Distribution of Ag(I), Li(I)-Cs(I) Picrates, and Na(I) Tetraphenylborate 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 (V_{org}/V) between water and oDCBz phases, where "org" shows an organic phase. Simultaneously, an analytic equation with the V_{org}/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 $NaB(C_6H_5)_4$ (=$NaBPh_4$) one into NB and DCE were studied at 298 K under the conditions of various V_{org}/V values. So, extraction constants (K_{ex}) for MPic into the org phases, their ion-pair formation constants ($K_{MA,org}$) for MA = MPic in the org ones, and standard distribution constants ($K_{D,M}^S$) 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 $K_{ex}(NaA)$, $K_{NaA,org}$, and $K_{D,A}^S$ values were done at $A^- = BPh_4^-$. Here, the symbols K_{ex}, $K_{MA,org}$, and $K_{D,M}^S$ or $K_{D,A}^S$ 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 K_{ex} and $K_{MPic,org}$ were examined at M = Li(I)-K(I) and org = oDCBz. From above, the conditional distribution constants, $K_{D,BPh4}$ and $K_{D,Cs}$, were classified by checking the experimental conditions of the I, I_{org}, and dep values.

Keywords

Standard Distribution Constants, Volume Ratios, Distribution Equilibrium

Potentials, Ionic Strength Dependence, Extraction Constant, Ion-Pair Formation Constant, *o*-Dichlorobenzene

1. Introduction

In electrochemistry at liquid/liquid interfaces, such as water/nitrobenzene (w/NB) and w/1,2-dichloroethane (w/DCE) ones, formal potentials ($\mathrm{dep}_j^{0\prime}$) 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 ($\mathrm{Ph_4As^+BPh_4^-}$) and so on [1] [2] [3] in many cases. In these studies, there are many data for the potentials $\mathrm{dep}_j^{0\prime}$ in the w/NB and w/DCE systems [1] [2] [3] [4], while there are some data [5] [6] for w/*o*-dichlorobenzene (*o*DCBz) one. Especially, the data [6] for the metal ions (M^{z+} at $z = 1$) seems to be very few. Also, the $\mathrm{dep}_j^{0\prime}$ values have been converted with the relation, $\mathrm{dep}_j^{0\prime} = -\left(1/z_j f\right)\ln K_{\mathrm{D},j}^{\mathrm{S}}$ [7] [8], at dep = 0 V into standard distribution constants ($K_{\mathrm{D},j}^{\mathrm{S}}$) 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 $\mathrm{dep}_{\mathrm{M}}^{0\prime} = -\left(0.05916\right)\log K_{\mathrm{D,M}}^{\mathrm{S}}$ {or $\mathrm{dep}_+^{0\prime} = -\left(0.05916\right)\log K_{\mathrm{D,+}}^{\mathrm{S}}$} with $j = \mathrm{M}^+$ holds at dep = 0 V and $T = 298.1_5$ K. Generally such $K_{\mathrm{D},j}^{\mathrm{S}}$ values have been determined by solvent extraction experiments with $j = \mathrm{M}^+$, 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, $K_{\mathrm{D},j}^{\mathrm{S}}$, at dep = 0 V and $T \approx 298$ K for $j = \mathrm{Ag}^+$, $\mathrm{Li}^+\text{-}\mathrm{Cs}^+$, and $\mathrm{BPh_4^-}$ into some diluents. The $K_{\mathrm{D,Ag}}^{\mathrm{S}}$ values were obtained from NB, DCE, *o*DCBz, and dichloromethane (DCM) systems with the reported $K_{\mathrm{D,Pic}}^{\mathrm{S}}$ value [5] [8] [11] of picrate ion (Pic$^-$), the $K_{\mathrm{D},j}^{\mathrm{S}}$ values at $j = \mathrm{Li}^+\text{-}\mathrm{Cs}^+$ from *o*DCBz one with that [5] of Pic$^-$, and the $K_{\mathrm{D,BPh4}}^{\mathrm{S}}$ values from NB and DCE ones with the $K_{\mathrm{D,Na}}^{\mathrm{S}}$ value [8] of Na$^+$. In the experiments corresponding to the above systems, volume ratios ($= V_{\mathrm{org}}/V = r_{\mathrm{org/w}}$) 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_{ex}, $K_{\mathrm{MA,org}}$, and $K_{\mathrm{D,MA}}$ values were obtained at 298 K from the same combinations of $\mathrm{M^+A^-}$ and the diluents. Here, the symbols K_{ex}, $K_{\mathrm{MA,org}}$, and $K_{\mathrm{D,MA}}$ were defined as $[\mathrm{MA}]_{\mathrm{org}}/[\mathrm{M^+}][\mathrm{A^-}]$, $[\mathrm{MA}]_{\mathrm{org}}/[\mathrm{M^+}]_{\mathrm{org}}[\mathrm{A^-}]_{\mathrm{org}}$, and $[\mathrm{MA}]_{\mathrm{org}}/[\mathrm{MA}]$, 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_{ex} and $K_{MPic,org}$ (M = Li-K) on the ionic strength of both w and oDCBz (=org) phases were examined. About the distribution with BPh_4^- or Cs^+, differences among its K_{D,BPh_4} or $K_{D,Cs}$ 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: ≥95.0%, Kanto Chemical) and NaBPh₄ {guaranteed pure reagent (GR): ≥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: 7.34_3% for M(I) = Li; 6.23_2 for Na; 1.23_0 for K; 2.76_7 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), oDCBz (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 AgNO₃ (GR: ≥ 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 NaBPh₄ Distribution

Aqueous solutions of MPic or NaBPh₄ were mixed with some diluents in the various $r_{org/w}$ (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 NaBPh₄ 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 NaBPh₄ distribution systems were back-extracted by using 0.1 mol/L HNO₃, 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 NaBPh$_4$ distribution into several diluents at 298 K with various $r_{org/w}$ conditions.

MA	Diluent (org)	$\log K_{D,\pm}$[a]	dep[b]/V	$\log(\ K^S_{D,Ag}\ $ or $\ K^{S\%}_{D,BPh_4}\ )$
AgPic	NB at $r_{org/w}$ = 1	-2.12 ± 0.03	0.13	-4.30[a,e]
	DCE at $r_{org/w}$ = 1[d]	-3.74	0.16	-6.47[a,e]
	DCE at $r_{org/w}$ = 0.12 - 8.3	$-3.8_5 \pm 0.1_6$	0.1_7	$-6.6_9 \pm 0.2_2$[a,e]
	oDCBz at $r_{org/w}$ = 1.2 - 20	-4.52 ± 0.07	0.11[f]	-6.30[e,g]
	DCM at $r_{org/w}$ = 1.0 - 27	$-3.9_5 \pm 0.1_5$	0.1_9	$-7.2_3 \pm 0.1_5$[e]
NaBPh$_4$	NB at $r_{org/w}$ = 0.50 - 7.5	$-0.5_0 \pm 0.2_1$	0.3_6	4.2 ± 0.2[a,h,i]
	DCE at $r_{org/w}$ = 1.0 - 8.0	$-3.7_4 \pm 0.2_8$	0.1_4	-1.4 ± 0.3[a,h,i]

I/mol·L^{-1}	$\log K_{ex}$	$\log K_{D,MA}$	I_{org}[e]/mol·L^{-1}	$\log K_{MA,org}$
0.022	-0.46 ± 0.03	-0.79 ± 0.05	1.6×10^{-4}	3.79 ± 0.05
0.020[e]	-1.49	-1.83[f]	3.6×10^{-6e}	5.992
0.023	$-1.0_2 \pm 0.3_9$	$-1.3_5 \pm 0.3_9$	3.2×10^{-6}	6.3 ± 0.4
0.043	$-2.5_2 \pm 0.3_7$	$-2.8_1 \pm 0.3_7$	1.3×10^{-6}	6.5 ± 0.4
0.044	$-1.5_8 \pm 0.2_8$	$-1.8_6 \pm 0.2_8$	4.9×10^{-6}	6.3 ± 0.4
0.00025	$3.9_0 \pm 0.2_7$	$2.7_6 \pm 0.2_7$	8.0×10^{-5}	4.9 ± 0.4
0.019	$-0.7_1 \pm 0.3_7$	$-1.7_6 \pm 0.3_7$	3.4×10^{-6}	6.8 ± 0.8

[a]Values at I & $I_{org} \to 0$. [b]Values calculated from Equation (3a). See the footnotes e & h for the $\log K^S_{D,Pic}$ & $\log K^{S\%}_{D,Na}$ values. [c]Average values. [d]Ref. [14]. [e]Values calculated from $\log K^S_{D,Pic} = 0.05$ at I & $I_{NB} \to 0$; -1.01_1 at I & $I_{DCE} \to 0$; -2.73_7 at [Li$_2$SO$_4$]$_t$ = 0.0035 mol/L, [PNP$^+$DCC$^-$]$_{t,oDCBz}$ = 0.01, & 295 K; -0.68 for the w/DCM system. See refs. [5], [8], & [11] & **Appendix B**. [f]Values calculated from the original data of ref. [14]. [g]Values determined at 295 - 298 K, where $\log K^S_{D,Ag}$ corresponds $\log K^{S\%}_{D,Ag}$. See the text & Equation (T8) in **Table 3** for the $\log K^{S\%}_{D,Ag}$ estimation. [h]Calculated from $\log K^{S\%}_{D,Na} = -5.18$ for w/NB; -6.09 for w/DCE. See ref. [8]. [i]The maximum values among errors used for calculation were described.

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

M	I/mol·L^{-1} ($r_{org/w}$ range)	$\log K_{D,\pm}$[a]	dep[b,c]/V	$\log K^{S\%}_{D,M}$[c,d]	$\log K_{ex}$	$\log K_{D,MPic}$	I_{org}[e]/mol·L^{-1}	$\log K_{MPic,org}$
	0.026 (1.0 - 4.0)	$-5.5_3 \pm 0.6_1$	0.1_7	$-8.3_2 \pm 0.6_1$	$-3.1_5 \pm 0.2_4$	-4.4	7.6×10^{-8}	7.9 ± 0.9
	0.058 (1.0 - 3.0)	$-5.4_4 \pm 0.2_8$	0.1_6	$-8.1_4 \pm 0.2_8$	$-3.5_9 \pm 0.1_7$	-4.5	2.1×10^{-7}	7.3 ± 0.4
Li	0.070 (1.0)	-6.0 ± 2.3	0.2	-9.2 ± 2.3	$-4.1_9 \pm 0.5_5$	-5.1	7.6×10^{-8}	$7._7 \pm 2._4$
	0.082 (2.0 - 4.1)	-5.3[f]	0.1_5	$-7.8_6 \pm 0.3_9$	-3.87 ± 0.09	-4.7	4.1×10^{-7}	6.7 ± 0.6
	0.082 (1.0 - 2.9)	-6.2 ± 1.2	0.2	$-9._7 \pm 1._2$	$-4.0_2 \pm 0.1_4$	-4.9	4.7×10^{-8}	$8._5 \pm 1._7$
	0.038 (1.0 - 7.5)	$-4.9_1 \pm 0.5_7$	0.1_3	$-7.0_9 \pm 0.5_7$	$-2.1_4 \pm 0.3_2$	-2.6	4.6×10^{-7}	7.7 ± 0.9
	0.049 (6.0 - 12)	-3.71 ± 0.01	0.057	-4.68	$-1.8_5 \pm 0.1_2$	-2.3	9.6×10^{-6}	5.6 ± 0.1
Na	0.070 (1.0 - 12)	$-5.1_0 \pm 0.4_1$	0.1_4	$-7.4_5 \pm 0.4_1$	$-2.6_4 \pm 0.3_9$	-3.1	5.6×10^{-7}	7.5 ± 0.7
	0.090 (4.0 - 15)	-4.8[f]	0.1_2	$-6.9_0 \pm 0.4_6$	$-2.5_2 \pm 0.2_0$	-2.9	1.4×10^{-6}	7.1 ± 0.7
	0.11 (1.2 - 6.0)	$-5.0_6 \pm 0.8_3$	0.1_4	$-7.3_8 \pm 0.8_3$	$-3.0_1 \pm 0.2_8$	-3.4	9.2×10^{-7}	$7._1 \pm 1._2$
	0.13 (1.0 - 12)	$-5.4_4 \pm 0.7_4$	0.1_6	$-8.1_4 \pm 0.7_4$	$-3.0_8 \pm 0.3_4$	-3.5	4.6×10^{-7}	$7._8 \pm 1._1$
	0.0017 (1.5 - 3.0)	-2.6 ± 1.0	-0.01	-2.5 ± 1.0	$0.5_6 \pm 0.1_2$	-0.5	3.8×10^{-6}	$5._8 \pm 1._4$
K	0.0040 (1.5 - 6.0)	$-3.4_9 \pm 0.2_2$	0.04_3	$-4.2_5 \pm 0.2_2$	$-0.5_5 \pm 0.2_3$	-1.3	1.3×10^{-6}	6.4 ± 0.4
	0.0078 (1.0 - 3.0)	$-3.7_6 \pm 0.3_1$	0.06_0	$-4.7_8 \pm 0.3_1$	$-1.3_7 \pm 0.1_8$	-2.1	1.4×10^{-6}	6.1 ± 0.5
	0.020 (1.2 - 4.0)	-3.9[f]	0.07_1	$-5.1_0 \pm 0.3_9$	$-1.6_7 \pm 0.2_0$	-2.3	2.5×10^{-6}	6.2 ± 0.6
Rb	0.0047 (1.7 - 6.0)	$-4.6_2 \pm 0.8_0$	0.1_1	$-6.5_0 \pm 0.8_0$	$-1.6_2 \pm 0.1_9$	-3.4	1.1×10^{-7}	$7._6 \pm 1._1$
	0.0071 (2.0 - 7.5)	-5.3 ± 1.2	0.2	$-7._9 \pm 1._2$	$-1.8_4 \pm 0.2_0$	-3.6	3.2×10^{-8}	$8._8 \pm 1._7$
Cs	0.0032 (1.1 - 12)	$-4.2_2 \pm 0.1_6$	0.1_4	$-6.6_3 \pm 0.1_9$	$-1.0_1 \pm 0.3_0$	-3.0	2.0×10^{-7}	7.4 ± 0.4
	0.0032 (1.0 - 12)	$-4.6_9 \pm 0.1_9$	0.06_0	$-5.6_9 \pm 0.1_6$	$-1.5_2 \pm 0.4_0$	-3.5	6.7×10^{-8}	7.9 ± 0.5

[a]Values at I & $I_{oDCBz} \to 0$. [b]Values calculated from $\log K^{S\%}_{D,Pic} = -2.73_7$ at [Li$_2$SO$_4$]$_t$ = 0.0035 mol/L, [PNP$^+$DCC$^-$]$_{t,org}$ = 0.01, & 295 K using Equation (3a). See ref. [5]. [c]Values determined at 295 - 298 K. [d]Values expressed as the errors which equal those of $\log K_{D,\pm}$. See the text. [e]Average values. [f]Ref. [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 $NaBPh_4$ 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 $K_{MA}\,^V[M^+]^2 + {}^V[M^+] - [M]_{t,w} = 0$ {see Equation (1) for the symbols $^V[M^+]$ & $[M]_{t,w}$} and then obtain from it $^V[M^+] = {}^V[A^-] = \left\{ (1 + 4K_{MA}[M]_{t,w})^{1/2} - 1 \right\} / 2K_{MA}$. From the latter equation, we calculated self-consistent $^V[A^-]$ and K_{MA} values by a successive approximation with $\log K_{MA} = \log K_{MA}^0 + 2\log y_{\pm}$ [8]. Here, the symbols, K_{MA}, K_{MA}^0, and $y_{\pm}$, denote an ion-pair formation constant for MA in water at concentration expression, that at $^V[A^-]$ (= ionic strength) $\to$ 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:

$$[M]_t V = [M]_{t,w} V + [M]_{t,org} V_{org}, \tag{1}$$

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 $^V[M^+] V$ and then rearranged into

$$r_{org/w} [M]_{t,org} \Big/ {}^V[M^+] = ([M]_t - [M]_{t,w}) \Big/ {}^V[M^+]$$
$$= r_{org/w} ([M^+]_{org} + [MA]_{org}) \Big/ {}^V[M^+], \tag{2}$$

using the mass balance relation of $[M]_{t,org} = [M^+]_{org} + [MA]_{org}$ in the org phase.

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

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

$$\text{dep} = \phi - \phi_{org} = 0.05916\left(\log K_{D,M} - \log K^S_{D,M}\right)$$
$$= -0.05916\left(\log K_{D,A} - \log K^S_{D,A}\right). \tag{3}$$

Here, the symbols ϕ (or ϕ_{org}), $K_{D,M}$, and $K_{D,A}$ denote an inner potential of the w (or org) phase, the conditional distribution constant of M^+, and that of A^-, respectively, in this equation; see the introduction for the symbols $K^S_{D,M}$ and $K^S_{D,A}$. This dep practically means a total energy which is necessary for the M^+ or 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).

$$\text{dep} = \text{dep}_\pm = 0.05916\left(\log K_{D,\pm} - \log K^S_{D,M}\right) = -0.05916\left(\log K_{D,\pm} - \log K^S_{D,A}\right) \tag{3a}$$

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

$$r_{org/w}\left[M\right]_{t,org}\Big/{^V\left[M^+\right]} = r_{org/w}D^{expl.}_M = K_{D,M} + K'_{ex}r_{org/w}{^V\left[A^-\right]}$$
$$= K_{D,\pm} + K'_{ex}r_{org/w}{^V\left[A^-\right]} \tag{4}$$

under the conditions of $K_{D,M} = K_{D,A}$ (see above) and $K^S_{D,M} \neq K^S_{D,A}$. Here $r_{org/w}D^{expl.}_M$ equals an experimental (expl.) value, $^V[M]_{t,org}/^V[M^+]$, corresponding to the distribution ratio of M(I) [8]. Hence, the plot of $r_{org/w}D^{expl.}_M$ *versus* $r_{org/w}{^V\left[A^-\right]}$ based on Equation (4) can give K'_{ex} as the slope and $K_{D,\pm}$ as the intercept. Interestingly, we can obtain the plot with changing $r_{org/w}$ under the constant condition of $^V[A^-]$, namely, the constant ionic strength (I) in the w phases. Here, we can see that the intercept is the $K_{D,\pm}$ value under the condition of $I (= {^V[A^-]} = {^V[A^-]_{org}}/K_{D,\pm}) \to 0$ [8] at least, because of $r_{org/w} > 0$. When $K_{D,\pm} > 0$, this fact, $I = {^V[A^-]_{org}}/K_{D,\pm} \to 0$, also means $^V[A^-]_{org} (= I_{org}) \to 0$ [8]. Therefore, the intercept, $K_{D,\pm}$, satisfies both the conditions of I and $I_{org} \to 0$. Equation (4) is essentially similar to the Czapkiewicz equation [18] with $P'^{1/2}$ $(\approx K_{D,\pm})$ at C_{II} $(= r_{org/w}{^V\left[A^-\right]}$ or $^V[A^-]) \to 0$ and P' $(\approx K_{ex})$.

The symbol K'_{ex} is converted with $r_{org/w}$ into $K_{ex}\left(= r_{org/w}K'_{ex}\right)$ which is thermodynamically expressed as

$\left(K_{D,\pm}\right)^2 K_{MA,org} = K_{D,M}K_{D,A}K_{MA,org} = K_{D,M}^S K_{D,A}^S K_{MA,org}$ (see the introduction for $K_{MA,org}$). Accordingly, we can obtain the $K_{MA,org}$ 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_{org}, and also $K_{D,A}^S$ and $K_{D,M}^S$ 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 $r_{DCE/w}D_{Ag}^{expl.} = \left(1.4_0 \pm 0.5_1\right)\times10^{-4} + \left(0.0366 \pm 0.0007\right)\times r_{DCE/w}{}^V\left[\text{Pic}^-\right]$ 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 $\log K_{ex}$ one was to be $-1.0_2 \pm 0.3_9$. In the latter K_{ex} evaluation, the K_{ex} values were obtained from $K_{ex} = r_{DCE/w}K'_{ex}$ for given $r_{DCE/w}$ values and then their values were averaged. Additionally, the $\log K_{D,Ag}^S$ and $\log K_{AgPic,DCE}$ values were calculated to be -6.6_9 $\left(= 2\log K_{D,\pm} - \log K_{D,Pic}^S\right)$ with the calculation error of $\pm0.2_2$ and 6.3 $(= \log K_{ex} - \log K_{D,\pm})$ with that of ±0.4 at $I_{DCE} = 3.2 \times 10^{-6}$ mol/L, respectively. Here, I_{DCE} (or I_{org}) refers to the ionic strength in the DCE (or org) phase. These values were in agreement with those [14] at $r_{DCE/w} = 1$ reported before within their experimental errors, except for the $\log K_{ex}$ and $\log K_{D,AgPic}$ values. About these two constants, the minimum $\log K_{ex}$ value $(= -1.4_1)$ was close to that $(= -1.49$ [14]) reported before and also the minimum $\log K_{D,AgPic}$ value $(= -1.7_4)$ was somewhat larger than the
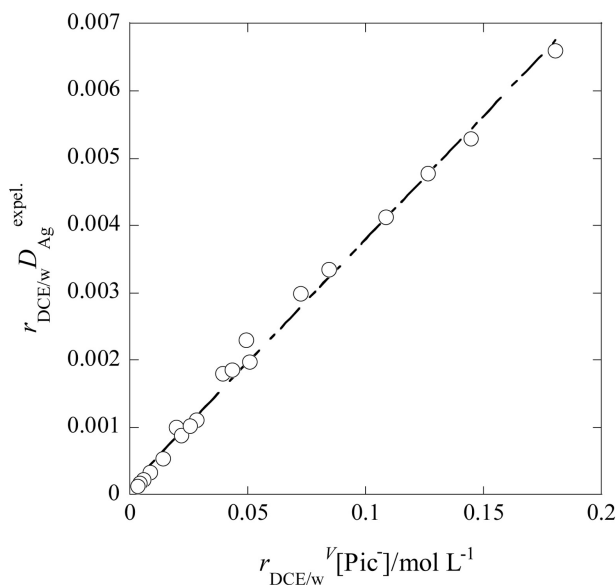

Figure 1. Plot of $r_{DCE/w}D_{Ag}^{expl.}$ *vs.* $r_{DCE/w}{}^V\left[\text{Pic}^-\right]$ for the Ag-Pic distribution into DCE at vari ous $r_{DCE/w}$ values (see **Table 1**). The broken line is a regression one based on Equation (4) (see the text).

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 NaBPh$_4$ distribution into several diluents and Table 2 does results for the LiPic-CsPic distribution into oDCBz.

In the relation of $2\log K_{D,\pm} = \log\left(K_{D,M}^{S} K_{D,A}^{S}\right)$, 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 $\log K_{D,Ag} = 2\log K_{D,\pm} - \log K_{D,Pic}$.

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.

$$D_{M}^{expl.} = K_{D,\pm}/r_{org/w} + K_{ex}'{}^{V}\left[A^{-}\right]. \tag{5}$$

As examples, these common logarithmic $K_{D,\pm}$ and K_{ex} values for the AgPic distribution into DCE were −3.2$_3$ ± 0.3$_8$ and −1.0$_2$ ± 0.3$_8$, respectively. From these values, the $\log K_{D,Ag}^{S}$ and $\log K_{AgPic,DCE}$ values were also estimated to be −5.4$_5$ ± 0.5$_3$ and 5.4 ± 0.7 at $I_{DCE} = 3.2 \times 10^{-6}$ 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 $r_{org/w}D_{M}^{expl.}$ *versus* $^{V}[A^{-}]$ based on Equation (4) was not able to give the straight line, indicating that the $K_{ex}'r_{org/w}$ (=K_{ex}) term in the plot is not the constant. This fact shows that the parameter $r_{org/w}{}^{V}\left[A^{-}\right]$ 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 (=$^{V}[A^{-}]$) 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 $I_{org} \rightarrow 0$ mol/L, that for K_{ex} in the I range of 0.020 to 0.044, and that for $K_{D,AgPic}$. Here, the $K_{D,AgPic}$ 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}^{0} 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 1.3×10^{-6} to 1.6×10^{-4} mol/L (Table 1). These orders seem to reflect polarities of the diluents, except for $K_{D,AfPic}$. Also, the $K_{D,Ag}^{S}$ values were in the order NB > oDCBz ≥ DCE > DCM (see Table 1), al-

though the value for the *o*DCBz system was calculated from $K_{D,Pic}^{S}$ [5] reported at $T = 295 \pm 3$ K and $K_{D,\pm}$ obtained here at 298 K. Moreover, it was assumed that the $\log K_{D,Pic}$ values for the *o*DCBz and DCM systems satisfy the conditions of I and $I_{org} \to 0$ and dep = 0; for the former system, that of I and $I_{org} \to 0$ or an activity expression was cleared as described in **Appendix B**.

Considering the experimental errors of $K_{D,\pm}$ (or $K_{D,M}^{S}$) in **Table 2**, except for the *o*DCBz 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.

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

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 $u_{t}//x_{t}$), its numerator shows the condition of $I_{org} \to 0$ (or the left hand side of // does the total concentration, u_{t}, 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_{t} in the w phase). According to Equation (6) at dep = 0 V, $K_{D,M}^{S} \left(= K_{D,M}^{Su/x} \right)$ equals $[M^{+}]_{org}/[M^{+}]$ as the concentration expression for a given $I = x$ or $I_{org} = u$, $K_{D,M}^{Su/0}$ does $[M^{+}]_{org}/a_{M}$ for a given $I_{org} = u$, and $K_{D,M}^{S0/x}$ does $a_{M,org}/[M^{+}]$ 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 $\log K_{D,Pic}^{\%}$ reported cyclic-volammetrically for the w/*o*DCBz system [5] satisfies the condition of dep = 0 V, the $\log K_{D,M}^{S\%}$ values were calculated from its $\log K_{D,Pic}^{\%}$ value (= -2.73_{7}, see **Appendix B** for the calculation) with $2\log K_{D,\pm}^{\%} = \log K_{D,M}^{\%} K_{D,A}^{\%}$ 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, $K_{D,\pm}^{\%}$ (for example see **Figure 2**), can be estimated easily. These $\log K_{D,M}^{S\%}$ values were $-8.3_{4} \pm 0.4_{1}$ for M = Li, $-5.4_{5} \pm 0.9_{6}$ for Na, $-3.1_{3} \pm 0.7_{2}$ for K, -6.7_{8} for Rb, and -5.9_{5} for Cs. Here, the errors corresponding to $\log K_{D,\pm}$ were approximately employed as the errors of $\log K_{D,M}^{S\%}$, 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 $K_{D,MPic}$ order was M = Li (log $K_{D,MPic,av} = -4.6 \pm 0.2$) < Na ($-2.8 \pm 0.4$) < K ($-1.0 \pm 0.6$) ≫ Rb ($-3.5$) < Cs ($-3.2$) (see **Table 2**). Here the symbol $K_{D,MPic,av}$ refers to the average value of $K_{D,MPic}$. These orders for

Table 3. Various equations of experimental $\log K_{D,j}$ based on some conditions.

Equation no	Unknown or known conditions[a]			Symbol for $K_{D,j}$	Equations
	I/mol·L⁻¹	I_{org}/mol·L⁻¹	dep/V		
T1 or 10	x	u	v	$K_{D,j}$[b] or $K_{D,j}^{u/x}$[b]	$\log K_{D,j} = \log K_{D,j}^{S\%} + (f/2.303) z_j v - A z_j^2 f(x) + A_{org} z_j^2 (u)^{1/2}$[c]
T2 or 6	x	u	0	$K_{D,j}^{S}$ or $K_{D,j}^{Su/x}$	$\log K_{D,j} = \log K_{D,j}^{S\%} - A z_j^2 f(x) + A_{org} z_j^2 (u)^{1/2}$
T3	x	0 or u_1	v	$K_{D,j}^{0/x}$[d]	$\log K_{D,j} = \log K_{D,j}^{S\%} + (f/2.303) z_j v - A z_j^2 f(x)$ or $\log K_{D,j}^{0/x} = \log K_{D,j} - A_{org} z_j^2 (0\ \text{or}\ u_1)^{1/2}$
T4	0 or x_1	u	v	$K_{D,j}^{u/0}$[e]	$\log K_{D,j} = \log K_{D,j}^{S\%} + (f/2.303) z_j v + A_{org} z_j^2 (u)^{1/2}$ or $\log K_{D,j}^{u/0} = \log K_{D,j} + A z_j^2 f(0\ \text{or}\ x_1)$
T5	x	0 or u_1	0	$K_{D,j}^{S0/x}$	$\log K_{D,j} = \log K_{D,j}^{S\%} - A z_j^2 f(x)$ or $\log K_{D,j}^{S0/x} = \log K_{D,j} - A_{org} z_j^2 (0\ \text{or}\ u_1)^{1/2}$
T6	0 or x_1	u	0	$K_{D,j}^{Su/0}$	$\log K_{D,j} = \log K_{D,j}^{S\%} + A_{org} z_j^2 (u)^{1/2}$ or $\log K_{D,j}^{Su/0} = \log K_{D,j} + A z_j^2 f(0\ \text{or}\ x_1)$
T7	0 or x_1	0 or u_1	v	$K_{D,j}^{\%}$[f]	$\log K_{D,j} = \log K_{D,j}^{S\%} + (f/2.303) z_j v$ or $\log K_{D,j}^{\%} = \log K_{D,j} + A z_j^2 f(0\ \text{or}\ x_1) - A_{org} z_j^2 (0\ \text{or}\ u_1)^{1/2}$
T8	0 or x_1	0 or u_1	0	$K_{D,j}^{S\%}$	$\log K_{D,j} = \log K_{D,j}^{S\%}$[g] or $\log K_{D,j}^{S\%} = \log K_{D,j} + A z_j^2 f(0\ \text{or}\ x_1) - A_{org} z_j^2 (0\ \text{or}\ u_1)^{1/2}$

[a]The parameters x, u, & v show unknown values & zero, u_1, & x_1 do the known ones. [b] $K_{D,j} = K_{D,j}^{u/x} = [j]_{org}/[j]$. [c]Basic equation. [d] $K_{D,j}^{0/x} = a_{j,org}/[j]$. $K_{D,j}^{u/0} = [j]_{org}/a_j$. [f] $K_{D,j}^{\%} = a_{j,org}/a_j$. [g]Defined as $K_{D,j}^{S\%} = a_{j,org}/a_j$ at dep = 0 V.
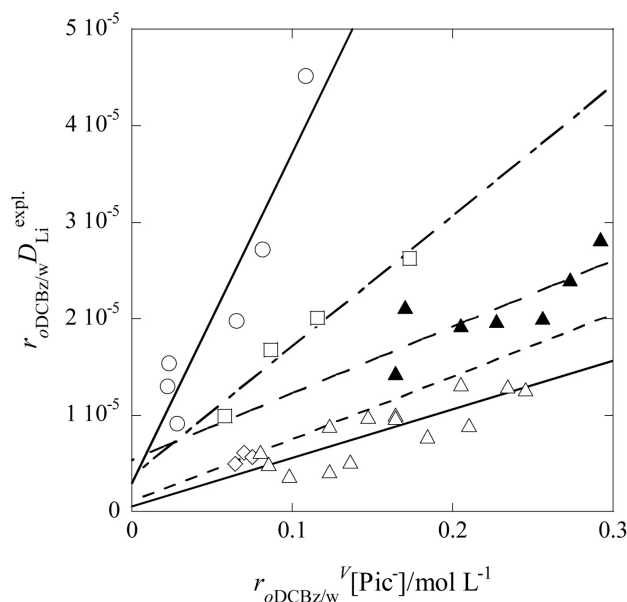

Figure 2. Plot of $r_{o\text{DCBz/w}} D_{\text{Li}}^{\text{expl.}}$ *vs.* $r_{o\text{DCBz/w}}{}^{V}[\text{Pic}^-]$ for the LiPic distribution into oDCBz at various $r_{\text{DCE/w}}$ values. The lines are straight ones based on the regression analysis with Equation (4). These plots are those under the 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.

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, −6.0$_9$ for Na, and −5.9$_5$ for K (−5.37 for Rb & −4.6$_0$ 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 $\log K_{D,Ag}^{S\%}$ value for the oDCBz system was estimated to be −6.30 (see Table 1) from the relation $\log K_{D,Ag}^{S\%} = 2 \log K_{D,\pm} - \log K_{D,Pic}^{S\%}$.

From Table 2, the maximum $\log y_+$ and $\log y_{+,org}$ values at org = oDCBz were calculated to be −0.02 {= −0.5114f(0.0017)} and 0.00 {= −(11.3)(3.2 × 10^{-8})$^{1/2}$}, 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 × 10^{-6}, respectively. These results indicate that, as a measure, the predicted changes of log $K_{D,M}$ due to I and I_{oDCBz} are less than about 0.1 {= |log[y_+(min.)/$y_{+,org}$(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 were calculated to be 0.96 to 3.$_3$. At least, the deviation of about 0.1 in log($y_+/y_{+,oDCBz}$) seems to be effective for deviations in the NB and DCE distribution systems.

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

Figure 3 shows a plot of logK_{ex} *versus* dep (see Table 2 & Appendix B) for the MPic distribution with M = Li-Cs and Ag into oDCBz. A regression line was logK_{ex} = (0.0$_6$ ± 0.3$_0$) − (19.$_7$ ± 2.$_3$) dep at R = 0.899 without the AgPic system (see the full circle in Figure 3 & Table 1). Thus we can see that the logK_{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, logK_{ex} is expressed as log ($K_{D,M}K_{D,A}K_{MA,org}$). Introducing Equation (3) in this cycle, we immediately obtain

$$
\begin{aligned}
\log K_{ex} &= -\text{dep}/0.05916 + \log\left(K_{D,M} K_{D,A}^{S} K_{MA,org}\right) \\
&= -16.90\text{dep} + \log\left(K_{D,M} K_{D,A}^{S} K_{MA,org}\right)
\end{aligned}
\tag{7}
$$

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 $K_{MPic,org}$ were −3.$_8$ ± 1.$_8$ and 7.8$_9$ ± 0.8$_9$, respectively, and $\log K_{D,Pic}^{S\%}$ was −2.73$_7$ (see Appendix B) for org = oDCBz at 295 K. A sum of the three values became +1.$_3$ ± 2.$_0$ (the approximate value calculated without the error of $\log K_{D,Pic}^{S\%}$). The estimated $\log\left(K_{D,M}^{S\%} K_{DD,A,M}^{S\%} K_{MA,org}\right)$ value was in accord
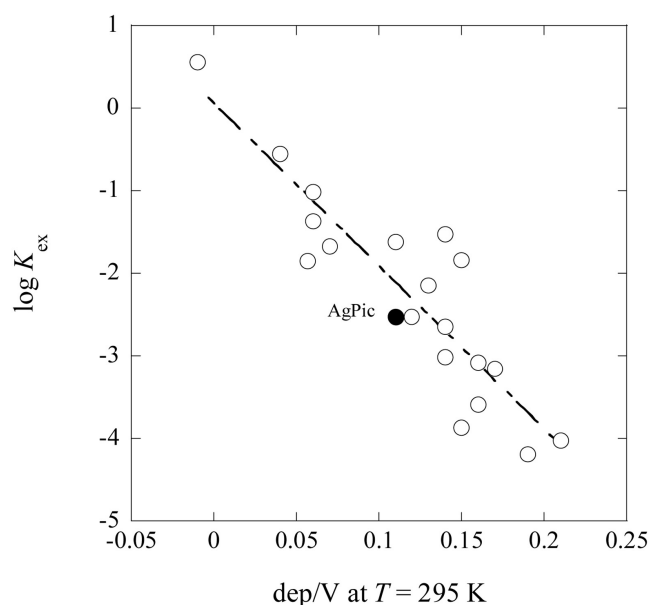
Figure 3. Plot of $\log K_{ex}$ *vs.* dep (at 295 K) for the MPic distribution with M = Li-Cs into *o*DCBz. The broken line is a regression one (see the text) corresponding to Equation (7), except for the point (full circle) of the AgPic system.

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* $\log K_{D,M}^{S\%}$ plot. This plot can come from the relation

$$\log K_{ex} = \log\left(y_+ K_{D,M}^{S\%} / y_{+,org}\right) + \log\left(y_- K_{D,A}^{S\%} / y_{-,org}\right) + \log K_{MA,org}$$
$$= \log K_{D,M}^{S\%} + \log\left(K_{D,A}^{S\%} K_{MA,org}\right) + 2\log\left(y_\pm / y_{\pm,org}\right). \tag{7a}$$

Additionally, the symbols, y_- and $y_{-,org}$, refer to the activity coefficients of A⁻ in the w and org phases, respectively; $y_\pm$ and $y_{\pm,org}$ show their mean activity ones. The corresponding regression line with the MPic system was $\log K_{ex} = \left(0.62 \pm 0.07\right)\log K_{D,M}^{S\%} + \left(1.9_1 \pm 0.4_8\right)$ at $R = 0.903$. Unfortunately, the slope and intercept were smaller than unity and the log (the product between $\log K_{D,Pic}^{S\%}$ and the average of $K_{MA,org}$) value of 5.2 ($\approx 7.8_9 - 2.73_7$) with the error of about ±0.9, respectively. While, the result obtained from the slope fixed at unity was $\log K_{ex} = \log K_{D,M}^{S\%} + \left(4.4_8 \pm 0.2_0\right)$ at $R = 0.716$. Considering $4.5 \approx 5.2 + 2\log(y_\pm/y_{\pm,org})$, this improvement of the intercept suggests $\log(y_\pm/y_{\pm,org}) < 0$. Similarly, from this result, it can be seen that the $K_{D,M}^{S\%}$ term is included in $\log K_{ex}$.

3.7. On the *I* Dependence of logK_{ex}

In this section, using the data in Table 2, we tried to examine a dependence of logK_{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

constants in the *I* ranges of less than 1 mol/L. Defining K_{ex}^0 as K_{ex} based on the activity expression, we can obtain

$$K_{ex}^0 = a_{MA,org} / a_M a_A = K_{ex} / y_+ y_- ,\qquad (8)$$

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:

$$\log K_{ex} \approx \log K_{ex}^0 - 2Af(I)\qquad (8a)$$

with $\log y_+ y_- = -2Af(I)$ (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 $\log K_{ex} = (-1.5_4 \pm 0.7_2) - 2 \times (6._2 \pm 2._0) f(I)$ at $R = 0.875$ for the LiPic distribution into *o*DCBz. Also, the lines for the NaPic and KPic distribution systems were $\log K_{ex} = (0.2_4 \pm 0.7_4) - 2 \times (7._3 \pm 1._9) f(I)$ at $R = 0.885$ and $= (1.2_4 \pm 0.6_7) - 2 \times (13._6 \pm 4._2) f(I)$ 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 ≤ K {>Rb $(\log K_{ex,av}^0 = -1.6_5) <$ Cs $(-1.1_4)\}$, where $K_{ex,av}^0$ denotes the average of K_{ex}^0.

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

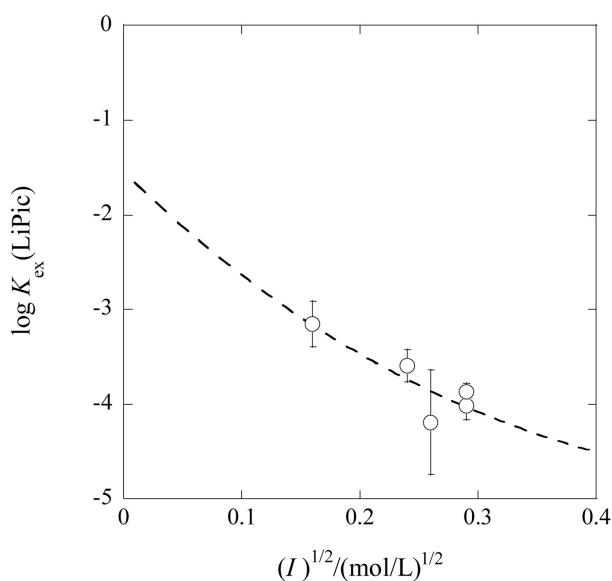As similar to the *I* dependence of $\log K_{ex}$, we considered $K_{MA,org}^0$ based on an

Figure 4. Plot of $\log K_{ex}$ *vs.* $(I)^{1/2}$ for the LiPic distribution into *o*DCBz. The broken line was a regression one based on Equation (8a).

activity ex pression as follows.

$$K_{\text{MA,org}}^0 = [\text{MA}]_{\text{org}} \big/ a_{\text{M,org}} a_{\text{A,org}} = K_{\text{MA,org}} \big/ y_{+,\text{org}} y_{-,\text{org}} \tag{9}$$

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

$$\log K_{\text{MA,org}} = \log K_{\text{MA,org}}^0 - 2A_{\text{org}} \left(I_{\text{org}} \right)^{1/2} \tag{9a}$$

with $-2A_{\text{org}} \left(I_{\text{org}} \right)^{1/2} = \log y_{+,\text{org}} y_{-,\text{org}}$. $\qquad$ (9b)

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

Figure 5 shows an example of the NaPic distribution system with org = *o*DCBz. The broken line was the experimental regression one, $\log K_{\text{NaPic,org}} = \left(8.1_6 \pm 0.1_3 \right) - 2 \times \left(422 \pm 43 \right) \left(I_{\text{org}} \right)^{1/2}$ at $R = 0.980$. Similar results were obtained from the other two systems: $\log K_{\text{LiPic,org}} = \left(8.9_8 \pm 0.2_8 \right) - 2 \times \left(1819 \pm 350 \right) \left(I_{\text{org}} \right)^{1/2}$ at $R = 0.949$ and $\log K_{\text{KPic,org}} = \left(6.8_8 \pm 0.4_0 \right) - 2 \times \left(260 \pm 134 \right) \left(I_{\text{org}} \right)^{1/2}$ at 0.809. These A_{org} values were 23- to 161-times larger than that {$=11.3$ (L/mol)$^{1/2}$} calculated for pure *o*DCBz (= 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 $\log K_{\text{MPic,}o\text{DCBz}}^0$ values at $I_{o\text{DCBz}} \to 0$ were in the order M = Li > Na > K ($\leq$ Rb $\approx$ Cs, see **Table 2**). This order recalls that (Li > Na $\leq$ 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 *o*DCBz phases in the hydration to M$^+$.
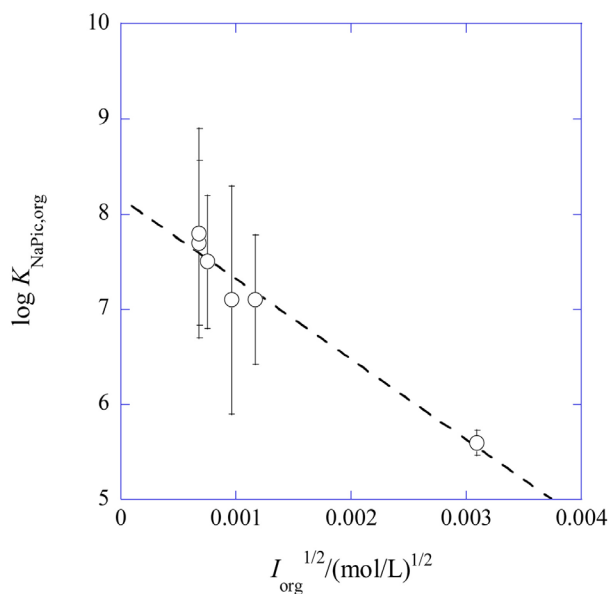

Figure 5. Plot of log $K_{\text{NaPic,org}}$ *vs.* $I_{\text{org}}^{1/2}$ for the distribution into org = *o*DCBz. The broken line was a regression one based on Equation (9a).

3.9. On the Differences between $K_{\text{D,BPh}_4}$ or $K_{\text{D,Cs}}$ Values in the NB, DCE, and oDCBz Systems

The $\log K_{\text{D,BPh}_4}^{\text{S\%}}$ 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 $I \to 0$ for the NB systems; 5.396 [20] at $[\text{MgSO}_4]_t = 1$ mol/L and $\left[\text{CV}^+\text{BPh}_4^-\right]_{\text{t,DCE}} = 0.05$ (CV$^+$: crystal violet cation) and 6.13 [18] at $I \to 0$ for the DCE ones. Their experimental $\log K_{\text{D,BPh}_4}^{\text{S\%}}$ 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 $\log K_{\text{D,BPh}_4}$ values, as described in the Section 3.5.

Although numbers of the data sets of $\log K_{\text{D,BPh}_4}$ and I or I_{org} were few, Equation (6) employed for A$^-$ has possibility for showing the I or I_{org} dependence of the $\log K_{\text{D,BPh}_4}$ values. So, using Equations (3) and (6), we can immediately derive the following basic equation:

$$\log K_{\text{D},j} = \log K_{\text{D},j}^{\text{S\%}} + \left(f/2.303\right)z_j\text{dep} - Az_j^2 f\left(I\right) + A_{\text{org}}z_j^2\left(I_{\text{org}}\right)^{1/2} \tag{10}$$
$$\approx \log K_{\text{D},j}^{\text{S}} + \left(f/2.303\right)z_j\text{dep}$$

with $j = \text{M}^+$, A$^-$ and $K_{\text{D},j}^{\text{S\%}} = y_{j,\text{org}}K_{\text{D},j}^{\text{S}}/y_j\left(= y_{j,\text{org}}K_{\text{D},j}^{\text{Su/x}}/y_j\right)$. This expression can be an overall one about $K_{\text{D},j} = [j]_{\text{org}}/[j]$. **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 $\log K_{\text{D},j}$ 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 $\log(y_j/y_{j,\text{org}}) \approx \pm 0.1$ 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
$$4.2 = \log K_{\text{D},j}^{\text{S\%}} + \left(f/2.303\right)z_j \times 0 - Az_j^2 f\left(0\right) + A_{\text{NB}}z_j^2 \times 0^{1/2} = \log K_{\text{D},j}^{\text{S\%}} + 0 - 0 + 0$$
with $A = 0.5114$, $b = 0.3$, and $A_{\text{NB}} = 1.725$ at $j = \text{BPh}_4^-$, we immediately obtained $\log K_{\text{D},j}^{\text{S\%}} = 4.2$ at $z_j = -1$. From $6.3 = 4.2 - \left(f/2.303\right)v - Af\left(x\right) + A_{\text{NB}}u^{1/2}$, the $-16.90v - Af(x) + A_{\text{NB}}u^{1/2}$ term at 298 K was obtained to be 2.1 at $z_j = -1$. Also, using $5.6 + Af\left(0\right) = 4.2 - \left(f/2.303\right)v + A_{\text{NB}}u^{1/2}$, the $-(f/2.303)v + A_{\text{NB}}u^{1/2}$ term equals 1.4 with $5.6 = \log K_{\text{D,BPh}_4}^{u/0} = 4.2 - 16.90v + 1.725u^{1/2}$. These cases suggest that the former of 6.3 is $\log K_{\text{D,BPh}_4}^{u/x}$ {Equation (10) or (T1) in **Table 3**} and the latter of 5.6 is $\log K_{\text{D,BPh}_4}^{u/0}$ {Equation (T4)}. Strictly speaking, it is difficult to compare 6.3 with 5.6.

Similarly, the relation $-1.4 = \log K_{\text{D},j}^{\text{S\%}} + 0 - 0 + A_{\text{DCE}} \times 0^{1/2}$ gave -1.4 as $\log K_{\text{D},j}^{\text{S\%}}$ with $A_{\text{DCE}} = 10.63$ at $j = \text{BPh}_4^-$. For
$$5.396\left(= \log K_{\text{D,BPh}_4}^{0.05//1}\right) = -1.4 - \left(f/2.303\right)v - Af\left(0.87\right) + A_{\text{DCE}} \times 0.0086^{1/2},$$ dep $(= v)$
became -0.3_5 V with $5.396 + 0.5114f(0.87) - 10.63 \times 0.0086^{1/2} = 4.52_7 = -1.4 -$

$16.90\,v$ at $b = 0.3$ and 298 K: see **Appendix C** for the estimation of $I = 0.86_7$ and $I_{DCE} = 0.0086$. The absolute value of this dep was in good agreement with the $E_{I=0}$ value $(=0.358$ V) reported by the polarographic measurements at the w/DCE interface [20]. Moreover, from $6.13 = -1.4 - (f/2.303)v - 0 + A_{DCE}u^{1/2}$, the $-(f/2.303)v + A_{DCE}u^{1/2}$ term at 298 K became 7.5 with $6.13 + Af(0) = -1.4 - 16.90v + 10.63u^{1/2}$. As similar to the w/NB results, the former of $5.396 + Af(0.87) - A_{DCE} \times 0.0086^{1/2}$ $(= 4.53)$ is $\log K^{\%}_{D,BPh_4}$ {Equation (T7)} and the latter of 6.13 is $\log K^{u/0}_{D,BPh_4}$ {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 $MgSO_4$)/oDCBz(0.05 CVBPh$_4$) 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 $\log K_{D,Cs}$, it corresponds to -2.03. So, using $\log K^{S\%}_{D,Cs} = -5.9_5$ (see Section 3.5) based on the average value in **Table 2**, the following relation holds: $-2.03 \left(= \log K^{0.05//1}_{D,Cs} \right) \approx -5.9_5 + (f/2.303)v - Af(0.87) + A_{oDCBz}u^{1/2}$. Hence, the relation $16.90v + 11.3u^{1/2} \approx 4.0$ was obtained with $-2.03 + Af(0.87) = -1.91 \approx \log K^{u/0}_{D,Cs} = -5.9_5 + 16.90v + 11.3u^{1/2}$. Here, we were not able to estimate the dep and I_{oDCBz} values, because the $K_{MA,oDCBz}$ value for $MA = CV^+BPh_4^-$ (the supporting electrolyte) in the oDCBz phase had not been found [6].

As another example, the $\log K^{S\%}_{D,Cs}$ value has been reported to be -6.3_5 [21] for the CsPic distribution into DCE at 298 K. Similarly, the relation $\log K_{D,Cs} + Af(x) - A_{DCE}u^{1/2} = -6.3_5 = \log K^{\%}_{D,Cs} = -4.6_0 + 16.90v$ holds. So, we can estimate its dep $(=v)$ value to be -0.1 V at 298 K. In these cases, the former of $-2.03 + Af(0.87)$ is approximately $\log K^{u/0}_{D,C}$ {Equation (T4)} and the latter of -6.3_5 is $\log K^{\%}_{D,Cs}$ {Equation (T7)}.

Thus, these results support the above understanding about the conditional K_{D,BPh_4} or $K_{D,Cs}$ and self-consistently suggest that their values are functions [16] [22] containing dep, I, and I_{org}, that is, $K_{D,BPh_4} = K^{S\%}_{D,BPh_4} \left(y_- / y_{-,org} \right) \exp(-f\text{dep})$ or $K_{D,Cs} = K^{S\%}_{D,Cs} \left(y_+ / y_{+,org} \right) \exp(f\text{dep})$. Also, the condition of dep $= 0$ V gives $K^{S}_{D,BPh_4} = K^{S\%}_{D,BPh_4} \left(y_- / y_{-,org} \right)$. From such an equation, we can see that the apparent I or I_{org} values, such as [supporting electrolyte]$_t$, [MA]$_t$, and [MA]$_{t,org}$, are not effective for estimating $K^{S}_{D,A}$ (or $K^{S}_{D,M}$), but their practical I or I_{org} 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 $K_{D,BPh4}$ value, because BPh_4^- is the standard material in the $\text{dep}^{0'}_j$ determination, as described in the introduction.

4. Conclusions

The $\log K_{ex}$ and $\log K_{MA,org}$ values were well expressed by Equation (8a) with I and Equation (9a) with I_{org}, respectively. Now, it is unclear why the experimental A and A_{org} values are much larger than their theoretical ones. Also, the MA distri-

bution experiments based on the V_{org}/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 $^V[A^-] = {}^V[M^+] =$ 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 $K_{D,M}^{S\%}$, $K_{D,M}^{Su/0}$, or $K_{D,M}^{S0/x}$ 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 $\log\left(K_{D,A}^{expl.1}/K_{D,A}^{expl.2}\right)$ term is approximately proportional to the $-(\text{dep}^{expl.1} - \text{dep}^{expl.2})$ 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_{org} 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) $K_{D,\pm}^2 = K_{D,+} K_{D,-}$.

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

$$\text{dep}_+^{0\prime} + \left(2.303/f\right)\log K_{D,+} = \text{dep}_-^{0\prime} - \left(2.303/f\right)\log K_{D,-} \tag{A1}$$

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

$$\left(2.303/f\right)\log K_{D,\pm} = \left(\text{dep}_-^{0\prime} - \text{dep}_+^{0\prime}\right)\Big/2 \tag{A2}$$

(B) Derivation of another equation based on (C2). Similarly, using $\left(2.303/f\right)\log K_{D,-}^{S} = \text{dep}_-^{0\prime}$, we rearranged Equation (3) as

$$\left(2.303/f\right)\log K_{D,-} = \left(2.303/f\right)\log K_{D,+} = \text{dep}_-^{0\prime} - \text{dep}_-. \tag{A3}$$

Introducing Equation (A3) in $\text{dep}_+ = \text{dep}_+^{0\prime} + \left(2.303/f\right)\log K_{D,+}$ {another expression of Equation (3)}, we can immediately obtain $\text{dep}_+ = \text{dep}_+^{0\prime} + \text{dep}_-^{0\prime} - \text{dep}_-$ under the condition of (C2). Rearranging this equation based on (C1) can yield

$$\text{dep}_+ = \text{dep}_- = \left(\text{dep}_+^{0\prime} + \text{dep}_-^{0\prime}\right)\Big/2. \tag{A4}$$

Here, we define $\left(\text{dep}_+^{0\prime} + \text{dep}_-^{0\prime}\right)\Big/2$ as $\text{dep}_\pm$ and accordingly this means $\text{dep}_+ = \text{dep}_- = \text{dep}_\pm$.

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

$$\text{dep}_\pm = \text{dep}_-^{0\prime} - \left(2.303/f\right)\log K_{D,\pm}. \tag{A5}$$

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

$$\text{dep}_\pm = \text{dep}_+^{0\prime} + \left(2.303/f\right)\log K_{D,\pm}. \tag{A6}$$

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 $\text{dep}_-^{0\prime} = \left(2.303/f\right)\log K_{D,-}^{S}$ and $\text{dep}_+^{0\prime} = -\left(2.303/f\right)\log K_{D,+}^{S}$.

Appendix B

The $I_{o\text{DCBz}}$ 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], μ-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 2×10^3 L/mol from conduc-

tivity data [5]. From the quadratic equation for $[C^+]_{\text{org}}$ (= $[A^-]_{\text{org}}$), therefore, we obtained

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

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

Similarly, the association constant ($K_{\mathrm{LiSO_4}}$) for $\mathrm{Li^+ + SO_4^{2-} \rightleftharpoons LiSO_4^-}$ 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,

$$\left[\mathrm{Li}^+\right]\Big/\mathrm{mol}\cdot\mathrm{L}^{-1}\approx\left\{\left(1+0.0140K_{\mathrm{LiSO_4}}\right)^{1/2}-1\right\}\Big/2K_{\mathrm{LiSO_4}}=0.0033_5\approx\left[\mathrm{SO_4^{2-}}\right] \quad (A8)$$

with $K_{\mathrm{LiSO_4}} \approx 13\,\mathrm{L/mol}$ and $I \approx 0.010_2$ mol/L under the condition of $[\mathrm{LiSO_4}]_t$ = 0.0035 mol/L [24] in the w phase at 298 K.

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

$$\log K_{\mathrm{D,Pic}}^{\%}\approx\log K_{\mathrm{D,Pic}}^{u/x}+Af\left(x\right)-A_{\text{org}}\left(u\right)^{1/2}\approx\log K_{\mathrm{D,Pic}}^{\%}-16.90v \qquad (A9)$$

holds in this case at 298 K. Using $x \approx 0.010_2$ mol/L and u = 0.0020 with b = 0.3 for the oDCBz systems, we immediately obtained $\log K_{\mathrm{D,Pic}}^{\%}\approx\log K_{\mathrm{D,Pic}}^{0.002/0.01}-0.46_0=-2.277-0.46_0=-2.73_7$. This value was assumed to be that at I and $I_{o\mathrm{DCBz}} \to 0$ (see the text) and then employed for the $\log K_{\mathrm{D,M}}^{\%}$ evaluation with $\log K_{\mathrm{D,M}}^{\%}=2\log K_{\mathrm{D,\pm}}-\log K_{\mathrm{D,Pic}}^{\%}=2\log K_{\mathrm{D,\pm}}+2.73_7$ in this study. Also, the dep values at 298 K in **Table 2** were calculated from the rearranged equation of Equation (3a):

$$\mathrm{dep} = 0.05916\left(\log K_{\mathrm{D,\pm}}-\log K_{\mathrm{D,M}}^{\mathrm{S\%}}\right). \qquad (A10)$$

Appendix C

As similar to **Appendix B**, the I and I_{DCE} values for the w(1 mol/L $\mathrm{MgSO_4}$)/DCE(0.05 $\mathrm{CVBPh_4}$) system were evaluated. The thermodynamic association constant (K_{MA}^0) for $\mathrm{Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4}$ (=MgA) in water at 298 K has been reported to be 135 L/mol [24]. With the successive approximation method, its $[\mathrm{Mg^{2+}}]$ (=$[\mathrm{SO_4^{2-}}]$) in the total concentration, $[\mathrm{MgSO_4}]_t$ = 1 mol/L [20], can be evaluated to be 0.21_7 mol/L, which was calculated from the equation

$$\left[\mathrm{Mg^{2+}}\right]=\left\{\left(1+4K_{\mathrm{MgA}}\right)^{1/2}-1\right\}\Big/2K_{\mathrm{MgA}}. \qquad (A11)$$

Consequently, the I (=$4[\mathrm{Mg^{2+}}]$) value of the aqueous $\mathrm{BPh_4^-}$ solution with 1 mol/L $\mathrm{MgSO_4}$ became 0.86_7 mol/L at which K_{MgA} was estimated to be 16.7 L/mol. In this computation, the K_{MgA} value was evaluated from $\log K_{\mathrm{MgA}} = \log K_{\mathrm{MgA}}^0 - 2\times0.5114\times(+2)^2\times f(I)$. Accordingly, $\log y_- = -0.114$ at I = 0.86_7 was approximately obtained from $-0.5114\times(-1)^2\times\left\{I^{1/2}\Big/\left(1+I^{1/2}\right)-0.3I\right\}$ for the $\mathrm{BPh_4^-}$ solution. Here, the symbol K_{MgA} denotes the concentration equilibrium constant. The estimated $\log y_-$ value suggests the ion-pair formation of $\mathrm{BPh_4^-}$ in water.

Similarly, the association constant ($K_{CVA,DCE}$) for $CV_{DCE}^+ + A_{DCE}^- \rightleftharpoons CVA_{DCE}$ in the DCE solution of 0.05 mol/L crystal violet cation CV^+ with $A^- = BPh_4^-$ at 298 K has been reported to be 560 L/mol [20]. Therefore,

$$\left[CV^+ \right]_{DCE} \Big/ mol \cdot L^{-1} = \left[A^- \right]_{DCE}$$
$$= \left\{ \left(1 + 0.20 K_{CVA,DCE} \right)^{1/2} - 1 \right\} \Big/ 2 K_{CVA,DCE} = 0.0086_0 \tag{A12}$$

which equals the I_{DCE} value.