

Brief Determination of Standard Formal Potentials for the Transfers of Several Pairing Anions across the Nitrobenzene/Water Interface by Na(I) Extraction with 18-Crown-6 Ether

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Abstract

Extraction constants (K_{ext}) for the extraction of sodium salts (NaA) with 18-crown-6 ether (18C6) from water (w) into nitrobenzene (NB) were determined at 298 K, together with the determination of individual distribution constants ($K_{\text{D,A}}$) of several pairing anions A^- . The symbols K_{ext} and $K_{\text{D,A}}$ were defined as $[\text{NaL}^+]_{\text{NB}}[\text{A}^-]_{\text{NB}}/([\text{Na}^+][\text{L}]_{\text{NB}}[\text{A}^-])$ at $L = 18\text{C6}$ and $[\text{A}^-]_{\text{NB}}/[\text{A}^-]$, respectively; the subscript "NB" shows the NB phase. Also, ion-pair formation constants for sodium 2,4-dinitrophenolate (NaDnp) and its ion pair complex with 18C6 in water were determined by potentiometry with a Na^+ -selective electrode. Standardized (S) $K_{\text{D,A}}$ values were briefly calculated from the following thermodynamic cycle: $K_{\text{D,A}}^{\text{S}} = K_{\text{ext}}/K_{\text{D,Na}}^{\text{S}}K_{\text{NaL,NB}}^{\text{S}}$. Here, $K_{\text{D,Na}}^{\text{S}}$ and $K_{\text{NaL,NB}}^{\text{S}}$ denote the standardized individual distribution-constant of Na^+ into and a complex formation constant for NaL^+ in the NB phase, respectively. Moreover, equilibrium potential differences ($\Delta\varphi_{\text{eq}}$) at the NB/w interface were estimated from the relation $\Delta\varphi_{\text{eq}} = 0.05916\log(K_{\text{D,A}}^{\text{S}}/K_{\text{D,A}})$ at 298 K. The $\Delta\varphi_{\text{eq}}$ values of $A^- = \text{F}_3\text{CCO}_2^-, \text{MnO}_4^-, \text{ReO}_4^-$ and Dnp^- were determined for comparison with the value of picrate ion. The plot of $\log K_{\text{ext}}$ versus $\Delta\varphi_{\text{eq}}$ gave a positive correlation at (correlation coefficient)² = 0.748.

Keywords: Standard formal potentials; Individual distribution constants; Extraction into nitrobenzene; Ion-pair formation constants; Potentiometry; 18-Crown-6 ether

Introduction

Individual distribution constants ($K_{\text{D,M}}$ and $K_{\text{D,A}}$) of cations $\{\text{M}^{z+}$ with the formal charge of $z (= 1, 2)\}$ and monovalent anions (A^-) are generally important for the determination of equilibrium constants, such as complex formation (or stability) constants ($K_{\text{ML,org}}$) for ML^{z+} and acid dissociation ones of HA in organic (o or org) phases, in electrochemistry at water/o solution interfaces [1-5]. With respect to these distribution constants, the authors have proposed the presence of interfacial equilibrium potentials ($\Delta\varphi_{\text{eq}}$) in solvent extraction processes with such interfaces and determined so far many $\Delta\varphi_{\text{eq}}$ values by applying this idea to the monovalent or divalent metal extraction with crown compounds (L) [6-10]. Here, the $\Delta\varphi_{\text{eq}}$ values have been obtained from the relation [2,8], $\Delta\varphi_{\text{eq}} = \Delta\varphi_{\text{Pic}}^{0'} - 0.05916\log K_{\text{D,Pic}}$ at 298 K, based on the standardized formal potentials ($\Delta\varphi_{\text{Pic}}^{0'}$) for the transfer of picrate ion (Pic^-) across the nitrobenzene/water (NB/w) [7-9,11], benzene (Bz)/w [10], dichloromethane (DCM)/w [6,11] or 1,2-dichloroethane (DCE)/w interface [6,8]. On the other hand, there are systematic studies for many A^- distribution from water into DCE or NB in the $K_{\text{D,A}}$ determination, using the CsA extraction with 24-crown-8 ether derivative [12] or the extraction of single salts [1,13], MA or MA_2 . However, the no relation between $K_{\text{D,A}}$ and $\Delta\varphi_{\text{eq}}$ had been reported in these extraction studies [1,12,13]. Therefore, it is difficult to check whether the $K_{\text{D,A}}$ values experimentally-obtained are equivalent to those standardized at $\Delta\varphi_{\text{eq}} = 0$ V (namely the $K_{\text{D,A}}^{\text{S}} = \{\exp(\Delta\varphi_{\text{A}}^{0'}/0.02569)\}$ at 298 K [2,8]) values or not. According to our previous paper [14], $K_{\text{D,A}}^{\text{S}}$ has been electrochemically derived at $\Delta\varphi_{\text{eq}} = 0$ V from the equation

$$\ln K_{\text{D,A}} = -F(\Delta\varphi_{\text{eq}} - \Delta\varphi_{\text{A}}^{0'})/RT \quad (1)$$

being the same as that [2] described above. Here, the minus sign of the right hand side (rhs) of this equation comes from the formal charge of A^- [11,14].

In order to clarify the presence of $\Delta\varphi_{\text{eq}}$ for the transfers of other A^- at the NB/w interface, as well as its presence for that of Pic^- , we performed here extraction experiments of sodium salts, NaA, by 18-crown-6 ether (18C6) into NB at $\text{A}^- = \text{MnO}_4^-, \text{ReO}_4^-, \text{F}_3\text{CCO}_2^-$ and 2,4-dinitrophenolate ion (Dnp^-). For increasing the actual distribution efficiency of $\text{A}(-\text{I})$ and $\text{Na}(\text{I})$ as much as possible, 18C6 was used in the above extraction systems as the more effective L, compared with benzo-18C6 and dibenzo-18C6 [15]. This idea had been actually employed by Levitskaia et al. [12]. Also, NB was used as a diluent for facilitating the dissociation of the ion-pair complex $\text{Na}(\text{18C6})^+\text{A}^-$ extracted in the o phase and then this caused totally an increase in extraction-ability of $\text{Na}(\text{I})$. Moreover, the ion-pair formation constants, K_{MA}^0 and K_{MLA}^0 , for NaDnp and $\text{Na}(\text{18C6})^+\text{Dnp}^-$ in water at $I \rightarrow 0$ mol dm^{-3} were determined at 298 K by potentiometry [16] with a commercial Na^+ -selective electrode ($\text{Na}^+\text{-SE}$). Here, the symbol I refers to ionic strength of the aqueous solution with Na^+Dnp^- or $\text{Na}(\text{18C6})^+\text{Dnp}^-$.

Experimental

Materials and reagents

Purities of $\text{Na}(\text{I})$ in commercial $\text{F}_3\text{CCO}_2\text{Na}$ (Aldrich, 98%) and NaReO_4 (Aldrich, 99.99%) were checked by AAS measurements at 589.0 nm, while those of $\text{NaDnp}\cdot\text{H}_2\text{O}$ (Tokyo Chemical Industries, >98.0%) and $\text{NaPic}\cdot\text{H}_2\text{O}$ (Wako Pure Chemical Industries, >90%)

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were done by spectrophotometric measurements at the Dnp⁻ absorption of 358 nm and the Pic⁻ one of 355, respectively. Water contents of the former three Na(I) salts and commercial 18C6 (Wako Pure Chemical Industries, 98.0%) were determined by a Karl-Fischer titration: F₃CCO₂Na·0.0392H₂O (0.517%); NaReO₄·0.018H₂O (0.12); NaDnp·0.505H₂O (4.23); 18C6·0.0309H₂O (0.210). Purity of NaMnO₄·H₂O (Aldrich, ≥ 97%) was determined by a redox titration with Na₂C₂O₄ (Wako, 99.96%). The concentration of a basic aqueous solution with commercial HDnp (Tokyo Chemical Industries, >98.0%) was determined spectrophotometrically at 358 nm. Nitrobenzene (Kanto Chemical Co., min. 99.5%) was washed three-times with pure water and then was kept at a state saturated with pure water. Other reagents used here were of guaranteed reagent grades. Tap water was distilled once with a stainless steel-still and purified through the Autopure system (type WT 101 UV, Millipore).

Extraction experiments

Extraction experiments were essentially the same as those [17-19] reported before for the NaMnO₄, NaO₂CCF₃ and NaReO₄ extraction by 18C6 into DCE or NB. Amounts of Na(I) extracted into the NB phases were determined by the AAS measurements, where the same atomic absorption spectrophotometer (Hitachi, Japan) as that described previously [9] was used with the same accessories; Na(I) extracted into the NB phase was two-times back-extracted into an acidic aqueous solution. All the *D* values were less than unity, where *D* denotes a distribution ratio of Na(I) species extracted into the NB phase. A stock solution of 0.02 mol dm⁻³ NaMnO₄ for the extraction experiments was diluted immediately before use and its diluted solution was used up within about 8 h [17].

Total concentrations, [NaA, HDnp or L]_t, for the extraction experiments were [NaMnO₄]_t = 3.2 × 10⁻³ mol dm⁻³ with [L]_t = 4.2 × 10⁻⁵-6.1 × 10⁻³ mol dm⁻³; [NaReO₄]_t = 9.0 × 10⁻³ with [L]_t = 4.4 × 10⁻⁵-4.4 × 10⁻³; [NaO₂CCF₃]_t = 3.0 × 10⁻³ with [L]_t = 4.4 × 10⁻⁴-3.6 × 10⁻²; [NaOH]_t = 3.2 × 10⁻⁴-2.7 × 10⁻³, [HDnp]_t or [NaDnp]_t = (1.2-9.1) × 10⁻⁴ with [L]_t = 1.4 × 10⁻⁴-2.9 × 10⁻²; see the *x*-axis in Figure 1 as a reference of [L]_t. In particular, the total concentrations of mixtures of NaOH with HDnp or NaDnp were determined by the AAS measurements.

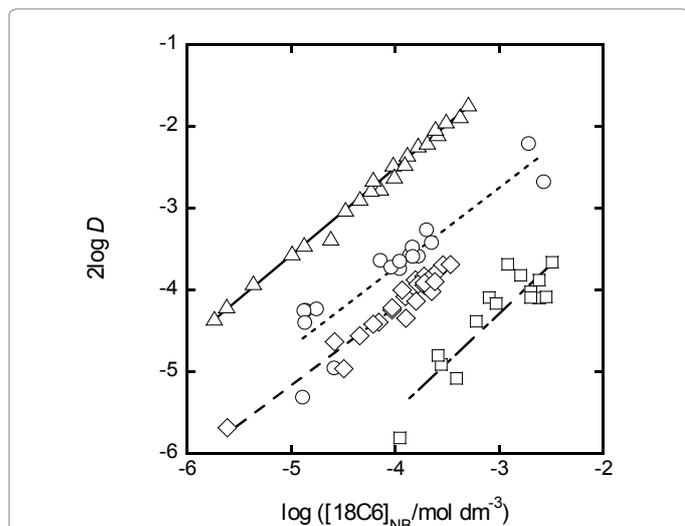


Figure 1: Plots of 2log *D* vs. log [18C6]_{NB} for the NaA extraction by 18C6 into NB at A⁻=MnO₄⁻ (triangle), Dnp⁻ (circle), ReO₄⁻ (diamond) and F₃CCO₂⁻ (square). See the text for the regression lines.

Data analysis

An extraction model for the data analysis was shown in Appendix A, supplementary information. In the [A⁻] calculation, the *K*_{HA} values were neglected by assuming that HA is strong acids in water for A⁻ = MnO₄⁻, ReO₄⁻ and F₃CCO₂⁻. Similarly, *K*_{D,HA} or *K*_{ex,HA} (= *K*_{HA}·*K*_{D,HA}) value was neglected. Therefore, the following equation was used: [A⁻] ≈ ([A]_t - *Ab*)/(1 + {*K*_{NaA} + (*K*_{NaL}·*K*₁/*K*_{D,L})[L]_{NB}}[Na⁺]) (see Appendix A) instead of the more-exact equation [A⁻] = ([A]_t - *Ab*)/(1 + {*K*_{NaA} + (*K*_{NaL}·*K*₁/*K*_{D,L})[L]_{NB}}[Na⁺] + (*K*_{HA} + *K*_{ex,HA})[H⁺]). Here, *K*_{HA}⁻¹, *K*_{D,HA} and *K*_{ex,HA} denote the acid dissociation constant of HA in water, the distribution one of HA into and an extraction one (mol⁻¹ dm³) for HA into the NB phase, respectively, and see Appendix A for the other equilibrium constants and the symbol *Ab*.

Similarly, the experiments for the NaDnp extraction system were almost performed in the pH range of more than 10. This pH value means the condition of [HDnp]/[Dnp⁻] ≤ 10⁻⁶ (≈ [H⁺]*K*_{HDnp} = 10^{-10.8}·10^{4.1} [20]). Hence, the *K*_{HA}, *K*_{D,HA} and *K*_{ex,HA} values were neglected in the calculation.

Emf measurements

The following cell was used for the determination of the *K*_{MA}⁰ and *K*_{MLA}⁰ values: Ag|AgCl|3.3 mol dm⁻³ KCl|0.1 mol dm⁻³ (C₂H₅)₄NCl|test solution|Na⁺-SE. Here, the test solutions were aqueous solutions of NaCl for preparing calibration curves and those of NaDnp and its solutions with 18C6 for the *K*_{MA}⁰ and *K*_{MLA}⁰ determination, respectively. Experimental slopes of the calibration curves were in the ranges of 59-74 mV/decade for the NaDnp system, 57-62 for NaPic, 69-76 for NaDnp-18C6 and 65-76 for NaPic-18C6.

The emf values of the above cell were measured at 25 ± 0.3°C using a Horiba pH/ion meter (type F-23) equipped with a Horiba Na⁺-SE (type 1512A). Liquid junction potentials (Δ*E*_{LJ}) at the 0.1 mol dm⁻³ (C₂H₅)₄NCl|test solution interface in the cell were not corrected. An effect of this treatment was examined by determining the *K*_{MA}⁰ and *K*_{MLA}⁰ values at MA = NaPic and MLA = Na(18C6)Pic, respectively (see below).

Results and Discussion

Potentiometric determination of ion-pair formation constants for NaDnp and Na(18C6)Dnp in water

The following equations were used for the determination of the *K*_{MA}⁰ and *K*_{MLA}⁰ values [16].

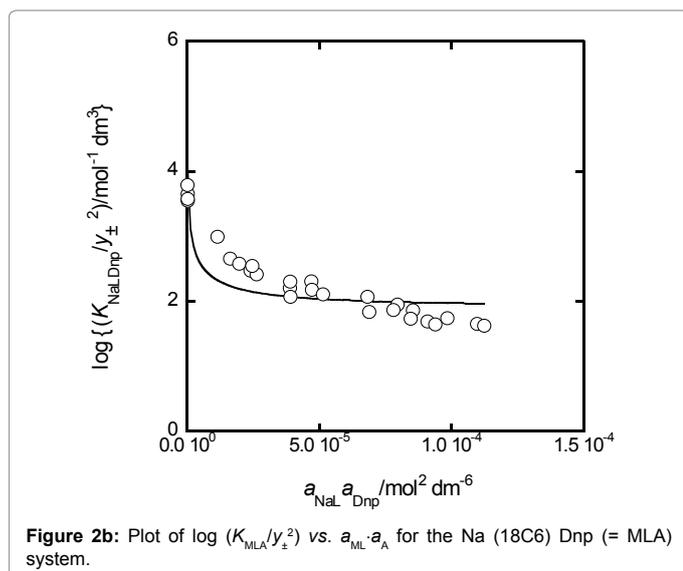
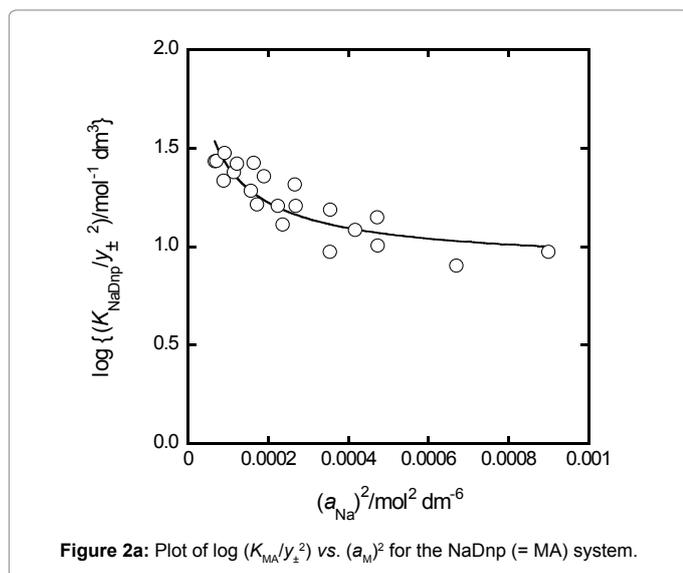
$$\log (K_{MA}^0 / y_{\pm}^2) = \log \{K_{MA}^0 + b_s (a_M)^{-2}\} \quad (2)$$

$$\text{with } K_{MA}^0 = [MA] / (a_M \cdot a_A) \text{ and}$$

$$\log (K_{MLA}^0 / y_{\pm}^2) = \log \{K_{MLA}^0 + b (a_{ML} \cdot a_A)^{-1}\} \quad (3)$$

with *K*_{MLA}⁰ = [MLA]/(*a*_{ML}·*a*_A). Here, *y*_± and *a*_{*j*} denote a mean activity coefficient and an activity (mol dm⁻³) of species *j* (= M⁺, A⁻, ML⁺) in water, respectively. Also, we assumed that the activity coefficients of MA and MLA are unity. Figures 2a and 2b show a plot of log (*K*_{MA}⁰/*y*_±²) versus (*a*_M)⁻² for MA = NaDnp and that of log (*K*_{MLA}⁰/*y*_±²) versus *a*_{ML}·*a*_A for MLA = Na(18C6)Dnp, respectively. Regression analyses of these plots at 298 K yielded *K*_{NaDnp}⁰ = 8.1 ± 1.2 mol⁻¹ dm³ with *b*_s = (1.7 ± 0.2) × 10⁻³ mol dm⁻³ at (correlation coefficient)² (*R*²) = 0.741 and *K*_{Na18C6Dnp}⁰ = 78 ± 18 with *b* = (1.5 ± 0.5) × 10⁻³ at *R*² = 0.801. The symbols *b*_s and *b* refer to empirical parameters for curve fittings [16]. Solid lines shown in Figures 2a and 2b were the regression ones based on the curve fittings of the plots into Equations (2) and (3).

In order to check the accuracy of these values, the *K*_{NaPic}⁰ and *K*_{Na18C6Pic}⁰ values were determined potentiometrically: *K*_{NaPic}⁰ = 7.7



$\pm 0.5 \text{ mol}^{-1} \text{ dm}^3$ with $b_s = (5.1 \pm 0.5) \times 10^{-4} \text{ mol dm}^{-3}$ at $R^2 = 0.941$ and $K_{\text{Na18C6Pic}}^0 = 136 \pm 15$ with $b = (6.8 \pm 0.5) \times 10^{-4}$ at $R^2 = 0.960$. The former value is close to that ($= 4.2 \text{ mol}^{-1} \text{ dm}^3$ [16]) reported before. On the other hand, the latter value is two-times larger than the literature one ($= 62$ [16]). These facts indicate that the K_{NaDnp}^0 value which was thus determined is essentially reliable, while the $K_{\text{Na18C6Dnp}}^0$ value is an approximate (see below for the analyses of extraction data). Additionally, it can be important that we obtained to a certain degree the reliable K_{MA}^0 and K_{MLA}^0 values without troublesome corrections of the ΔE_{Lj} values in the emf measurements. Hence, the two values were used for the calculation [17-19] of the $[\text{Na}^+]$, $[\text{18C6}]_{\text{NB}}$, and $[\text{Dnp}^-]$ values in the analyses on the extraction experiments (see Appendix A). Moreover, we think that this simple procedure has a possibility for the K_{MA}^0 - or K_{MLA}^0 -determination, namely can become the procedure without the troublesome ΔE_{Lj} corrections.

Determination of composition of the extracted species

Procedures for determining the composition of Na(I):L:A(-I) at $L = 18\text{C6}$ were the same as those [11,17-19] reported before. That is, plots

of $\log (D/[A^-])$ (call this procedure plot I) and $2\log D$ (call it plot II) versus $\log [L]_{\text{NB}}$ are useful for the composition determination of both the ion-pair (NaL^+A^-) extraction and the NaL^+ extraction with the pairing (or counter) anion A^- into the NB phase, respectively. Also, the intercepts of the plots I and II correspond to the approximate values of $\log K_{\text{ex}}$ and $\log K_{\text{ex}\pm}$, respectively [6,8,11,17-19]; K_{ex} is defined as $[\text{MLA}]_0/P$ and $K_{\text{ex}\pm}$ as $[\text{ML}^+]_0[\text{A}^-]_0/P$ with $P = [\text{M}^+][\text{L}]_0[\text{A}^-]$. Figure 1 shows their plots for the NaA extraction by 18C6 into NB. Basic data for the systems employed were a slope of 1.07 and an intercept of 1.76 at $R^2 = 0.990$ in the plot II for the MnO_4^- system, 0.96 and -0.37 at $R^2 = 0.942$ in that for ReO_4^- , 0.96 and -1.38 at $R^2 = 0.755$ in that for F_3CCO_2^- and 0.97 and 0.17 at $R^2 = 0.832$ in that for Dnp^- . The above slopes being in the range of 0.9 to 1.1 [11] indicate the extraction of species with $\text{Na(I):18C6:A(-I)} = 1:1:1$ into the NB phase at least. In this study, all the slopes of the plots I were less than 0.9, indicating the detectable dissociation of NaL^+A^- in the NB phase [17].

Determination of the $K_{\text{D,A}}$, $K_{\text{ex}\pm}$ and K_{ex} values

The $K_{\text{D,A}}$, $K_{\text{ex}\pm}$ and K_{ex} values were determined by the same methods as those [6,8,10,11,17] reported before, together with the $K_{\text{1,org}}$ ($= K_{\text{ex}}/K_{\text{ex}\pm}$) value. That is, the following extraction constants parameters ($K_{\text{ex}}^{\text{mix}}$) [6,8,10,11,17] were fundamentally used for the determination:

$$\log K_{\text{ex}}^{\text{mix}} \approx \log \{ K_{\text{ex}} + K_{\text{D,A}}([\text{M}^+][\text{L}]_0)^{-1} \} \quad (4)$$

$$= \log \{ K_{\text{ex}} + (K_{\text{ex}\pm}/P)^{1/2} \} \quad (4a)$$

with $K_{\text{ex}}^{\text{mix}} = ([\text{MLA}]_0 + [\text{ML}^+]_0 + [\text{M}^+]_0 + \dots)/P (= Ab/P)$ under the condition of $[\text{MLA}]_0 + [\text{ML}^+]_0 \gg [\text{M}^+]_0 + \dots$ in the o phase. Non-linear regression analyses based on Equations (4) and (4a) yield the $K_{\text{D,A}}$ and $K_{\text{ex}\pm}$ values, together with the K_{ex} one, respectively [6,8,10,11,17]. Figures 3 and 4 show the plots based on Equations (4) and (4a), respectively; the figures were examples of the F_3CCO_2^- and Dnp^- systems. The R^2 values of the regression lines obtained from Equations (4) and (4a) were 0.910 and 0.773 for $\text{A}^- = \text{MnO}_4^-$, 0.884 and 0.689 for ReO_4^- , 0.721 and 0.701 for F_3CCO_2^- and 0.884 and 0.933 for Dnp^- , respectively.

The $K_{\text{1,org}}$ value is easily calculated from the above relation [6,8,10,11,17]. Also, the $K_{\text{D,NaL}} (= [\text{NaL}^+]_{\text{NB}}/[\text{NaL}^+])$ values at $L = 18\text{C6}$ were estimated from the relation, $I_{\text{NB}} K_{\text{D,L}}/(K_{\text{NaL}}[\text{Na}^+][\text{L}]_{\text{NB}})$, in each run. Here, $K_{\text{D,NaL}}$, $K_{\text{D,L}}$ and K_{NaL} denote the individual distribution constant of NaL^+ , that ($= [\text{L}]_{\text{NB}}/[\text{L}]$) of L into the NB phase and the complex formation constant ($= [\text{NaL}^+]/[\text{Na}^+][\text{L}]$) for NaL^+ in water, respectively (see Appendix A); these latter two values were available in references. Table 1 lists the above equilibrium constants determined at 298 K.

A^-	$\log K_k$				
	$K_k = K_{\text{ex}}^{\text{a}}$	K_{ex}^{b}	$K_{\text{D,A}}^{\text{b}}(I)^{\text{c}}$	$K_{\text{1,NB}}^{\text{d}}(I)_{\text{NB}}^{\text{e}}$	$K_{\text{D,NaL}}^{\text{f}}$
MnO_4^-	$0.8_4 \pm 0.1_2$	5.12 ± 0.03	-1.95 ± 0.05 (0.0028)	$4.2_9 \pm 0.1_3$ (3.4×10^{-5})	$0.8_5 \pm 0.1_1$
ReO_4^-	$-0.9_7 \pm 0.1_4$	3.79 ± 0.03	-2.68 ± 0.07 (0.0081)	$4.7_5 \pm 0.1_4$ (1.8×10^{-5})	$-0.0_5 \pm 0.1_3$
F_3CCO_2^-	$-1.2_8 \pm 0.2_2$	3.34 ± 0.06 $2.6_1 \pm 0.7_0^{\text{a}}$	$-2.7_8 \pm 0.1_2$ (0.0026)	$3.8_9 \pm 0.7_3$ (4.8×10^{-6})	$-0.9_0 \pm 0.2_9$
Dnp^-	0.61 ± 0.06	$4.5_5 \pm 0.3_2$	-1.34 ± 0.09 (0.0012)	$3.9_4 \pm 0.3_2$ (2.9×10^{-5})	$0.4_5 \pm 0.4_1$
Pic^-^{g}	$1.5_1, 2.6^{\text{h}}$	$7.19, 7.0_2$	-2.5_0 (0.00033)	5.7 (1.0×10^{-6})	1.1

^aValues determined by Equation (4a) with the fixed K_{ex} values, except for the F_3CCO_2^- system. ^bValues determined by Equation (4). ^cIonic strength at the w phase. ^dValues calculated from $K_{\text{ex}}/K_{\text{ex}\pm}$. ^eValue at the NB phase. ^fValues calculated from $I_{\text{NB}} K_{\text{D,L}}/(K_{\text{ML}}[\text{M}^+][\text{L}]_{\text{NB}})$. ^g[11]. ^hEstimated value [23].

Table 1: Fundamental data for the NaA extraction with $L = 18\text{C6}$ into NB at 298 K.

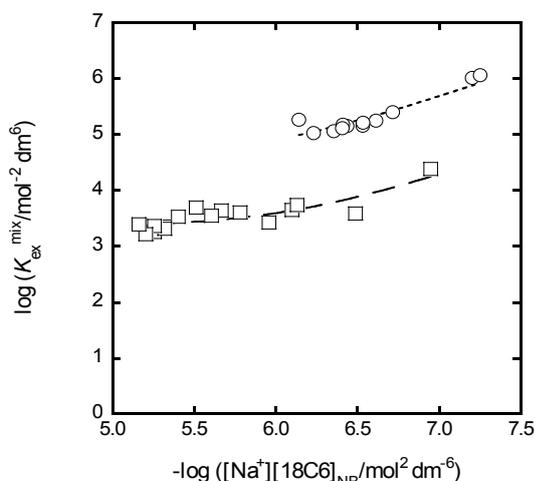


Figure 3: Plot of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log ([\text{Na}^+][18\text{C6}]_{\text{NB}})$ for the NaA-18C6 system at $\text{A}^- = \text{F}_3\text{CCO}_2^-$ (square) and Dnp^- (circle). See the $K_{\text{D,A}}$ and K_{ex} values in Table 1 about the data of the regression lines.

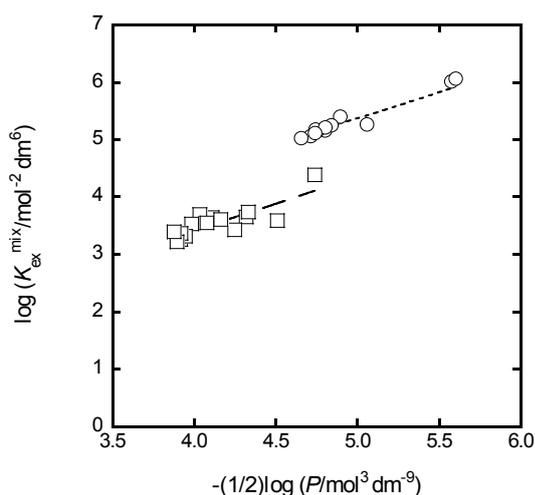


Figure 4: Plot of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-(1/2)\log P$ for the NaA-18C6 system at $\text{A}^- = \text{F}_3\text{CCO}_2^-$ (square) and Dnp^- (circle). See the K_{ex} and K_{ex} values in Table 1 about the data of the regression lines.

The $\log K_{\text{ex}}$ and $\log K_{\text{ex}}^{\text{mix}}$ values were in the orders $\text{A}^- = \text{F}_3\text{CCO}_2^- < \text{ReO}_4^- < \text{Dnp}^- < \text{MnO}_4^- < \text{Pic}^-$. The $\log K_{\text{D,NaL}}$ values were in the same order as those for $\log K_{\text{ex}}$ and $\log K_{\text{ex}}^{\text{mix}}$. Also, the $\log K_{\text{D,A}}$ values were in the order $\text{F}_3\text{CCO}_2^- \leq \text{ReO}_4^- < \text{Pic}^- < \text{MnO}_4^- < \text{Dnp}^-$.

The order of the $\log K_{1,\text{NB}}$ values was $\text{F}_3\text{CCO}_2^- \leq \text{Dnp}^- \leq \text{MnO}_4^- < \text{ReO}_4^- < \text{Pic}^-$. Ionic radii [21] of A^- are assumed to be H_3CCO_2^- (2.32 Å) $\leq \text{F}_3\text{CCO}_2^- < \text{MnO}_4^-$ (2.40) $< \text{ReO}_4^-$ (2.60) $< \text{Dnp}^- < \text{Pic}^-$. On the other hand, the ion size parameters [16,22] in aqueous solutions were in the order MnO_4^- (3.5) $< \text{ReO}_4^-$ (3.9) $< \text{H}_3\text{CCO}_2^-$ and $\text{H}_2\text{ClCCO}_2^-$ (4.5 Å) $\leq \text{F}_3\text{CCO}_2^- < \text{Dnp}^- < \text{Pic}^-$ (7). Here, the positions for F_3CCO_2^- , Dnp^- and Pic^- in the both orders were predicted empirically. Hence, the $\log K_{1,\text{NB}}$ order suggests there are two groups: MnO_4^- and ReO_4^- ; F_3CCO_2^- , Dnp^- and Pic^- . Unfortunately, we cannot now explain a reason about the $K_{1,\text{NB}}$ order.

Happily, the difference in a set of K_{NaPic}^0 and $K_{\text{Na18C6Pic}}^0$ ($\text{mol}^{-1} \text{dm}^3$) between 4.2 and 62 [16] and 7.7 and 136 did not affect the main results

of the data analyses in the NaPic extraction by 18C6 into NB, as follows. The K_{ex} , $K_{\text{D,Pic}}$ or $K_{1,\text{NB}}$ value well agreed with each other and the $K_{\text{ex}}^{\text{mix}}$ one calculated from 7.7 and $136 \text{ mol}^{-1} \text{dm}^3$ was in agreement with its corresponding value in Table 1 within the experimental error of ± 0.5 . Their logarithmic values were 7.19 ± 0.07 at K_{ex} , $-2.5_0 \pm 0.3_9$ at $K_{\text{D,Pic}}$, $1.4_7 \pm 0.5_3$ at $K_{\text{ex}}^{\text{mix}}$ and $5.7_3 \pm 0.5_3$ at $K_{1,\text{NB}}$. These results suggest that the extraction data for the NaDnp system with 18C6 are also reliable.

Estimate methods of the $K_{\text{D,A}}^{\text{s}}$, $\Delta\varphi_{\text{eq}}$ and $K_{\text{D,ML}}^{\text{s}}$ values at the NB/w interfaces

When the $K_{\text{D,M}}^{\text{s}}$ value, $K_{\text{D,M}}$ at $\Delta\varphi_{\text{eq}} = 0 \text{ V}$, is available from some references and the $K_{\text{ex}}^{\text{mix}}$ value was obtained from the present extraction experiment, the $K_{\text{D,A}}^{\text{s}}$ value can be easily calculated from the following thermodynamic relation:

$$\log K_{\text{D,A}}^{\text{s}} = \log K_{\text{ex}}^{\text{mix}} - \log (K_{\text{D,M}}^{\text{s}} \cdot K_{\text{ML,org}}^{\text{s}}) \quad (5)$$

Similarly, $K_{\text{ML,org}}^{\text{s}}$ is introduced as the reference value in this equation: $\log K_{\text{NaL,NB}}^{\text{s}} \{= \log ([\text{NaL}^+]_{\text{NB}} / [\text{Na}^+]_{\text{NB}} [L]_{\text{NB}})\} = 7.7$ [23] at $L = 18\text{C6}$ and 298 K ; $\log K_{\text{D,Na}}^{\text{s}} (= -\Delta\varphi_{\text{Na}}^{0'}/0.05916 = -16.90\Delta\varphi_{\text{Na}}^{0'}) = -5.18$ [13] (see Appendix A).

Also, the thus-obtained $K_{\text{D,A}}^{\text{s}}$ value is introduced in

$$\Delta\varphi_{\text{eq}} = (2.303RT/F)\log (K_{\text{D,A}}^{\text{s}}/K_{\text{D,A}}) \quad (1a)$$

with

$$\Delta\varphi_{\text{A}}^{0'} = (2.303RT/F)\log K_{\text{D,A}}^{\text{s}}. \quad (1b)$$

So we can immediately obtain the $\Delta\varphi_{\text{eq}}$ and $\Delta\varphi_{\text{A}}^{0'}$ values from Equations (1a) and (1b), respectively. Of course, the $K_{\text{D,A}}$ values can be determined experimentally (Table 1).

Furthermore, the $K_{\text{D,ML}}^{\text{s}}$ values averaged were calculated from two procedures as follows. (A): procedure estimated from a thermodynamic cycle. Its cycle is

$$K_{\text{D,ML}}^{\text{s}} = K_{\text{ex}}^{\text{mix}} K_{\text{D,L}} / (K_{\text{ML}} \cdot K_{\text{D,A}}^{\text{s}}). \quad (6)$$

Except for the $K_{\text{D,L}}$ and K_{ML} values, the other values were determined here. For the two values, we adopted $\log K_{\text{NaL}} = 0.73$ [15] and $\log K_{\text{D,L}} = -1.00$ [24] at $L = 18\text{C6}$ (see Appendix A) and accordingly $\log (K_{\text{D,L}}/K_{\text{NaL}})$ becomes -1.73 .

(B): procedure estimated from the $\Delta\varphi_{\text{eq}}$ and $K_{\text{D,ML}}$ values. Its equation is

$$\log K_{\text{D,ML}}^{\text{s}} = (F/2.303RT)\Delta\varphi_{\text{eq}} + \log K_{\text{D,ML}} \quad (6a)$$

which is derived from $\Delta\varphi_{\text{eq}} = \Delta\varphi_{\text{ML}}^{0'} + (2.303RT/F)\log K_{\text{D,ML}}^{\text{s}}$ with $\log K_{\text{D,ML}}^{\text{s}} = -(F/2.303RT)\Delta\varphi_{\text{ML}}^{0'}$ at $z = 1$. The experimental $K_{\text{D,ML}}$ values were individually calculated from the relation $K_{\text{D,ML}} \approx [\text{A}^-]_{\text{NB}} / [\text{ML}^+] (= I_{\text{NB}} K_{\text{D,L}} / K_{\text{ML}} [\text{M}^+] [\text{L}]_{\text{NB}})$ under the approximate condition (see the footnote f in Table 1) of $[\text{A}^-]_{\text{NB}} \approx [\text{ML}^+]_{\text{NB}}$, which comes from the charge balance equation $[\text{A}^-]_{\text{NB}} = [\text{M}^+]_{\text{NB}} + [\text{ML}^+]_{\text{NB}}$ {see Equation (B1) in Appendix B, supplementary information}, and then their values were averaged. Here, the fact that the $\Delta\varphi_{\text{eq}}$ value is in common for a given extraction system was over-interpreted in the mean calculation {see Equation (1a)}. The above procedures, (A) and (B), are described as fundamental ones in the calculations, although other procedures were able to be considered practically and were tried. The $K_{\text{D,A}}^{\text{s}}$, $\Delta\varphi_{\text{eq}}$ and $K_{\text{D,NaL}}^{\text{s}}$ values obtained from the above are listed in Table 2, together with the $\Delta\varphi_{\text{A}}^{0'}$ values.

The $\log K_{\text{D,A}}^{\text{s}}$ order was $\text{F}_3\text{CCO}_2^- < \text{ReO}_4^- < \text{Dnp}^- < \text{MnO}_4^- < \text{Pic}^-$; this means that the $\Delta\varphi_{\text{A}}^{0'}$ values were in the same order. This order

A ⁻	log K _{D,A} ^{S a} (Δφ _A ^{0 b/V})	Δφ _{eq} ^{c/V}	log K _{D,NaL} ^{S d}
MnO ₄ ⁻	-1.6 ₈ , -1.16 ^e (-0.1 ₀ , -0.069)	0.01 ₆ , 0.047 ^f	0.7 ₂ , 0.5 ₈ ^g , 0.05 ₉ ^{fg}
ReO ₄ ⁻	-3.4 ₉ (-0.2 ₁)	-0.04 ₈	0.7 ₂ , 0.7 ₆ ^g
F ₃ CCO ₂ ⁻	-3.8 ₀ (-0.2 ₂)	-0.06 ₂	0.7 ₂ , 0.1 ₄ ^g
Dnp ⁻	-1.9 ₁ , -2.0 ^e (-0.1 ₁ , -0.1 ₂)	-0.03 ₄ , -0.03 ₆ ^f	0.7 ₂ , 1.0 ₂ ^g , 1.1 ₂ ^{fg}
Pic ^{-h}	0.05 ^e (0.0030)	0.1 ₅ , 0.11 ⁱ	-0.2 ₇ , -1.4 ₃ ^g , -0.7 ₈ ^{ij}
Without A ⁻	--- ^k	--- ^k	0.7 ^l

^aValues calculated from Equation (5) at M = Na. ^bValues reduced from the log K_{D,A}^S values with Equation (1b). ^cValues calculated from Equation (1a). ^dValues calculated from the procedure (A). ^e[13]. ^fValue calculated from Equation (1a) with the value of the footnote e. ^gValues calculated from the procedure (B). ^h[11]. ⁱValue calculated from the charge balance equation for the NB phase without any approximations [8] and Appendix B. ^jValue calculated from the procedure (B) with the value of the footnote i. ^kNot have the corresponding values. ^lValue obtained at 298 K and I_{NB} = 0.05 mol dm⁻³ (Bu₄N⁺BPh₄⁻) from ion-transfer polarographic measurements [25].

Table 2: Log K_{D,A}^S, Δφ_A⁰, Δφ_{eq} and log K_{D,NaL}^S values for the NaA extraction with L = 18C6 into NB at 298 K.

was reflected to the log K_{ex} and log K_{ex±} orders. The K_{D,A}^S values for A⁻ = MnO₄⁻ and Dnp⁻ were close to those [13,23] reported before. Also, the log K_{D,NaL}^S order was Pic⁻ < F₃CCO₂⁻ ~ MnO₄⁻ ~ ReO₄⁻ ≤ Dnp⁻. Especially, the latter four values (0.7-0.8 = log K_{D,NaL}^S) were in agreement with that (0.7 [25]) at the NB/w interface directly-determined by ion-transfer-polarographic measurements. These facts suggest that 0.7 is appropriate to the log K_{D,NaL}^S value.

Correlation between log K_{ex±} and Δφ_{eq}

A plot of log K_{ex±} versus Δφ_{eq} gave a positive correlation: log K_{ex±} = (13.2 ± 2.9)Δφ_{eq} + (0.3 ± 0.2), at R² = 0.748 (Figure 5); the point of MnO₄⁻ due to ref. [13] was removed from the regression calculation because of uncertainty of the Δφ_{eq} value. This plot can come from Equation (5). For example, by adding the Δφ_{eq} term in the both sides of Equation (5), Equation (5) can be modified as

$$\log K_{\text{ex}\pm} = 16.90\Delta\phi_{\text{eq}} + \log K_{\text{D,A}} + \log (K_{\text{D,Na}}^{\text{S}} \cdot K_{\text{NaL,NB}}) \quad (5a)$$

with log K_{D,A} = -16.90Δφ_{eq} + log K_{D,A}^S [see Equation (1a) and Appendix B] at 298 K and the rhs of Equation (5a) becomes 16.90Δφ_{eq} + log K_{D,A} + 2.5₂. Also, the log K_{D,A} values for the five extraction systems were in the range of -2.8 to -1.3. Therefore, the value of log K_{D,A} + 2.5₂ can be estimated at -0.3 to 1.2. This range which corresponds to the intercept of the plot includes the experimental intercept (= 0.4). This fact indicates that the plot is essentially based on Equation (5a), namely Equation (5).

Moreover, the log K_{D,A} values can cause the larger deviation of the plots from the regression line (Figure 5), because their values are not constant among A⁻ employed. This is proved by the plot of log (K_{ex±}/K_{D,A}) versus Δφ_{eq}. The regression analysis of this plot yielded the equation, log (K_{ex±}/K_{D,A}) = log ([NaL⁺]_{NB}/[Na⁺][L]_{NB}) = 15.3Δφ_{eq} + 2.4 at R² = 0.896. This improvement on R² clearly shows a variance effect of log K_{D,A}.}

Similar correlations have been observed in the plots of log K_{ex±} versus Δφ_{eq} for the NaPic extraction with the four L into the two diluents [10,11]. These plots are based on the other modified form of Equation (5a): log K_{ex±} = 16.90(-Δφ_{eq}) + log K_{D,Na} + log (K_{D,Pic}^S · K_{NaL,org}) [11] at org = DCM and DCE. For the Bz extraction system, a similar plot has been obtained, but its slope (= 84 V⁻¹ [10]) was much larger than the theoretical value, 16.90 (= F/2.303RT) at 298 K. These facts also support that Equation (5a) is effective for an explanation of the above correlation.

Correlation between log K_{D,NaLA} and log K_{D,A}^S

The log K_{D,NaLA} [= log ([NaLA]_{NB}/[NaLA])] value was calculated from the thermodynamic relation [15,17].

$$\log K_{\text{D,NaLA}} = \log K_{\text{ex}} - \log (K_{\text{NaL}} \cdot K_1) + \log K_{\text{D,L}} \quad (7)$$

since NaLA is a neutral ion pair, its distribution constant naturally satisfies the condition of Δφ_{eq} = 0 V [26]. Here, the symbol K₁ is defined as [NaLA]/[NaL⁺][A⁻] (see Appendix A) and its values slightly changed with changes of I. The log K_{D,NaLA} values obtained were 1.01 for A⁻ = MnO₄⁻, -0.44 for ReO₄⁻, -0.97 for F₃CCO₂⁻ and 0.96 for Dnp⁻; its value for Pic⁻ was reported to be 3.68 [11]. Figure 6 shows a plot of log K_{D,NaLA} versus log K_{D,A}^S for the present extraction systems with A⁻. There was a good linear correlation between them at R² = 0.974. This result indicates that a distribution property of Na(18C6)A into the NB phase reflects that of A⁻. In other words, it means that the following relation

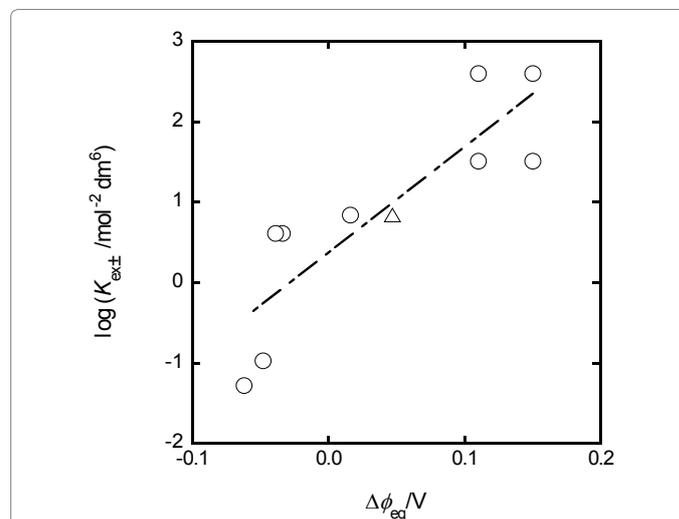


Figure 5: Plot of log K_{ex±} vs. Δφ_{eq} for the NaA extraction by 18C6 into NB. The regression line was log K_{ex±} = (13.2 ± 2.9) Δφ_{eq} + (0.3 ± 0.2), at R² = 0.748, except for the triangle point of MnO₄⁻. See Tables 1 and 2 for the plot data.

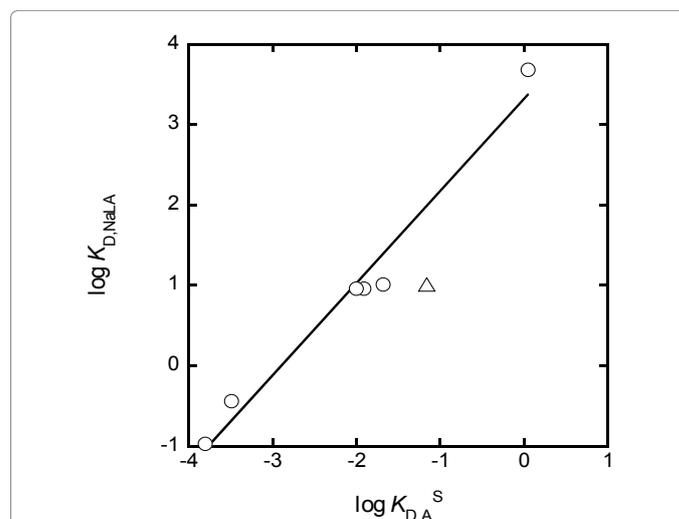


Figure 6: Plot of log K_{D,NaLA} vs. log K_{D,A}^S at L=18C6 and A=MnO₄⁻ (2 data), ReO₄⁻, F₃CCO₂⁻, Dnp⁻ (2 data) and Pic⁻. The regression line was log K_{D,NaLA} = (1.15 ± 0.09) log K_{D,A}^S + (3.32 ± 0.23) at R² = 0.974, except for the triangle point of MnO₄⁻.

holds in the present extraction systems: $\log K_{D,NaLA}^s = \log K_{D,A}^s + \log (K_{NaL,NB}/K_{NaL}) + \log (K_{D,Na}^s \cdot K_{D,18C6}) + \log (K_{1,NB}/K_1) \approx \log K_{D,A}^s + 0.7_2 + \log (K_{1,NB}/K_1)$, although the coefficient of $\log K_{D,A}^s$ was somewhat larger than unity. Here, this relation is derived from $\log K_{ex} = \log K_{ex}^s + \log K_{1,NB}$ {see Equations (6) and (7)}. The average values of $K_1/\text{mol}^{-1} \text{dm}^3$ were $10^{1.77}$ for $A^- = \text{Pic}^-$, $10^{2.31}$ for MnO_4^- , $10^{2.43}$ for ReO_4^- , $10^{1.86}$ for Dnp^- and $10^{2.51}$ for F_3CCO_2^- . Therefore, an estimate of the intercept, $0.7_2 + \log (K_{1,NB}/K_1)$, becomes in the range of 2.1 to 4.7. Its experimental value was $3.3_2 \pm 0.2$, (see the caption in Figure 6), overlapping this estimate. On the other hand, a plot of $\log K_{D,NaLA}^s$ versus $\log K_{D,A}^s$ at $\Delta\phi_{eq} \neq 0$ V did not yield the correlation ($R^2 = 0.038$).

Conclusion

The authors clarified the presence of $\Delta\phi_{eq}$ at the NB/w interfaces in the NaA extraction systems with 18C6, as well as the NaPic extraction one. Also, the positive correlation of $\log K_{ex}^s$ to $\Delta\phi_{eq}$ among A^- was observed in a given combination of Na^+ , NB, and 18C6. This fact makes the previously-reported correlation among L in given combinations of NaPic and diluents more-sure. Moreover, it was demonstrated that this method makes the $\Delta\phi_{eq}^{0'}$ - or $K_{D,A}^s$ -determination of a single A^- having the lower extraction-ability easier. In particular, using the more general L, such as 18C6, is important for the present method, because this promises the high versatility of the method.

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