$$\begin{array}{c|c|cc}
\text{III} & & & \\
\begin{array}{c}y\ \text{mol dm}^{-3}\ \text{LiCl}\\ c\ \text{mol dm}^{-3}\ \text{LiPic}\\ \text{(W)}\end{array} & \text{AgCl} & \text{Ag,} & \text{(A)}
\end{array}$$

where (W) and (N) stand for the aqueous and the nitrobenzene phases, respectively. The interface between phases II and III is the test interface at which the Pic^--ion transfer takes place. The left-hand reference electrode Ag/AgCl/0.1 mol dm^{-3} TBACl(W) was connected to the nitrobenzene phase (II) through sintered glass.[1)] The potential drop across the interface between phases I and II is determined by the distribution potential of TBA^+ ion in the two phases.[8,9)] In electrochemical measurements, a two-electrode cell system[1)] was used. The solution resistance between the two reference electrodes, R_u, was measured with a laboratory-made linear bridge[1)] with a 10 kHz a.c. generator and the ohmic drop due to R_u was compensated for by positive feedback.[1)] The observed values of R_u were in the range between 0.96 and 3.27 kΩ. The details of electrochemical measurements have been described elsewhere.[1)] The electrolytic cell was thermostated at 25±0.1 °C.

Lithium picrate (LiPic) was prepared by the reported method.[10)] The other chemicals and the preparation of electrolyte solutions have been described elsewhere.[1)]

Results

In the following, the potential E applied to Cell A is defined by the potential of the right-hand reference electrode, E_{right}, referred to the potential of the left-hand reference electrode, E_{left}, that is, $E=E_{\mathrm{right}}-E_{\mathrm{left}}$. The flow of the positive charge from the aqueous to the nitrobenzene phase is taken as the positive current.

Cyclic Voltammetry. Cyclic voltammograms for the Pic$^-$-ion transfer at the interface between aqueous solution of LiCl and nitrobenzene solution of TBATPB at various concentrations of the electrolytes as listed in Tables 1—3 were recorded at the voltage scan rate of 5 mV s^{-1}. At all concentrations used, well-defined reversible cyclic voltammograms were obtained at the scan rate of 5 mV s^{-1} (Fig. 1). The peak separation was 63±2 mV being close to the theoretical value of 60 mV for the reversible cyclic voltammogram. The midpoint potential, E_{mid}, which is considered to be equal to the reversible half-wave potential, agreed with the summit potential, E_s, of the admittance curves in a.c. polarography (see Figs. 2 and 3 and Tables 1—3) within the experimental errors (±4 mV). Figure 2 shows the dependence of E_{mid} and E_s on the logarithm of the mean activity of LiCl, $a_{\mathrm{LiCl}}^{\pm,\mathrm{W}}$, in the aqueous solution (phase III in Cell A). The experimental points in Fig. 2 lie on a straight line with the slope of −58 mV which is close to $-2.30RT/F=-59$ mV at 25 °C. Similarly, the change of E_{mid} and E_s with the change of TBATPB concentration was close to −59 mV per decade (Table 3). These results indicate that the ion-pair formation of Pic$^-$-ion with Li$^+$ and TBA$^+$ ions is negligibly small in the concentration range studied (see Discussion).

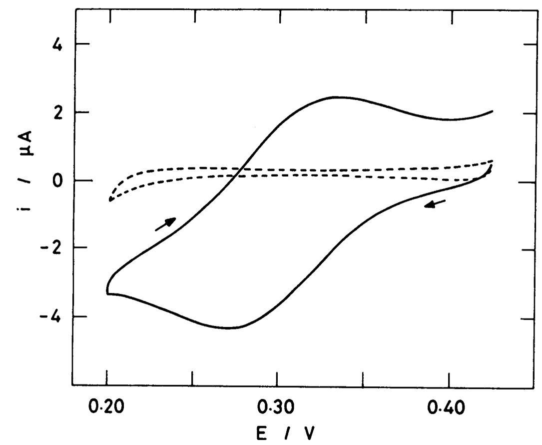

Fig. 1. A cyclic voltammogram for the transfer of 0.5 10^{-3} mol dm^{-3} Pic$^-$ ion from a 0.1 mol dm^{-3} LiCl aqueous solution to a 0.1 mol dm^{-3} TBATPB nitrobenzene solution at the voltage scan rate of 5 mV s^{-1}. Dashed line shows a cyclic voltammogram in the absence of Pic$^-$ ion.

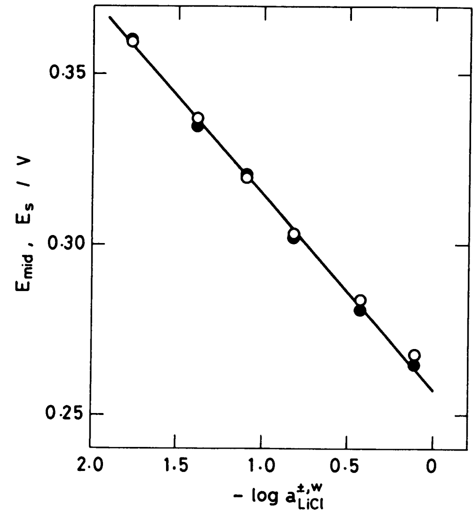

Fig. 2. Dependence of the midpoint potential (○) and the summit potential (●) on the logarithm of mean activity of LiCl in the aqueous phase when the concentration of TBATPB is 0.1 mol dm^{-3}. The slope of the straight line is −58 mV.

A.c. Polarography. In a.c. polarography, a small a.c. voltage (usually 5 mV peak to peak) was superimposed on the d.c. applied potential E_{dc} (usually at the scan rate of 5 mV s^{-1}), and the real (Y'_t) and the imaginary (Y''_t) components of the admittance, $Y_t=Y'_t+jY''_t (j=(-1)^{-1/2})$, of the test interface in Cell A were measured at seven frequencies from 10 to 100 Hz. Curves a in Fig. 3 show representative plots of Y'_t and Y''_t against E_{dc}. Also plotted in Fig. 3 (curves b) are the real (Y'_B) and the imaginary (Y''_B) components of the admittance of the base aqueous solution/base nitrobenzene solution interface, $Y_B=Y'_B+jY''_B$. Thus, the ion-transfer admittance, $Y_F=Y'_F+jY''_F$, is determined by subtraction of Y_B from Y_t[1]:

$$Y'_F = Y'_t - Y'_B, \tag{1}$$

$$Y''_F = Y''_t - Y''_B. \tag{2}$$

Y'_F and Y''_F are plotted against E_{dc} in Fig. 3 (curves c). The summit potentials of the Y'_F and Y''_F *vs.* E_{dc} curves coincided with each other and were virtually equal to the corresponding reversibe half-wave potentials obtained from cyclic voltammetry, irrespective of the frequency, the Pic$^-$-ion concentration, and the supporting-electrolyte concentrations. The summit potentials are summarized in Tables 1—3.

From the ion-transfer admittance, the ion-transfer impedance, Z_F, which is expressed by a series combination of resistance (r_s) and capacitance (c_s), *i.e.* $Z_F=r_s-j(1/\omega c_s)$, was calculated:

$$r_s = Y'_F/(Y'^2_F + Y''^2_F), \tag{3}$$

$$1/\omega c_s = Y''_F/(Y'^2_F + Y''^2_F), \tag{4}$$

where ω is the angular frequency of the a.c. signal

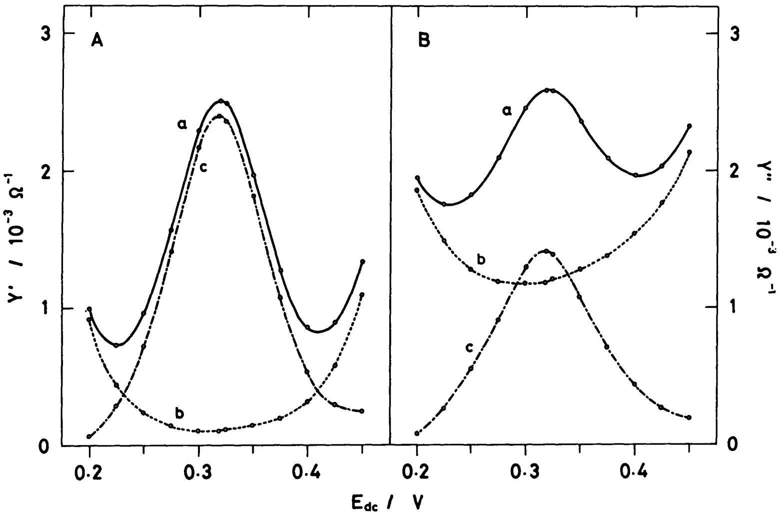

Fig. 3. Real (A) and imaginary (B) components of the admittance of the interface between a 0.1 mol dm^{-3} LiCl aqueous solution and a 0.1 mol dm^{-3} TBATPB nitrobenzene solution, at f=50 Hz, in the presence (a) and absence (b) of 0.5×10^{-3} mol dm^{-3} Pic$^-$ ion in the aqueous phase. Curve c shows the ion-transfer admittance, Y_F' and Y_F'', for the Pic$^-$ ion transfer corrected for the base admittance.

($\omega=2\pi f$, f being the frequency).

Determination of the Kinetic Parameters. For the sake of simplicity, we assume a linear kinetic equation:

$$I = I(E, C^{W}, C^{N}) = zFA[\vec{k}(E)C^{W}-\overleftarrow{k}(E)C^{N}], \tag{5}$$

for the ion-transfer current I, which is a function of the potential, E, and the surface concentrations of the transferred ion in the aqueous and nitrobenzene phases, C^{W} and C^{N}, respectively. Here, z is the ionic valence of the transferred ion ($z=-1$ for Pic$^-$ ion), F the Faraday constant, A the surface area of the interface, and $\vec{k}(E)$ and $\overleftarrow{k}(E)$ are the rate constants of ion transfer from the aqueous to the nitrobenzene phase and from the nitrobenzene to the aqueous phase, respectively, both being considered to be functions of the potential E. On the basis of the information obtained by cyclic voltammetry, we assume that the mass transfer of the ion is due to semi-infinite linear diffusion and that the ion-transfer reaction at the interface is d.c. reversible at the d.c. voltage scan rate of 5 mV s^{-1}, that is, the Nernst equation is valid for the mean surface concentrations or the d.c. components of the surface concentration of the transferred ion in both sides of the interface, $\bar{C}^{W}$ and $\bar{C}^{N}$:

$$E_{dc} = E^{\ominus} + (RT/zF)\ln(\bar{C}^{N}/\bar{C}^{W}), \tag{6}$$

where $E^{\ominus}$ is the standard ion-transfer potential (with respect to the reference electrodes in Cell A), R the gas constant, and T the absolute temperature. We also assume that the ion-pair formation of the transferred ion is negligibly small in both phases.

On the above assumptions, the ion-transfer impedance can be expressed, by analogy with the faradaic impedance theory of electrode reaction, by[1)]

$$r_s = (\sigma/\omega^{1/2})[1+(2\omega)^{1/2}\lambda^{-1}], \tag{7}$$

$$1/\omega c_s = \sigma/\omega^{1/2}, \tag{8}$$

with

$$\sigma = \frac{4RT\cosh^2(\xi/2)}{z^2F^2A(2D^{W})^{1/2}C^{W,o}}, \tag{9}$$

$$\lambda = \frac{\vec{k}}{(D^{W})^{1/2}} + \frac{\overleftarrow{k}}{(D^{N})^{1/2}}, \tag{10}$$

$$\xi = zF(E_{dc}-E^{r}_{1/2})/RT, \tag{11}$$

$$E^{r}_{1/2} = E^{\ominus} + (RT/zF)\ln(D^{W}/D^{N})^{1/2}, \tag{12}$$

where $\vec{k}$ and $\overleftarrow{k}$ are the ion-transfer rate constants defined by $\vec{k}=\vec{k}(E=E_{dc})$ and $\overleftarrow{k}=\overleftarrow{k}(E=E_{dc})$ (see Eq. 5), respectively, and D^{W} and D^{N} are the diffusion coefficients of the transferred ion in the aqueous and nitrobenzene phases, respectively; $C^{W,o}$ is the bulk concentration of the ion in the aqueous phase (the bulk concentration in the nitrobenzene phase is assumed to be zero). When the ion-transfer reaction is d.c. reversible, we have $k\bar{C}^{W}=k\bar{C}^{N}$ from Eq 5. Using Eqs. 6, 11, and 12, we then have $\vec{k}=(D^{W}/D^{N})^{1/2}\overleftarrow{k}\exp(\xi)$. Consequently, Eq. 10 can be rewritten as

$$\ln[\vec{k}/(D^{W})^{1/2}] = \ln[\lambda/(1+\exp(-\xi))], \tag{13}$$

or

$$\ln[\overleftarrow{k}/(D^{N})^{1/2}] = \ln[\lambda/(1+\exp(\xi))]. \tag{14}$$

Here λ can be obtained by Eqs. 7 and 8 as

$$\lambda = (2\omega)^{1/2}/(r_s c_s \omega - 1). \tag{15}$$

Thus these relationships enable us to determine the ion-transfer rate constants from the ion-transfer impedance.

We assume Butler-Volmer type equations for the potential dependence of the rate constants:

$$\overrightarrow{k} = k_s \exp[\overrightarrow{\alpha} zF(E_{dc} - E^{\ominus})/RT], \tag{16}$$

$$\overleftarrow{k} = k_s \exp[-\overleftarrow{\alpha} zF(E_{dc} - E^{\ominus})/RT], \tag{17}$$

where k_s is the standard rate constant, $\overrightarrow{\alpha}$ and $\overleftarrow{\alpha}$ ($\overrightarrow{\alpha} + \overleftarrow{\alpha} = 1$) are the transfer coefficients. Then, using Eqs. 10—12, Eqs. 13 and 14 can be rewritten as

$$\ln[\overrightarrow{k}/(D^{W})^{1/2}] = \ln \Lambda + \overrightarrow{\alpha}\xi, \tag{18}$$

$$\ln[\overleftarrow{k}/(D^{N})^{1/2}] = \ln \Lambda - \overleftarrow{\alpha}\xi, \tag{19}$$

with

$$\Lambda = k_s \left(\frac{1}{(D^{W})^{1/2}}\right)^{\overleftarrow{\alpha}} \left(\frac{1}{(D^{N})^{1/2}}\right)^{\overrightarrow{\alpha}}. \tag{20}$$

In Fig. 4, r_s and $1/\omega c_s$ at the summit potential are plotted against $\omega^{-1/2}$ for x=0.1 mol dm^{-3}, y=0.1 mol dm^{-3}, and c=0.5×10^{-3} mol dm^{-3} in Cell A. According to Eqs. 7 and 8, both plots gave straight lines with a common slope giving the diffusion coefficient of Pic$^-$ ion in the aqueous phase, D^{W}_{Pic}=8.8×10^{-6} cm^2 s^{-1} by Eqs. 9 and 11. For all compositions of the solution measured in this study (Tables 1—3) similar linear plots were obtained for the ion-transfer impedance in the d.c. potential range of $|E_{dc} - E_s| < 80$ mV. The D^{W}_{Pic} values obtained at various compositions of the solutions are summarized in Tables 1—3.

The potential dependence of the rate constants

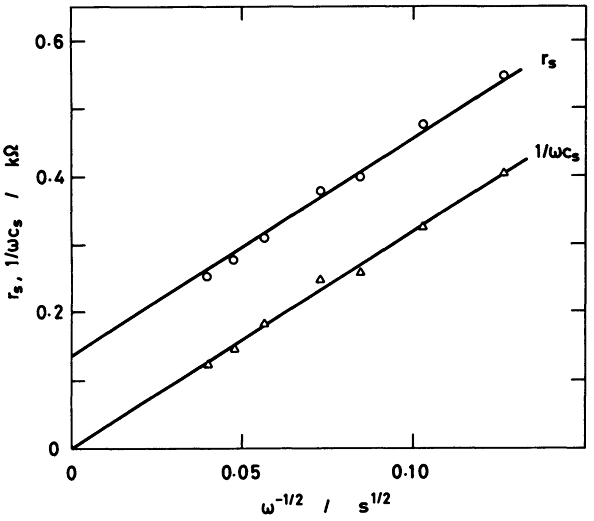

Fig. 4. Plot of the real (r_s) and imaginary ($1/\omega c_s$) components of ion-transfer impedance at the summit potential against $\omega^{-1/2}$ for the transfer of 0.5×10^{-3} Pic$^-$ ion at the interface between a 0.1 mol dm^{-3} LiCl aqueous solution and a 0.1 mol dm^{-3} TBATPB nitrobenzene solution.

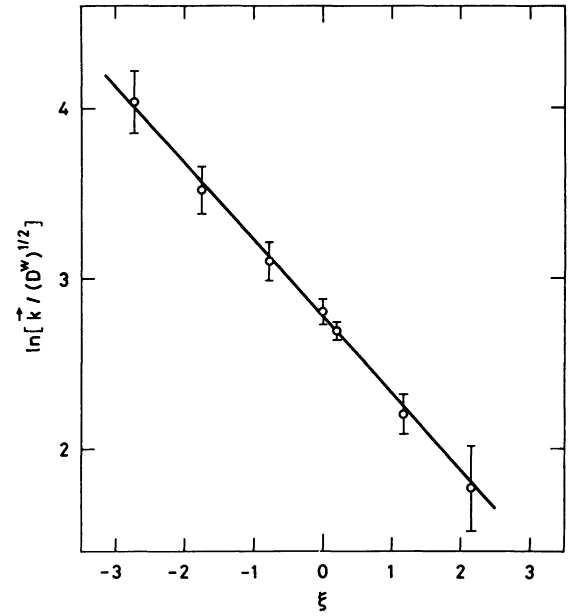

Fig. 5. Plot of $\ln[\overrightarrow{k}/(D^{W})^{1/2}]$ *vs.* $\xi(=zF(E_{dc} - E^{r}_{1/2})/RT)$ for the transfer of 0.5×10^{-3} mol dm^{-3} Pic$^-$ ion at the interface between a 0.1 mol dm^{-3} LiCl aqueous solution and a 0.1 mol dm^{-3} TBATPB nitrobenzene solution. Vertical bars indicate the standard deviations.

TABLE 1. KINETIC PARAMETERS OF Pic$^-$-ION TRANSFER AT THE INTERFACE BETWEEN A 0.1 mol dm^{-3} LiCl AQUEOUS SOLUTION AND A 0.1 mol dm^{-3} TBATPB NITROBENZENE SOLUTION, DETERMINED AT VARIOUS CONCENTRATIONS OF Pic$^-$ ION IN THE AQUEOUS PHASE

C^{W}_{Pic} / 10^{-3} mol dm^{-3}	E_s / mV	$\ln \Lambda$	k_s / 10^{-2} cm s^{-1}	$\overrightarrow{\alpha}$	D^{W}_{Pic} / 10^{-6} cm^2 s^{-1}
0.30	319	2.86±0.04	3.9	0.61±0.05	8.0
0.50	320	2.77±0.04	3.7	0.45±0.04	8.8
0.75	320	2.85±0.06	3.8	0.57±0.04	7.7
1.00	319	2.68±0.09	3.2	0.56±0.05	7.3
average	320	2.79±0.06	3.7±0.3	0.55±0.05	8.0±0.6

were analysed using Eqs. 13—15. A typical plot of $\ln[\vec{k}/(D^{\mathrm{W}})^{1/2}]$ against ξ for $x=0.1\ \mathrm{mol\ dm^{-3}}$, $y=0.1\ \mathrm{mol\ dm^{-3}}$, and $c=0.5\times10^{-3}\ \mathrm{mol\ dm^{-3}}$ in Cell A is shown in Fig. 5. Similar linear plots were obtained for all compositions of the solutions examined in this study. By fitting the $\ln[\vec{k}/(D^{\mathrm{W}})^{1/2}]$ *vs.* ξ plot to Eq. 18, Λ and $\vec{\alpha}$ were determined. Then k_{s} was determined from Λ using Eq. 20 with $D^{\mathrm{W}}_{\mathrm{Pic}}=7.46\times10^{-6}\ \mathrm{cm^2\ s^{-1}}$ and $D^{\mathrm{N}}_{\mathrm{Pic}}=D^{\mathrm{W}}_{\mathrm{Pic}}/2.07$[11]$=3.60\times10^{-6}\ \mathrm{cm^2\ s^{-1}}$. The kinetic parameters of Pic$^-$-ion transfer obtained at various Pic$^-$-ion concentrations at the interface between 0.1 mol dm^{-3} LiCl aqueous solution and 0.1 mol dm^{-3} TBATPB nitrobenzene solution are shown in Table 1. Also, the kinetic parameters of Pic$^-$-ion transfer obtained at various concentrations of LiCl in the aqueous solution and TBATPB in the nitrobenzene solution are shown in Tables 2 and 3.

Discussion

The cyclic voltammetric measurements show that the Pic$^-$-ion transfer at the water/nitrobenzene interface is d.c. reversible (nernstian) at the scan rate of 5 mV s^{-1}. This experimental finding ensures the validity of the Nernst equation for the mean surface concentration (Eq. 6) in a.c. polarography with the d.c. voltage scan rate of 5 mV s^{-1}. The d.c. reversibility of Pic$^-$-ion transfer at the water/nitrobenzene interface has been described also by Homolka and Mareček.[12] Thus the mid-point potential, E_{mid}, can be equated to the reversible half-wave potential, $E^{\mathrm{r}}_{1/2}$, which is related to the standard ion-transfer potential, $E^{\ominus}$, by Eq. 12. The standard ion-transfer potential of Pic$^-$-ion $E^{\ominus}_{\mathrm{Pic}}$, observed with Cell A is expressed by

$$E^{\ominus}_{\mathrm{Pic}} = \Delta\phi^{\ominus}_{\mathrm{Pic}} + \Delta E^{\mathrm{A}}_{\mathrm{ref}}, \tag{21}$$

where $\Delta\phi^{\ominus}_{\mathrm{Pic}}$ is the standard ion-transfer potential of Pic$^-$ ion at the water/nitrobenzene interface, and $\Delta E^{\mathrm{A}}_{\mathrm{ref}}$ is the constant determined solely by the left- and right-hand reference electrodes in Cell A. In the present case the left- and right-hand reference electrodes are reversible to TBA$^+$ and Cl$^-$ ions, respectively, and $\Delta E^{\mathrm{A}}_{\mathrm{ref}}$ is given as a function of the activities of TBA$^+$ and Cl$^-$ ions, $a^{\mathrm{N}}_{\mathrm{TBA}}$ and $a^{\mathrm{W}}_{\mathrm{Cl}}$, in the nitrobenzene (II) and aqueous (III) solutions, respectively, by

$$\Delta E^{\mathrm{A}}_{\mathrm{ref}} = \mathrm{constant} - (2.30RT/F)\log(a^{\mathrm{N}}_{\mathrm{TBA}}a^{\mathrm{W}}_{\mathrm{Cl}}). \tag{22}$$

Furthermore, if the ion-pair formation of Pic$^-$-ion with Li$^+$ and TBA$^+$ ions is appreciable, $\Delta\phi^{\ominus}_{\mathrm{Pic}}$ in Eq. 21 should be replaced by $\Delta\phi^{\ominus\prime}_{\mathrm{Pic}}$:

$$\Delta\phi^{\ominus\prime}_{\mathrm{Pic}} = \Delta\phi^{\ominus}_{\mathrm{Pic}} + \frac{RT}{F}\ln\frac{1+K^{\mathrm{N}}_{\mathrm{LiPic}}K^{\mathrm{N/W},\Delta\phi}_{\mathrm{Li}}a^{\mathrm{W}}_{\mathrm{Li}}+K^{\mathrm{N}}_{\mathrm{TBAPic}}a^{\mathrm{N}}_{\mathrm{TBA}}}{1+K^{\mathrm{W}}_{\mathrm{LiPic}}a^{\mathrm{W}}_{\mathrm{Li}}+K^{\mathrm{W}}_{\mathrm{TBAPic}}(K^{\mathrm{N/W},\Delta\phi}_{\mathrm{TBA}})^{-1}a^{\mathrm{N}}_{\mathrm{TBA}}}, \tag{23}$$

where $K^{\alpha}_{\mathrm{LiPic}}$ and $K^{\alpha}_{\mathrm{TBAPic}}$ (α=N and W) are the association constants of the ion pairs Li$^+$Pic$^-$ and TBA$^+$Pic$^-$ in the α phases, respectively, whereas $K^{\mathrm{N/W},\Delta\phi}_{\mathrm{TBA}}$ and $K^{\mathrm{N/W},\Delta\phi}_{\mathrm{Li}}$ are the ionic distribution co-

Table 2. Kinetic parameters of Pic$^-$-ion transfer[a] at the interface between a nitrobenzene solution of 0.1 mol dm^{-3} TBATPB and an aqueous solution of 0.02 to 1.0 mol dm^{-3} LiCl

$C^{\mathrm{W}}_{\mathrm{LiCl}}$ / mol dm^{-3}	E_{s} / mV	$\ln\Lambda$	k_{s} / 10^{-2} cm s^{-1}	$\vec{\alpha}$	$D^{\mathrm{W}}_{\mathrm{Pic}}$ / 10^{-6} cm^2 s^{-1}
0.02	360	2.86±0.07	4.0	0.45±0.06	6.3
0.05	335	2.80±0.07	3.8	0.50±0.08	8.3
0.10	320	2.77±0.04	3.7	0.45±0.04	8.8
0.20	302	2.80±0.03	3.7	0.50±0.04	7.5
0.50	281	2.66±0.04	3.1	0.65±0.05	6.5
1.00	265	2.82±0.06	3.5	0.74±0.09	6.2

a) Determined at 0.50×10^{-3} mol dm^{-3} Pic$^-$ ion in the aqueous phase.

Table 3. Kinetic parameters of Pic$^-$-ion transfer[a] at the interface between an aqueous solution of 0.1 mol dm^{-3} LiCl and a nitrobenzene solution of 0.05 to 0.17 mol dm^{-3} TBATPB

$C^{\mathrm{N}}_{\mathrm{TBATPB}}$ / mol dm^{-3}	E_{s} / mV	$\ln\Lambda$	k_{s} / 10^{-2} cm s^{-1}	$\vec{\alpha}$	$D^{\mathrm{W}}_{\mathrm{Pic}}$ / 10^{-6} cm^2 s^{-1}
0.05	333	2.76±0.08	3.5	0.60±0.06	7.1
0.10	320	2.77±0.04	3.7	0.45±0.04	8.8
0.17	310	2.64±0.03	3.2	0.49±0.02	8.5

a) Determined at 0.50×10^{-3} mol dm^{-3} Pic$^-$ ion in the aqueous phase.

efficients of TBA$^+$ and Li$^+$ ions, respectively, between nitrobenzene and water when the interfacial potential difference is $\Delta\phi$, and are given by

$$K_{\mathrm{j}}^{\mathrm{N/W},\Delta\phi} = \exp\,[z_{\mathrm{j}}F(\Delta\phi-\Delta\phi_{\mathrm{j}}^{\ominus})/RT],$$
$$\mathrm{j} = \mathrm{Li}^+ \text{ and } \mathrm{TBA}^+ \text{ and } z_{\mathrm{j}} = +1. \tag{24}$$

The change in the effective diffusion coefficients caused by the ion-pair formation in this case hardly affects the $E_{1/2}^{\mathrm{r}}$ values (see Eq. 12). The experimental results (Fig. 2 and Tables 2 and 3) show that the change of $E_{1/2}^{\mathrm{r}}$ ($\approx E_{\mathrm{Pic}}^{\ominus}$) with Cl$^-$ or TBA$^+$ activity is close to $-2.30RT/F$=-59 mV per decade, indicating that the variation in $\Delta\phi_{\mathrm{Pic}}^{\ominus\prime}$ with Li$^+$ and TBA$^+$ activities is negligibly small. Therefore the ion-pair formation of Pic$^-$-ion with Li$^+$ and TBA$^+$ ions should be negligible in the concentration range of the electrolytes used in this study.

The plot of $\ln[\overrightarrow{k}/(D^{\mathrm{W}})^{1/2}]$ against ξ for the Pic$^-$-ion transfer generally gave a straight line (Fig. 5). This is in contrast to the tetramethylammonium-ion transfer, in which the plot gave an appreciably upward convex curve (see Fig. 12 in Ref. 1). Thus we applied the Butler-Volmer type equations (Eqs. 16 and 17) to the rate constants of Pic$^-$-ion transfer to determine the kinetic parameters A, k_{s}, and $\overrightarrow{\alpha}$. The results are summarized in Tables 1—3. Table 1 shows that the observed kinetic parameters are hardly dependent on Pic$^-$-ion concentration in the range from 0.3×10^{-3} to 1.0×10^{-3} mol dm^{-3} indicating the validity of assuming the linear kinetic equation for the ion transfer (Eq. 5). As seen in Tables 2 and 3, the kinetic parameters, except the transfer coefficients, were virtually independent of the concentrations of LiCl and TBATPB in the aqueous and nitrobenzene solutions, respectively.

The electrical double layer of the interface between aqueous solution of LiCl and nitrobenzene solution of TBATPB consists of the inner layer which is sandwiched by the two diffuse double layers on the aqueous and nitrobenzene solution sides.[13] Accordingly, when an ion is transferred from one solvent to the other, the ion is transferred through the three layers, *i.e.* the diffuse double layer in one phase, the inner layer, and the other diffuse double layer in the other in series. The effect of the potential of the diffuse double layer on the concentrations of transferred ion at the reaction planes where the transfer of ion from one solvent to the other will take place can be expressed, in the first approximation, by the Frumkin equation for the double-layer correction:

$$C_2^{\mathrm{W}} = C^{\mathrm{W}} \exp\,[zF(\phi^{\mathrm{W}}-\phi_2^{\mathrm{W}})/RT], \tag{25}$$
$$C_2^{\mathrm{N}} = C^{\mathrm{N}} \exp\,[zF(\phi^{\mathrm{O}}-\phi_2^{\mathrm{O}})/RT], \tag{26}$$

where C_2^{α} (α=W or N) is the concentration of the transferred ion at the reaction plane on the aqueous (α=W) or nitrobenzene (α=N) solution side and C^{α} (α=W or N) is the surface concentration, *i.e.* the concentration of the transferred ion just outside the diffuse double layer. ϕ^{W} and ϕ^{O} are the inner potentials in the bulk of the aqueous and nitrobenzene solutions, respectively, and ϕ_2^{W} and ϕ_2^{O} are the potentials of the reaction planes on the respective solution sides. Consequently, Eq. 5 can be rewritten as

$$I = zFA(\overrightarrow{k}_{\mathrm{corr}}C_2^{\mathrm{W}}-\overleftarrow{k}_{\mathrm{corr}}C_2^{\mathrm{N}}), \tag{27}$$

with

$$\overrightarrow{k}_{\mathrm{corr}} = \overrightarrow{k}\exp\,[-zF(\phi^{\mathrm{W}}-\phi_2^{\mathrm{W}})/RT], \tag{28}$$
$$\overleftarrow{k}_{\mathrm{corr}} = \overleftarrow{k}\exp\,[-zF(\phi^{\mathrm{O}}-\phi_2^{\mathrm{O}})/RT], \tag{29}$$

where $\overrightarrow{k}_{\mathrm{corr}}$ and $\overleftarrow{k}_{\mathrm{corr}}$ are the "true" rate constants or the rate constants for the ion-transfer reaction taking place from the reaction plane on one solvent side to the reaction plane on the other. Upon assuming that the reaction planes are located on the OHP's on each solution side, the values of ϕ^{W}—ϕ_2^{W} and ϕ^{O}—ϕ_2^{O} can be calculated (in the absence of specific adsorption) by the Gouy-Chapman theory by knowing the surface charge density which was calculated from the double-

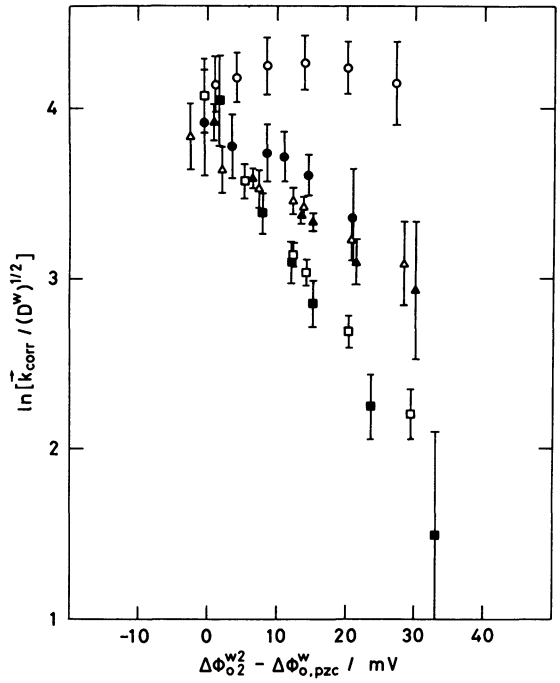

Fig. 6. Plot of $\ln[\overrightarrow{k}_{\mathrm{corr}}/(D^{\mathrm{W}})^{1/2}]$ *vs.* $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}-\Delta\phi_{\mathrm{O,pzc}}^{\mathrm{W}}$ for the Pic$^-$-ion transfer at the interface between a nitrobenzene solution of 0.1 mol dm^{-3} TBATPB and an aqueous solution of (○) 0.02, (●) 0.05, (△) 0.10, (▲) 0.20, (□) 0.50, and (■) 1.0 mol dm^{-3} LiCl. Vertical bars indicate the standard deviations.

layer capacity data[14] and the potential of zero charge (pzc) data.[13] In Fig. 6, the values of $\ln[\overrightarrow{k}_{\mathrm{corr}}/(D^{\mathrm{W}})^{1/2}]$ thus obtained for various concentrations of LiCl in the aqueous solution are plotted against the potential drop across the inner layer, $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}=\phi_{2}^{\mathrm{W}}-\phi_{2}^{\mathrm{O}}$, referred to the potential drop across the inner layer at the pzc, $\Delta\phi_{\mathrm{O,pzc}}^{\mathrm{W}}=\phi_{\mathrm{pzc}}^{\mathrm{W}}-\phi_{\mathrm{pzc}}^{\mathrm{O}}$.[14] It has been shown[13,14] that the inner layer capacity of the interface between an aqueous solution of LiCl and a nitrobenzene solution of TBATPB depends only on the surface charge density (or the inner layer potential difference) and not on the concentration of LiCl in the aqueous solution. Therefore it is expected that the corrected rate constants obtained at various LiCl concentrations lie on a single curve representing the dependence of $\overrightarrow{k}_{\mathrm{corr}}$ on $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}$. In contrast to this expectation, the $\ln[\overrightarrow{k}_{\mathrm{corr}}/(D^{\mathrm{W}})^{1/2}]$ *vs.* $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}-\Delta\phi_{\mathrm{O,pzc}}^{\mathrm{W}}$ plots varies considerably with the concentration of LiCl in the aqueous solution (Fig. 6). Considerable variation of the $\ln[\overleftarrow{k}_{\mathrm{corr}}/(D^{\mathrm{N}})^{1/2}]$ *vs.* $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}-\Delta\phi_{\mathrm{O,pzc}}^{\mathrm{W}}$ plots with the change of TBATPB concentration in the nitrobenzene solution was also found for the corrected rate constants obtained at various TBATPB concentrations (data not shown). These results (Fig. 6) suggest that the formalism of Frumkin correction based on the assumption that the reaction planes are located on the OHP's on respective solution sides is not valid for this case, especially in moderately concentrated supporting electrolyte solutions.

In the above discussion, the potentials of OHP's were estimated by the basic Gouy-Chapman theory. Modifications of the basic Gouy-Chapman theory have been described.[16] In view of the smallness of the surface charge density (less than $4\,\mu\mathrm{C\,cm^{-2}}$) and the moderate concentration of the electrolytes (less than $0.20\,\mathrm{mol\,dm^{-3}}$ except in a few extreme cases), however, we may conclude that the error caused by applying the basic Gouy-Chapman theory to the present system is probably small.

In the above discussion it is also assumed that the ion-pair formation of $\mathrm{Pic^-}$ ion is negligible which is in harmony with the d.c. voltammetric data on $\mathrm{Pic^-}$ ion. Available data on the ion-pair formation of $\mathrm{Pic^-}$ ion in water and nitrobenzene are limited. However, according to Poonia *et al.*[15] $K_{\mathrm{LiPic}}^{\mathrm{W}}=12.8$, which suggests that the ion-pair formation of $\mathrm{Pic^-}$ ion would be appreciable in concentrated LiCl aqueous solution. Accordingly, it is worth while discussing the possible effect of the ion-pair formation on the kinetic parameters of the ion transfer at the water/nitrobenzene interface. If the rate constants of the association and dissociation of the ion-pair are sufficiently large (*e.g.*(the first order rate constant)$/\omega \gg 1$), the a.c. faradaic impedance theory predicts that $\overrightarrow{k}$ and $\overleftarrow{k}$ in Eqs. 10, 13, 14 and the following equations should be replaced, respectively, by

$$\overrightarrow{k}' = \frac{\overrightarrow{k}}{1+K_{\mathrm{LiPic}}^{\mathrm{W}}a_{\mathrm{Li}}^{\mathrm{W}}+K_{\mathrm{TBAPic}}^{\mathrm{W}}(K_{\mathrm{TBA}}^{\mathrm{N/W},\Delta\phi})^{-1}a_{\mathrm{TBA}}^{\mathrm{N}}} \tag{30}$$

and

$$\overleftarrow{k}' = \frac{\overleftarrow{k}}{1+K_{\mathrm{LiPic}}^{\mathrm{N}}K_{\mathrm{Li}}^{\mathrm{N/W},\Delta\phi}a_{\mathrm{Li}}^{\mathrm{W}}+K_{\mathrm{TBAPic}}^{\mathrm{W}}a_{\mathrm{TBA}}^{\mathrm{N}}}. \tag{31}$$

Thus, the $\ln[\overrightarrow{k}_{\mathrm{corr}}/(D^{\mathrm{W}})^{1/2}]$ *vs.* $\Delta\phi_{\mathrm{O2}}^{\mathrm{W2}}-\Delta\phi_{\mathrm{O,pzc}}^{\mathrm{W}}$ plots, such as those in Fig. 6 should be also corrected by Eq. 30. However, it is clear that such a correction will not modify the scattered plots to align them on a single curve. Therefore we may conclude that the ion-pair formation of $\mathrm{Pic^-}$ ion with $\mathrm{TBA^+}$ and/or $\mathrm{Li^+}$ ion, if any, would not seriously affect the above discussion.

The ion transfer from one solvent to the other should consist of desolvation of one solvent and resolvation with the other and could take place in the reaction layer of a certain thickness, possibly extending beyond the inner layer into the diffuse double layers (or even beyond the diffuse double layers in concentrated electrolyte solutions). The Frumkin correction, if any, should be applied to the concentrations of the transferred ion at the reaction planes which are supposed to be located distant from the OHP's toward the bulk of respective solutions. Samec and his coworkers, using relatively dilute LiCl solutions (0.05 and $0.01\,\mathrm{mol\,dm^{-3}}$), found that the corrected rate constants of the transfer of $\mathrm{Cs^+}$ [6] and choline and acetylcholine ions[7] at the aqueous solution of LiCl/nitrobenzene solution of TBATPB interface change little with the potential across the interface. This result led these authors to conclude that the observed potential dependence of the "apparent" rate constants arises largely from the effect of the porential on the concentration of the transferred ions at the reaction planes which are located at the OHP's. Actually, the potential dependence of the "corrected" rate constants in $0.02\,\mathrm{mol\,dm^{-3}}$ LiCl aqueous solution was relatively small (see Fig. 6). However, as discussed above, the strong potential dependence of the "corrected" rate constants of $\mathrm{Pic^-}$-ion transfer observed in moderately concentrated electrolyte solutions seems to indicate that the observed potential dependence may reflect the real potential dependence of the $\mathrm{Pic^-}$-ion transfer rate constants at the water/nitrobenzene interface.

References

1) T. Osakai, T. Kakutani, and M. Senda, *Bull. Chem. Soc. Jpn.*, **57**, 370 (1984).

2) Z. Samec, *J. Electroanal. Chem. Interfacial Electrochem.*, **99**, 197 (1979).

3) O. R. Melroy and R. P. Buck, *J. Electroanal. Chem. Interfacial Electrochem.*, **136**, 19 (1982).

4) B. d'Epenoux, P. Seta, G. Amblard, and C. Gavach, *J. Electroanal. Chem. Interfacial Electrochem.*, **99**, 77 (1979).

5) Z. Koczorowski and G. Geblewicz, *J. Electroanal. Chem. Interfacial Electrochem.*, **139**, 177 (1982).

6) Z. Samec, V. Mareček, J. Weber, and D. Homolka, *J. Electroanal. Chem. Interfacial Electrochem.*, **126**, 105 (1981).

7) Z. Samec, V. Mareček, and D, Homolka, *J. Electroanal. Chem. Interfacial Electrochem.*, **158**, 25 (1983).

8) T. Kakutani, T. Osakai, and M. Senda, *Bull. Chem. Soc. Jpn.*, **56**, 991 (1983).

9) M. Senda, T. Kakutani, and T. Osakai, *Denki Kagaku*, **49**, 322 (1981).

10) I. M. Kolthoff, *Can. J. Chem.*, **59**, 1548 (1981).

11) T. Osakai, T. Kakutani, Y. Nishiwaki, and M. Senda, *Bunseki Kagaku*, **32**, E81 (1983).

12) D. Homolka and V. Mareček, *J. Electroanal. Chem. Interfacial Electrochem.*, **112**, 91 (1980).

13) T. Kakiuchi and M. Senda, *Bull. Chem. Soc. Jpn.*, **56**, 1753 (1983).

14) T. Osakai, T. Kakutani, T. Kakiuchi, and M. Senda, unpublished results.

15) N. S. Poonia, S. K. Sarad, A. Jayakumar, and G. C. Kumar, *J. Inorg. Chem.*, **41**, 1759 (1979).

16) For a review, see a) J. O'M Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, Vol. 2, New York (1970), pp. 623—843; b) R. Reeves, "Comprehensive Treatise of Electrochemistry," ed by J. O'M Bockris, B. E. Conway, and E. Yeager, Plenum Press, Vol. 1, New York (1980) pp. 83—134.