

# Liquid Membrane Transports of Na(I) Ions by Crown Compounds into Dichloromethane and *o*-Dichlorobenzene: About Analytical Model Simplified for Potentiometric Experiments

Yoshihiro Kudo<sup>1</sup>, Tomohiro Goto<sup>2</sup>, Saya Morioka<sup>1</sup>, Chiya Numako<sup>1</sup>

<sup>1</sup>Graduate School of Science, Chiba University, Chiba 263-8522, Japan; <sup>2</sup>Department of Chemistry, Faculty of Science, Chiba University, Chiba 263-8522, Japan

## ABSTRACT

Membrane transport experiments into Dichloromethane (DCM) and *o*-Dichlorobenzene (*o*DCBz) were performed at 298 K using basic mixtures of NaCl, picrate ion, and crown compounds (L). Here, L shows 15-crown-5 ether (15C5), benzo-15C5 (B15C5), 18-crown-6 ether (18C6), or B18C6. A used cell was (-) ref. electrode|0.05 mol/L (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NCl|org (=DCM or *o*DCBz) |mixture| ref. electrode (+), where the ref. electrode is a commercial one composed of 3 mol/L NaCl|AgCl|Ag. First-order rate constants (k/minute<sup>-1</sup>) and a parameter,  $f\Delta E'$ , with potential differences  $\Delta E'/V$  at the (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NCl<sub>aq</sub>|org interfaces and  $f=F/RT$ , were determined. The natural logarithm of the apparent distribution constant (KD') defined before for the ion transfer into the organic phases was displaced by this parameter  $f\Delta E'$ . Also, a negative correlation was observed at T=298 K in the plots of  $f\Delta E'$  vs.  $\ln k$ . Here, "dep" is the abbreviation of the distribution equilibrium potential for the extraction system with L and the values were determined from re-analyzing the corresponding extraction data. Additionally, the experimental emf values were discussed based on the equation  $\pm \text{emf} \approx 0.02569 kt + \Delta E'$ , where t shows an elapsed time (minute).

**Keywords:** Membrane transport; Rate constants; Distribution equilibrium potentials; Potentiometry; Na(I) ion; Crown compounds; Dichloromethane; *o*-Dichlorobenzene

## INTRODUCTION

We studied transports of Na<sup>+</sup> with crown compounds (L), such as 15-crown-5 ether (15C5) and 18-crown-6 one (18C6), from water (w) into Nitrobenzene (NB) and 1,2-Dichloroethane (DCE) as bulk liquid membranes with potentiometry [1]. Although such potentiometric measurements do not detect neutral Na(I) species that transfer across the w/membrane interfaces, we could obtain any data about their ion transfers. In addition, such experiments can support the membrane transport experiments that have been studied by using non-potentiometric procedures [2-4]. In the previous paper [1], a parameter,  $\ln K_D'$ , was introduced in order to analyze such experimental data. This parameter has been defined as a function that includes  $\Delta E_{ij}$ ,  $iR$ ,  $K_D^S$ ,  $\Delta \phi$  eq, and so on [1]. Here these four symbols denote liquid junction potentials for some interfaces,  $iR$  drop through some phases, a standard distribution constant of the ion between the organic (org) and w phases at 0 V of a distribution equilibrium potential (dep or  $\Delta \phi$  eq [5,6]), and dep due to mainly picrate ion (pic<sup>-</sup>), respectively.

However, they were ambiguous for understanding or expressing the parameter. Consequently, it made an understanding of the above membrane transports difficult.

In this study, the ion transfers with L into the Dichloromethane (DCM) and *o*-Dichlorobenzene (*o*DCBz) were studied by potentiometric at 298 K. As L, 15C5, benzo-15C5 (B15C5), 18C6, and B18C6 were used, since there are many extraction data [7-9] for these L. Basic mixtures of NaCl and pic<sup>-</sup> with L were prepared as source phases. From such experiments, we obtained at 298 K the first-order rate constants (k/min<sup>-1</sup>) and newly potential differences ( $\Delta E'/V$ ) between the w and org phases. For this purpose, a simplified analytical model was proposed here, compared with the previously-shown model [1], as described partially above. Additionally, another meaning of dep [5] was discussed based on a modified form of the Arrhenius equation [6] with  $\ln k$  and  $F\text{dep}/RT$ . The dep values were determined from data [7-9] reported in the extraction experiments of NaPic by the above four Ls into *o*DCBz.

**Correspondence to:** Yoshihiro Kudo, Graduate School of Science, Chiba University, Chiba 263-8522, Japan, Tel: +0432902786; E-mail: iakudo@faculty.chiba-u.jp

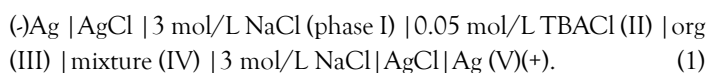
**Received:** December 27, 2020; **Accepted:** December 30, 2020; **Published:** February 03, 2020

**Citation:** Yoshihiro Kudo (2020) Liquid Membrane Transports of Na(I) Ions by Crown Compounds into Dichloromethane and *o*-Dichlorobenzene: About Analytical Model Simplified for Potentiometric Experiments 10:216.

**Copyright:** © 2020 Kudo Y et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

## MATERIALS AND CHEMICALS

The used cell was as follows:



Here the symbol TBACl denotes  $(C_4H_9)_4NCl$  and the parts of  $Ag|AgCl|3 \text{ mol/L NaCl}$  were commercial electrodes (BAS Co. Ltd., type RE-1B). The org phases III were DCM {Guaranteed Pure Reagent (GPR), >99.5%; Kanto Chemical} and oDCBz (GR, >99.0%; Kanto), where these commercial org solvents were washed three times with pure water and then saturated with pure water. The aqueous mixtures IV were fundamentally composed of 0.050 mol/L NaCl,  $5.0 \times 10^{-4}$  NaOH,  $3.3 \times 10^{-4}$  HPic, and  $2.2 \times 10^{-5}$  mol/L for L=B15C5, 18C6, and B18C6 and  $7.1 \times 10^{-5}$  for 15C5. Other chemicals and treatments were the same as those [1] reported previously.

The emf measurements of the cell (Figure 1) were performed at 298 K by using a pH/ion meter (TOA, type IM-20E) with handmade connection terminals [1]. The numbers of the emf measurements for the org systems with the mixtures were about 5 times.

## RESULTS AND DISCUSSION

### Renewal of analytical model

The used cell was  $(-)Ag|AgCl|3 \text{ mol/L NaCl (phase I)} | 0.05 \text{ mol/L TBACl (II)} | \text{org (III)} | \text{basic mixture (IV)} | 3 \text{ mol/L NaCl} | AgCl | Ag \text{ (V)(+)}$ . According to the Nernst and Henderson equations [6], the potential difference between the phases I and II and that between phase IV with 0.05 mol/L  $Cl^-$  and phase V were evaluated to be both  $|0.17| \text{ V}$  ( $=0.19-0.02$ ). Hence, the net potential difference of the measured emf under the steady-state conditions [1] was approximately expressed as:

$$emf = 0.17 + (\phi_{IV} - \phi_{III}) + (\phi_{III} - \phi_{II}) + (-0.17) \\ \approx (\phi_{IV} - \phi_{III}) + (\phi_{III} - \phi_{II}) \quad (2)$$

Additionally, the difference  $\phi_{III} - \phi_{II}$  can be constant, because of the constant composition of the org and aqueous TBACl phases. Also, the former in *emf* is similar to the definition of *dep*, namely  $\phi_w - \phi_{org}$  [5], where the subscript “w” shows a water phase.

Therefore, based on Eq. (2), we can express *emf* as follows:

$$emf \approx dep + \Delta E' \quad (3)$$

$$dep = \phi_{IV} - \phi_{III} (= \phi_w - \phi_{org}) \text{ and } \Delta E' = \phi_{III} - \phi_{II}$$

Also, this equation can be rearrange into

$$emf \approx \ln[(K_D / K_D^S) / zf + \Delta E'] = kt / zf + \Delta E' \quad (3a)$$

$$\ln(K_D / K_D^S) = (\ln K_D^F) = kt$$

where  $K_D$  shows a conditional distribution constant at  $dep \neq 0$  [10]. In this equation, we re-defined  $\ln K_D^F$  as *kt*. Thus, the model [1] for the membrane transport, proposed before, was more simplified here. So, the  $\ln K_D^F$  values [1] reported previously in the NB and DCE systems were interpreted as the *zfΔE'* ones.

Multiplying *zf* for the both sides of Eq. (3a), we can immediately obtain

$$zf \times emf \approx kt + zf \Delta E' \quad (4)$$

Essentially, the  $\Delta E'$  term can be treated as a constant for a given org, although kinds of L differ from each other. The plot of  $-f \times emf$  versus *t* at  $z \pm 1$  gives *k* as a slope and  $f\Delta E'$  as an intercept for a given L at fixed org. Here, the minus sign of  $-f \times emf$  was employed for easily analyzing the  $+emf$ -versus-*t* plots because their actual plots were curves monotonically decreasing with an increase in *t* for the present DCM and oDCBz systems.

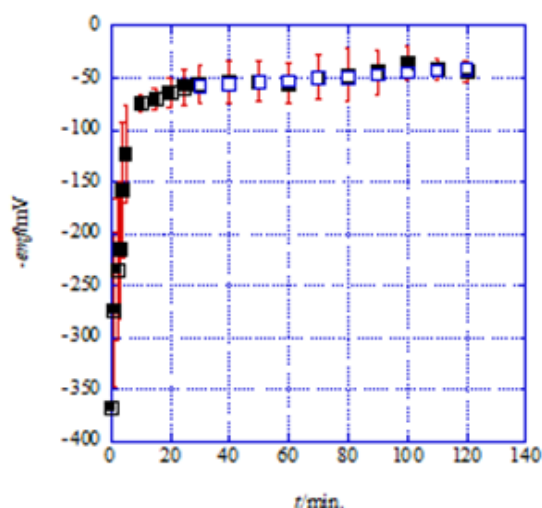
**Table 1:** Fundamental data of *k* and  $f\Delta E'$  for the membrane transports of Na(I) ion by some crown ethers at 298 K.

Organic	L	k/min <sup>-1</sup>		fΔE' (ΔE'/V)		
			S. E. <sup>b</sup>		S. E. <sup>b</sup>	dep <sup>c</sup> /V
DCM	15C5	0.0038	0.0005	-2.50 (-0.064)	0.05	0.104
	B15C5	0.0074	0.0015	-2.40 (-0.061)	0.12	0.126
	18C6	0.0066	0.0005	-2.53 (-0.065)	0.04	0.073
	B18C6	0.0028	0.0005	-2.48 (-0.064)	0.04	0.113
oDCBz	15C5	0.011	0.001	-6.69 (-0.17)	0.28	0.10d
	B15C5	0.018	0.001	-7.84 (-0.20)	0.33	0.078d
	18C6	0.013	0.001	-4.54 (-0.11)	0.19	0.056d
	B18C6	0.011	0.001	-6.33 (-0.16)	0.27	0.074d
NBe	15C5	0.0016		-2.44 (-0.082)		0.12
	B15C5	0.027, 0.028		-2.99 (-0.076), -2.81 (-0.072)		0.024
	18C6	0.0029		-1.68 (-0.043)		0.15
	B18C6	0.018		-2.51 (-0.064)		0.098
DCEe	15C5	0.025		-4.12 (-0.10)		0.11
	15C5f	0.0105	0.0008	-3.24 (-0.083)	0.07	
	B15C5	0.019		-3.70 (-0.095)		0.14
	18C6	0.044		-5.72 (-0.14)		
	18C6f	0.0171	0.0009	-4.12 (-0.11)	0.05	0.022
	B18C6	0.036		-3.92 (-0.10)		0.078

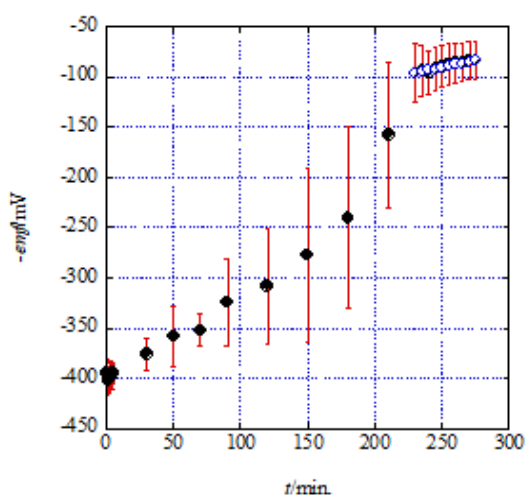
### On features of the membrane transport systems

Figure 1 and Figure 2 show  $-emf$  vs  $t$  plots being the basis of the above actual plots. The  $|emf|$  values of the DCM system were stabilized in a short time, while those of  $oDCBz$  were done in the longer time. Also, the former system is superior to the latter one about the reproducibility of  $emf$  see the error bars of  $-emf$  in Figures 1 and 2. On the other hand, the  $emf$  or  $f-emf$  plots for the NB and DCE systems have monotonically increased with  $t$  [1]. The thus-determined  $k$  and  $f\Delta E'$  values are listed in Table 1, together with the same ones [1] reported before for the NB and DCE systems. <sup>a</sup>Materials of the bulk liquid membranes <sup>b</sup>Standard error, <sup>c</sup>Values determined at 298 K from extraction experiments [7-9]. <sup>d</sup>Values re-calculated from the reported extraction data.

The  $k$  values determined from the cell (1) for DCE were the same as those reported before in order, while their  $f\Delta E'$  ( $=\ln K_D'$ ) values were different from the reported ones [1] (Table 1). We cannot now understand that the latter finding is caused by whether the 3 mol/L NaCl phase is present or not between Ag|AgCl and 0.05 mol/L TBACl [1] in both cells.



**Figure 1:** Plots of  $-emf$  vs.  $t$  for the DCM system with NaPic and B15C5. Full and open squares show experimental and calculated values, respectively.



**Figure 2:** Plots of  $-emf$  vs  $t$  for the DCM system with NaPic and B15C5. Full and open squares show experimental and calculated values, respectively.

The  $k$  values were in the orders:

$L=B18C6 < 15C5 < 18C6 < B15C5$  for the DCM systems,  $15C5 = B18C6 \leq 18C6 < B15C5$  for  $oDCBz$ ,  $15C5 \leq 18C6 < B18C6 < B15C5$  for NB [1], and  $B15C5 \approx 15C5 < B18C6 \approx 18C6$  for DCE [1].

For the DCE system, their values depend on the ring size of L. Also, the dependence on the L's hydrophobicity for the NB system has been reported [1]. There is no such dependence for the DCM and  $oDCBz$  systems, although the orders of both the systems are similar to each other.

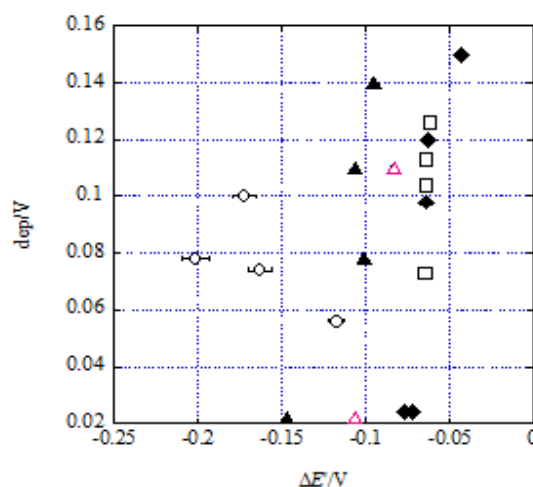
At a fixed L, the  $k$  values were in the orders:

$org=NB \leq DCM < oDCBz < DCE$  for  $L=15C5$ ,  $DCM < oDCBz \leq DCE \leq NB$  for  $B15C5$ ,  $NB < DCM < oDCBz < DCE$  for  $18C6$ , and  $DCM < oDCBz < NB < DCE$  for  $B18C6$ .

The order for  $15C5$  was almost the same as that for  $18C6$ . The order for  $B15C5$  was also similar to that for  $B18C6$ . The findings of the benzo derivatives might suggest a good affinity between the NB molecules and the benzo groups of L. Additionally, the orders are independent of those in distribution properties,  $K_{D,L}=[L]_{org}/[L]$  (Table 2), of the free Ls [7-9,11]: as an example, the  $K_{D,B15C5}$  order was  $oDCBz < NB < DCE < DCM$ . Moreover, these  $k$  orders essentially depend on the frequency factors (A) in the Arrhenius equation [6], except for the NB systems in the benzo derivatives. The average A values were in the order  $NB \leq DCM \leq oDCBz \leq DCE$ .

### Re-examination of plots of $dep$ vs. $\ln K_D'$

As similar to the plots of  $dep$  versus  $\ln K_D$  [1], the  $\Delta E'$  values were plotted against the  $dep$ ones (Figure 3). Here, the  $dep$  values for the  $oDCBz$  system were evaluated from the extraction data [7-9] previously reported by our colleagues in Table 2. The plots may hardly reflect the positive correlation [1] between them. These  $f\Delta E'$  ( $=\ln K_D'$ ) data in Table 1 indicate that the plots of  $dep$  versus  $\ln K_D'$  cannot be indirect proof of the presence of  $dep$  in the extraction system with L. In addition to this, by only Figure 3, we cannot explain whether such positive relations between  $dep$  and  $\Delta E'$  are present or not (Figure 3).



**Figure 3:** Plots of  $dep$  vs.  $\Delta E'$  for all the org systems with NaPic and L. Organic=DCM (square),  $oDCBz$  (circle), NB (full diamond), and DCE (full & open triangles). The data of the full symbols were cited from [1].

Table 2: Extraction data for NaPic with L into oDCBz at 298 K.

L	I b/mol L-1 (log KD, L)a	log K <sub>c</sub> ex	log Kex d ± (I <sub>o</sub> e DCBz /mol L-1)	log KD, P f	depg/V
B15C5-0.50	0.0044	4.198 ± 0.004 5.45h	-3.44 ± 0.58 (4.3 · 10 <sup>-7</sup> )	-4.01 ± 0.29	0.1
B15C-1.362	0.0053	3.726 ± 0.006 3.908h	-2.89 ± 0.24 (1.4 · 10 <sup>-6</sup> )	-3.59 ± 0.14	0.078
B18C6-1.13	0.0071	3.984 ± 0.007 4.432h	-1.29 ± 0.02 (4.7 · 10 <sup>-6</sup> )	-3.22 ± 0.03	0.056 ± 0.001
B18C6-1.225	0.0037	3.500 ± 0.005 3.633h	-2.74 ± 0.03 (1.1 · 10 <sup>-6</sup> )	-3.53 ± 0.04	0.074 ± 0.002

### For Contents of Emf Values

For each org system with L, the mean  $\Delta E'$  values, symbolized as  $\Delta E'_m$ , were estimated to be  $-0.064 \pm 0.001$  V (relative standard deviation: 1.5%) for the DCM system,  $-0.16 \pm 0.03$  (ca. 18%) for oDCBz,  $-0.064 \pm 0.012$  (ca. 18) for NB, and  $-0.11 \pm 0.02$  (ca. 18) for DCE. These values were in the order oDCBz  $\leq$  DCE  $<$  DCM  $\leq$  NB. This order was in accordance with that of the  $\Delta\phi_{tr}^0$  and  $-\Delta G_{tr}^0$  values for the TBA<sup>+</sup> transfer across these org/w interfaces, where the symbols  $\Delta\phi_{tr}^0$  and  $\Delta G_{tr}^0$  denote a standard ion-transfer potential and its Gibbs free energy [5,12], respectively. For example,  $\Delta\phi_{tr}^0$  ( $-\Delta G_{tr}^0$ ) at  $T=298$  K were 0.226 V (21.8 kJ/mol) for org = DCE, 0.230 (22.2) for DCM, and 0.248 (24.2) for NB [12] and it at  $T=295.3$  K for oDCBz was 0.177 V (15 kJ/mol) [13]. Especially, the plot of  $\Delta\phi_{tr}^0$  (TBA<sup>+</sup>) versus  $\Delta E'_m$  for given organic phases gave a straight line,  $\Delta\phi_{tr}^0$  (TBA<sup>+</sup>) = (0.6,  $\pm 0.1$ ) $\Delta E'_m$  + (0.28  $\pm 0.02$ ), at  $R = 0.931$

This fact supports the hypothesis that  $\Delta E'$  is a constant for a given org phase. On the other hand, there was no clear correlation with  $\Delta\phi_{tr}^0$  (or  $-\Delta G_{tr}^0$ ) for the Cl<sup>-</sup> transfer into NB, DCE, and DCM [5,12], the authors were not able to find the data corresponding to oDCBz. The above results suggest that the potential differences at the 0.05 mol/L TBACl|org interfaces are controlled by the TBA<sup>+</sup> transfer across the w/org interfaces, in other words, the TBA<sup>+</sup> distribution between phases II and III.

From Eq. (2) and Eq. (3), and the above facts, we can express the contents of mean emf ( $emf_m$ ) as follows.

$$\begin{aligned}
 -emf_m &= 0.17 + (\phi_{IV} - \phi_{III}) + (\phi_{III} - \phi_{II}) + (-0.17) \approx dep + \Delta E'_m \\
 &= 0.02569kt - 0.16 \text{ for oDCBz,} \\
 &= 0.02569kt - 0.16 \text{ for oDCBz,} \\
 +emf &= 0.30 + (\phi_{IV} - \phi_{III}) + (\phi_{III} - \phi_{II}) + (-0.30) \approx dep + \Delta E'_m \\
 &= 0.02569kt - 0.11 \text{ for DCE,} \\
 &= 0.02569kt - 0.06_4 \text{ for NB at } T = 298 \text{ K}
 \end{aligned}$$

Here, the reference electrode of Ag|AgCl|3 mol/L NaCl in the cell equation (1) was replaced simply by the Ag|AgCl electrode for the NB and DCE systems [1]. Accordingly, the electrode potential at the 0.05 mol/L TBACl|AgCl|Ag interface and 298 K was calculated to be +0.30 V from the Nernst equation [5,6].

At least, the emf values under the steady-state conditions can be estimated from the equation like  $\pm emf_m = 0.02569kt + \Delta E'_m$  at a fixed org. Representative examples for the DCM system with B15C5 and oDCBz with B18C6 are shown in Figures 1 and 2, respectively. Both the experimental  $-emf$  values were in agreement with their values, calculated from  $-emf_m = 0.02569kt + \Delta E'_m$ , in the evaluated time ranges. The same was essentially true of the other org systems with Ls.

### Another Meaning of Dep

According to the Arrhenius equation [6], one can obtain:

$$lnk = lnA - E_a / RT, \quad (5)$$

$$fdep \approx lnA - lnk \quad (6)$$

where A and  $E_a$  denote the frequency factor, as described above, and the activation energy for the reaction, respectively. This equation is usually used for indicating the T dependence of k. From the relation:

$$zFdep = RTlnK_D^F = \Delta G \quad (7)$$

with  $f = F/RT$ , we can easily derive:

$$zFdep = RTlnK_D^F = \Delta G \quad (8)$$

and then obtain:

$$fdep \approx lnA - lnk \quad (9)$$

Therefore, substituting  $E_a$  by  $\Delta G^+$  and then rearranging it, the following equation is obtained:

$$fdep \approx lnA - lnk \quad (10)$$

Figure 4 shows the plots of  $fdep$  versus  $lnk$  based on Eq. (6). The plots for the NB, DCE, and oDCBz systems seem to show negative correlations between  $lnk$  and  $fdep$ . Obtained values for the slope and the  $lnA$  were  $-1.41 \pm 0.50$  and  $-3.3 \pm 2.4$  at  $R = 0.85$  for the NB system,  $-0.80 \pm 0.89$  and  $0.1 \pm 3.8$  at 0.54 for DCE, and  $-1.0 \pm 10.6$  and  $-0.9 \pm 2.4$  at 0.26 for oDCBz, respectively. For the DCM system, the plot was analyzed with the fixed slope of  $-1$ : the  $lnA$  value was  $-1.29 \pm 0.46$  at  $R = 0.36$ . Although the R values were very low, the obtained slopes included  $-1$  within their experimental errors. Experimental slope ranges were  $-0.9$  to  $-1.9$  for NB,  $0.0$  to  $-1.7$  for DCE, and  $-12$  to  $+10$  for oDCBz. These results indicate that the  $dep$  value can be comparable to a measure about a barrier for the ion transfer across the w/org interfaces, although the oDCBz system shows a larger experimental error in its slope.

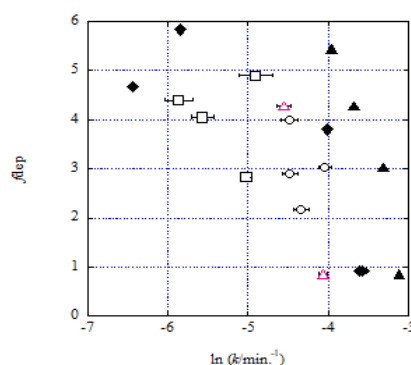


Figure 4: Plots of  $fdep$  vs.  $lnk$  for all the org systems with NaPic and L. Org=DCM (square), oDCBz (circle), NB (full diamond), and DCE (full & open triangles). The data of the full symbols were cited from [1].

## CONCLUSION

The following two points were mainly changed here, compared with the previous study:

1. The apparent distribution parameter  $\ln K_D'$  was changed into  $zf\Delta E'$ . This change cancels the correlation between  $\text{dep}$  and  $K_D'$  and thereby the presence of  $\text{dep}$  in the liquid membrane transports became uncertain.
2. The relation of  $\ln K_D^F (= \ln (K_D/K_D^S)) = kt$  was postulated instead of that of  $\ln K_D = kt$ . This treatment changed the model to the simpler one. So, this makes the understanding of the transport phenomena easier, and then the understanding of the emf measurements, based on Eq. (3), was improved.

By using the modified Arrhenius equation (6), a new interpretation of  $\text{dep}$  was proposed here. That is, it is that  $\text{dep}$  means the barrier, such as the activation energy, about the distribution of ions from water into org phases. It will be necessary to improve their R values of the plots based on Eq. (6). Also, the  $\Delta \phi_{tr}^0$  (TBA<sup>+</sup>) dependence of  $\Delta E'_m$  and the reproduction of the  $\pm$  emf values with Eq. (3a) indicated that the TBA<sup>+</sup> transfer across the water/org interfaces generates the potential differences between the II (or water) and III (org) phases.

## REFERENCES

1. Kudo Y, Suzuki Y. Potentiometric study of liquid membrane transports of ionic Na(I) species with some crown ethers into nitrobenzene and 1,2-dichloroethane. *J Anal Pharm*. 2018;7:375-381.
2. Kazemabad M, Verliefe A, Cornelissen ER, D'Haese A. Crown ether containing polyelectrolyte multilayer membranes for lithium recovery. *J Membr Sci*. 2020;595:432-442.
3. Bibi N, Rehman HU, Kahn K, Kanwal A, Gul R, Ali K. Extraction and facilitated transport of cd(ii) ions across triethylenediamine-carbon tetrachloride supported liquid membrane. *J Membr Sci Thech*. 2019;9:194-199.
4. Nghiem LG, Mornane P, Potter ID, Perera JM, ChattrallRW, KolevSD. Extraction and transport of metal ions and small organic compounds using Polymer Inclusion Membranes (PIMs). *J Membr Sci*. 2006;281:7-41.
5. Kakiuchi T. Equilibrium electric potential between two immiscible electrolyte solutions in liquid-liquid interfaces: theory and methods. Edited by Volkov AG & Dramer DW, CRC Press, New York, NY. 1996;1.
6. Bard AJ, Faulkner LR. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons. 2001;19:52-88.
7. Takeda Y. Extraction of alkali metal picrate with 18-crown-6, benzo-18-crown-6, and dibenzo-18-crown-6 into various organic solvents. Elucidation of fundamental equilibria governing extraction-ability and selectivity. *Bunseki Kagaku*. 2002;51:515-525.
8. Takeda Y, Hatai S, Hayakawa H, Ono Y, Yahata T, Endō K, et al. Solvent effects on extraction of alkali metal picrates with 15-crown-5 into various organic solvents. *Talanta*. 1998;47:67-75.
9. Takeda Y, Hashimoto K, Yoshiyama D, Katsuta S. Extraction of alkali metal (Li, Na, K) picrates with benzo-15-crown-5 into various organic solvents. Elucidation of fundamental equilibria determining extraction-ability and selectivity. *J Incl Phenom Macrocycl Chem*. 2002;42:313-321.
10. Kudo Y, Katsuta S. On an expression of extraction constants without interfacial equilibrium-potential differences for the extraction of univalent and divalent metal picrates by crown ether into 1,2-dichloroethane and nitrobenzene. *Amer J Anal Chem*. 2015;6:350-363.
11. Kudo Y, Amano T, Ikeda S. Determination of distribution equilibrium-potential differences based on extraction with several crown ethers by nitrobenzene, 1,2-dichloroethane and dichloromethane. *Int J Chem*. 2017;9:110-123.
12. Markin VS, Volkov AG. The Gibbs free energy of ion transfer between two immiscible liquids. *Electrochim Acta*. 1989;34:93-107.
13. Hundhammer B, Müller C. Ion transfer across the water-o-dichlorobenzene interface. *J Electroanal Chem*. 1991;319:125-135.
14. Kudo Y. On Two Kinds of Equilibrium Constants in an Extraction System: Does an Interfacial Equilibrium Potential Control the Equilibrium Constants. *J Anal Pharm Res*. 2016;3:78-80.