

## Research Article

# Extraction of Sodium Picrate by 3*m*-Crown-*m* Ethers and Their Monobenzo Derivatives (*m* = 5, 6) into Benzene: Estimation of Their Equilibrium-Potential Differences at the Less-Polar Diluent/Water Interface by an Extraction Method

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Individual distribution constants ( $K_{D,A}$ ) of picrate ion ( $\text{Pic}^-$ ) and extraction constants ( $K_{\text{ext}}$ ) of NaPic by some crown ethers (L) into benzene (Bz) at 25°C were calculated from data reported previously. These constants were defined as  $K_{D,\text{Pic}} = [\text{Pic}^-]_o/[\text{Pic}^-]$  and  $K_{\text{ext}} = [\text{NaL}^+]_o[\text{Pic}^-]_o/([\text{Na}^+][\text{L}]_o[\text{Pic}^-])$ , respectively. Here, the subscript “o” denotes an organic (o) phase and practically o = Bz. 15-Crown-5 ether (15C5), 18-crown-6 one (18C6), and their monobenzo (B) derivatives (B15C5 and B18C6) were selected as L. Interfacial equilibrium-potential differences ( $\Delta\phi_{\text{eq}}$ ) at extraction were estimated at 298 K. A plot of  $\log K_{\text{ext}}$  versus  $-\Delta\phi_{\text{eq}}$  for the four L extraction systems gave a straight line with slope = 84 V<sup>-1</sup>. This slope was compared with those, reported before, of the dichloromethane (DCM), 1,2-dichloroethane (DCE), and nitrobenzene (NB) extraction systems. The slopes of the regression lines were in the order NB < DCM ≤ DCE < Bz. Also, the individual distribution constants of the complex ion  $\text{NaL}^+$  and an ion-pair complex ( $\text{NaL}^+\text{Pic}^-$ ) into Bz phase were calculated from the above extraction data. At least, a comparison between these values suggests that Bz molecules mainly interact with  $\text{NaL}^+$  moiety of  $\text{NaL}^+\text{Pic}^-$ .

## 1. Introduction

A presence of interfacial equilibrium-potential differences ( $\Delta\phi_{\text{eq}}$ ) at extraction processes with polar diluents, such as dichloromethane (DCM), 1,2-dichloroethane (DCE), and nitrobenzene (NB), has been clarified [1, 2]. For example, crown compounds (L) extract silver picrate into DCE [1, 2] or alkaline-earth metal (Ca-Ba) picrates [1] into NB. In these studies [1, 2], an individual distribution constant ( $K_{D,A}$ ) of a pairing anion ( $A^-$ ), such as picrate ion ( $\text{Pic}^-$ ), has been determined in the course of  $K_{\text{ex}}$  determination. Here,  $K_{D,A}$  and  $K_{\text{ex}}$  have been defined as  $[A^-]_o/[A^-]$  and  $[\text{MLA}_z]_o/P$  with  $P = [M^{z+}][L]_o[A^-]^z$ , respectively; the symbols  $\text{MLA}_z$ ,  $M^{z+}$  and the subscript “o” denote an ion-pair complex, a metal ion with the formal charge  $z$  ( $= 1, 2$ ), and an organic (o) phase, respectively. The  $\Delta\phi_{\text{eq}}$  values have been determined by using the experimental  $K_{D,A}$  values and the electrochemical equation of  $\log K_{D,A} = -(F/2.303RT)(\Delta\phi_{\text{eq}} - \Delta\phi_A^{0'})$  [1],

where  $\Delta\phi_A^{0'}$  refers to a standard formal potential for an  $A^-$  transfer across the o/water (w) interface and  $F$ ,  $R$ , and  $T$  have usual meanings. Thus the presence of  $\Delta\phi_{\text{eq}}$  at the polar diluent/w interfaces has been examined and proved experimentally [1, 2]. Also,  $\Delta\phi_{\text{eq}}$  presence had been already described in the distribution study of protonated amino acids into NB [3]. However, the presence of  $\Delta\phi_{\text{eq}}$  has not been clearly considered for the extraction of simple salts into NB [4], that of metal salts by extractants, such as calix[4]arene and dibenzo-24-crown-8 ether derivative, into NB [5] or DCE [6], and that of  $\text{R}_4\text{N}^+\text{A}^-$  into DCE [7] in the field of extraction chemistry and for electrochemical extraction studies [8–10] at the liquid/liquid interfaces. Besides, the presence of  $\Delta\phi_{\text{eq}}$  at less-polar diluent/w interfaces has not been clarified so far. Its cause seems to be the lower concentrations of ions present in the less-polar diluents, compared with their concentrations in the polar diluents. Additionally, the correlation between the extraction chemistry and the electrochemistry at the

TABLE 1: Extraction data of the NaPic systems with L into Bz at 25°C.

L	$\log K_{D,A}^a$ ( $\Delta\phi_{eq}/V$ ) <sup>b</sup>	$\log K_{ex\pm}^c$ ( $I$ ) <sup>d</sup>	$\log K_{ex}^{a,c}$	$\log K_{1,Bz}^e$ ( $I_{Bz}$ ) <sup>d</sup>	$\log K_{D,NaL}^f$ ( $\Delta\phi_{NaL}^{0'}/V$ ) <sup>g</sup>
15C5	$-4.11 \pm 0.27$ (-0.24)	$-3.14 \pm 0.22,$ $-4.11 \pm 0.38^h$ (0.0060)	$3.909 \pm 0.007^a,$ $3.889 \pm 0.008^c,$ 4.67 [12–15]	$7.0 \pm 0.2$ ( $3.5 \times 10^{-7}$ )	$-1.51 \pm 0.38,$ $-1.3^i$ (-0.15)
B15C5	$-4.7 \pm 3.4$ (-0.21)	$-5.99 \pm 6.7,$ $-6.50 \pm 0.39^h$ (0.023)	$3.178 \pm 0.008^a,$ $3.18 \pm 0.01^c,$ 3.378 [12–15]	$9.7 \pm 0.4^j$ ( $1.3 \times 10^{-7}$ )	$-1.13 \pm 0.39,$ $-0.6^i$ (-0.1)
18C6	$-4.21 \pm 0.16$ (-0.24)	$-3.18 \pm 0.31,$ $-3.73 \pm 0.23^h$ (0.010)	$3.45 \pm 0.02^a,$ $3.40 \pm 0.03^c,$ 3.84 [12–15]	$6.6 \pm 0.3$ ( $5.3 \times 10^{-7}$ )	$-1.55 \pm 0.24,$ $-1.6^i$ (-0.14)
B18C6	$-5.2 \pm 3.7$ (-0.18)	$-7.8 \pm 15.5,$ $-8.03 \pm 0.38^h$ (0.010)	$3.062 \pm 0.002^a,$ $3.060 \pm 0.004^c,$ 3.162 [12–15]	$11.1 \pm 0.4^j$ ( $2.4 \times 10^{-8}$ )	$-2.73 \pm 0.38,$ $-2.7^i$ (-0.0)

<sup>a</sup>Values obtained from the analyses of the  $\log K_{ex}^{mix}$  versus  $-\log([Na^+][L]_{Bz})$  plots. <sup>b</sup>See the text for the evaluation. <sup>c</sup>Values obtained from the analyses of the  $\log K_{ex}^{mix}$  versus  $-(1/2)\log P$  plots. <sup>d</sup>Mean values of ionic strength for the w or the Bz phase. <sup>e</sup>Values calculated from the thermodynamic relation,  $\log K_{1,Bz} = \log K_{ex}^a - \log K_{ex\pm}^c$ . <sup>f</sup>Mean values calculated from the relation,  $K_{D,ML} \approx I_{Bz}K_{D,L}/K_{ML}[M^+][L]_{Bz}$ . <sup>g</sup>Mean values calculated from the relation,  $\Delta\phi_{ML}^{0'} = \Delta\phi_{eq} - 0.05916 \log K_{D,ML}$  at 25°C. <sup>h</sup>Mean values calculated from the relation,  $K_{ex\pm} \approx I_{Bz}^2/P$ . <sup>i</sup>Values calculated from the thermodynamic relation,  $\log K_{D,ML} = \log K_{ex\pm} + \log(K_{D,L}/K_{ML}) - \log K_{D,A}$ . <sup>j</sup>Values calculated from the values of footnote h for convenience, because the  $K_{ex\pm}$  values of footnote c showed the larger calculation errors.

liquid/liquid interfaces had not been reported, except for our studies [1–3] and a description [11] with respect to the distribution of a simple salt, such as  $Bu_4NBr$ .

In the present paper, selecting benzene (Bz) as the representative less-polar diluent, we determined from available extraction data [12–15]  $\Delta\phi_{eq}$  values at the Bz/w interface. Also, the thus-determined values at 25°C were compared with  $\Delta\phi_{eq}$  ones for the DCM, DCE, and NB extraction systems. For the comparison, 15-crown-5 ether (15C5), 18-crown-6 one (18C6), benzo-15C5 (B15C5), and B18C6 were selected as L and NaPic was done as an extract. Moreover, individual distribution constants of the ion-pair complexes  $NaL^+Pic^-$  and the complex ions ( $NaL^+$ ), which constitute parts of the complexes, into the four diluents were estimated from the above results and then their properties for solute-solvent interaction were discussed.

## 2. Experimental Section

This study was performed by reusing the extraction data [12–16] reported previously at 25°C. Also, analytic procedures were the same as those [12–16] described before. Hence, experiments for the extraction into Bz have not been newly performed here at all; see Takeda et al.’s studies [12–16] for the experimental details.

The fundamental data of  $[Na^+]$ ,  $[L]_{Bz}$ , and  $[Pic^-]$  were calculated from the extraction data in successive approximations [12–16]. In the analysis of an overall extraction equilibrium, the following component equilibria were considered [2, 16]:  $L \rightleftharpoons L_{Bz}$  (the equilibrium constant for this equilibrium:  $K_{D,L}$ ; see Section 3.5);  $Na^+ + L \rightleftharpoons NaL^+$  ( $K_{NaL}$ ; see Section 3.5);  $NaL^+ + Pic^- \rightleftharpoons NaLPic$  ( $K_1$ ; see Section 3.5);  $NaLPic \rightleftharpoons NaLPic_{Bz}$  ( $K_{D,NaLPic}$ ; see Section 3.5);  $NaLPic_{Bz} \rightleftharpoons NaL^+_{Bz} + Pic^-_{Bz}$  ( $K_{1,Bz}^{-1}$ ; see Section 3.2); and  $Na^+ + Pic^- \rightleftharpoons NaPic$ . In

addition to these equilibria, one can understand the presence of other component equilibria:  $NaL^+ \rightleftharpoons NaL^+_{Bz}$  ( $K_{D,NaL}$ ; see Section 3.2 and Table 1) and  $Pic^- \rightleftharpoons Pic^-_{Bz}$  ( $K_{D,Pic}$ ; see Section 1 and Table 1).

## 3. Results and Discussion

**3.1. Redetermination of Compositions of the Ion-Pair Complexes Extracted into Bz.** Plots [16] for redetermining a  $Na(I) : L : Pic(-I)$  composition in the four extraction systems yielded regression lines of a slope = 0.99<sub>7</sub> and an intercept = 3.89 ( $\approx \log K_{ex}$  at  $z = 1$ ) at a correlation coefficient ( $R$ ) = 0.998 for the 15C5 system, of 0.99<sub>9</sub> and 3.17 at  $R = 0.999$ , for the B15C5 one, of 0.90<sub>3</sub> and 3.04 at  $R = 0.996$  for the 18C6 one, and of 1.02 and 3.09 at  $R = 0.999$  for the B18C6 one; see  $\log(D/[Pic^-])$  versus  $\log[L]_{Bz}$  plots in Figure 1, where  $D$  denotes a distribution ratio of species with  $Na(I)$  into the Bz phase.

These slopes of about unity obviously indicate that the compositions of extracted species, mainly ion-pair complex, are  $Na(I) : L : Pic(-I) = 1 : 1 : 1$  [16]. These results were in good agreement with those [12–15] described previously.

**3.2. Determination of Extraction Constants and Their Several Component Equilibrium Constants.** The  $K_{D,A}$  and  $K_{ex}$  values at  $A = Pic(-I)$  and  $z = 1$  were determined by the plot of  $\log K_{ex}^{mix}$  versus  $-\log([Na^+][L]_{Bz})$  (Figure 2) based on the equation

$$\log K_{ex}^{mix} \approx \log \left( K_{ex} + \frac{K_{D,A}}{[Na^+][L]_{Bz}} \right), \quad (1)$$

where  $K_{ex}^{mix}$  has been defined as  $([MLA]_o + [ML^+]_o + [M^+]_o + \dots)/P$  [1, 2, 16]. Also,  $K_{ex\pm}$  values were determined by the

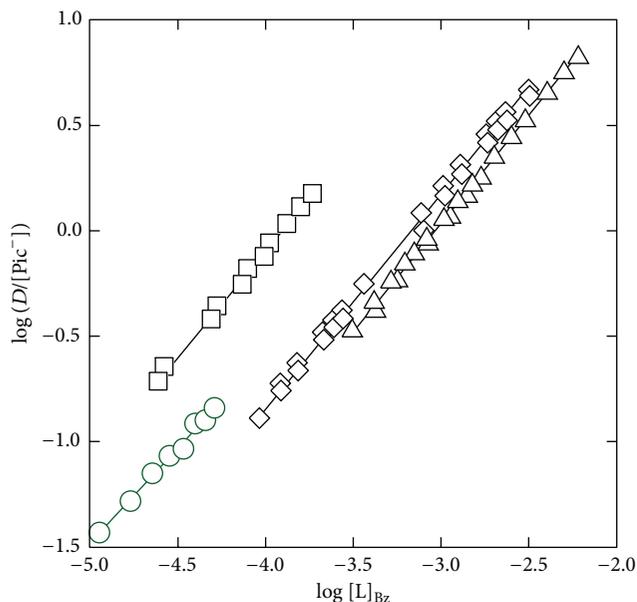


FIGURE 1: Plots of  $\log(D/[Pic^-])$  versus  $\log[L]_{Bz}$  for the 15C5 (square), B15C5 (diamond), 18C6 (circle), and B18C6 (triangle) extraction systems. See the text for regression results of the solid lines. The symbol of  $1 \text{ mol dm}^{-3} = 1 \text{ M}$  was used.

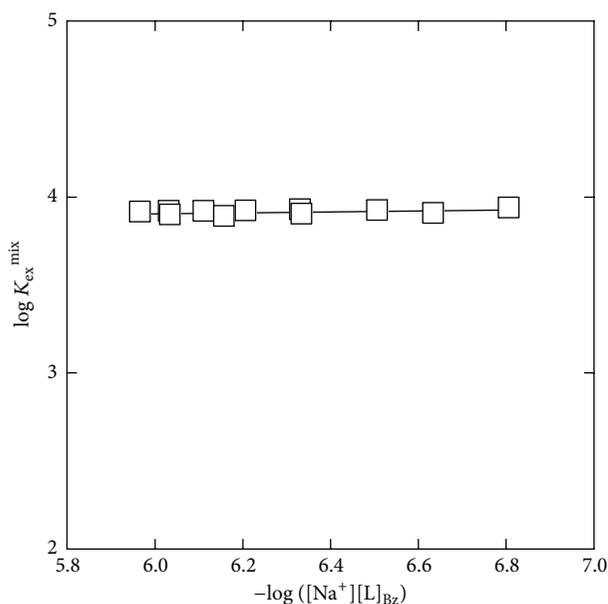


FIGURE 2: Plot of  $\log K_{ex}^{mix}$  versus  $-\log([Na^+][L]_{Bz})$  for the NaPic extraction with  $L = 15C5$ . The  $K_{D,Pic}$  and  $K_{ex}$  values obtained from a nonlinear regression analysis with (1) were  $(7.7 \pm 4.8) \times 10^{-5}$  and  $8115 \pm 133 \text{ M}^{-2}$ , respectively.

plot of  $\log K_{ex}^{mix}$  versus  $-(1/2) \log P$  (Figure 3) based on the equation

$$\log K_{ex}^{mix} \approx \log \left\{ K_{ex} + \left( \frac{K_{ex\pm}}{P} \right)^{1/2} \right\}, \quad (2)$$

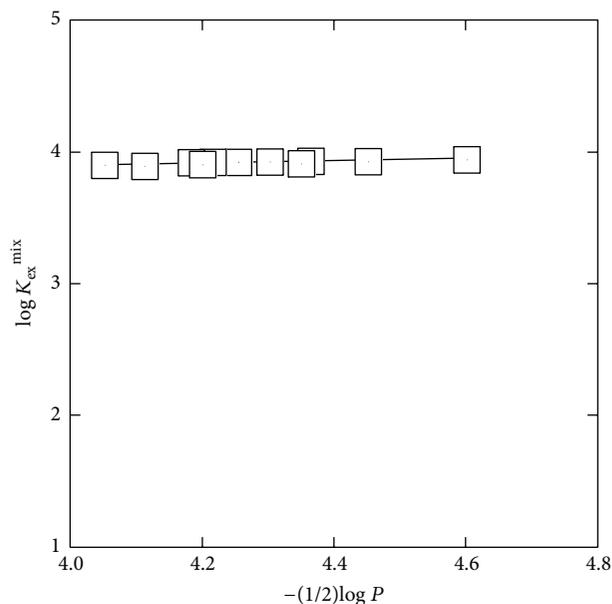


FIGURE 3: Plot of  $\log K_{ex}^{mix}$  versus  $-(1/2) \log P$  for the NaPic extraction with  $L = 15C5$ . The  $K_{ex\pm}$  and  $K_{ex}$  values were obtained to be  $(7.3 \pm 3.8) \times 10^{-4} \text{ M}^{-1}$  and  $7747 \pm 149 \text{ M}^{-2}$  from the nonlinear regression analysis with (2).

where the symbol  $K_{ex\pm}$  has been defined as  $[ML^+]_o[A^-]_o/P$  [1, 2, 6] at  $z = 1$ .

The thus-determined values at  $25^\circ\text{C}$  are listed in Table 1 (see Appendix A for reference), together with their component equilibrium constants,  $K_{D,Pic}$ ,  $K_{D,NaL}$  ( $= [NaL^+]_{Bz}/[NaL^+] [1]$ ), and  $K_{1,Bz}$  ( $= K_{ex}/K_{ex\pm} = [NaLPic]_{Bz}/[NaL^+]_{Bz}[Pic^-]_{Bz}$  [1, 2, 16]).  $K_{ex}$  values were in the order  $B18C6 < B15C5 < 18C6 < 15C5$ , although the ionic strength ( $I$ ) for the water phase of the 15C5 system is somewhat smaller than those of the other systems. This order was in accord with those [12–15] reported before (Table 1) and reflected the order of the (intercept/slope) values for the plots of  $\log(D/[Pic^-])$  versus  $\log[L]_{Bz}$  (see Section 3.1). Similarly,  $K_{ex\pm}$  values showed the order  $B18C6 \leq B15C5 < 18C6 \leq 15C5$ , although the values of the benzo derivatives have large errors. This order agreed with that of  $K_{ex}$ . These facts indicate that the present analyses are essentially valid.

3.3. On  $\Delta\phi_{eq}$  Estimation and Its Correlation with  $\log K_{ex\pm}$ . We can formally calculate the  $\Delta\phi_{eq}$  values from the relation

$$\Delta\phi_{eq} = \Delta\phi_A^{0'} - \left( \frac{2.303RT}{F} \right) \log K_{D,A} \quad (3)$$

[1, 2, 21] (see Table 1), when  $\Delta\phi_A^{0'}$  values are available. Fyles had evaluated the free energy of the  $Pic^-$  transfer from w to Bz [22]; then,  $\Delta\phi_{Pic}^{0'}$  value at the Bz/w interface was estimated from its free energy to be  $-0.486 \text{ V}$  at  $25^\circ\text{C}$ . The thus-estimated  $\Delta\phi_{eq}$  values are listed in Table 1.  $\Delta\phi_{eq}$  values were in the order  $15C5 \approx 18C6 < B15C5 \approx B18C6$ , although their experimental errors were large. Also, one can see that  $\Delta\phi_{eq}$  values for the Bz system with L are negative, indicating that

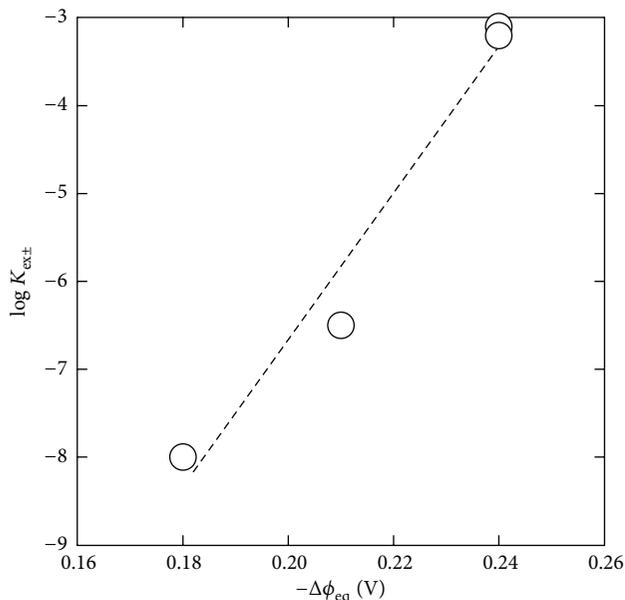


FIGURE 4: Plot of  $\log K_{ex\pm}$  versus  $-\Delta\phi_{eq}$  for the NaPic extraction with L into Bz. See the text for the regression line.

$K_{D,Pic}$  values are larger than  $K_{D,Pic}^S$  ones which are defined as  $\exp(\Delta\phi_{Pic}^{0'}/0.02569)$  [1–3] at 25°C. On the other hand, the values reported before for the DCM, DCE, and NB systems have been accidentally all positive [1, 2].

As Figure 4 shows, a plot of  $\log K_{ex\pm}$  versus  $-\Delta\phi_{eq}$  yielded the straight line:  $\log K_{ex\pm} = (84 \pm 12)(-\Delta\phi_{eq}) - (23.6 \pm 2.6)$  at  $R = 0.981$ . Similar lines were observed in NaPic extraction by L into DCM and DCE. Adding the data of NB systems, these slope values at  $\Delta\phi_{eq}$  (not  $-\Delta\phi_{eq}$ ) were in the order Bz (slope =  $-84 \text{ V}^{-1}$ ) < DCE ( $-26$ ) ≤ DCM ( $-21$ ) < NB (3). This order was close to that of dielectric constants ( $\epsilon_r$ ) [23] of the pure diluents at 298.15 K: Bz ( $\epsilon_r = 2.27$ ) < DCM (8.93) < DCE (10.23) < NB (34.82), although these diluents were saturated with water. These results can be explained in terms of a model like a parallel-plate capacitor at the diluent/w interface [24]. Namely, its capacitance ( $C$ ) is expressed as the following equation [24]:

$$C = \frac{q}{E} \approx \epsilon_r \frac{S}{d}. \quad (4)$$

Here, the symbols  $q$ ,  $E$ ,  $S$ , and  $d$  refer to a charge stored on the capacitor, a potential across the capacitor, an area of the plate, and an interplate spacing, respectively [24].

So assuming that the slopes in  $\text{V}^{-1}$  of  $\log K_{ex\pm}$  versus  $-\Delta\phi_{eq}$  plots correspond to  $C$  terms, then their values have to be proportional to  $\epsilon_r$  ones under the condition of a fixed  $S/d$  in (4). The symbol  $S$  can be considered to be the area of the o/w interface and  $S$  value corresponding to its area in test tubes which had been used for the extraction experiments into the four diluents was estimated to be  $2.4 \text{ cm}^2$  from their mean inner diameter ( $=1.75_0 \text{ cm}$ ). A plot of slope versus  $\epsilon_r$  showed a positive correlation. From this fact, as an example, it can be considered that  $d$  value for Bz is smaller than those

for others. Unfortunately, we have no experimental ground with respect to this consideration.

**3.4. On Some Tendencies of the  $K_{D,Pic}$  and  $K_{1,Bz}$  Values.** The experimental  $\log K_{D,Pic}$  values of the Bz systems agreed with each other within experimental errors among L listed in Table 1. At least, the values for L = 15C5 and 18C6 were much larger than  $\log K_{D,Pic}^S$  one ( $= -8.208$  [22] =  $\Delta\phi_{Pic}^{0'}/0.05916$  at 25°C) without L. This fact indicates that the presence of L, namely, the distribution of  $\text{NaL}^+$ , in the extraction largely facilitates  $\text{Pic}^-$  transfer at Bz/w interfaces.

A plot of  $\log(I_{Bz}/I)$  ( $= y$ ) versus  $\log K_{D,Pic}$  ( $= x$ ) gave a straight line with a slope of  $1.45 \pm 0.23$  and an intercept of  $1.7 \pm 1.1$  at  $R = 0.975$ . Although the slope value is larger than unity, this linear relation is similar to those reported before for the extraction systems of  $\text{CdPic}_2$  [21] and  $\text{PbPic}_2$  [25] with 18C6 into various diluents containing Bz. Such a similarity also suggests that the present analysis is valid.

$\log K_{1,Bz}$  values were in the order L = 18C6 ≤ 15C5 < B15C5 < B18C6 (Table 1). This order is close to 18C6 < 15C5, B18C6 < B15C5, which was predicted from a combined parameter,  $B + M' + V$ , of basicity of the donor O atoms (parameter:  $B$ ), selectivity of L against  $\text{Na}^+$  ( $M'$ ) with a molecular volume ( $V$ ); see Table 3 and Appendix B for the parameters. Also, an addition of a benzo group to the ring skeletons is causing an increase in  $K_{1,Bz}$ : 15C5 < B15C5 and 18C6 < B18C6. That is, its addition which spontaneously changes the parameters  $B$ ,  $S$ , and  $V$  of L (see Table 3 and Appendix B for  $S$ ) has a positive effect on  $K_{1,Bz}$ .

$K_{1,Bz}$  value at L = 15C5 was larger than  $K_{1,DCE}$ ,  $K_{1,DCM}$ , and  $K_{1,NB}$  ones;  $K_{1,DCM} = 10^{6.2} \text{ M}^{-1}$  at average  $I_{DCM} = 3.0 \times 10^{-6} \text{ M}$ ,  $K_{1,DCE} = 10^{6.5}$  at  $1.7 \times 10^{-6}$ , and  $K_{1,NB} = 10^{5.3}$  at  $3.1 \times 10^{-6}$ . Also, the same is true for  $K_{1,org}$  values for the other L. These facts indicate that although  $\text{NaL}^+\text{Pic}^-$  in Bz phases are less dissociable than those in DCM, DCE, and NB phases, the ions are present even in Bz phases. In other words, it suggests that the occurrence of  $\Delta\phi_{eq}$  is possible at Bz/w interface.

**3.5. On the Distribution of  $\text{NaL}^+$  and  $\text{NaL}^+\text{Pic}^-$  into Bz.** The following relation can be used for  $K_{D,NaL}^S$  evaluation:

$$\log K_{D,ML}^S = \log K_{D,ML} - \frac{\Delta\phi_{eq}}{0.05916} \quad \text{at } 25^\circ\text{C} \quad (5)$$

[1, 3] and the symbol  $K_{D,NaL}^S$  denotes the distribution constant,  $K_{D,NaL}$ , of  $\text{NaL}^+$  into the Bz phase at  $\Delta\phi_{eq} = 0 \text{ V}$ . As can be seen from Table 2 (see the values of footnote d and Appendix A for reference),  $\log K_{D,NaL}^S$  values were in the orders DCE < DCM < NB < Bz for L = 15C5, DCE < DCM < Bz < NB for B15C5, NB < DCM < DCE < Bz for 18C6, and DCM < Bz < DCE < NB for B18C6. These orders indicate that the addition of the benzo group to the ring skeleton causes an increase in an interaction between  $\text{NaL}^+$  and NB molecules.

The larger  $K_{D,NaL}^S$  values for Bz systems (Table 2) do not necessarily show surprising results. Consider  $K_{D,NaL}^S$  value, using the thermodynamic relation,  $\log K_{D,ML}^S = \log K_{ex\pm} + \log(K_{D,L}/K_{ML}) - \log K_{D,A}^S$ . Here,  $K_{D,L}$  and  $K_{ML}$  refer to the

TABLE 2: Individual distribution constants of  $\text{NaL}^+$  and  $\text{NaL}^+\text{Pic}^-$  into some diluents at 25°C.

(a)				
L	$\log K_{\text{D,NaL}}^{\text{S}^{\text{a}}} (\log K_{\text{D,NaL}})^{\text{b}}$			
	o = Bz	DCM	DCE	NB
15C5	2.6 (-1.5)	-1.14 (1.0)	-1.54 (0.3)	0.0, -0.3 <sup>d</sup> , 0.62 <sup>e</sup> (1.7)
B15C5	2 (-1.1)	-0.34 (2.3)	-0.54 (2)	2.2, 3.7 <sup>d</sup> , 2.1 <sup>e</sup> (4.1)
18C6	2.4 (-1.6)	-0.44 (0.77)	0.47 (0.84)	-0.3, -1.4 <sup>d</sup> , 0.7 <sup>e</sup> (1.1)
B18C6	0.3 (-2.7)	0.19 (2.62)	1.16 (2.47)	1.5, 2.0 <sup>d</sup> , 2.1 <sup>f</sup> , (3.7)
Without L	— <sup>g</sup>	-5.73 <sup>h</sup>	-6.09 <sup>i</sup> , -4.38 [17]	-5.18 <sup>i</sup> , -5.95 [17]
(b)				
L	$\log K_{\text{D,NaLPic}}$			
	Bz	DCM <sup>c</sup>	DCE <sup>c</sup>	NB <sup>c</sup>
15C5	0.94	2.87	2.47	3.82
B15C5	1.29 (1.42 [13])	3.01 (3.13 [13])	2.61 (2.73 [13])	3.75
18C6	-0.26	1.88	1.16	3.68
B18C6	0.48 (1.18 [13, 15])	2.47 (3.36 [13, 15])	2.06 (2.97 [13, 15])	3.71
Without L				

<sup>a</sup>Standard values calculated from the thermodynamic relation,  $\log K_{\text{D,ML}}^{\text{S}} = \log K_{\text{ex}\pm} + \log(K_{\text{D,L}}/K_{\text{ML}}) - \log K_{\text{D,A}}^{\text{S}}$ . <sup>b</sup>See footnote f in Table 1. <sup>c</sup>Unpublished data by Kudo. <sup>d</sup>Standard values calculated from (5). <sup>e</sup>Values determined by ion-transfer polarographic measurements at the presence of 0.05 M  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{B}(\text{C}_6\text{H}_5)_4^-$  in the NB phase. See [18]. <sup>f</sup>Values determined by the ion-transfer polarographic measurements at the presence of 0.05 M  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{B}(\text{C}_6\text{H}_5)_4^-$  in the NB phase. See [19]. <sup>g</sup>Not determined. <sup>h</sup>The values are a logarithmic individual distribution-constant of a single Na(I) ion into the DCM, DCE, or NB phase and are standardized at  $\Delta\phi_{\text{eq}} = 0$  V. <sup>i</sup>See [20] and footnote h.

TABLE 3: A measure of basic parameters for a comparison between Ls.

L	Cavity size (parameter: C)	Molecular volume (V)	Number of donor O atoms (N)	Basicity of donor O atoms (B)	Softness of ring skeleton (S)	$\text{Na}^+$ selectivity (M')
15C5	1	0	5	2	2	2
B15C5	1	2	5	1	1	2
18C6	2	1	6	2	2	0
B18C6	2	3	6	1	1	0
DB18C6	2	4	6	0	0	0

distribution constant ( $=[\text{L}]_0/[\text{L}]$ ) of L into the o phase and a complex formation one ( $=[\text{ML}^+]/[\text{M}^+][\text{L}]$ ) of  $\text{M}^+$  with L in water, respectively.

Comparing Bz system with NB one at L = 15C5, for example, a difference between  $\log K_{\text{ex}\pm, \text{Bz}}$  and  $\log K_{\text{ex}\pm, \text{NB}}$  was  $-5.2_7$   $\{= \log(K_{\text{ex}\pm, \text{Bz}}/K_{\text{ex}\pm, \text{NB}}) = -3.9_1 - 1.3_6\}$ . Similarly,  $\log\{K_{\text{D,15C5}}(\text{Bz})/K_{\text{D,15C5}}(\text{NB})\}$  and  $-\log\{K_{\text{D,Pic}}^{\text{S}}(\text{Bz})/K_{\text{D,Pic}}^{\text{S}}(\text{NB})\}$  were  $-0.15$   $\{= -0.81$  [12]  $- (-0.66$  [18]) $\}$  and  $+8.25_8$   $\{= -(-8.208 - 0.05$  [20]) $\}$ , respectively. Therefore,  $\log\{K_{\text{D,NaL}}^{\text{S}}(\text{Bz})/K_{\text{D,NaL}}^{\text{S}}(\text{NB})\}$  value becomes  $2.8_3$ . From such handling, we can see that the difference ( $= +8.26$ ) in  $\log K_{\text{D,Pic}}^{\text{S}}$  between these diluents greatly contributes the positive difference ( $=2.8$ ) in  $\log K_{\text{D,NaL}}^{\text{S}}$  between them. Also, the same is true for other Ls systems with Bz. The same explanation holds in comparison with DCM or DCE system because  $\log K_{\text{D,Pic}}^{\text{S}}$  values have been reported to be  $-1.01_1$  [20] for DCE and  $-0.68$  [23] for DCM. In other words, accuracy of  $K_{\text{D,Pic}}^{\text{S}}$  value for Bz system can become important for the discussion of the above larger  $K_{\text{D,NaL}}^{\text{S}}$  values; Fyles had

estimated  $\log K_{\text{D,NaL}}^{\text{S}}$  value for DCM at  $-0.44$  [22], compared to  $-0.68$  [23].

On the other hand, the orders of the actual  $K_{\text{D,NaL}}$  values, the values at  $\Delta\phi_{\text{eq}} \neq 0$ , were  $\text{Bz} < \text{DCM} < \text{DCE} < \text{NB}$  for L = 18C6 and  $\text{Bz} < \text{DCE} < \text{DCM} < \text{NB}$  for the other three (Table 2). Also, the  $\log K_{\text{D,NaLPic}}$  ( $=\log K_{\text{D,NaLPic}}^{\text{S}}$  in practice [1]) orders were  $\text{Bz} < \text{DCE} < \text{DCM} < \text{NB}$  for all the Ls employed. Here, the thermodynamic relation  $\log K_{\text{D,MLA}} = \log K_{\text{ex}} + \log(K_{\text{D,L}}/K_{\text{ML}}) - \log K_1$ , was used for the calculation [12–16] and the symbol  $K_1$  denotes the ion-pair formation constant in  $\text{M}^{-1}$  for  $\text{ML}^+\text{A}^-$  in water. The orders of  $K_{\text{D,NaLPic}}$  determined in the benzo derivatives systems were in agreement with the corresponding orders [13, 15] reported before. This agreement shows a validity of such  $K_{\text{D,NaLPic}}$  evaluations. For 15C5 and 18C6 systems,  $\log K_{\text{D,NaLPic}}$  values were not cited here because of limitations [26] of their analytic procedures. Both orders of  $K_{\text{D,NaL}}$  and  $K_{\text{D,NaLPic}}$  essentially agreed with each other (see Table 2). These facts suggest that an interaction of the diluent molecules with  $\text{NaL}^+\text{Pic}^-$  is fundamentally similar to that with  $\text{NaL}^+$ . Again, its main interaction with

Bz molecules occurs around  $\text{NaL}^+$  moiety of the ion-pair complex.

#### 4. Conclusions

The compositions of the ion-pair complexes,  $\text{NaLPic}$ , extracted into the Bz phases were clarified again and their few dissociations were shown from the magnitudes of  $\log K_{1,\text{Bz}}$  values. The  $\Delta\phi_{\text{eq}}$  values at the Bz/w interfaces were easily calculated from the experimentally obtained  $\log K_{\text{D,Pic}}$  values. Namely, the presence of  $\Delta\phi_{\text{eq}}$  at a less-polar diluent/w interface was clarified, as well as those at the polar diluents/w interfaces. Also,  $\log K_{\text{ex}\pm}$  values for the  $\text{NaPic}$  extraction with L into Bz were proportional to the  $-\Delta\phi_{\text{eq}}$  ones and the slope of its regression line was about  $84 \text{ V}^{-1}$ . The order of the slopes is  $\text{NB} < \text{DCM} \leq \text{DCE} < \text{Bz}$ , although its meaning is not still clear. Besides, by comparing the actual  $K_{\text{D,NaL}}$  with  $K_{\text{D,NaLPic}}$  values, it was suggested that the main interaction site of Bz molecules with  $\text{NaL}^+\text{Pic}^-$  is  $\text{NaL}^+$  moiety in their ion pairs. The authors hope that the present study will become a topic which connects the extraction chemistry with the electrochemistry at the o/w interfaces.

#### Appendix

##### A. Check of the Employed Data by Benford's Law

As reference, Benford's law [27] was checked on data of 228 in Tables 1 and 2 and the text. These results were 49 frequencies (21%) for Figure 1, 52 (23%) for Figure 2, 51 (22%) for Figure 3, 19 (8.3%) for Figure 4, 10 (4.4%) for Figures 5 and 6, 9 (3.9%) for Figure 7, 16 (7.0%) for Figure 8, and 12 (5.3%) for Figure 9. On the other hand, the theoretically calculated rates are 30% for Figure 1, 18% for Figure 2, 12% for Figure 3, 10% for Figure 4, 8% for Figure 5, 7% for Figure 6, 6% for Figure 7, and 5% for Figures 8 and 9 [27]. Although the rate of Figure 1 (or Figure 3) was somewhat smaller (or larger) than the calculated rate of the corresponding figure, we can see that the law was roughly satisfied in our data determined and cited here. Consequently, the above analysis shows that the data are not being falsified knowingly.

##### B. Empirical Parameters Which Express L's Characteristics with Their Exchanges

For example, changing L from 15C5 to B15C5 simultaneously causes changes among their molecular volumes, the basicity of the donor oxygen atoms, and ring flexibilities of L. Namely, in the comparison between these Ls, the three parameters vary at least. Such conditions can hold on the comparisons between other Ls. So we classified the conditions for some Ls in the following table. Here, these figures in Table 3 are empirical values in many cases. Accordingly, only the relative order expressed by the figures is important for the discussion in the text (see Section 3.4). These orders were essentially based on data available in references: estimated cavity sizes [28] of L for C, the molar volumes [12–15] for V, group electronegativities ( $\chi$ ) of  $-\text{OCH}_3$  ( $\chi = 2.68$  [29]) and  $-\text{OC}_6\text{H}_5$  (2.65, evaluated

here from the procedure in [25]) for B, ratio between the  $\text{Na}^+$  radius [30] and the cavity size [28] of L for  $M'$ , and the presence or absence of benzo groups for S.

Assuming the additivity among the figures for a given phase (except for the w phase), we can easily obtain various orders for properties of L from Table 3. For example, the sums between the parameters C and S were 3 (=1 + 2) for L = 15C5, 2 (=1 + 1) for B15C5, 4 (=2 + 2) for 18C6, 3 (=2 + 1) for B18C6, and 2 (=2 + 0) for DB18C6. This estimate suggests the order in the L's flexibility: B15C5, DB18C6 < 15C5, B18C6 < 18C6. Also, an ion-pair formation ability in the o phase,  $B + M' + V$ , was in the order 18C6 (sum = 3) < 15C5, B18C6, DB18C6 (4) < B15C5 (5). Besides, a bonding-ability with the complex formation for  $\text{NaL}^+$  in the o phase,  $C + N + S$ , was B15C5 (7) < 15C5, DB18C6 (8) < B18C6 (9) < 18C6 (10); a shielding effect of L for  $\text{Na}^+$ ,  $B + M'$ , was DB18C6 (0) < B18C6 (1) < 18C6 (2) < B15C5 (3) < 15C5 (4). Particularly, these combined parameters can be effective for a prediction of the order of  $K_{1,\text{org}}$  (see the text) or  $K_{\text{ML,org}}$  (complex formation constant in a  $M^{-1}$  unit). As the case may be, Table 3 should be improved step by step.

In addition to the above estimation based on the combined parameters, Table 3 can be employed as follows. Consider a comparison of L = 15C5 with 18C6. Comparing the rows of two Ls, one can see that changing from 15C5 to 18C6 means changes of the four parameters C, V, N, and  $M'$  at least. That is, one can understand immediately parameters which are changed by the exchange of L. Such comparisons with changes in some parameters make an explanation of differences in properties between Ls more difficult. However, we believe that such an idea is useful for considering the essence of the exchanges of L.

#### Competing Interests

The authors do not have any possible conflict of interests with any trademarks mentioned in the paper. Of course, they do not receive any financial gains from any companies at all.

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