Potentiometric study of liquid membrane transports of ionic Na(I) species with some crown ethers into nitrobenzene and 1,2-dichloroethane

Abstract

Potentiometric measurements of the following liquid-membrane-transport cell were performed at 298 K. Cell: (−) Ag/AgCl | 0.05mol dm⁻³ (C₅H₅NO₃)⁻| nitrobenzene (NB) or 1,2-dichloroethane (DCE) | + 0.05mol dm⁻³ NaCl with L, NaOH, and picric acid | AgCl/Ag (+), where the symbols | and L denote an interface with a sintered glass and a crown ether, respectively. 15-Crown-5 ether (15C5), benzo-15C5, 18-crown-6 one (18C6), and benzo-18C6 were used as L. Assuming \( \text{emf} = \text{distribution equilibrium potentials} (\Delta \phi_{\text{org}} / V) \) around the NB- or DCE/water interface expressed by the asterisk) + other potentials in the cell, the relation of \( (F/RT)\text{emf} = k + \ln K'_{\text{org}} \), was derived under the conditions of \( K'_{\text{org}} > 1 \) and a steady state. Here, \( \text{emf}, k, t, K'_{\text{org}} \) refer to an emf (mV) measured between the two Ag/AgCl electrodes, an apparent first-order-reaction rate constant (minute⁻¹) for the distribution of Na(I) species, a monitored time (minute), a conditional distribution constant of the Na(I) species into the NB or DCE phase, and its modified \( K'_{\text{org}} \), respectively. With \( \Delta \phi_{\text{org}} \) values previously reported at 298K, positive correlations of the \( \ln K'_{\text{org}} \) values obtained from the \((F/RT)\text{emf}-\text{vs.-t} \) plots were observed in the systems with the four L employed; their correlation coefficients obtained from \( \Delta \phi_{\text{org}} - \text{vs.-ln} K'_{\text{org}} \) plots were 0.909 for the NB system and 0.896 for DCE. These good correlations indirectly confirmed the presence of \( \Delta \phi_{\text{org}} \), for the liquid-membrane transport systems. The emf values of another cell was also analyzed.

Keywords: potentiometry, liquid-membrane transports, distribution equilibrium-potential, crown ethers, nitrobenzene

Introduction

There are distribution equilibrium potentials \( (\text{dep} \text{ or } \Delta \phi_{\text{org}}) \) for single ion transfers across liquid/liquid interfaces\(^{4–5} \) in the field of electrochemistry and then it has been reported that these dep values between bulk organic (org) and water phases are present in univalent- and divalent-cation extraction systems without or with crown ethers \( (L) \).\(^{4–12} \) Also, in these studies, the term of “a conditional distribution constant” has been used for distinguishing the distribution constant of the ion with the dep \( \neq 0 \) V from that of neutral species with usually dep-0V.\(^{10–12} \) However, in the present state, such studies have been limited to the narrow field, such as the above extraction phenomena.\(^{4–12} \) This fact can cause the supposition that the presence of dep in the extraction systems is a rare case. On the other hand, as an experiment similar to the extraction ones, the experiments of liquid-membrane transport or separation of cations \((M^{n+})\) with various \( L \) have been reported so far at \( M^{n+} = \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Sr}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}, \) protonated \( \text{Phe} \) and \( L - \text{Phe} \), and so on.\(^{10} \)

In the present paper, in order to clarify the dep presence based on the present paper, we tried to review liquid-membrane transport experiments of Na’ with L into nitrobenzene (NB) and 1,2-dichloroethane (DCE) at 298K by using potentiometry. In such potentiometric measurements, handmade Ag/AgCl electrodes were immersed in the so-called solution phase of the Na(I) species, such as \( \text{Na}^+ \) and \( \text{NaL}^- \), with \( \text{Cl}^- \), \( \text{OH}^- \), and picric acid \( (\text{HPic}) \) and their receiving phase with \( (\text{C}_5\text{H}_5\text{NO}_3)^- \) (TBA \( \text{Cl}^- \)) and thereby an \( \text{emf} \) value between these two electrodes was monitored during the ion transport measurements with the liquid membrane of NB or DCE. As \( L^{11} \), 15-crown-5 ether \((15\text{C}5) \), benzo-15C5 \((18\text{C}6) \), and benzo-18C6 \((18\text{C}6) \) were employed.

Also, theoretical relations were derived for the analyses of the \( \text{emf} \)-versus-time \((t) \) plots of two kinds of cells (see the \( \text{emf} \) measurements section). From these analyses, apparent rate constants, such as \( k \), and the conditional distribution constants and other ones, such as \( K'_{\text{org}} \) and \( K'_{\text{NB}} \), for the membrane transport of \( \text{Na}^+ \) with \( L \) were obtained. So, the plots of \( \Delta \phi_{\text{org}} \) versus \( \ln K'_{\text{org}} \) for the NB and DCE systems with the four \( L \) employed gave good linear correlations. Besides, the speed of the process \( \text{NaL}^- \) vs. \( \text{Na}^+ \) and \( \text{NaL}^- \) vs. \( \text{Na}^+ \) were compared with those of the processes, \( \text{NaL}^- \) vs. \( \text{Na}^+ \) and \( \text{NaL}^- \) vs. \( \text{Na}^+ \).

Materials and methods

Materials

Sodium chloride \((\text{guaranteed reagent (GR): >99.5%}, \text{Kanto Chemical, Tokio})\) was dried at \( >100°C \) for more than 8h. Tetrabutylammonium chloride \((>98.0%, \text{Tokyo Chemical Industry})\) and NaOH \((\text{extra pure: >93.0%}, \text{Wako Pure Chemical Industries, Tokio})\) were used without further purifications. An aqueous solution of HPic \( \times \text{H}_2\text{O} \) \((\text{GR: >99.5%}, \text{added water: 15-25%}, \text{Wako})\) was prepared with pure water and its concentration was determined by the acid-base titration with phenolphthalein. Benzo-15C5 and 18C6 were purchased from Tokyo Chemical Industry and the former was dried \( \text{in vacuo} \) at a room temperature for 10h. 15-Crown-5 ether and 18C6 were purchased from Kanto Chemical and Acros Organics, respectively. The melting points of these ethers except for 15C5 were measured. When the observed ranges of their points were about one degree \( C \), the others were used without any purification. Nitrobenzene \((\text{GR: >99.5%}, \text{Kanto & Wako})\) and DCE \((\text{GR: >99.5%}, \text{Kanto})\) were washed three times with pure water and stored in states saturated with water.\(^{5,11} \) Other chemicals were of GR grades. Pure water was prepared with the same procedure as that reported before.\(^{10,11} \)
**Emf measurements**

The emf measurements were performed with Cells (A) and (B) at T = 298 K and P = 1013 hPa.

**Cell (A):** (−) Ag/AgCl | 0.05 mol dm$^{-3}$ TBACl (phase I) | NaCl, NaOH, and HPic (III) | AgCl/Ag (+).

Here, a sintered glass, depicted by $\varphi$ in the cells, separated the phase I from the phase II and also did the phase III from the phase II. Aqueous solutions of NaCl in the phase III and TBACl in the I were prepared at the concentrations of 0.05 mol dm$^{-3}$ and 0.051, respectively.

In the cell (A) of the NB/water system, the concentrations of L, HPic, and NaOH were in the ranges of (1.7 - 4.2) × $10^{-3}$ mol dm$^{-3}$ for the four L and additionally 0.0026, and 0.0026, respectively.11 Also, in the DCE/water systems, those of L, HPic, and NaOH were in the range or concentrations of (1.6 - 3.0) × $10^{-3}$ mol dm$^{-3}$, 0.0026, and 0.0026, respectively.11

**Cell (B):** (−) Ag/AgCl | 0.05 mol dm$^{-3}$ TBACl (phase I) | L = B15C5 or B18C6 in NB or DCE (II) | 0.05 mol dm$^{-3}$ NaCl with NaOH, and HPic (III) | AgCl/Ag (+).

In this cell, the concentrations, C$_{\text{org}}$, of L = B18C6 in the Nb (or DCE) phase, B15C5, and B18C6 in the DCE ones were 3.01 × $10^{-3}$ mol dm$^{-3}$, 0.00165, and 0.00206, respectively, and those of the materials in the other phases were the same as the concentrations in the cell (A), except for the absence of L in the phase III. Silver/silver chloride electrodes were of handmade in a common procedure in which the aqueous solutions of 1% K[Ag(CN)$_2$] (GR: >99%, Kanto) and 0.1 mol dm$^{-3}$ NaCl were used for their electrolytic preparation. The potentials of the handmade Ag/AgCl electrodes were regularly checked with the following cell: (−) Ag/AgCl | 0.1 mol dm$^{-3}$ NaCl | AgCl/Ag (+).

From the TBACl in the phase I (about 3 cm$^3$) contacted with the Ag/AgCl electrode, the mixture (about 3 cm$^3$) of NaCl, L, HPic, and NaOH in the III with the electrode were separated by the phase II of NB or DCE. Here, the phases I and III with Ag/AgCl electrodes were sealed up in glass containers of about 3 cm$^3$; their containers have been used in a cell for the ion-transfer polarographic measurements.21 A U-type-like cell was made between the org phase II (about 40 cm$^3$) in a 100 cm$^3$ beaker and the two containers put up perpendicularly. The phase II prepared in the beaker was magnetically stirred with a Teflon-coated stainless bar at a constant speed during the emf monitoring. After a setting of the cell (A) or (B), the monitoring time $t$ was measured from a start of the agitation of the org phase II. The pH/ion meter (TOA, type IM-20E) was used for the emf measurements (within ±1 mV) of the cells, in which the phase II was kept at 25 ± 0.4°C as priority. The same measurements with the other meter (Horiba, type F23) were not able to indicate stable emf readings, though their reasons are unclear.

**Theoretical handling**

A theoretical handling of the measured emf values based on the membrane transport models13,14,17 of the ion with L is described as follows. We monitored an emf value of the following bulk-liquid-membrane cell:

**Cell (A):** (−) Ag/AgCl | 0.05 mol dm$^{-3}$ TBACl (phase I) | NaCl, NaOH, and HPic (III) | AgCl/Ag (+).

Using inner potentials of the five phases, its emf value measured can be expressed as

\[
\text{Emf} = \phi_{\text{Ag/AgCl}} - \phi_{\text{Ag/AgCl}} + (\phi_{\text{II}} - \phi_{\text{I}}) + (\phi_{\text{III}} - \phi_{\text{II}}) + \phi_{\text{III}}
\]

\[\text{(1)}\]

where the symbol $\phi$ denotes the inner potential of the phase $q$ (Ag/AgCl, I, II, and III). Actually Eq. (1) becomes

\[
\text{Emf} = \phi_{\text{Ag/AgCl}} - \phi_{\text{Ag/AgCl}} + (\phi_{\text{II}} - \phi_{\text{I}}) + (\phi_{\text{III}} - \phi_{\text{II}})
\]

with

\[\text{(1a)}\]

\[\text{(1b)}\]

\[\text{(1c)}\]

Then, assuming that this process is simply of the first order reaction15,19 (the assumption 1) and accordingly its forward rate constant ($k_1$) is larger than the corresponding backward constant (k$^{-1}$) (the assumption 2), we can employ the general relation15,19,22:

\[C = C_0 \exp(-kt) \]

(2a)

Here, $C$ and $C_0$ refer to the concentration of the ion at the time $t$ and an initial one of $j$ in the phase II, respectively. Moreover, using the mass balance equation, $C_0 = C_0 = C_0 = C_0 = C_0$, at $t$ and rearranging Eq. (2a), we can immediately obtain

\[K_0 = \exp(kt) \]

(2b)

Then, assuming the process is simply of the first-order reaction15,19,22 (the assumption 1) and accordingly its forward rate constant ($k_1$) is larger than the corresponding backward constant ($k^{-1}$) (the assumption 2), we can employ the general relation15,19,22:

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\[K_0 = \exp(kt) \]

(2b)

According to our previous papers10-12 the $K_0$ value can be related to the $\Delta\phi_{\text{org}}$ or dep as follows:

\[\Delta \phi = (RT/2F)(\ln K_{\text{D}^\circ} - \ln K_{\text{D}^\circ}) \]

(4)

Here, $z$ shows a formal charge of $j$ with the sign and $K_{\text{D}^\circ}$ does a standard distribution constant of $j$ into the org phase, namely $K_{\text{D}^\circ}$ at $\Delta \phi = 0$ V.11 Rearranging Eq. (1a) and rearranging Eq. (2a) based on Eq. (4) gives the following equation.

\[\text{Emf} = \Delta \phi \cdot \exp(RT/2F)(\ln K_{\text{D}^\circ} - \ln K_{\text{D}^\circ}) + \alpha \]

(1b)

with $\alpha = \Delta E_A + iR \cdot (\Delta \phi_{\text{org}} - \phi_{\text{org}})$, where $\Delta E_A$ and $iR$ denote a liquid junction potential between the phases II and III13 and an ohmic potential drop in the cell, respectively, and this potential $\alpha$ was considered to be a constant within an experimental error. At equilibrium $\Delta \phi_{\text{org}}$ equals $|\Delta \phi_{\text{org}}|$, while at the steady state (the assumption 4, see below) $\Delta \phi_{\text{org}}$ can be a little different from $|\Delta \phi_{\text{org}}|$. Introducing Eq. (3) in Eq. (1b) and then rearranging it, we can immediately obtain

\[(zF/RT) \cdot \text{emf} = k \cdot \ln K_D \]

(5)

with $\ln K_{\text{D}^\circ} = (zF/RT) \cdot \alpha - \ln K_{\text{D}^\circ}$.

(5a)

Here, the subscripts, $j$ and $j'$, were omitted for visual simplicity of Eqs. (5) and (5a). Therefore, we can obtain the $k$ and $\ln K_D$ values from the plot of $(zF/RT) \cdot \text{emf versus } t$ (Figure 1). In Eq. (5), we can think that the $K_D$ term is a conditional distribution constant for $j$ with $\Delta \phi_{\text{org}} = 0$V for the membrane transport system, as well as the NaPic
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POTENTIAL STUDY OF LIQUID MEMBRANE TRANSPORTS OF IONIC Na(I) SPECIES WITH SOME CROWN ETHERS INTO NITROBENZENE AND 1,2-DICHLOROETHANE

extraction ones with L. One can also suppose that the $K_{c}'$ and $(F/RT)t$ terms of Eq. (5a) correspond to the $(F/RT)\Delta\phi_m$ and $K_{c,org}$ ones, respectively, at $z_i=1$ in comparison with Eq. (4). Moreover, considering the cell constitution, it is valid that the $k$ term means the apparent first-order-reaction rate constant for the ion transfers from the bulk phase III to the II.

![Figure 1](image1.png)

**Figure 1** Plots of $(F/RT)\Delta\phi_m$ vs. $t$ for the NB system with 15C5 (circle), B15C5 (square), 18C6 (diamond), and B18C6 (triangle) at $T=298K$. The correlation coefficients ($R$) were 0.211 for 15C5, 0.968 for B15C5, 0.972 for 18C6, and 0.923 for B18C6.

Similarly, the cell (B) was employed for the emf monitoring of only the systems with the benzo derivatives in the org phase. The constitution of this cell comes from the distribution properties, only the systems with the benzo derivatives in the org phase. The $K_{c,org}$ is similarly called the distribution constant and defined as $[L]_{org}/[L]_{mem}$. In this case, the ion transfer process is mainly

$$Na^{+} + L_{org} \rightarrow NaL_{org}$$

with $K_{c,org} = [NaL_{org}]/[Na^{+}][L]_{org}$. (6a)

As the rate law prepared for Eq. (6), we can derive

$$-d[Na^{+}] = d[L]_{org}/d\tau = d[NaL_{org}]/d\tau = k_{c}[Na^{+}][L]_{org}$$

(7)

where the symbols $k$ denote the rate constants at $t=1$ or 2. Commonly, $k_{c}$ corresponds to the rate constant of the process $Na^{+} + L_{org} \rightarrow NaL_{org}$, while $k_{c}$ does to that of $NaL_{org} \rightarrow Na^{+} + L_{org}$. Introducing Eq. (6a) in Eq. (7) and rearranging it, the following equation is obtained:

$$-d[Na^{+}]/d\tau = [L]_{org}k_{c}K_{c,org}[Na^{+}] = k'[Na^{+}]$$

(8a)

so, Eq. (8) can express the modified rate law for the process $Na^{+} + L_{org} \rightarrow NaL_{org}$ and Eq. (8a) corresponds to a pseudo-second-order-reaction rate-constant. Comparing Eq. (8) with the rate law, $-d[Na^{+}]/d\tau = k[f]$, of Eq. (2), we can see easily that Eq. (2a) is useful for the analysis of the emf data obtained from the cell (B) too.

From Eqs. (2a) and (2b), we can obtain $C_{emf} = C_{exp} (-k't)$ and $K_{c,org} = C_{exp} + 1 = exp (-k't)$, respectively, with the mass balance equation, $C_{emf} = C_{exp} = [Na^{+}]_{org} + C_{org}$. Then, rearranging the latter equation with the term $K_{c,org} = C_{org}$, we can easily derive $K_{c,org} = exp (k't)[1 - exp (-k't)]$. By taking a natural logarithm of the both sides of this equation, the following equation can be given: ln $K_{c,org} = k't + ln C_{org}$. Consequently it becomes

$$ln K_{c,org} = k't + ln C_{org} \approx ln K_{c,org} = k't + ln C_{org}(1)$$

(3a)

with $K_{c,org} = [NaL_{org}]/[Na^{+}][L]_{org}$. So, from Eqs. (11b) and (3a), we can easily obtain

$$(F/RT)\Delta\phi_m + ln C_{org} = k't + ln K_{c,org}$$

(9)

Equation (9) at $z=1$ and $\alpha=q$ under the assumption of $F=constant$ value (the assumption 3b). Using Eq. (9) and assuming that $C_{exp}$ equals a total concentration of L in the org phase (see the emf measurements section), a plot of $(F/RT)\Delta\phi_m + ln C_{org}$ versus $t$ yields $k'$ as the slope and $ln K_{c,org}/T$ as the intercept (Figure 2). Also, Eq. (9a) is similar to Eq. (5a) in its equation form.

For the assumptions employed in the above handling, the assumptions 1 to 3 and 3b were essentially satisfied with the above experiments with emf: see the following results and discussion sections. On the other hand, the validity of the assumption 4 may be shown in the fact that the $K_{c,org}$ hardly reflects the $K_{c,org}$ and $K_{c,org}$ ones. Strictly speaking, it is difficult to clarify whether the assumption 4 is satisfied or not.

**Results**

The following results were obtained from only the measurements of $emf$ with $t$. Figure 3 & Figure 4 show $emf$-versus-$t$ plots of Cell (A) (see the $emf$ measurements section) at 298K for the NaCl/HPic-15C5 system with NB and -18C6 one with DCE, respectively. Here, the symbol $t$ means the monitoring time in min. of $emf$. As shown in these figures, the NB systems were superior to the DCE ones in the stability of the $emf$ measurements. Average values of the data sets of 3 to 5 for a given $t$ were used for the analyses of the $emf$-versus-$t$ plots based on Eq. (5) (see the theoretical handling section) at $z=1$. In order to bring the data sets close to the equilibrium condition, considering the steady state condition of the system (the assumption 4, see the theoretical handling section), the $emf$ values over $t=20$ or 10 minutes

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were employed for the data analyses; the triangle data in Figure 4 were neglected because of their less stability.

Figure 3 Plots of emf vs. t for the NaCl/HPic-15C5 system with NB of the cell (A) (see the theoretical handling section) at $C_{15C5} = 4.22 \times 10^{-5}$ mol dm$^{-3}$.

Figure 4 Plots of emf vs. t for the NaCl/HPic-18C6 system with DCE of the cell (A) at $C_{18C6} = 0.00303$ mol dm$^{-3}$.

Figure 5 Plots of emf (average) vs. t for the cell (B). The NB system with B18C6 (circle) and the DCE ones with B15C5 (square) and B18C6 (triangle).

Figure 6 Plots of dep vs. ln $K_D^{'}$ for the NB (circle) and DCE (square) systems with the four ethers.

The plots of dep versus ln $K_D^{'}$ for the both systems are shown in Figure 6. These regression lines were $\Delta \phi_{eq} = (0.10 \pm 0.03) \ln K_D^{'} + (0.34 \pm 0.01)$ for NB and $\Delta \phi_{eq} = (0.04 \pm 0.01) \ln K_D^{'} + (0.30 \pm 0.08)$ at 0.896 for DCE.

**Discussion**

**Characterization of the k and ln $K_D^{'}$ values**

In the NB systems, the $k$ values of the benzo derivatives were by one order larger than those of the simple ethers (Table 1). On the other hand, in the DCE systems, there were no large differences in $k$ among the L employed. Or, it seems that the $k$ values of the 18C6 derivatives are larger than those of the 15C5 ones among the DCE systems. These values for the 15C5 and 18C6 with NB (Table 1) were close to the observed first-order rate constants ($=0.0039-0.0079$ min.$^{-1}$) at 298K for the Na$^+$ complexes of the carboxylic 18C6 derivative with CHCl$_3$, while those for all the L with DCE were comparable to the rate constants ($=0.047 \& 0.056$ min.$^{-1}$) observed at 298K for the Na$^+$ complexes of B15C5 and B18C6 with CH$_2$Cl$_2$. These agreements indicate the validity of the present method described in the theoretical handling.

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section. Also, it is interesting that the rate constants reported for the transfer of all species, such as $M^{+}$, $ML^{-}$, and MLA (neutral ion-pair complex with a pairing anion $A^{-}$), are comparable to those evaluated here. This suggests that the major transport species in the membrane transport experiments are ionic, not neutral ones.

According to our previous paper, the log $K_{D,NaL}$ values (Table 1) were in the orders $L=15C5<18C6=B15C5=B18C6$ for both the NB and DCE systems. Also, the log $K_{D,NaL}$ values were in the orders $18C6$ ($\log K_{D,NaL}=−2.5$) $<15C5$ ($−2.0$) $<B18C6$ ($−1.6$) $<B15C5$ ($−0.4$) for NB and $B15C5$ ($−3.3$) $<15C5$ ($−2.90$) $<B18C6$ ($−2.32$) $<18C6$ ($−1.38$) for DCE. On the other hand, the $\ln K_{D}'$ values in Table 1 were in the orders $B15C5<B18C6=15C5<18C6$ for NB and $18C6<15C5<18C6=B15C5$ for DCE. The NB systems show the tendency of hydrophobic $L$ $<$ hydrophilic $L$, but the DCE ones do its reverse tendency. The above orders indicate that the $K_{D,NaL}$ and $K_{D,NaL}$ values "at equilibrium" hardly reflect the $K_{D}'$ ones "at the steady state". Being different from the $K_{D,NaL}$ and $K_{D,NaL}$ ($<K_{D,NaL}$) values, however, only the $K_{D,NaL}$ values satisfy the assumption 3 described in the theoretical handling section. The charge balance equation, $[\text{Na}^+]_i-[\text{NaL}^+]_i=[\text{Pic}_i]^-$, in the extraction experiments shows the distribution of $\text{Na}^+$, $\text{NaL}^-$ and $\text{Pic}^-$ (especially $\text{NaL}^-$ & $\text{Pic}^-)$ into the org phase, in addition to the distribution of the charge-less $\text{NaPic}^-$. The log $K_{D,NaL}$ values have revealed the relations of $\text{org}=$NB $>$ DCE for all the $L$ (Table 1). The same is true of the relation, NB $>$ DCE, of the log $K_{D,NaL}$ values, except for 18C6. The $\ln K_{D}'$ values showed the same relations, except for the case of NB $<$ DCE for $L=B18C6$. These results suggest that a strength of the ion-solvent interaction controls a magnitude of $\ln K_{D}'$. On the basis of the above results, the $K_{D}'$ values seem to reflect a comprehensive distribution of $\text{Na}^+$ & $\text{Pic}^-.$

### Table 1 Fundamental data obtained from the analyses of the liquid-membrane transport cell (A) with NaCl/Pic and some L at 298K

| $L$ | $k'^{-1}$ (sec$^{-1}$) | $\ln K_{D}'$ | $\Delta \phi_{eq}^i \psi (\text{log } K_{D,NaL}')$ |
|-----|-----------------|--------------|---------------------------------|
|     | $\text{org}=$NB | DCE | NB | DCE | NB | DCE |
| 15C5 | $0.001\pm0.003(4.1\times10^{-5})$ | $0.025\pm0.005(28)$ | $-2.4\pm0.2$ | $-4.1\pm0.2$ | $0.1(2.0)$ | $0.11(0.4)$ |
| B15C5 | $0.027\pm0.003(26)$ | $0.028\pm0.005(25)$ | $-2.9\pm0.1$ | $-3.7\pm0.8$ | $0.024(2.6)$ | $0.1(1.8)$ |
| 18C6 | $0.0029\pm0.0002(2.4\times10^{-5})$ | $0.044\pm0.009(16)$ | $-1.68\pm0.04$ | $-5.7\pm0.6$ | $0.1(2.2)$ | $0.022(0.84)$ |
| B18C6 | $0.018\pm0.004(39)$ | $0.036\pm0.009(19)$ | $-2.5\pm0.2$ | $-3.9\pm0.5$ | $0.09(4.2)$ | $0.078(4.57)$ |

*Data determined by extraction experiments in ref. 11. Experimental values to the initial concentration of 0.00310mol dm$^{-3}$ B15C5.*

### Indirect evidence for the presence of dep

The dep or $\Delta \phi_{eq}$ order list in Table 1 was $B15C5=B18C6=15C5=18C6$ for NB and $18C6=B18C6=15C5<B15C5$ for DCE. These orders are close to those of the $\ln K_{D}'$ values (see above). Additionally, as described in the theoretical section, we can see the possibility that the $(F/R)\Delta \phi_{eq}$ term is comparable to the $\ln K_{D}'$ one: see Eqs. (4) and (5a) (see the theoretical handling section). Figure 6 indirectly proves the presence of the dep between the two bulk phases II and III with the NB/- or DCE/water interface. Also, the results indicate that there are the dep values in the liquid membrane transport, as well as solvent extraction and electrochemistry at liquid/liquid interfaces. Moreover, the intercepts show the $\Delta \phi_{eq}$ values for the hypothetical L system which satisfies the condition of $\ln K_{D}'=0$, namely $\alpha=(R/T)\ln K_{org}^i$ in Eq. (5a). In other words, this makes us suppose $\alpha$ is a constant under the constant condition of $P$ and $T$.

### Determination of the $\ln K_{NaNaL}'$ and $k_a$ values

The authors examined the assumption 3b (see the theoretical handling section) using the definition of $I'=\ln [1−\exp (−k_t)]$ with the above experimental $k'$ (Table 2) and $t$ values. The calculated $I'$ values were $−1.5\pm0.4$, for the B18C6 with NB in the $t$ range of 20-95min., $−0.5\pm0.1$, for B15C5 with DCE in that of 35-85 and $−0.6\pm0.3$, for B18C6 with DCE in that of 14-55. On the basis of these values, the corresponding $\ln K_{NaNaL}'$ values were estimated to be $−12.1\pm0.4$, $−8.2\pm0.2$, and $−8.9\pm0.3$, respectively. Such experimental errors of $I'$ and $\ln K_{NaNaL}'$ for $L=$benzo derivatives were comparable to those of $\ln K_{D}'$ in Table 1. The $\ln K_{NaNaL}'$ values (=the intercept, and Table 2, Figure 2 & the theoretical handling section) for NB was somewhat smaller than the $\ln K_{NaNaL}'$ one, while the intercepts for DCE were close to the $\ln K_{NaNaL}'$ values. These results essentially satisfy the assumption 3b for the present case and indicate that the intercepts of the $F(B)$-versus-$t$ plots are adequately close to the $\ln K_{NaNaL}'$ values.

### Table 2 Fundamental data obtained from the analyses of the liquid-membrane transport cell (B) with NaCl/Pic and some L at 298K

| $L$ | $k'^{-1}$ (sec$^{-1}$) | $\ln K_{NaNaL}'$ |
|-----|-----------------|------------------|
|     | $\text{org}=$NB | DCE | NB | DCE |
| B15C5 | $\cdots$ | $C_{NaNaL}'=0.00165$ | $0.015\pm0.002(46)$ | $\cdots$ | $-8.7\pm0.1$ |
| B18C6 | $C_{NaNaL}'=3.01\times10^{-5}$ | $0.0045\pm0.009(1.5\times10^{-5})$ | $0.00206$ | $0.0273\pm0.0003(26)$ | $-13.69\pm0.06$ | $-9.59\pm0.09$ |

*Data determined by extraction experiments in ref. 11. Experimental values to the initial concentration of 0.00310mol dm$^{-3}$ B15C5.*

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*Not determined. Experimental values/mol dm$^{-3}$. 
*Forward rate constant of the cell (A) in the text. The half life calculated from $t_{1/2}=\ln 2/k$. See ref. 22.
Also, the log $K_{NaNaL}$ values were calculated to be 3.4, for L=B18C6 with NB, 0, for B15C5 with DCE, and 1.27 for B18C6 with DCE from the thermodynamic relation.\textsuperscript{12} $K_{NaNaL}=k'/k_1[NaL]_{org}$ From the relation\textsuperscript{26} at equilibrium of $K_{NaNaL}=k'/k_1[NaL]_{org}$ and the above $k'/[L]_{org}$ and $K_{NaNaL}$ values, the $k_1$ values were estimated to be 0.05 min\textsuperscript{-1} for L=B18C6 with NB, 4 for B15C5 with DCE, and 0.70 for B18C6 with DCE. Only the obtained $k_1$ value for B18C6 with NB was close to that (0.056min\textsuperscript{-1} at 298K\textsuperscript{25}) for B18C6 with CH\textsubscript{2}Cl\textsubscript{2}. The corresponding pseudo-second-order-reaction rate-constants $k'/[L]_{org}$ were $1.5\times10^{-3}$dm\textsuperscript{3}min\textsuperscript{-1}, 8.8, and 13, respectively. These facts simply show $k'/k_1$, although their units differ from each other. On the other hand, we can derive the limitation of $k_1/k_2$ from Eq. (8a), since both the relations of $K_{NaNaL}>1$ and $k_2>0$ holds (see the above results). This accordance between the inequalities suggests that $k_1/k_2$ is proportional to $k'/k_1[NaL]_{org}$.

For the rate of the ion transfer from the org to the water phase

Assuming that the relation of $-\sigma[NaL]/dt=k[NaL^-]-k[NaL]_{org}$ holds, we can estimate the apparent backward-rate-constant $k_1$ from the relation\textsuperscript{26} of $K_{NaNaL}=k/k_k'$. The estimated $k_1$ values were $1.5\times10^{-3}$ min\textsuperscript{-1} at L=B15C5, $6.6\times10^{-3}$ and $7.2\times10^{-3}$ at B15C5, $1.2\times10^{-3}$ at 18C6, and $1.3\times10^{-3}$ at B18C6 for the NB systems and 0.01 at 15C5, $3.0\times10^{-3}$ at 15C5, 0.0064 at 18C6, and $9.6\times10^{-3}$ at B18C6 for the DCE ones. One can see that the relation $k_1=k_2$ holds in all the L and satisfies the assumption 2 (see the theoretical handling section), although the 15C5 system with DCE does not adequately satisfy the assumption 3 of $K_{NaNaL}>1$ (see the $K_{NaNaL}=2$ in Table 1). These results suggest that the Na-L transfers from the org phase to the water one are slow, compared with the transfer from water phase to the org one. It is interesting that the process of Na-L transfers from the org phase to the water phase is more speedy than that of NaB18C6\textsubscript{org}→NaB18C6\textsubscript{org}. The same is true for the B15C5 and B18C6 systems with DCE. Besides, the good correlations of the dep-versus-In $K_{NaL}$ plots indirectly confirmed the presence of the dep between the two bulk phases for the liquid-membrane transport systems, as well as extraction systems.

As shown in the materials and methods section, the study proposes a simple procedure which monitors $emf$ with $t$. This gives the possibility that many unprofessional workers can do thus transport experiments, because the experiments do not need comparatively expensive instruments, such as AAS\textsuperscript{13,15,17} and HPLC.\textsuperscript{19} On the other hand, needless to say, the neutral species, such as NaLPic and NaPic, cannot be detected with this method. This limitation becomes a weak point of the method, as well as the traditional methods reported before. This study should be acceptable for readers as primary experiments. Additional experiments will be required for confirming these results more directly, if possible.

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Conflict of interest

The author declares that there is no conflict of interest.

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