Distribution of Ag(I), Li(I)-Cs(I) Picrates, and Na(I) Tetracyanoborate with Differences in Phase Volume between Water and Diluents

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Abstract

Ionic strength conditions in distribution experiments with single ions are very important for evaluating their distribution properties. Distribution experiments of picrates (MPic) with M = Ag(I) and Li(I)-Cs(I) into o-dichlorobenzene (oDCBz) were performed at 298 K by changing volume ratios (Vorg/V) between water and oDCBz phases, where “org” shows an organic phase. Simultaneously, an analytic equation with the Vorg/V variation was derived in order to analyze such distribution systems. Additionally, the AgPic distribution into nitrobenzene (NB), dichloromethane, and 1,2-dichloroethene (DCE) and the NaB(C6H5)4 (=NaBPh4) one into NB and DCE were studied at 298 K under the conditions of various Vorg/V values. So, extraction constants (Kex) for MPic into the org phases, their ion-pair formation constants (KMA,org) for M = MPic in the org ones, and standard distribution constants (SD,M) for the M(I) transfers between the water and org bulk phases with M = Ag and Li-Cs were determined at the distribution equilibrium potential (dep) of zero V between the bulk phases and also the Kex(Na), KNaA and SD,A values were done at \( V_{org}/V \). Here, the symbols Kex, KMA,org and KSD,M or KSD,A were defined as [MA]org/[M+][A−], [MA]org/[M+]org[A−]org and [M+]org/[M+] or [A−]org/[A−] at dep = 0, respectively. Especially, the ionic strength dependences of Kex and KMPic,org were examined at M = Li(I)-K(I) and org = oDCBz. From above, the conditional distribution constants, KD,BPh4 and KD,Cs, were classified by checking the experimental conditions of the I, Iorg, and dep values.

Keywords

Standard Distribution Constants, Volume Ratios, Distribution Equilibrium
1. Introduction

In electrochemistry at liquid/liquid interfaces, such as water/nitrobenzene (w/NB) and w/1,2-dichloroethane (w/DCE) ones, formal potentials (dep\_\(j\)) for the transfer of single ions j across the interfaces have been determined [1] [2]. These potentials have been obtained at 298 K from standardized potentials of cations or anions based on the extra-thermodynamic assumption for the distribution of tetraphenylarsonium tetraphenylborate (Ph\(_4\)As\(^+\)BPh\(_4\)^-) and so on [1] [2] [3] in many cases. In these studies, there are many data for the potentials dep\_\(j\) in the w/NB and w/DCE systems [1] [2] [3] [4], while there are some data [5] [6] for w/\(o\)-dichlorobenzene (oDCBz) one. Especially, the data [6] for the metal ions (M\(^{z+}\) at \(z = 1\)) seems to be very few. Also, the dep\_\(j\) values have been converted with the relation, dep\_\(j\) = \(-\left(\frac{1}{2}z_j f\right)\ln K_{D,j}^S\) [7] [8], at dep = 0 V into standard distribution constants (\(K_{D,j}^S\)) of j in a mol/L unit. Here, the symbols, \(z_j\), f, and dep, denote a formal charge of j with its sign, \(F/RT\) (these symbols are usual meanings), and a distribution equilibrium potential between w and organic (org) bulk phases, respectively. That is, the relation of dep\_\(M\) = \(-(0.05916)\log K_{D,M}^S\) {or dep\_\(j\) = \(-(0.05916)\log K_{D,j}^S\)} with j = M\(^+\) holds at dep = 0 V and \(T = 298.15\ K\). Generally such \(K_{D,j}^S\) values have been determined by solvent extraction experiments with j = M\(^+\), M\(^{2+}\), univalent cation, and its anion (A\(^-\)) [3] [7] [8] [9] [10]. However, there are few studies [7] [10] for understanding distribution and extraction phenomena based on the dep values. So, it is expected that the above studies facilitate both an electrochemical understanding of the distribution and extraction phenomena and an extraction-chemical one of the ion transfers across the liquid/liquid interfaces.

In this study, we determined the standard distribution constants, \(K_{D,j}^S\), at dep = 0 V and \(T = 298\ K\) for j = Ag\(^+\), Li\(^+\)-Cs\(^+\), and BPh\(_4\)^- into some diluents. The \(K_{D,Ag}^S\) values were obtained from NB, DCE, oDCBz, and dichloromethane (DCM) systems with the reported \(K_{D,Pic}^S\) value [5] [8] [11] of picrate ion (Pic\(^-\)), the \(K_{D,j}^S\) values at j = Li\(^+\)-Cs\(^+\) from oDCBz one with that [5] of Pic\(^-\), and the \(K_{D,BPh4}^S\) values from NB and DCE ones with the \(K_{D,Na}^S\) value [8] of Na\(^+\). In the experiments corresponding to the above systems, volume ratios (=\(V_{org}/V = r_{org/w}\)) of the both phases were changed and accordingly an equation for analyzing such systems was derived; \(V_{org}\) and \(V\) refer to an experimental volume (L unit) of the org phase and that of the w one, respectively. Also, the \(K_{exs}\) \(K_{MA,orgs}\) and \(K_{D,MA}\) values were obtained at 298 K from the same combinations of M\(^{z+}\) and the diluents. Here, the symbols \(K_{exs}\) \(K_{MA,orgs}\) and \(K_{D,MA}\) were defined as \([MA]_{org}/[M^+][A^-]\), \([MA]_{org}/[M^+]_{org}[A^-]_{org}\) and \([MA]_{org}/[MA]\), respectively. Moreover, extraction, ion-pair formation, and distribution properties for the above systems were
discussed based on their equilibrium constants. Additionally, using the Davies equation or the Debye-Hückel limiting law [12], dependences of $K_a$ and $K_{\text{MPic,org}}$ ($M = \text{Li-K}$) on the ionic strength of both $w$ and $o\text{DCBz (=org)}$ phases were examined. About the distribution with $\text{BPh}_4^-$ or $\text{Cs}^+$, differences among its $K_{D,\text{BPh}_4}$ or $K_{D,\text{Cs}}$ values were considered in their experimental conditions and thereby classified into two groups, such as $K_{D,j}$ and $K_{D,j}^S$.

2. Experimental

2.1. Chemicals

The procedures for the preparation of MPic, except for NaPic, were the same as those [13] [14] reported before. Commercial NaPic (monohydrate, extra pure reagent: $\geq$95.0%, Kanto Chemical) and NaBPh$_4$ (guaranteed pure reagent [GR]: $\geq$95.0%, Kanto) were dissolved into pure water and then recrystallized by concentrating their aqueous solutions with a rotary evaporator. The thus-obtained crystals were filtered and then dried for > 20 h in vacuum. Amounts of the water of crystallization in these picrates were determined with a Karl-Fischer titration: $7.343\%$ for $M(\text{I}) = \text{Li}$; $6.232\%$ for Na; $1.230\%$ for K; $2.767\%$ for Rb; $0.414\%$ for Cs. Water was not detected for the AgPic crystal [14].

Commercial NB (GR: > 99.5%, Kanto), DCE (GR: > 99.5%, Kanto), $o\text{DCBz (GR: > 99.0%, Kanto)}$, and DCM (GR: > 99.5%, Kanto), used as the diluents, were washed three times with pure water and kept at states saturated with water until use [15]. Commercial nitric acid (GR: 60% – 61%, Wako Pure Chemical Industries) and hydrochloric acid (for amino acid analysis, GR: 35.0% – 37.0%, Kanto) were employed for the preparation of the calibration curves with AgNO$_3$ (GR: $\geq$ 99.8%, Kanto) and LiCl-CsCl (GR, Kanto, Wako, & Nacalai Tesque). Used pure water was purified by the same procedure as that [15] reported previously.

2.2. Experiments for the MPic and NaBPh$_4$ Distribution

Aqueous solutions of MPic or NaBPh$_4$ were mixed with some diluents in the various $r_{\text{org}}/w$ (see Table 1 & Table 2 for their ratios) in stoppered glass tubes of about 30 mL and then they were shaken for 3 minutes (in the experiments with the AgPic and NaBPh$_4$ distribution) or one minute (in those with the LiP-ic-CsPic one) by hand. After this operation, these tubes were mechanically agitated at 25°C ± 0.3°C for 2 h and centrifuged for 5 minutes in order to separate the two phases. The separated diluent phases were taken into the glass tubes and treated as follows. The diluent phases of AgPic, NaPic, and NaBPh$_4$ distribution systems were back-extracted by using 0.1 mol/L HNO$_3$, pure water, and 0.02 mol/L HCl, respectively. For the NaPic system, the $w$ phases back-extracted were separated, transferred to 5 mL tubes produced by polypropylene, and then their separated phases were diluted with the HCl solution. Total amounts of Ag(I) and Na(I) in these aqueous solutions were analyzed at 328.1 nm for Ag and 589.0 for Na with a Hitachi atomic absorption spectrometer (type Z-6100). In addition to
Table 1. Fundamental data for AgPic and NaBPh₄ distribution into several diluents at 298 K with various $r_{\text{org/\text{w}}}$ conditions.

| MA | Diluent (org) | log$K_{\text{DS}}$a | $\text{dep}^b/V$ | log($K_{\text{DS},\text{Ag}}^\text{org}$ or $K_{\text{DS},\text{BPh}}^\text{org}$) |
|----|---------------|----------------------|------------------|----------------------------------|
| AgPic | NB at $r_{\text{org/\text{w}}}$ = 1 | $-2.12 \pm 0.03$ | 0.13 | $-3.30^e$ |
|   | DCE at $r_{\text{org/\text{w}}}$ = 1d | $-3.74$ | 0.16 | $-6.47^d$ |
|   | DCE at $r_{\text{org/\text{w}}}$ = 0.12 - 8.3 | $-3.85 \pm 0.1$ | 0.1 | $-6.69 \pm 0.2^e$ |
|   | oDCBz at $r_{\text{org/\text{w}}}$ = 1.2 - 20 | $-4.52 \pm 0.07$ | 0.11f | $-6.30^e,g$ |
|   | DCM at $r_{\text{org/\text{w}}}$ = 1.0 | $-4.95 \pm 0.15$ | 0.19 | $-7.23 \pm 0.15^e$ |
| NaBPh₄ | NB at $r_{\text{org/\text{w}}}$ = 0.50 - 7.5 | $-0.52 \pm 0.2$ | 0.3 | $4.12 \pm 0.2^h,i$ |
|   | DCE at $r_{\text{org/\text{w}}}$ = 1.0 | $-1.4 \pm 0.1$ | 0.3 | $4.12 \pm 0.3^j$ |

Table 2. Fundamental data for MPic (M = Li-Cs) distribution into org = oDCBz at 298 K with various I and $r_{\text{org/\text{w}}}$ conditions.

| M | I/mol·L⁻¹ ($r_{\text{org/\text{w}}}$ range) | log$K_{\text{DS}}$a | $\text{dep}^b/V$ | log$K_{\text{DS},\text{M}}^{\text{org}}$ | log$K_{\text{DS},\text{M}}$ | log$K_{\text{DS},\text{M}}^{\text{org}}$ | log$K_{\text{DS},\text{M}}$ |
|---|-------------------|----------------------|------------------|-----------------------------|----------------|-----------------------------|----------------|
| Li | 0.026 (1.0 - 4.0) | $-5.52 \pm 0.61$ | 0.1 | $-8.36 \pm 0.61$ | $-3.11 \pm 0.2$ | $-4.4$ | $7.6 \times 10^{-8}$ | $7.9 \pm 0.9$ |
|   | 0.058 (1.0 - 3.0) | $-5.42 \pm 0.2$ | 0.1 | $-8.14 \pm 0.2$ | $-3.52 \pm 0.1$ | $-4.6$ | $2.1 \times 10^{-7}$ | $7.3 \pm 0.4$ |
|   | 0.070 (1.0) | $-6.2 \pm 2.1$ | 0.2 | $-9.2 \pm 2.1$ | $-4.11 \pm 0.5$ | $-5.1$ | $7.6 \times 10^{-8}$ | $7.2 \pm 1.0$ |
|   | 0.082 (2.0 - 4.1) | $-5.3$ | 0.1 | $-7.8 \pm 0.3$ | $-3.87 \pm 0.09$ | $-4.7$ | $4.1 \times 10^{-7}$ | $6.7 \pm 0.6$ |
|   | 0.082 (1.0 - 2.9) | $-6.2 \pm 1.2$ | 0.2 | $-9.1 \pm 1.2$ | $-4.01 \pm 0.4$ | $-4.9$ | $4.7 \times 10^{-8}$ | $8.3 \pm 1.7$ |
| Na | 0.038 (1.0 - 7.5) | $-4.92 \pm 0.5$ | 0.1 | $-7.0 \pm 0.5$ | $-2.1 \pm 0.3$ | $-2.6$ | $4.6 \times 10^{-7}$ | $7.7 \pm 0.9$ |
|   | 0.049 (6.0 - 12) | $-3.71 \pm 0.01$ | 0.05 | $-4.68$ | $-1.8 \pm 0.1$ | $-2.3$ | $9.6 \times 10^{-6}$ | $5.6 \pm 0.1$ |
|   | 0.070 (1.0 - 12) | $-5.1 \pm 0.4$ | 0.1 | $-7.4 \pm 0.4$ | $-2.6 \pm 0.3$ | $-3.1$ | $5.6 \times 10^{-7}$ | $7.5 \pm 0.7$ |
|   | 0.090 (4.0 - 15) | $-4.8^f$ | 0.1 | $-6.9 \pm 0.4$ | $-2.5 \pm 0.2$ | $-2.9$ | $1.4 \times 10^{-6}$ | $7.1 \pm 0.7$ |
|   | 0.11 (1.2 - 6.0) | $-5.0 \pm 0.8$ | 0.1 | $-7.3 \pm 0.8$ | $-3.0 \pm 0.2$ | $-3.4$ | $9.2 \times 10^{-7}$ | $7.8 \pm 1.0$ |
|   | 0.13 (1.0 - 12) | $-5.4 \pm 0.7$ | 0.1 | $-8.1 \pm 0.7$ | $-3.0 \pm 0.3$ | $-3.6$ | $4.6 \times 10^{-7}$ | $8.1 \pm 1.1$ |
| K | 0.0017 (1.5 - 3.0) | $-2.8 \pm 1.0$ | $-0.01$ | $-2.9 \pm 1.0$ | $0.52 \pm 0.1$ | $-0.5$ | $3.8 \times 10^{-6}$ | $5.4 \pm 1.1$ |
|   | 0.0040 (1.5 - 6.0) | $-3.4 \pm 0.2$ | 0.04 | $-4.2 \pm 0.2$ | $-0.5 \pm 0.2$ | $-1.3$ | $1.3 \times 10^{-6}$ | $6.4 \pm 0.4$ |
|   | 0.0078 (1.0 - 3.0) | $-3.7 \pm 0.3$ | 0.06 | $-4.7 \pm 0.3$ | $-1.3 \pm 0.1$ | $-2.1$ | $1.4 \times 10^{-6}$ | $6.1 \pm 0.5$ |
|   | 0.020 (1.2 - 4.0) | $-3.9^g$ | 0.07 | $-5.1 \pm 0.3$ | $-1.6 \pm 0.2$ | $-2.3$ | $2.5 \times 10^{-6}$ | $6.2 \pm 0.6$ |
| Rb | 0.0047 (1.7 - 6.0) | $-4.6 \pm 0.8$ | 0.1 | $-6.5 \pm 0.8$ | $-1.6 \pm 0.1$ | $-3.4$ | $1.1 \times 10^{-7}$ | $7.8 \pm 1.1$ |
|   | 0.0071 (2.0 - 7.5) | $-5.5 \pm 1.1$ | 0.2 | $-7.5 \pm 1.1$ | $-1.8 \pm 0.2$ | $-3.6$ | $3.2 \times 10^{-8}$ | $8.4 \pm 1.7$ |
| Cs | 0.0032 (1.1 - 12) | $-4.2 \pm 0.1$ | 0.1 | $-6.7 \pm 0.1$ | $-1.0 \pm 0.3$ | $-3.0$ | $2.0 \times 10^{-7}$ | $7.4 \pm 0.4$ |
|   | 0.0032 (1.2 - 10) | $-4.6 \pm 0.1$ | 0.06 | $-5.6 \pm 0.4$ | $-1.5 \pm 0.4$ | $-3.6$ | $7.6 \times 10^{-7}$ | $7.9 \pm 0.5$ |

aValues at I & IoDCBz → 0. bValues calculated from log$K_{\text{DS},\text{Pic}}^{0.05} = -1.01$ at [Li$_2$SO$_4$] = 0.0035 mol/L, [PNP⁺DCC⁻] = 0.01, & 295 K. cAverage values. dRef. [14]. eValues calculated from log$K_{\text{DS},\text{Pic}}^{0.05} = -2.73$ at [Li$_2$SO$_4$] = 0.0035 mol/L, [PNP⁺DCC⁻] = 0.01, & 295 K. fValues determined at 295 - 298 K. gValues expressed as the errors which equal those of log$K_{\text{DS},\text{Ag}}$. hAverage values. iRef. [17].
589.0 for Na, amounts of the other M(I) were analyzed at 670.8 nm for M(I) = Li, 766.5 for K, 780.0 for Rb, and 852.1 for Cs by a flame spectrophotometry.

Total concentrations of MPic in the w phases before the distribution experiments into oDCBz were as follows: 0.025 & 0.052 mol/L for the AgPic distribution, 0.026 - 0.034, 0.083, 0.094 - 0.12, & 0.13 - 0.14 for LiPic, 0.042, 0.056, 0.084, 0.11, 0.13, & 0.17 for NaPic, 0.0017, 0.0040, 0.0081, & 0.022 for KPic, 0.0061 & 0.010 for RbPic, and 0.0043 for CsPic. In the AgPic distribution into other org phases, the total concentrations were 1.0 × 10⁻⁴ - 0.041 mol/L for org = NB, 0.012 - 0.030 for DCE, and 0.025, 0.040, & 0.049 for DCM. In the NaBPh₄ distribution into NB and DCE, the concentrations were 4.9 × 10⁻⁵ - 0.0061 mol/L and 0.0040 - 0.035, respectively.

2.3. Data Analyses

Based on the ion-pair formation, \( M^+ + A^- \rightleftharpoons MA \), in water, we can easily propose a quadratic equation

\[
\left[M^+\right]^2 - 2\left[M^+\right]\left[M\right]_{t,w} + \left[M\right]_{t} = 0
\]

[see Equation (1) for the symbols \( \gamma[M^+] \) & \( [M]_{t,w} \) and then obtain from it]

\[
\left[M^+\right] = \frac{\left[M^+\right]}{\gamma[M^+]^2} = \left[\frac{1 + 2K_{MA} [M]_{t,w}^2}{\gamma[M^+]} - 1\right]^{1/2}K_{MA}.
\]

From the latter equation, we calculated self-consistent \( \gamma[A^-] \) and \( K_{MA} \) values by a successive approximation with \( \log K_{MA} = \log K_{MA}^0 + 2\log \gamma_s [8] \). Here, the symbols, \( K_{MA}, K_{MA}^0 \), and \( \gamma_s \), denote an ion-pair formation constant for MA in water at concentration expression, that at \( \gamma[A^-] \) (= ionic strength) → 0 mol/L, and a mean activity coefficient for M⁺ and A⁻ in water, respectively.

3. Results and Discussion

3.1. Derivation of Analytic Equation under the Conditions of Different Phase Volumes

Under the condition that \( V_{org} \) is different from \( V \) in the MA distribution into the org phase, we considered the following equation as a total mass balance at mol unit:

\[
[M]_t V = [M]_{t,w} V + [M]_{t,org} V_{org},
\]

where \([M]_t, [M]_{t,w}\), and \([M]_{t,org}\) denote a total concentration of the 1:1 electrolyte MA in the w phase before the extraction experiment, that of species with M(I) in the w one, and that of those in the org phase after the experiment (namely, at equilibrium), respectively. In these concentrations, the \([M^+]_{t,org}\) value can be experimentally determined with some analytical methods, such as AAS, flame spectrophotometry, and potentiometry with ISE. Equation (1) was divided by \( [M^+] \) \( V \) and then rearranged into

\[
\frac{r_{org/w} [M]_{t,org}}{[M^+] - [M]_{t,w}} = \frac{\left([M]_t - [M]_{t,w}\right) / [M^+]^2}{\gamma[M^+]} = r_{org/w} \frac{\left([M^+]_{t,org} + [MA]_{t,org}\right) / [M^+]^2}{\gamma[M^+]},
\]

using the mass balance relation of \([M]_{t,org} = [M^+]_{t,org} + [MA]_{t,org}\) in the org phase.
Here, the symbols, $[{\text{M}}^+]$ and $r_{\text{org/w}}[{\text{M}}^+]_{\text{org}}$, show the concentration of $\text{M}^+$ in the $w$ phase of the volume $V$ and that of $\text{M}^+$ in the org phase of $V$, respectively. In other words, the $[{\text{M}}^+]_{\text{org}}$ value is converted with $r_{\text{org/w}}$ into $[{\text{M}}^+]_{\text{org}}$ the concentration of $\text{M}^+$ in the org phase of $V$: namely $[{\text{M}}^+]_{\text{org}} = (V_{\text{org}}/V)[{\text{M}}^+]_{\text{org}}$. Therefore, we can define $r_{\text{org/w}}[{\text{M}}^+]_{\text{org}}/[{\text{M}}^+]_w$ as a conditional distribution constant $[7]$, $K_{D,M}$, of $\text{M}^+$ and additionally do $[\text{MA}]_{\text{org}}/[{\text{M}}^+]_w[\text{A}^-]$ as the apparent extraction constant, $K_{\text{ex}}$, of $\text{MA}$, respectively. Obviously, from the charge balance relations of $[{\text{M}}^+]_{\text{org}} = [{\text{A}}^-]_{\text{org}}$ and $[{\text{M}}^+] = [{\text{A}}^-]$ in the $\text{MA}$ distribution system, we can see immediately that $K_{D,M} = (r_{\text{org/w}}[{\text{M}}^+]_{\text{org}}/[{\text{M}}^+]_w) = r_{\text{org/w}}[{\text{A}}^-]_{\text{org}}/[{\text{A}}^-] = K_{D,A}$.

According to our previous paper [7], the $K_{D,M}$ and $K_{D,A}$ values at 298 K have been expressed as

$$\text{dep} = \phi - \phi_{\text{org}} = 0.05916 \left( \log K_{D,M} - \log K_{D,A}^S \right)$$

$$= -0.05916 \left( \log K_{D,A} - \log K_{D,M}^S \right).$$

Here, the symbols $\phi$ (or $\phi_{\text{org}}$), $K_{D,M}$, and $K_{D,A}$ denote an inner potential of the $w$ (or org) phase, the conditional distribution constant of $\text{M}^+$, and that of $\text{A}^-$, respectively, in this equation; see the introduction for the symbols $K_{D,M}^S$ and $K_{D,A}^S$. This dep practically means a total energy which is necessary for the $\text{M}^+$ or $\text{A}^-$ transfer across the interface between the two bulk phases at equilibrium. Equation (3) is the modified form of the Nernst equation [16]; this expression has a little problem in its definition (see ref. [17]). As similar to Equation (3), the following equation can hold (see Appendix A for its derivation).

$$\text{dep} = \text{dep}_e = 0.05916 \left( \log K_{D,A} - \log K_{D,M}^S \right) = -0.05916 \left( \log K_{D,M} - \log K_{D,A}^S \right)$$

So from rearranging Equation (2) with $K_{D,±}^S$ which is defined as $K_{D,M}^S K_{D,A}^S (=K_{D,M} K_{D,A}$: the condition (C3) in Appendix A), the following equation was obtained.

$$r_{\text{org/w}}[{\text{M}}]_{\text{org}}/V = r_{\text{org/w}} D_{\text{M}}^{\text{eq}} = K_{D,M} + K_{\text{ex}} r_{\text{org/w}} [\text{A}^-]$$

under the conditions of $K_{D,M} = K_{D,A}$ (see above) and $K_{D,M}^S \neq K_{D,A}^S$. Here $r_{\text{org/w}} D_{\text{M}}^{\text{eq}}$ equals an experimental (expl.) value, $[\text{M}]_{\text{org}}/\phi_{\text{org}}$, corresponding to the distribution ratio of $\text{M}(I)$ [8]. Hence, the plot of $r_{\text{org/w}} D_{\text{M}}^{\text{eq}}$ versus $r_{\text{org/w}} [\text{A}^-]$ based on Equation (4) can give $K_{\text{ex}}$ as the slope and $K_{D,±}$ as the intercept. Interestingly, we can obtain the plot with changing $r_{\text{org/w}}$ under the constant condition of $[\text{A}^-]$, namely, the constant ionic strength ($I$) in the $w$ phases. Here, we can see that the intercept is the $K_{D,±}$ value under the condition of $I (= [\text{A}^-] / K_{D,±}) \to 0$ [8] at least, because of $r_{\text{org/w}} > 0$. When $K_{D,±} > 0$, this fact, $I = [\text{A}^-] / K_{D,±} \to 0$, also means $[\text{A}^-]_{\text{org}} (= K_{D,±}) \to 0$ [8]. Therefore, the intercept, $K_{D,±}$, satisfies both the conditions of $I$ and $L_{\text{org}} \to 0$. Equation (4) is essentially similar to the Czapkiewicz equation [18] with $P_{\text{II}}^{1/2} (= K_{D,±})$ at $C_{\text{II}}$ ($= r_{\text{org/w}} [\text{A}^-]$ or $[\text{A}^-]) \to 0$ and $P (= K_{D,±})$. 

DOI: 10.4236/ajac.2020.111003
The symbol $K'_\text{ex}$ is converted with $r_{\text{org/w}}$ into $K_{\text{ex}} = r_{\text{org/w}} K'_\text{ex}$, which is thermodynamically expressed as

$$\left(K_{D,\pm}\right)^2 K_{\text{MA,org}} = K_{D,M} K_{D,A} K_{\text{MA,org}} = K_{D,M}^S K_{D,A}^S K_{\text{MA,org}}$$

(see the introduction for $K_{\text{MA,org}}$). Accordingly, we can obtain the $K_{\text{MA,org}}$ value from the intercept and the modified slope based on Equation (4). In the relation of $\left(K_{D,\pm}\right)^2 = K_{D,M} K_{D,A} = K_{D,M}^S K_{D,A}^S$, the $K_{D,M}$ and $K_{D,A}$ values must satisfy the same experimental conditions, such as $I$ and $I_{\text{org}}$, and also $K_{D,M}^S$ and $K_{D,A}^S$ ones do the same condition.

### 3.2. Reproducibility of the Experimental Values in Equation (4)

Figure 1 shows an example of the AgPic extraction into DCE. The straight line was

$$r_{\text{DCE/w}} D_{\text{Ag}}^{\text{exp}} = (1.4_6 \pm 0.5_1) \times 10^{-3} + (0.0366 \pm 0.0007) \times r_{\text{DCE/w}}^{-} \left[\text{Pic}^-\right]$$

at correlation coefficient ($R$) = 0.997. From these intercept and slope, the log $K_{D,\pm}$ value was evaluated to be $-3.8_5 \pm 0.1_6$, while the log $K_{\text{ex}}$ one was to be $-1.0_2 \pm 0.3_3$. In the latter $K_{\text{ex}}$ evaluation, the $K_{\text{ex}}$ values were obtained from $K_{\text{ex}} = r_{\text{DCE/w}} K'_\text{ex}$ for given $r_{\text{DCE/w}}$ values and then their values were averaged. Additionally, the log $K_{D,\text{Ag}}^S$ and log $K_{A,\text{Pic,DCE}}$ values were calculated to be $-6.6_9$ ($= 2 \log K_{D,\pm} - \log K_{D,\text{Pic}}^S$) with the calculation error of $\pm 0.2$; and 6.3 ($= \log K_{\text{ex}} - \log K_{D,\text{Ag}}$) with that of $\pm 0.4$ at $I_{\text{DCE}} = 3.2 \times 10^{-6}$ mol/L, respectively. Here, $I_{\text{DCE}}$ (or $I_{\text{org}}$) refers to the ionic strength in the DCE (or org) phase. These values were in agreement with those [14] at $r_{\text{DCE/w}} = 1$ reported before within their experimental errors, except for the log $K_{\text{ex}}$ and log $K_{D,\text{AgPic}}$ values. About these two constants, the minimum log $K_{\text{ex}}$ value ($= -1.4_1$) was close to that ($= -1.49$ [14]) reported before and also the minimum log $K_{D,\text{AgPic}}$ value ($= -1.7_4$) was somewhat larger than the
calculated one (\(= -1.83\)); see Table 1. The deviation of the latter value (\(= \log K_{ex} - \log K_{AgPic}\), see the section 3.4 for \(K_{AgPic}\)) can depend on the error of \(\log K_{ex}\). Table 1 lists the results for the AgPic and NaBPh₄ distribution into several diluents and Table 2 does results for the LiPic-CsPic distribution into oDCBz.

In the relation of \(2 \log K_{D,\pm} = \log \left( K_{D,M}^{S} \times K_{D,A}^{S} \right)\), the pair of the \(K_{D,M}^{S}\) and \(K_{D,A}^{S}\) values must satisfy the same experimental conditions. In other words, the use of \(\log K_{D,Ag}^{S} = 2 \log K_{D,\pm} - \log K_{D,Pic}^{S}\) basically reflects the experimental conditions of \(K_{D,Pic}^{S}\) in the \(K_{D,Ag}^{S}\) estimation. The same is also true of \(\log K_{D,Ag}^{S} = 2 \log K_{D,\pm} - \log K_{D,Pic}^{S}\).

### 3.3. Comparable Validity of Equation (4)

For \(K_{D,\pm}\) and \(K_{ex}\) determination, another simple analytic equation was derived from Equation (4) as follows.

\[
D_{M}^{expl} = K_{D,\pm} R_{org/w} \left( A^{-} \right) + K_{ex}^{'} \left( A^{-} \right),
\]

(5)

As examples, these common logarithmic \(K_{D,\pm}\) and \(K_{ex}\) values for the AgPic distribution into DCE were \(-3.2 ± 0.3\) and \(-1.0 ± 0.3\), respectively. From these values, the \(\log K_{D,Ag}^{S}\) and \(\log K_{AgPic,DCE}\) values were also estimated to be \(-5.4 ± 0.5\) and \(5.4 ± 0.7\) at \(I_{DCE} = 3.2 × 10^{-6}\) mol/L, respectively. However, except for the \(\log K_{ex}\) and \(\log K_{AgPic,DCE}\) values, their values were in less agreement with those [14] (see Table 1) reported before, compared with the values determined in terms of Equation (4).

The form of Equation (5) was simpler than that of Equation (4). Although the difference in reproducibility between the two equations was few, we did not adopt here Equation (5) for the \(K_{D,\pm}\) and \(K_{ex}\) determination. Also, the plot of \(R_{org/w} \times D_{M}^{expl}\) versus \(\left[ A^{-} \right]\) based on Equation (4) was not able to give the straight line, indicating that the \(K_{ex}^{'} R_{org/w} \left( = K_{ex} \right)\) term in the plot is not the constant. This fact shows that the parameter \(R_{org/w} \left( = K_{ex}^{'} \right)\) is more important than the \(K_{ex}^{'} R_{org/w}\) one in Equation (4). Simultaneously, both the plots lose the advantage of the constant \(I \left( = I_{A^{-}} \right)\) condition in the experiments. On the basis of the above results, we employed here Equation (4) for the determination of the \(K_{D,\pm}\) and \(K_{ex}\) values.

### 3.4. On Features of the AgPic Distribution Systems

Table 1 showed the order of \(org = NB > DCE ≥ DCM > oDCBz\) for the \(K_{D,\pm}\) values at \(I\) and \(L_{ag} \rightarrow 0\) mol/L, that for \(K_{ex}\) in the \(I\) range of 0.020 to 0.044, and that for \(K_{AgPic}\). Here, the \(K_{AgPic}\) value was calculated from the thermodynamic relation of \(K_{D,AgPic} = K_{ex}/K_{AgPic}\) with \(K_{AgPic} = [AgPic]/[Ag^{+}][Pic^{-}]\), which was evaluated from the \(K_{AgPic}^{S}\) value (\(= 2.8 \ L/mol\) [19]) reported at \(I \rightarrow 0\) and 298 K. On the other hand, the \(K_{AgPic,org}\) values showed the reverse order: \(org = NB < DCE ≤ DCM ≤ oDCBz\) in the \(I_{org}\) range of \(1.3 \times 10^{-6}\) to \(1.6 \times 10^{-4}\) mol/L (Table 1). These orders seem to reflect polarities of the diluents, except for \(K_{D,AgPic}\). Also, the \(K_{D,Ag}^{S}\) values were in the order \(NB > oDCBz ≥ DCE > DCM\) (see Table 1), al-
though the value for the oDCBz system was calculated from $K_{D,Pic}^S$ [5] reported at $T' = 295 \pm 3$ K and $K_{D,A}$ obtained here at 298 K. Moreover, it was assumed that the log$K_{D,Pic}$ values for the oDCBz and DCM systems satisfy the conditions of $I$ and $L_{org} \to 0$ and dep = 0; for the former system, that of $I$ and $L_{org} \to 0$ or an activity expression was cleared as described in Appendix B.

Considering the experimental errors of $K_{D,A}$ (or $K_{D,M}^S$) in Table 2, except for the oDCBz system of Table 1, we can suppose that the differences in $K_{D,M}^S$ between $T = 295 \pm 3$ [5] and 298 K are negligible. However, the $K_{D,Pic}^S$ determination at 298 K will be necessary for the determination of the more-exact $K_{D,M}^S$ values.

### 3.5. log$K_{D,M}^{S%}$ Estimation

We derived the following equation from the definition of $K_{D,M}^{S%} = y_{+org} K_{D,M}^S / y_+$ for the present distribution systems at dep = 0 V, the individual activity coefficients $y_{+org} (=y_{M,org})$ and $y_+ (=y_{M})$ and rearranged it.

$$\log K_{D,M}^S = \log \left( y_+ y_{+org} / y_{+org} \right) = \log K_{D,M}^{S%} - Az^2 f(I) + A_{org} z^2 (I_{org})^{1/2} \quad (6)$$

Here, the symbol, $K_{D,M}^{S%}$, denotes a thermodynamic equilibrium constant ($=a_{M,org}/a_M$ in activity unit) of $K_{D,M}$ at $I_{org}$ and $I \to 0$ mol/L and the superscripts, $S$ and $\%$, mean the experimental conditions of dep = 0 V and the ionic strength for the both phases, respectively. As the description of the superscript $\%$ (or $u//u_+$), its numerator shows the condition of $I_{org} \to 0$ (or the left hand side of // does the total concentration, $u$, of an electrolyte in the org phase), while its denominator does that of $I \to 0$ (or its right hand side does the total one $x$). According to Equation (6) at dep = 0 V, $K_{D,M}^{S%}$ ($=K_{D,M}^{Su/x}$) equals $[M^+]/[M^+]$ as the concentration expression for a given $I = x$ or $I_{org} = u$, $K_{D,M}^{Su//0}$ does $[M^+]/[M^+]$ for a given $L_{org} = u$, and $K_{D,M}^{S0/x}$ does $a_{M,org}/a_M$ for a given $I = x$; the latter two equations are both the semi-activity expressions (see the footnotes b, d-f in Table 3).

Assuming that log$K_{D,Pic}^{S%}$ reported cyclic-volammetrically for the w/oDCBz system [5] satisfies the condition of dep = 0 V, the log$K_{D,M}^{S%}$ values were calculated from its log$K_{D,Pic}^{S%}$ value (=-2.73, see Appendix B for the calculation) with $2 \log K_{D,M}^{S%} = \log K_{D,M}^{S%} K_{D,A}^{S%}$ at dep = 0 V. From the data in Table 2, the logarithmic values of the average $K_{D,M}^{S%}$, which was calculated from the intercepts, $K_{D,A}^{S%}$ (for example see Figure 2), can be estimated easily. These log$K_{D,M}^{S%}$ values were $-8.34 \pm 0.41$ for M = Li, $-5.45 \pm 0.96$ for Na, $-3.13 \pm 0.72$ for K, $-6.78$ for Rb, and $-5.95$ for Cs. Here, the errors corresponding to log$K_{D,M}^{S%}$ were approximately employed as the errors of log$K_{D,Pic}^{S%}$, because of a lack [5] of the log$K_{D,Pic}^{S%}$’s error (see Table 1 & Table 2). The $K_{D,M}^{S%}$ values were in the order M = Li < Na < K > Rb < Cs. This order is the same as that of the distribution with the neutral MPic. The log$K_{D,M}^{MPic,av}$ order was M = Li (log$K_{D,M}^{MPic,av} = -4.6 \pm 0.2$) < Na (−2.8 ± 0.4) < K (−1.0 ± 0.6) ≫ Rb (−3.5) < Cs (−3.2) (see Table 2). Here the symbol $K_{D,M}^{MPic,av}$ refers to the average value of $K_{D,M}^{MPic}$. These orders for
Table 3. Various equations of experimental log$K_{D,j}$ based on some conditions.

| Equation no | Unknown or known conditions* | Symbol for $K_{D,j}$ Equations |
|-------------|------------------------------|--------------------------------|
| T1 or 10    | $x$ $u$ $v$ $K_{D,j}^{b}$ or $K_{D,j}^{c}$ | $\log K_{D,j} = \log K_{D,j}^{b} + (f/2.303)z_{j} + A_{D,j}^{c}$ |
| T2 or 6     | $x$ $u$ $v$ $K_{D,j}^{a}$ or $K_{D,j}^{c}$ | $\log K_{D,j} = \log K_{D,j}^{a} - A_{D,j}^{c}f(x) + A_{D,j}^{c}(u)$ |
| T3          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} + (f/2.303)z_{j} - A_{D,j}^{c}f(x)$ |
| T4          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} + (f/2.303)z_{j} + A_{D,j}^{c}(u)$ |
| T5          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} - A_{D,j}^{c}(0+u)$ |
| T6          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} + A_{D,j}^{c}(0+u)$ |
| T7          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} + (f/2.303)z_{j} - A_{D,j}^{c}(0+u)$ |
| T8          | $x$ $0$ or $u$ $v$ $K_{D,j}^{a}$ | $\log K_{D,j} = \log K_{D,j}^{a} + A_{D,j}^{c}(0+u)$ |

*The parameters $x$, $u$, & $v$ show unknown values & zero, $u$, & $x$ do the known ones. $b$ $K_{D,j}^{b} = [j_{aq}/[j]]$. $K_{D,j}^{c} = [j_{aq}/[j]]$. $K_{D,j}^{a} = [j_{aq}/[j]]$. $*$Defined as $K_{D,j}^{a} = [j_{aq}/[j]]$ at $x$ = 0. $^c$Defined as $K_{D,j}^{a} = [j_{aq}/[j]]$. $^d$Basic equation. $f$ $K_{D,j}^{a} = [j_{aq}/[j]]$. $^g$Defined as $K_{D,j}^{a} = [j_{aq}/[j]]$ at $x$ = 0. $^h$Defined as $K_{D,j}^{a} = [j_{aq}/[j]]$ at $x$ = 0.

Figure 2. Plot of $r_oDCB_z/w D^c_{LI}$ vs. $r_oDCB_e/w [Pic^-]$ for the LiPic distribution into oDCBz at various $r_oDCB_e/w$ values. The lines are straight ones based on the regression analysis with Equation (4). These plots are those under the conditions of $I = 0.026$ mol/L (circle), $0.058$ (square), $0.070$ (diamond), and $0.082$ (full & open triangles). Essentially, all the intercepts must indicate the same value.

DOI: 10.4236/ajac.2020.111003
M = Li-K are in agreement with those for the MPic distribution into NB [3,8] and DCE; that is, the order increases in going from M = Li to K (monotonically to Cs). The data of log $K_{D,M}^{S\%}$ for the MPic distribution into DCE at 298 K were −8.07 for M = Li, −6.09 for Na, and −5.96 for K (−5.37 for Rb & −4.60 for Cs), reported by one (Y. K.) of the authors in Chemistry Journal, 2013, vol. 3, pp. 37-43 (now this journal has not been open access). Further experiments will be needed for the RbPic and CsPic distribution into oDCBz. Similarly, the log $K_{D,A}^{S\%}$ value for the oDCBz system was estimated to be −6.30 (see Table 1) from the relation log $K_{D,A}^{S\%} = 2\log K_{D,\pm} - \log K_{D,Pic}^{S\%}$.

From Table 2, the maximum log $y_\pm$ and log $y_\pm,org$ values at org = oDCBz were calculated to be −0.02 (= −0.5114(0.0017)) and 0.00 (= −(11.3)(3.2 × 10^-6))^2, respectively. On the other hand, their minimum values were done to be −0.11 from I = 0.13 mol/L and −0.03 from $I_{org} = 9.6 \times 10^{-6}$, respectively. These results indicate that, as a measure, the predicted changes of log $K_{D,M}$ due to $I$ and $I_{org}$ are less than about 0.1 (= |log[y_\pm(min.)/y_\pm,org(max.)]|). In other words, this suggests the larger dep dependence of log $K_{D,M}$ (or log $K_{D,A}$), compared with its $I$ and $I_{org}$ dependences. The suggestion is supported by the following results. The many dep values, except for KPic distribution at $I = 0.0017$ mol/L, were present in the range of 0.057 to 0.2 V in Table 2. The [dep/0.05916] terms (see Equations (7) & (10)) at 298 K corresponding to log $y_\pm$ were calculated to be 0.96 to 3.3. At least, the deviation of about 0.1 in log($y_\pm/y_\pm,org$) seems to be effective for deviations in the NB and DCE distribution systems.

### 3.6. Correlation between log $K_{ex}$ and Dep or log $K_{D,M}^{S\%}$

**Figure 3** shows a plot of log $K_{ex}$ versus dep (see Table 2 & Appendix B) for the MPic distribution with M = Li-Cs and Ag into oDCBz. A regression line was log $K_{ex} = (0.0_\pm 0.3_\pm) - (19.7_\pm 2.3_\pm)$ dep at $R = 0.899$ without the AgPic system (see the full circle in Figure 3 & Table 1). Thus we can see that the log $K_{ex}$ values decrease with an increase in the dep values. Also, this fact suggests that the dep values are barriers to the distribution or extraction of M$^+$ with Pic$^-$ (or Pic$^-$ with M$^+$) into oDCBz. On the other hand, according to the $K_{ex}$ definition by the thermodynamic cycle, log $K_{ex}$ is expressed as log ($K_{D,M}K_{D,A}K_{MA,org}$). Introducing Equation (3) in this cycle, we immediately obtain

$$
\text{log } K_{ex} = -\text{dep}/0.05916 + \text{log} \left( K_{D,M}^{S\%}K_{D,A}^{S\%}K_{MA,org}^{S\%} \right) \\
= -16.90\text{dep} + \text{log} \left( K_{D,M}^{S\%}K_{D,A}^{S\%}K_{MA,org}^{S\%} \right)
$$

at $T = 298$ K. Comparing this equation with the experimental regression line, one can suppose that the experimental slope of −20 V$^{-1}$ is close to the theoretical one of −17 at 298 ( & 295) K. In addition to this fact, the logarithmic values of average $K_{D,M}^{S\%}$ and $K_{MPC,org}$ were $-3.3_\pm 1.8_\pm$ and $7.8_\pm 0.8_\pm$, respectively, and log $K_{D,Pic}^{S\%}$ was $-2.73$ (see Appendix B) for org = oDCBz at 295 K. A sum of the three values became $+1.3_\pm 2.0$ (the approximate value calculated without the error of log $K_{D,Pic}^{S\%}$). The estimated log($K_{D,M}^{S\%}K_{D,A}^{S\%}K_{MA,org}^{S\%}$) value was in accord
Figure 3. Plot of log$K_{ex}$ vs. dep (at 295 K) for the MPic distribution with $M = \text{Li-Cs}$ into oDCBz. The broken line is a regression one (see the text) corresponding to Equation (7), except for the point (full circle) of the AgPic system.

3.7. On the I Dependence of log$K_{ex}$

In this section, using the data in Table 2, we tried to examine a dependence of log$K_{ex}$ on the I values at 298 K. In general, it is empirically known that the Davies equation [12] is effective for analyzing the I dependences of equilibrium

with the intercept (= 0.1) of the plot within both the errors, ±2 for the estimated value and ±0.3 for the intercept. These results indicate that the regression line is essentially based on Equation (7). Also, from the above, it can be seen that the dep term is included in log $K_{ex}$ at least.

The same is also true of the plot of log$K_{ex}$ versus $S\%D,M$ plot. This plot can come from the relation

$$
\log K_{ex} = \log \left( y_+ K_{D,M}^{\text{org}} / y_{y,\text{org}} \right) + \log \left( y_- K_{D,A}^{\text{org}} / y_{y,\text{org}} \right) + \log K_{MA,\text{org}}
$$

$$
= \log K_{D,M}^{\text{org}} + \log \left( K_{D,A}^{\text{org}} K_{MA,\text{org}} \right) + 2 \log \left( y_+ / y_{y,\text{org}} \right).
$$

Additionally, the symbols, $y_+$ and $y_{y,\text{org}}$, refer to the activity coefficients of $A^+$ in the $w$ and org phases, respectively; $y_-$ and $y_{y,\text{org}}$ show their mean activity ones. The corresponding regression line with the MPic system was

$$
\log K_{ex} = (0.62 \pm 0.07) \log K_{D,M}^{\text{org}} + (1.9 \pm 0.4) \quad R = 0.903.
$$

Unfortunately, the slope and intercept were smaller than unity and the log (the product between $K_{D,M}^{\text{org}}$ and the average of $K_{MA,\text{org}}$) value of 5.2 ($\approx 7.89 - 2.737$) with the error of about ±0.9, respectively. While, the result obtained from the slope fixed at unity was

$$
\log K_{ex} = \log K_{D,M}^{\text{org}} + (4.4 \pm 0.2) \quad R = 0.716.
$$

Considering $4.5 \approx 5.2 + 2\log(y_+ / y_{y,\text{org}})$, this improvement of the intercept suggests $\log(y_+ / y_{y,\text{org}}) < 0$. Similarly, from this result, it can be seen that the $K_{D,M}^{\text{org}}$ term is included in log $K_{ex}$.

3.7. On the I Dependence of log$K_{ex}$

In this section, using the data in Table 2, we tried to examine a dependence of log$K_{ex}$ on the I values at 298 K. In general, it is empirically known that the Davies equation [12] is effective for analyzing the I dependences of equilibrium

with the intercept (= 0.1) of the plot within both the errors, ±2 for the estimated value and ±0.3 for the intercept. These results indicate that the regression line is essentially based on Equation (7). Also, from the above, it can be seen that the dep term is included in log $K_{ex}$ at least.

The same is also true of the plot of log$K_{ex}$ versus $S\%D,M$ plot. This plot can come from the relation

$$
\log K_{ex} = \log \left( y_+ K_{D,M}^{\text{org}} / y_{y,\text{org}} \right) + \log \left( y_- K_{D,A}^{\text{org}} / y_{y,\text{org}} \right) + \log K_{MA,\text{org}}
$$

$$
= \log K_{D,M}^{\text{org}} + \log \left( K_{D,A}^{\text{org}} K_{MA,\text{org}} \right) + 2 \log \left( y_+ / y_{y,\text{org}} \right).
$$

Additionally, the symbols, $y_+$ and $y_{y,\text{org}}$, refer to the activity coefficients of $A^+$ in the $w$ and org phases, respectively; $y_-$ and $y_{y,\text{org}}$ show their mean activity ones. The corresponding regression line with the MPic system was

$$
\log K_{ex} = (0.62 \pm 0.07) \log K_{D,M}^{\text{org}} + (1.9 \pm 0.4) \quad R = 0.903.
$$

Unfortunately, the slope and intercept were smaller than unity and the log (the product between $K_{D,M}^{\text{org}}$ and the average of $K_{MA,\text{org}}$) value of 5.2 ($\approx 7.89 - 2.737$) with the error of about ±0.9, respectively. While, the result obtained from the slope fixed at unity was

$$
\log K_{ex} = \log K_{D,M}^{\text{org}} + (4.4 \pm 0.2) \quad R = 0.716.
$$

Considering $4.5 \approx 5.2 + 2\log(y_+ / y_{y,\text{org}})$, this improvement of the intercept suggests $\log(y_+ / y_{y,\text{org}}) < 0$. Similarly, from this result, it can be seen that the $K_{D,M}^{\text{org}}$ term is included in log $K_{ex}$.
constants in the I ranges of less than 1 mol/L. Defining $K_{ex}^0$ as $K_a$ based on the activity expression, we can obtain

$$K_{ex}^0 = a_{MA,org}/a_M a_A = K_a/y_j y_j,$$

(8)

where $a_j$ denotes the activities of $j = M^+$ and $A^-$ in the w phase and $a_{MA,org}$ does that of MA in the org phase, being equal to a molar concentration $[MA]_{org}$. Taking logarithms of both the sides of Equation (8) and then rearranging it, the following equation was obtained:

$$\log K_{ex}^0 \approx \log K_{ex}^0 - 2Af(I)$$

(8a)

with

$$\log y_j y_j = -2Af(I)$$

(8b)

and

$$f(I) \approx I^{1/2}/(1+I^{1/2}) - 0.3I.$$  

(8c)

Hence, a non-linear regression analysis of the plots of $\log K_{ex}$ versus $I^{1/2}$ can yield experimental $\log K_{ex}^0$ and $A$ values.

Figure 4 shows an example of such plots. The regression line was $\log K_{ex} = (-1.54 \pm 0.72) - 2 \times (6.2 \pm 2.0)f(I)$ at $R = 0.875$ for the LiPic distribution into oDCBz. Also, the lines for the NaPic and KPic distribution systems were $\log K_{ex} = (0.24 \pm 0.74) - 2 \times (7.3 \pm 1.9)f(I)$ at $R = 0.885$ and $= (1.24 \pm 0.67) - 2 \times (13.6 \pm 4.3)f(I)$ at 0.916, respectively. These $A$ values were 12- to 27-times larger than that $[-0.5114 (L/mol)^{1/2}]$ calculated for pure water at 298 K. The $\log K_{ex}^0$ values for the MPic distribution were in the order $M = Li < Na \leq K > Rb > Cs (-1.14)$, where $K_{ex,av}^0$ denotes the average of $K_{ex}^0$.

3.8. On the $I_{org}$ Dependence of $\log K_{MA,org}$

As similar to the $I$ dependence of $\log K_{ex}$ we considered $K_{MA,org}^0$ based on an
activity expression as follows.

\[ K_{MA,org}^0 = \frac{[MA]}{[A_{org}]} = K_{MA,org} \frac{[M]}{[A_{org}]} = K_{MA,org} \frac{Y_{+,org}}{Y_{-,org}} \]  

(9)

Taking logarithms of both sides of this equation and then rearranging it, the following equation was obtained:

\[ \log K_{MA,org} = \log K_{MA,org}^0 - 2A_{org} \left( I_{org} \right)^{1/2} \]  

(9a)

with \( -2A_{org} \left( I_{org} \right)^{1/2} = \log y_{+,org}y_{-,org} \).

(9b)

A plot of \( \log K_{MA,org} \) versus \( I_{org}^{1/2} \) can give a straight line with the slope of \( -2A_{org} \) and the intercept of \( \log K_{MA,org}^0 \).

Figure 5 shows an example of the NaPic distribution system with \( org = oDCBz \). The broken line was the experimental regression one,

\[ \log K_{NaPic,org} = (8.1 \pm 0.1) - 2 \times (422 \pm 43) \left( I_{org} \right)^{1/2} \]  

at \( R = 0.980 \). Similar results were obtained from the other two systems:

\[ \log K_{LiPic,org} = (8.9 \pm 0.2) - 2 \times (1819 \pm 350) \left( I_{org} \right)^{1/2} \]  

at \( R = 0.949 \) and

\[ \log K_{KPic,org} = (6.8 \pm 0.4) - 2 \times (260 \pm 134) \left( I_{org} \right)^{1/2} \]  

at \( R = 0.809 \). These \( A_{org} \) values were 23- to 161-times larger than that \( = 11.3 \) (L/mol) \( 1/2 \) calculated for pure \( oDCBz \) (= org) at 298 K. These results are similar to those of \( A_{DCE} \) for the AgPic extraction system with benzo-18-crown-6 ether into DCE [14]. The \( K_{MPic,DCBz}^0 \) values at \( I_{DCBz} \to 0 \) were in the order \( M = Li > Na > K \) (≤ Rb ≤ Cs, see Table 2). This order recalls that \( Li > Na ≤ K \) of \( K_{MPic}^0 \) [19] in water potentiometrically-determined at 298 K to us. The difference in order between Na (=M) and K may reflect that between the water and \( oDCBz \) phases in the hydration to \( M^+ \).
3.9. On the Differences between $K_{D,BPh}$ or $K_{D,Cs}$ Values in the NB, DCE, and oDCBz Systems

The log $K_{D,BPh}$ values determined with the present experiments (see Table 1) were much smaller than the values reported from the distribution [3] [8] [18] and electrochemical experiments [20]. Their values have been reported to be 6.3 [3] at $I = x$ and 5.6 [8] at $I → 0$ for the NB systems; 5.396 [20] at [MgSO$_4$]$_t = 1$ mol/L and [CV’‘BPh]$_{D, DCE} = 0.05$ (CV’: crystal violet cation) and 6.13 [18] at $I → 0$ for the DCE ones. Their experimental log $K_{D,BPh}$ values were obtained here to be 4.2 for NB and −1.4 for DCE (Table 1). These differences may be understood by the dep dependence of the log $K_{D,BPh}$ values, as described in the Section 3.5.

Although numbers of the data sets of log $K_{D,BPh}$ and $I$ or $I_{org}$ were few, Equation (6) employed for $A^-$ has possibility for showing the $I$ or $I_{org}$ dependence of the log $K_{D,BPh}$ values. So, using Equations (3) and (6), we can immediately derive the following basic equation:

$$\log K_{D,j} = \log K_{D,j}^{SN} + (f/2.303)z_j \text{dep} - A_{j}z_j f(I) + A_{org}z_j f(I_{org})$$

with $j = M^+, A^-$ and $K_{D,j}^{SN} = y_{j,org} K_{D,j}^{SN}/y_j = y_{j,org} K_{D,j}^{SN}/y_j$. This expression can be an overall one about $K_{D,j} = [j]_{org}/[j]$. Table 3 summarizes variation of Equation (10) based on the conditions of $I$, $I_{org}$, and dep. These equations can be classified into two groups in whether the equation contains the dep term or not. So this difference can give the larger difference in log $K_{D,j}$ between the two groups, such as Equations (10), (T3), (T4), and (T7) and Equations (6), (T5), (T6), and (T8). In particular, we can expect that differences in value among Equations (6), (T5), (T6), and (T8) are the smaller than those among Equations (10), (T3), (T4), and (T7), since $\log(y/y_{j,org}) = ±0.1$ and $|\text{dep}/0.05916| = 1$ to 3, as estimated above (the section 3.5).

Based on Equation (10) or (T1), we can handle the above data for the w/NB systems as follows. Using the relation

$$4.2 = \log K_{D,j}^{SN} + (f/2.303)z_j \times 0 - A_{j}z_j f(0) + A_{NB}z_j \times 0^{1/2} = \log K_{D,j}^{SN} + 0 - 0 + 0$$

with $A = 0.5114$, $b = 0.3$, and $A_{NB} = 1.725$ at $j = BPh^+_4$, we immediately obtained log $K_{D,j}^{SN} = 4.2$ at $z_j = -1$. From $6.3 = 4.2 - (f/2.303)v - A_{f}(x) + A_{eq}u^{1/2}$, the $-16.90v - A_{f}(x) + A_{eq}u^{1/2}$ term at 298 K was obtained to be 2.1 at $z_j = -1$. Also, using $5.6 + A_{f}(0) = 4.2 - (f/2.303)v + A_{eq}u^{1/2}$, the $-(f/2.303)v + A_{eq}u^{1/2}$ term equals 1.4 with $5.6 = \log K_{D,BPh}^{SN} = 4.2 - 16.90v + 1.725u^{1/2}$. These cases suggest that the former of 6.3 is log $K_{D,BPh}^{SN}$ [Equation (10) or (T1)] in Table 3 and the latter of 5.6 is log $K_{D,BPh}^{SN}$ [Equation (T4)]. Strictly speaking, it is difficult to compare 6.3 with 5.6.

Similarly, the relation $-1.4 = \log K_{D,j}^{SN} + 0 - 0 + A_{DCE} \times 0^{1/2}$ gave $-1.4$ as log $K_{D,j}^{SN}$ with $A_{DCE} = 10.63$ at $j = BPh^+_4$. For $5.396 = \log K_{D,BPh}^{SN} = -1.4 - (f/2.303)v - A_{f}(0.87) + A_{DCE} \times 0.0086^{1/2}$, dep ($= v$) became $-0.35$ V with $5.396 + 0.5114f(0.87) - 10.63 \times 0.0086^{1/2} = 4.527 = -1.4 -$
16.90ν at b = 0.3 and 298 K: see Appendix C for the estimation of I = 0.86ν and 
E_DCE = 0.0086. The absolute value of this dep was in good agreement with the 
E_d0 value (=0.358 V) reported by the polarographic measurements at the w/DCE in-
terface [20]. Moreover, from 6.13 = −1.4 − (f /2.303)ν − 0 + A_DCEν/2 , the
−(f/2.303)ν + A_DCEν/2 term at 298 K became 7.5 with
6.13 + Aν(0.87) = −1.4 − 16.90ν + 10.63u/2. As similar to the w/NB results, the for-
mer of 5.396 + Aν(0.87) − A_DCE × 0.0086ν/2 (≈ 4.53) is log K^∞_{D,BPh} [Equa-
tion (T7)] and the latter of 6.13 is log K^∞_{D,DCE} [Equation (T4)]. Therefore, we cannot
directly compare 5.396 (or 4.53) with 6.13.

A half-wave potential for the Cs+ transfer across the w (1 mol/L MgSO4)/
oDCBz(0.05 CVBPh4) interface has been reported to be 0.12 V at 298 K [6]. It is
well known that this value is generally close to the standard electrode potential
(namely, its free energy) in electrochemical measurements. Reducing its value to
logK_D,Cs it corresponds to −2.03. So, using log K^∞_{D,Cs} = −5.94 (see Section 3.5)
based on the average value in Table 2, the following relation holds:
−2.03 = log K^0_{D,Cs} + (f /2.303)ν − Aν(0.87) + A_DCBzν/2 . Hence, the rela-
tion 16.90ν + 1.3v/2 = 4.0 was obtained with
−2.03 + Aν(0.87) = −1.91 ≈ log K^∞_{D,Cs} = −5.94 + 16.90ν + 1.3v/2 . Here, we were
not able to estimate the dep and J_GCBz values, because the K_MA,oDCBz value for
MA = CV’BPh4− (the supporting electrolyte) in the oDCBz phase had not been
found [6].

As another example, the log K^∞_{D,Cs} value has been reported to be −6.35 [21]
for the CsPic distribution into DCE at 298 K. Similarly, the relation
log K_{D,Cs} + Aν(x) − A_DCEν/2 = −6.35 = log K^∞_{D,Cs} = −4.60 + 16.90ν holds. So,
we can estimate its dep (= ν) value to be −0.1 V at 298 K. In these cases, the former
of −2.03 + Aν(0.87) is approximately log K^∞_{D,C} [Equation (T4)] and the latter of
−6.35 is log K^∞_{D,Cs} [Equation (T7)].

Thus, these results support the above understanding about the conditional
K^S_{D,BPh4} or K_{D,Cs} and self-consistently suggest that their values are functions [16]
[22] containing dep, I and L_eq that is, K^S_{D,BPh4} = K^S_{D,BPh4} (y_i/y_i eq) exp(−fdep)
or K_{D,Cs} = K^S_{D,Cs} (y_i/y_i eq) exp(−feq). Also, the condition of dep = 0 V gives
K^S_{D,BPh4} = K^S_{D,BPh4} (y_i/y_i eq). From such an equation, we can see that the ap-
parent I or L_eq values, such as [supporting electrolyte]o, [MA], and [MA]_eq are
not effective for estimating K^S_{D,A} (or K^S_{D,M}), but their practical I or L_eq values
become more effective. This indicates that comparing such conditional K_{D,A} and
K_{D,M} values is very difficult. Especially, it is very important for evaluating the
K^S_{D,BPh4} value, because BPh4− is the standard material in the dep determination,
as described in the introduction.

4. Conclusions

The logK rx and logK MA,eq values were well expressed by Equation (8a) with I and
Equation (9a) with L_eq, respectively. Now, it is unclear why the experimental A
and A_eq values are much larger than their theoretical ones. Also, the MA distri-
bution experiments based on the $V_{eq}/V$ variation provided us a procedure for the $K_{D,M}^S$ or $K_{D,A}^S$ determination under the constant condition of $I$, namely $[^1[A^-] =[^1[M^+]]$ = a constant value. So, in the single MA distribution, we could get the experimental procedure without the addition of any ionic strength conditioners (ISC) into the w phase. Besides, by introducing $K_{D,M}^{S_{\text{w}}}$, $K_{D,M}^{S_{\text{w}}/0}$, or $K_{D,M}^{S_{\text{w}}/x}$ in the $K_{D,M}$ expression, a possibility for interpreting differences among various experimental values of $K_{D,M}$ or $K_{D,A}$ was shown with Equation (10). The effect of the activity coefficients terms for both the phases on the $K_{D,A}^S$ determination was smaller than that of the dep term at least. This result indicates that the $\log\left(\frac{K_{D,A}^{\exp 1}}{K_{D,A}^{\exp 2}}\right)$ term is approximately proportional to the $-(\text{dep}^{\exp 1} - \text{dep}^{\exp 2})$ one by using Equation (T7) for the same $A^-$ and diluent. In comparing various experimental $K_{D,A}$ or $K_{D,M}$ values, readers need a suitable attention to the experimental concentrations of the salts, the supporting electrolytes, and ISC added in both phases. So, it is difficult to critically evaluate various $K_{D,M}$ or $K_{D,A}$ values without such a precise description of experimental conditions.

From the above, we propose a clear description of the $I$ and $I_{eq}$ conditions in the distribution experiments at least. If possible, ion-pair formation or ion association data for the supporting electrolytes or ISC in the phases should be also added.

**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix A

We derived Equation (3a) as follows. First, the following reasonable conditions in the present distribution system were assumed for the derivation: (C1) \( \text{dep}_+ = \text{dep}_- \), (C2) \( K_{D,+} = K_{D,-} \), and (C3) \( K^2_{D,\pm} = K_{D,+} K_{D,-} \).

(A) Derivation of a basic equation starting from (C1). Next, we obtained from Equation (3) the relation

\[
(2.303/f) \log K_{D,\pm} = (\text{dep}_+ - \text{dep}_-)/2 \tag{A1}
\]

with \( f = F/RT \). Applying (C3) to this relation and rearranging it, the following equation was derived.

\[
(2.303/f) \log K_{D,\pm} = (\text{dep}_+ - \text{dep}_-)/2 \tag{A2}
\]

(B) Derivation of another equation based on (C2). Similarly, using

\[
(2.303/f) \log K^5_{D,\pm} = \text{dep}_+ \tag{A3}
\]

Introducing Equation (A3) in \( \text{dep}_+ = \text{dep}_+ + (2.303/f) \log K_{D,+} \) (another expression of Equation (3)), we can immediately obtain

\[ \text{dep}_+ = \text{dep}_+ + \text{dep}_- - \text{dep}_- \] under the condition of (C2). Rearranging this equation based on (C1) can yield

\[
\text{dep}_+ = \text{dep}_- = \left( \text{dep}_+ + \text{dep}_- \right)/2. \tag{A4}
\]

Here, we define \( \left( \text{dep}_+ + \text{dep}_- \right)/2 \) as \( \text{dep}_+ \) and accordingly this means \( \text{dep}_+ = \text{dep}_- = \text{dep}_0 \).

Lastly, adding Equation (A2) in Equation (A4) in each side and then rearranging it give the equation

\[
\text{dep}_0 = \text{dep}_+ - (2.303/f) \log K_{D,\pm}. \tag{A5}
\]

Also, subtracting Equation (A4) from Equation (A2) in each side and then rearranging it give

\[
\text{dep}_0 = \text{dep}_+ + (2.303/f) \log K_{D,\pm}. \tag{A6}
\]

These equations, (A5) and (A6), are applicable to the MA distribution system with the univalent anion \( A^- \) and that with the cation \( M^+ \), respectively. Therefore, the combination of Equations (A5) and (A6) becomes Equation (3a) with the relations of

\[
(2.303/f) \log K^5_{D,\pm} = \text{dep}_+ \]

Appendix B

The \( I_{DCBz} \) value for the oDCBz solution in 0.01 mol/L CA and the \( I \) value for the 0.0035 mol/L Li_2SO_4 solution were estimated in the following way. Here, the symbol CA means PNP+DCC⁻\[5\], \( \mu \)-nitrido-bis(triphenylphosphorus) 3,3-como-bis(undecahydro-1,2-dicarba-3-cobalta-closododecarbo)ate. The association constant \( (K_{CA,org}) \) for \( C^+_{org} + A^-_{org} \rightleftharpoons CA_{org} \) in the oDCBz (= org) solution of 0.01 mol/L CA at 295 K has been reported to be \( 2 \times 10^3 \) L/mol from conduc-
tivity data [5]. From the quadratic equation for $[C^+]_{org}$ (= $[A^-]_{org}$), therefore, we obtained

$$[C^+]_{org}/\text{mol} \cdot \text{L}^{-1} = \left(1 + 0.04K_{CA,org}\right)^{1/2} - 1\right) / 2K_{CA,org} = 0.0020$$  \hspace{1cm} (A7)

with $K_{CA} = 2 \times 10^3$. This $[C^+]_{org}$ value basically equals the I_{DCBz} one.

Similarly, the association constant $(K_{LiSO_4})$ for $Li^+ + SO_4^{2-} \rightleftharpoons LiSO_4^-$ in the aqueous solution of $I = 0.244$ mol/kg at 298 K has been reported to be $10^{0.77}$ kg/mol [23]. Therefore,

$$[Li^+] / \text{mol} \cdot \text{L}^{-1} \approx \left(1 + 0.0140K_{LiSO_4}\right)^{1/2} - 1\right) / 2K_{LiSO_4} = 0.0033 \approx [SO_4^{2-}]$$  \hspace{1cm} (A8)

with $K_{LiSO_4} \approx 13$ L/mol and $I \approx 0.0102$ mol/L under the condition of $[LiSO_4]_t = 0.0035$ mol/L [24] in the w phase at 298 K.

On the basis of the above calculation, the log $K_{D,Pic}^{w/x}$ value (= -2.277 [5]) was changed into the log $K_{D,Pic}^{w}$ one as follows. According to Equation (T7) in Table 3, the relation

$$\log K_{D,Pic}^{w/x} \approx \log K_{D,Pic}^{w} + Af(x) - A_{org}(u)^{1/2} \approx \log K_{D,Pic}^{w} - 16.90v$$  \hspace{1cm} (A9)

holds in this case at 298 K. Using $x \approx 0.0102$ mol/L and $u \approx 0.0020$ with $b = 0.3$ for the oDCBz systems, we immediately obtained

$$\log K_{D,Pic}^{w/x} \approx \log K_{D,Pic}^{w} + 0.0140 \approx -2.277.$$  \hspace{1cm} (A9)

This value was assumed to be that at $I$ and $I_{DCBz} \rightarrow 0$ (see the text) and then employed for the log $K_{D,M}^{w}$ evaluation with $\log K_{D,M}^{w} = 2\log K_{D,A} - \log K_{D,Pic} = 2\log K_{D,+} + 2.73$, in this study. Also, the dep values at 298 K in Table 2 were calculated from the rearranged equation of Equation (3a):

$$\text{dep} = 0.05916 \left(\log K_{D,+} - \log K_{D,M}^{w}\right).$$  \hspace{1cm} (A10)

### Appendix C

As similar to Appendix B, the $I$ and $I_{DCE}$ values for the w(1 mol/L MgSO_4)/DCE(0.05 CVBPh_4) system were evaluated. The thermodynamic association constant $(K_{MgA}^w)$ for $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4^-(=MgA)$ in water at 298 K has been reported to be 135 L/mol [24]. With the successive approximation method, its $[Mg^{2+}](=[SO_4^{2-}])$ in the total concentration, $[MgSO_4]_t = 1$ mol/L [20], can be evaluated to be 0.21 mol/L, which was calculated from the equation

$$[Mg^{2+}] = \left(1 + 4K_{MgA}\right)^{1/2} - 1\right) / 2K_{MgA} \cdot$$  \hspace{1cm} (A11)

Consequently, the $I (=4[Mg^{2+}])$ value of the aqueous BPh_4^- solution with 1 mol/L MgSO_4 became 0.86; mol/L at which $K_{MgA}$ was estimated to be 16.7 L/mol. In this computation, the $K_{MgA}$ value was evaluated from

$$\log K_{MgA} = \log K_{MgA}^w - 2 \times 0.5114 \times (2)^{1/2} \times f(I).$$  \hspace{1cm} (A11)

Accordingly, $\log y^- = -0.114$ at $I = 0.86$ was approximately obtained from $-0.5114 \times (-1)^{1/2} \times \left(1 + 0.5114 \times (2)^{1/2} - 0.3I\right)$ for the BPh_4^- solution. Here, the symbol $K_{MgA}$ denotes the concentration equilibrium constant. The estimated $\log y$ value suggests the ion-pair formation of BPh_4^- in water.
Similarly, the association constant \( (K_{\text{CVA,DCE}}) \) for \( CV^+_{\text{DCE}} + A^-_{\text{DCE}} \leftrightarrow CVA_{\text{DCE}} \) in the DCE solution of 0.05 mol/L crystal violet cation \( CV^+ \) with \( A^- = B\text{Ph}_4^- \) at 298 K has been reported to be 560 L/mol [20]. Therefore,

\[
\left[ CV^+ \right]_{\text{DCE}} \text{ mol} \cdot \text{L}^{-1} = \left[ A^- \right]_{\text{DCE}} \\
= \left( 1 + 0.20K_{\text{CVA,DCE}} \right)^{1/2} - 1 \right)^2 K_{\text{CVA,DCE}} = 0.0086 \\
\]

which equals the \( J_{\text{DCE}} \) value.