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Silver(I) Extraction with Benzo-18-Crown-6 Ether from Water into 1,2-Dichloroethane: Analyses on Ionic Strength of the Phases and their Equilibrium Potentials

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Abstract: Extraction constants (K_{ex} & $K_{\text{ex}\pm}$) for the extraction of silver picrate (AgPic) by benzo-18-crown-6 ether (B18C6) into 1,2-dichloroethane (DCE) were determined at 298 K and various ionic strength (I)-values of a water phase with or without excess HNO_3 . Here the symbols, K_{ex} and $K_{\text{ex}\pm}$, were defined as $[\text{AgLPic}]_{\text{DCE}}/P$ and $[\text{AgL}^+]_{\text{DCE}}[\text{Pic}^-]_{\text{DCE}}/P$ with $P = [\text{Ag}^+][\text{L}]_{\text{DCE}}[\text{Pic}^-]$ and $L = \text{B18C6}$, respectively; $[\]_{\text{DCE}}$ refers to the concentration of the corresponding species in the DCE phase at equilibrium. Simultaneously, $K_{\text{D,Pic}} (= [\text{Pic}^-]_{\text{DCE}}/[\text{Pic}^-])$ and $K_{1,\text{DCE}} (= K_{\text{ex}}/K_{\text{ex}\pm})$ values for given I and I_{DCE} values were determined, where the symbol I_{DCE} shows I of the DCE phase. Also, equilibrium potential differences ($\Delta\phi_{\text{eq}}$) based on the Pic^- transfer at the water/DCE interface were obtained from the analysis of the $K_{\text{D,Pic}} [= K_{\text{D,Pic}}^{\text{S}} \exp\{-(F/RT) \Delta\phi_{\text{eq}}\}]$ values; the symbol $K_{\text{D,Pic}}^{\text{S}}$ shows $K_{\text{D,Pic}}$ at $\Delta\phi_{\text{eq}} = 0$ V. On the basis of these results, I dependences of $\log K_{\text{ex}}$ and $\log K_{\text{ex}\pm}$ and I_{DCE} ones of $\log K_{1,\text{DCE}}$ and $\log K_{\text{ex}\pm}$ were examined. Extraction experiments of AgClO_4 and AgNO_3 by B18C6 into DCE were done for comparison. The $\log K_{\text{ex}\pm}$ -versus- $\Delta\phi_{\text{eq}}$ plot for the above Ag(I) extraction systems with Pic^- , ClO_4^- , and NO_3^- gave a good positive correlation.

Keywords: extraction constants; conditional distribution constants of ions; equilibrium potential difference between water and organic phases; ionic strength; silver salts; benzo-18-crown-6 ether; 1,2-dichloroethane

1. Introduction

It is well known that crown compounds (L) extract alkali and alkaline-earth metal ions (M^{z+} , $z = 1, 2$) from water (w) into various diluents [1–4]. In many extraction experiments, extraction constants for L have been determined so far [1–8]. For example, the two representative constants, K_{ex} and $K_{\text{ex}\pm}$, for the extraction of a univalent metal salt (M^1A) by L have been defined as $[\text{MLA}]_{\text{org}}/P$ [2,3] and $[\text{ML}^+]_{\text{org}}[\text{A}^-]_{\text{org}}/P$ [1,4] with $P = [\text{M}^+][\text{L}]_{\text{org}}[\text{A}^-]$, respectively. Generally, the K_{ex} value is effective for the evaluation of an extraction-ability and -selectivity of L against M^+ into low-polar diluents, while the $K_{\text{ex}\pm}$ value is for those of L into high-polar ones. Here, the subscript “org” denotes an organic phase and A^- does a univalent pairing anion. For the latter $K_{\text{ex}\pm}$, its thermodynamic equilibrium constants have been reported [4]. For the former K_{ex} , its thermodynamic treatment seems to be few. The authors were not able to find out the study with respect to a dependence of $\log K_{\text{ex}}$ on the ionic strength (I) of the w phase.

Presences of equilibrium potential differences ($\Delta\phi_{\text{eq}}$) between aqueous and diluent solutions have been recently reported for the extraction of some M^+ or M^{2+} with L [5–7]. This symbol $\Delta\phi_{\text{eq}}$ was defined

as $\sum\{\text{inner potential } (\phi) \text{ of ionic species in the } w \text{ phase}\} - \sum\{\phi \text{ of those in the org or diluent phase}\}$ [8], according to the definition [9,10], $\phi_w - \phi_{\text{org}}$, of an interfacial equilibrium potential-difference in the electrochemistry at liquid/liquid interfaces. In the above studies, an approximation method [5–8] for the $\Delta\phi_{\text{eq}}$ determination, namely the method with a use of a “conditional” distribution constant ($K_{D,A}$) of A^- into the org phase, has been described in comparison with its more-precise method with solving higher-degree equations [6]. Here the “conditional” is due to the fact that the $K_{D,A}$ values change depending on the $\Delta\phi_{\text{eq}}$ ones, even at fixed pressure and temperature. However, it is still not clarified whether the $\Delta\phi_{\text{eq}}$ values determined by the $K_{D,A}$ values equal those coming from the distribution of M^+ into the org phases or not.

In the present paper, we determined the K_{ex} , $K_{\text{ex}\pm}$, and $K_{D,A}$ values [6,8] at 298 K by the extraction experiments into 1,2-dichloroethane (DCE) with silver picrate (AgPic) and benzo-18-crown-6 ether (B18C6), in order to elucidate mainly the above two subjects for I and $\Delta\phi_{\text{eq}}$. The same experiments were performed under the condition of the presence of excess HNO_3 in the w phases. Then, an ion-pair formation constant ($K_{1,\text{DCE}}/\text{mol}^{-1}\cdot\text{dm}^3$) for $\text{Ag}(\text{B18C6})^+\text{Pic}^-$ in the DCE phase, DCE saturated with water, and the $\Delta\phi_{\text{eq}}$ values were calculated from the relations, $K_{1,\text{DCE}} = K_{\text{ex}}/K_{\text{ex}\pm}$ [6,8] and $\Delta\phi_{\text{eq}} = -(2.303RT/F)\{\log K_{D,A} - \log(K_{D,A} \text{ standardized at } \Delta\phi_{\text{eq}} = 0 \text{ V})\}$ [11], respectively. Here, R , T , and F are usual meanings. On the basis of these data, the dependences of $\log K_{\text{ex}}$ and $\log K_{\text{ex}\pm}$ on the I values and those of $\log K_{1,\text{DCE}}$ and $\log K_{\text{ex}\pm}$ on the I values (I_{DCE}) of the DCE phases were examined. Moreover, a relation between the $\Delta\phi_{\text{eq}}$ values determined by the $K_{D,A}$ ones and the conditional distribution constants ($K_{D,\text{Ag}}$) of Ag^+ into the DCE phases was discussed indirectly. For comparison, the $K_{\text{ex}\pm}$ and K_{ex} values were experimentally determined at 298 K for the AgClO_4^- and AgNO_3 -B18C6 extraction into DCE. As basic data, the $K_{D,\text{Ag}}^{\text{S}}$ value was determined in terms of a simple Ag^+Pic^- extraction experiment into DCE. The symbol $K_{D,\text{Ag}}^{\text{S}}$ denotes the distribution constant of Ag^+ into the DCE phase standardized at $\Delta\phi_{\text{eq}} = 0 \text{ V}$, that is, the standard distribution one.

2. Results

2.1. Determination of $\text{Log}K_{D,\text{Ag}}^{\text{S}}$

According to our previous paper [12], the $K_{D,M}^{\text{S}}$ value has been obtained from a plot of D_A' versus $[A^-]$ based on the equation

$$D_A' = [A]_{\text{t,org}}/[A^-] = K_{\text{ex,MA}}[A^-] + K_{D,\pm} \quad (1)$$

with

$$K_{D,\pm}^2 = K_{D,M}^{\text{S}} \cdot K_{D,A}^{\text{S}} = K_{D,M} \cdot K_{D,A} \quad (2)$$

and $K_{\text{ex,MA}} = K_{\text{MA,org}}(K_{D,\pm})^2 (= [\text{MA}]_{\text{org}}/[\text{M}^+][\text{A}^-])$, where $K_{\text{MA,org}}$ is $[\text{MA}]_{\text{org}}/[\text{M}^+]_{\text{org}}[\text{A}^-]_{\text{org}}$ and $[A]_{\text{t,org}}$ denotes a total concentration, $[\text{MA}]_{\text{org}} + [\text{A}^-]_{\text{org}}$, of $A(-I)$ in the org phase. A regression analysis of the plot (see Figure 1) yields a straight line with a slope of $K_{\text{ex,AgPic}}$ and an intercept of $K_{D,\pm}$. We call this $K_{D,\pm}$ a mean distribution constant.

Using the $K_{D,\text{Pic}}^{\text{S}}$ value ($= 10^{-1.011}$ [12]), we immediately can obtain the $K_{D,\text{Ag}}^{\text{S}}$ one from Equation (2). The thus-determined values were $\log K_{D,\pm} = -3.74 \pm 0.04$, $\log K_{\text{ex,AgPic}} = -1.49 \pm 0.05$, and $\log K_{\text{AgPic,DCE}} = 5.992 \pm 0.008$ and then the $\log K_{D,\text{Ag}}^{\text{S}}$ value became -6.47 ± 0.04 from the logarithmic form of Equation (2). This $K_{D,\text{Ag}}^{\text{S}}$ value was used only for the $K_{\text{AgL,DCE}}$ calculation (see Tables 1 and 2).

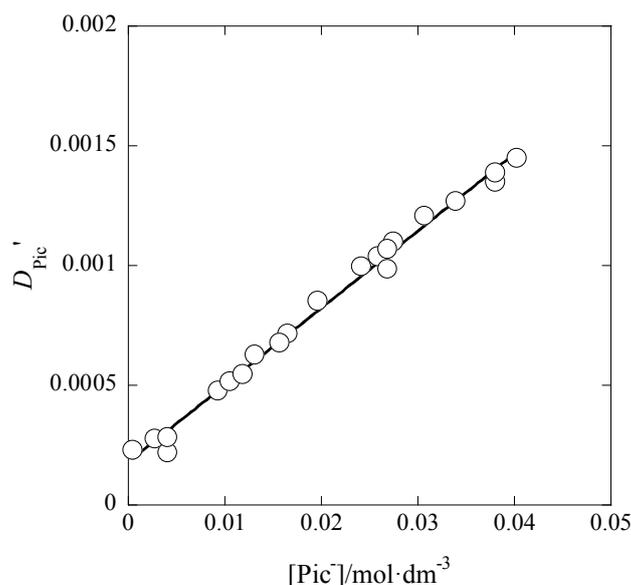


Figure 1. A plot of $D_{\text{Pic}'}'$ vs. $[\text{Pic}^-]$ for the AgPic extraction into 1,2-dichloroethane (DCE). The straight line was $D_{\text{Pic}'}' = (1.81 \times 10^{-4})\{1 + (1.81 \times 10^{-4})(9.81 \times 10^5)[\text{Pic}^-]\}$ at r (correlation coefficient) = 0.996.

Table 1. Fundamental data for the extraction with AgPic, AgClO₄, or AgNO₃ (= AgA) and B18C6 (= L) into DCE at 298 K.

A ⁻ ($I^1/10^{-3}$)	$\log K_{\text{ex}\pm}$	$\log K_{\text{D,A}}$ [$\Delta\phi_{\text{eq}}/V$]	$\log K_{\text{ex}}$	$\log K_{1,\text{DCE}}$ ($I_{\text{DCE}}^1/10^{-5}$)	$\log K_{\text{AgL,DCE}}$
Pic ⁻ (2.5)	0.33 ± 0.03	-2.40 ± 0.03 [0.082]	5.31 ± 0.03	4.98 ± 0.05 (0.93)	7.81
(2.7) ²	0.51	-2.60 [0.094]	5.336	4.82 (1.1)	7.99 ³
(2.8) ²	0.25	-2.33 [0.078]	5.17	4.92 (0.40)	7.73 ³
(3.1)	0.40 ± 0.09	-2.07 ± 0.05 [0.063]	4.93 ± 0.05	4.53 ± 0.10 (2.2)	7.88
(3.6) ²	0.17	-2.70 [0.10]	5.55	5.38 (0.64)	7.65 ³
ClO ₄ ⁻ (2.8)	-1.24 ± 0.02	-2.13 ± 0.11 [-0.032]	2.99 ± 0.11	4.23 ± 0.11 (2.1)	8.07
NO ₃ ⁻ (3.1)	-4.40 ± 0.07	-3.47 ± 0.04 [-0.14]	1.04 ± 0.03	5.44 ± 0.08 (0.11)	7.98

¹ Unit: mol·dm⁻³; ² Values in this line were cited from Ref. [6]; ³ Values re-calculated from the relation $\log K_{\text{AgL,DCE}} = \log K_{\text{ex}\pm} - \log K_{\text{D,Ag}}^{\text{S}} \cdot K_{\text{D,Pic}}^{\text{S}} = \log K_{\text{ex}\pm} + 7.481$, since the $K_{\text{D,Ag}}^{\text{S}}$ value was re-determined in this study.

Table 2. Fundamental data for the extraction with AgPic and B18C6 (= L) into DCE in the presence of excess HNO₃ in the water phases at 298 K.

$I/10^{-2}$ mol·dm ⁻³	$\log K_{\text{ex}\pm}$	$\log K_{\text{D,Pic}}$ [$\Delta\phi_{\text{eq}}/V$]	$\log K_{\text{ex}}$	$\log K_{1,\text{DCE}}$ ($I_{\text{DCE}}^1/10^{-6}$)	$\log K_{\text{AgL,DCE}}$
2.4	0.38 ± 0.10	-2.33 ± 0.05 [0.078]	5.35 ± 0.04	4.97 ± 0.11 (3.0)	7.87
5.0	0.00 ± 0.06	-2.30 ± 0.03 [0.076]	5.41 ± 0.03	5.41 ± 0.07 (2.0)	7.49
9.7 ²	-0.13	-1.68 [0.040]	5.07	5.20 (5.5)	7.35 ³
11	-0.23 ± 0.06	-2.26 ± 0.02 [0.074]	5.45 ± 0.02	5.68 ± 0.06 (0.97)	7.26
26	-0.78 ± 0.06	-1.88 ± 0.03 [0.051]	5.11 ± 0.02	5.89 ± 0.07 (1.3)	6.70

¹ Unit: see *I*; ² See the footer 2 in Table 1; ³ See the footer 3 in Table 1.

2.2. Composition Determination of Complex Species Extracted into DCE

Compositions of species extracted into DCE have been determined by a plot of $2\log D$ or $\log(D/[A^-])$ versus $\log[L]_{\text{org}}$ [2,7,13]. When the slope of both plots is in unity, it independently gives the compositions of ML^+ with A^- or MLA as the extracted major species. Among their plots, experimental slopes of all the $\log(D/[Pic^-])$ -versus- $\log[B18C6]_{\text{org}}$ plots were less than unity, suggesting the dissociation of $Ag(B18C6)Pic$ in the DCE phases [13]. On the other hand, the $2\log D$ -versus- $\log[L]_{\text{org}}$ plots were in the slope ranges of 1.01–1.11 for the $AgPic$ extraction with $L = B18C6$, in the slopes of 1.09 for the $AgClO_4$ one and of 1.08 for the $AgNO_3$ one (Figure 2). These results indicate the $AgB18C6^+$ extraction into DCE with $A^- = Pic^-, ClO_4^-,$ or NO_3^- . That is, the extraction systems were accompanied with the dissociation process, $Ag(B18C6)A_{\text{DCE}} \rightleftharpoons AgB18C6^+_{\text{DCE}} + A^-_{\text{DCE}}$ (see Appendix A).

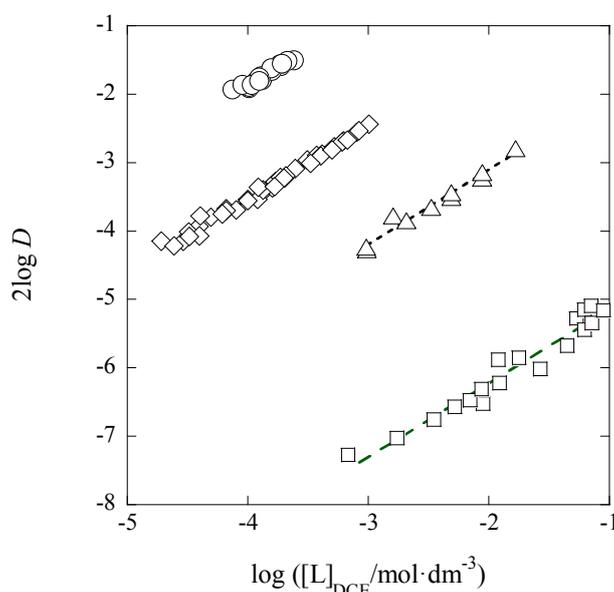


Figure 2. Plots of $2\log D$ vs. $\log[L]_{\text{DCE}}$ for the $AgPic$ (circle: without excess HNO_3 ; diamond: $0.05 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 in the w phase), $AgClO_4$ (triangle), and $AgNO_3$ (square) extraction with $B18C6$ ($= L$) into DCE.

2.3. Determination of Various Equilibrium Constants for the Extraction Systems

For the determination of $K_{D,A}$, $K_{\text{ex}\pm}$, and K_{ex} , the following extraction-constant parameter ($K_{\text{ex}}^{\text{mix}}/\text{mol}^{-2}\cdot\text{dm}^6$) has been employed [7,8,11].

$$\log K_{\text{ex}}^{\text{mix}} = \log\{([MLA]_{\text{org}} + [ML^+]_{\text{org}} + [M^+]_{\text{org}})/P\} \quad (3)$$

Rearranging this equation, we immediately obtain

$$\log K_{\text{ex}}^{\text{mix}} \approx \log\{K_{\text{ex}} + (K_{D,A}/[M^+][L]_{\text{org}})\} \quad (3a)$$

$$\approx \log\{K_{\text{ex}} + (K_{\text{ex}\pm}/P)^{1/2}\} \quad (3b)$$

under the assumption of $[MLA]_{\text{org}} + [ML^+]_{\text{org}} \gg [M^+]_{\text{org}}$. So we can determine the $K_{D,A}$ and $K_{\text{ex}\pm}$ values from the plots of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log([M^+][L]_{\text{org}})$ {see Equation (3a)} and $-(1/2)\log P$ {see Equation (3b)}, respectively, together with the K_{ex} values. Figures 3 and 4 show examples for such plots. Additionally, the ion-pair formation constant, $K_{1,\text{org}}$, for MLA in the org phase was calculated from $K_{1,\text{org}} = K_{\text{ex}}/K_{\text{ex}\pm}$ for a given I_{org} on average.

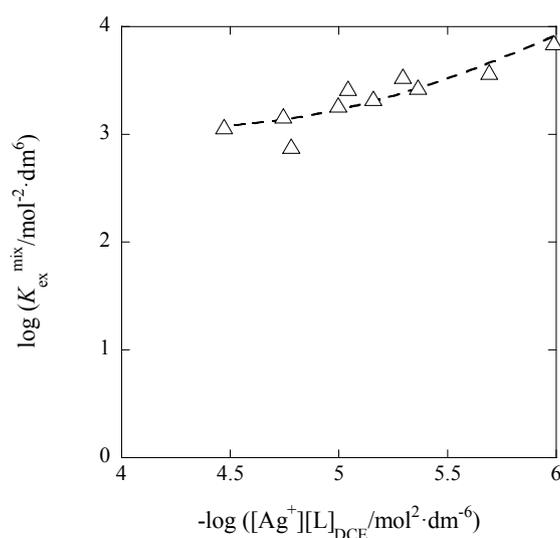


Figure 3. A plot of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log([\text{Ag}^+][\text{L}]_{\text{DCE}})$ for the AgClO_4 extraction with B18C6 (= L) into DCE. The regression line was $\log K_{\text{ex}}^{\text{mix}} = \log\{9.7 \times 10^2 + (7.4 \times 10^{-3})/([\text{Ag}^+][\text{L}]_{\text{DCE}})\}$ at $r = 0.891$.

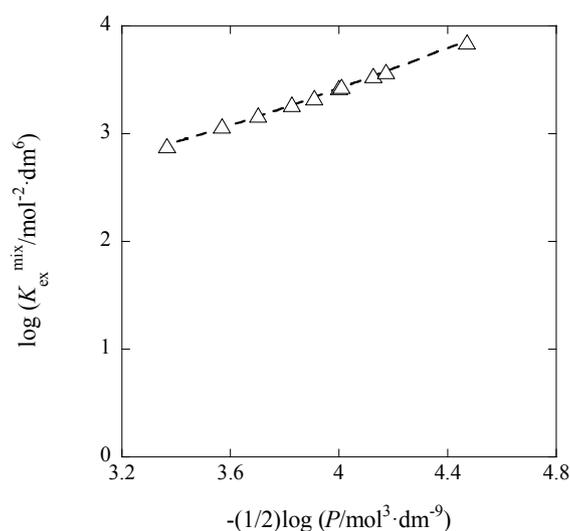


Figure 4. A plot of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-(1/2)\log P$ for the AgClO_4 extraction with B18C6 (= L) into DCE. The regression line was $\log K_{\text{ex}}^{\text{mix}} = \log(2.5 \times 10^2 + \sqrt{0.0575/P})$ at $r = 0.999$.

Similarly, a complex formation constant ($K_{\text{AgB18C6,DCE}}/\text{mol}^{-1}\cdot\text{dm}^3$) for AgB18C6^+ in the DCE phase was estimated from the thermodynamic relation of $K_{\text{AgB18C6,DCE}} = K_{\text{ex}\pm}/(K_{\text{D,Ag}}^{\text{S}}\cdot K_{\text{D,Pic}}^{\text{S}})$. Tables 1 and 2 list the logarithmic $K_{\text{D,A}}$, $K_{\text{ex}\pm}$, K_{ex} , $K_{1,\text{DCE}}$, and $K_{\text{AgB18C6,DCE}}$ values thus-obtained, together with the average I and I_{DCE} values.

2.4. Determination of Equilibrium Potential Differences between the Water and DCE Phases

The $\log K_{\text{D,A}}$ values were obtained from the plots based on Equation (3a). Next, the equilibrium potential differences $\Delta\phi_{\text{eq}}$ can be evaluated from using the following equation [11]:

$$\Delta\phi_{\text{eq}} = -(2.303RT/F)(\log K_{\text{D,A}} - \log K_{\text{D,A}}^{\text{S}}) \quad (4)$$

with

$$\log K_{\text{D,A}}^{\text{S}} = (F/2.303RT)\Delta\phi_{\text{A}}^{\text{O}'} \quad (4a)$$

where the symbols, $K_{D,A}^S$ and $\Delta\phi_A^{0'}$, are called the standard distribution constant of A^- into the org phase, namely $K_{D,A}$ at $\Delta\phi_{eq} = 0$ V, and a standard formal potential for the A^- transfer at the w/diluent interface, respectively; see Section 2.1 for the $K_{D,Pic}^S$ value. The thus-evaluated values are listed in Tables 1 and 2.

Strictly speaking, $\Delta\phi_{eq}$ and $\Delta\phi_A^{0'}$ are the equilibrium potential differences between the two bulk phases. However, they can be regarded approximately as the equilibrium potential differences at the liquid/liquid interfaces [9,10].

3. Discussion

3.1. I Dependences of $\log K_{ex}$ and $\log K_{ex\pm}$

The dependences of $\log K_{ex}$ and $\log K_{ex\pm}$ on I are considered below. On the basis of their definitions, the K_{ex} value can be dependent on $[M^+]$ and $[A^-]$, while, in addition to these concentrations, the $K_{ex\pm}$ value can be on $[ML^+]_{org}$ and $[A^-]_{org}$. Therefore, K_{ex} is mainly a function of I , while $K_{ex\pm}$ is a function with the two parameters, I and I_{org} ; the relations [14] of $[M^+] = a_M/y_+(I)$ and $[A^-]_{org} = a_{A,org}/y_{-,org}(I_{org})$ hold as examples (see below for the symbols a and y). The I dependence of $\log K_{ex\pm}$ is of an approximate.

Figure 5 shows the $\log K_{ex}$ -versus- I plot for the AgPic-B18C6 extraction system with DCE; in the plot, the average value of I was employed as I (x -axis) of each system. Using the extended Debye-Hückel (DH) equation [14], the extraction constant (K_{ex}^0) at $I \rightarrow 0$ mol·dm⁻³ is expressed as

$$\begin{aligned} \log K_{ex}^0 &= \log([MLA]_{org}/a_M[L]_{org}a_A) = \log K_{ex} - \log(y_+y_-) \\ &= \log K_{ex} + 2A\sqrt{I}/(1 + Ba\sqrt{I}) \end{aligned} \quad (5)$$

where the symbols, a_j and y , denote the activity of species j ($= M^+, A^-$) and its activity coefficient with I , respectively [14]. Rearranging Equation (5), the following equation was obtained immediately:

$$\log K_{ex} = \log K_{ex}^0 - 2A\sqrt{I}/(1 + Ba\sqrt{I}) \quad (5a)$$

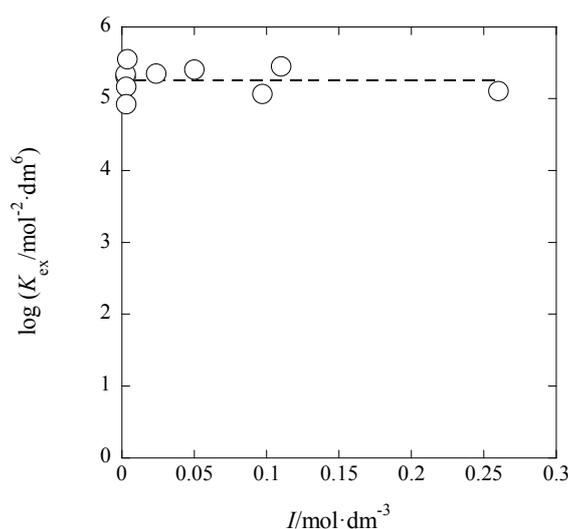


Figure 5. A plot of $\log K_{ex}$ vs. I for the AgPic extraction with B18C6 into DCE. See the text for the regression line (broken line). Error bars were added for only the present experimental values in Figures 5–10. There are some cases where the bars were smaller than the points, such as circle and square. Especially, all the bars were smaller than the size of the circles in Figure 5.

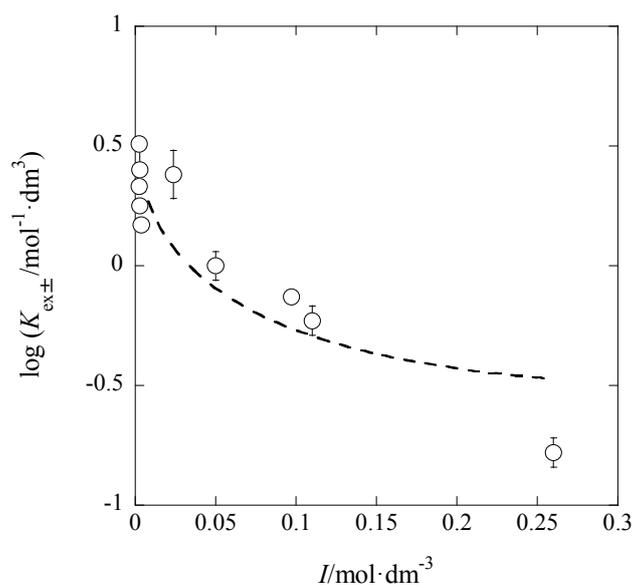


Figure 6. A plot of $\log K_{\text{ex}\pm}$ vs. I for the AgPic extraction with B18C6 into DCE. The regression line (broken line) based on the Davies equation was $\log K_{\text{ex}\pm} = 0.596 - 2 \times 2.05 \left\{ \sqrt{I} / (1 + \sqrt{I}) - 0.3I \right\}$ at $r = 0.884$ and $N = 10$.

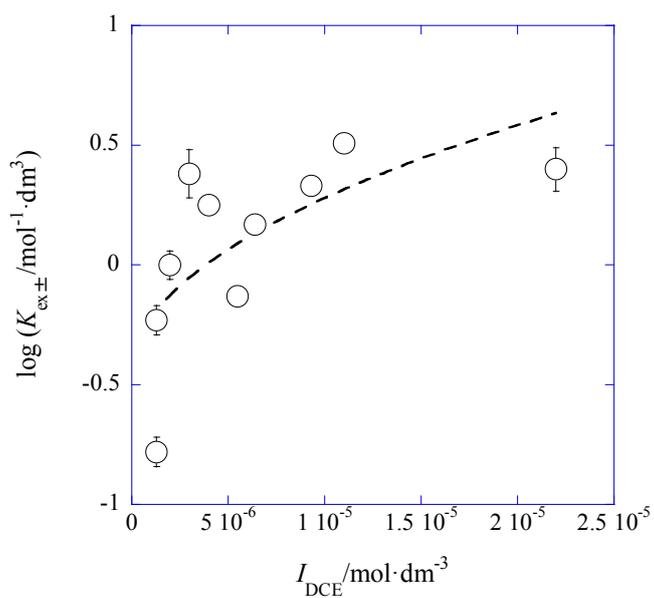


Figure 7. A plot of $\log K_{\text{ex}\pm}$ vs. I_{DCE} for the AgPic extraction with B18C6 into DCE. See the text for the regression line (broken line).

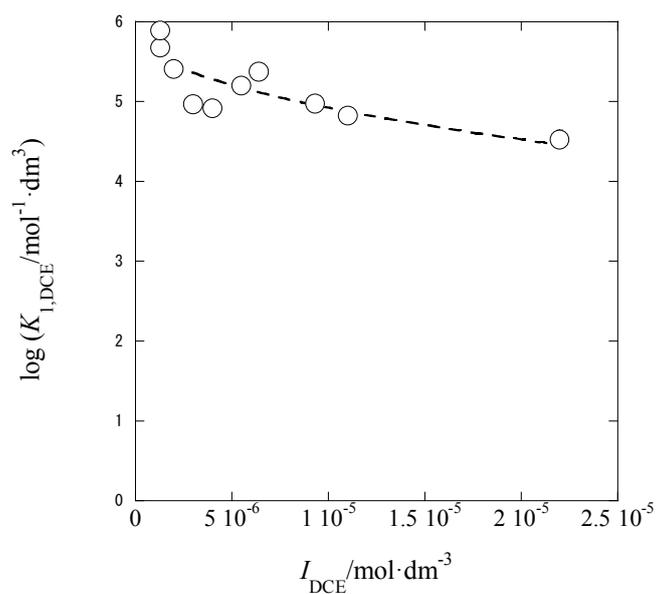


Figure 8. A plot of $\log K_{1,DCE}$ vs. I_{DCE} for the AgPic extraction with B18C6 into DCE. The regression line was $\log K_{1,DCE} = 5.89 - 2 \times (1.52 \times 10^2) \sqrt{I_{DCE}}$ (broken line) at $r = 0.821$ and $N = 10$.

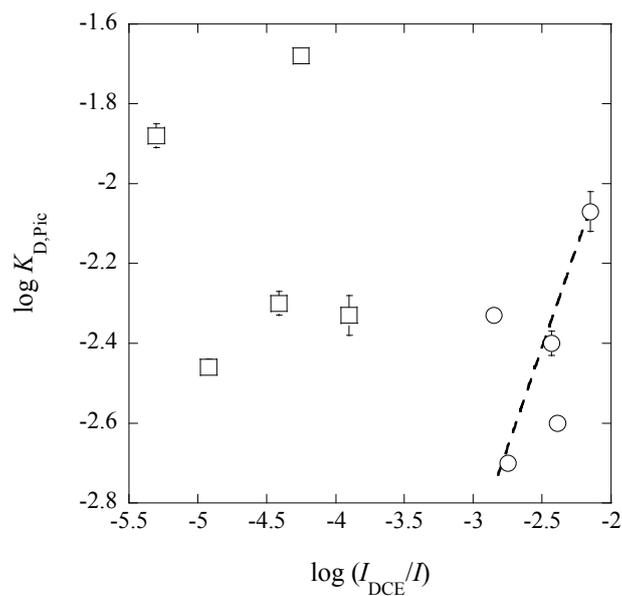


Figure 9. A plot of $\log K_{D,Pic}$ vs. $\log(I_{DCE}/I)$ for the AgPic extraction with B18C6 into DCE. The broken line shows a theoretical one for the slope fixed at unity: see the text. The plots (square) were of the extraction with the excess addition of HNO_3 in the w phases.

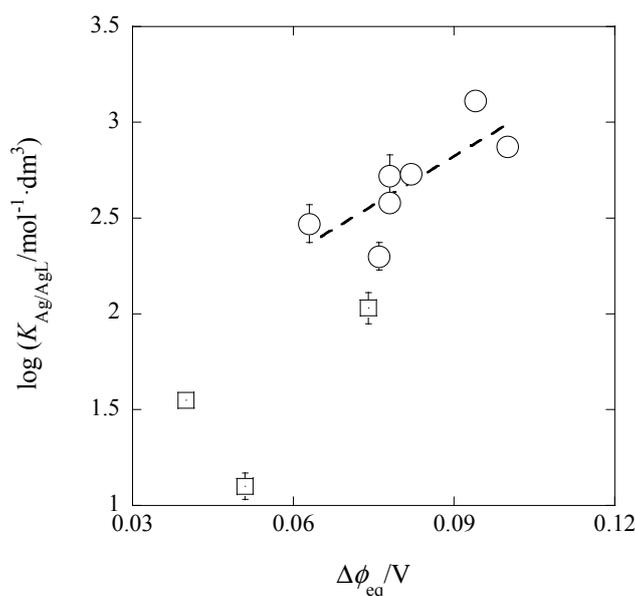


Figure 10. A plot of $\log K_{\text{Ag}/\text{AgL}}$ vs. $\Delta\phi_{\text{eq}}$ for the AgPic extraction with B18C6 (= L) into DCE. See the text for the regression line (broken line).

The regression analysis of the plot in Figure 5 based on this equation yielded the regression line with $\log(K_{\text{ex}}^0 / \text{mol}^{-2} \cdot \text{dm}^6) = 5.28 \pm 0.25$ and $B\hat{a} = 44 \pm 661 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2} \text{ \AA}$ at $r = 0.024$ and N (number of data) = 10, the fixed A value (= 0.5114) in pure water, and 298 K. Considering the error of the experimental $B\hat{a}$ value, it is difficult to discuss the $B\hat{a}$ or \hat{a} value in this result. When the three parameters, $\log K_{\text{ex}}^0$, A , and $B\hat{a}$, had been used for the regression analysis, it gave the results of $\log K_{\text{ex}}^0 > 0$, $A < 0$, and $B\hat{a} < 0$. Consequently, we gave up such an analysis.

Similarly, the extraction constant ($K_{\text{ex}\pm}^0$) at $I \rightarrow 0$ is expressed as

$$\begin{aligned} \log K_{\text{ex}\pm}^0 &= \log(a_{\text{ML,org}} a_{\text{A,org}} / a_{\text{M}} [\text{L}]_{\text{org}} a_{\text{A}}) \\ &= \log K_{\text{ex}\pm} + \log(y_{\text{ML,org}} y_{-, \text{org}}) - \log(y_{+} y_{-}) \end{aligned} \quad (6)$$

where the subscript “ML” means the complex ion ML^+ . Rearranging this equation, we can immediately obtain

$$\log K_{\text{ex}\pm} = \log K_{\text{ex}\pm}^{0'} - 2A\sqrt{I} / (1 + Ba\sqrt{I}), \quad (6a)$$

where $K_{\text{ex}\pm}^{0'}$ denotes $K_{\text{ex}\pm}^0 / (y_{\text{ML,org}} y_{-, \text{org}})$ ($= [\text{ML}^+]_{\text{org}} [\text{A}^-]_{\text{org}} / a_{\text{M}} [\text{L}]_{\text{org}} a_{\text{A}}$). Unfortunately, the analysis of the plot based on Equation (6a) did not yield the suitable result which satisfies the condition of $B\hat{a} > 0$.

On the other hand, using the Davies equation without $B\hat{a}$ instead of the extended DH equation [14], $\log K_{\text{ex}\pm}^{0'} = 0.60 \pm 0.11$ and $A = 2.05 \pm 0.38 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$ were obtained (Figure 6). The Davies equation is $\log \gamma = -Az^2 \left\{ \sqrt{I} / (1 + \sqrt{I}) - 0.3I \right\}$ [14], where z shows a formal charge of ionic species with a sign (refer to the Introduction).

The analysis of the $\log K_{\text{ex}}$ -versus- I plot by the Davies equation yielded $\log K_{\text{ex}}^0 = 5.29 \pm 0.11$ with $A = 0.08 \pm 0.40 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$. Within the calculation error of ± 0.3 , this $\log K_{\text{ex}}^0$ value was in accord with 5.3 determined by the DH equation (see above in this section).

3.2. I_{DCE} Dependence of $\text{Log} K_{\text{ex}\pm}$

Applying the DH limiting law [14] for the system and rearranging Equation (6) at org = DCE, we can easily obtain

$$\log K_{\text{ex}\pm} \approx \log K_{\text{ex}\pm}^{0''} + 2A_{\text{DCE}} \sqrt{I_{\text{DCE}}}. \quad (6b)$$

Hence, a plot of $\log K_{\text{ex}\pm}$ versus I_{DCE} yields $\log K_{\text{ex}\pm}^{0'}$ and A_{DCE} values immediately. Here, $K_{\text{ex}\pm}^{0'}$ is defined as $a_{\text{ML,DCE}}a_{\text{A,DCE}}/([\text{M}^+][\text{L}]_{\text{DCE}}[\text{A}^-]) (=y_+y_-K_{\text{ex}\pm}^0)$. Figure 7 shows its plot for the AgPic-18C6 extraction systems with DCE.

Also the average values of I_{DCE} were used for the plot (see Section 3.1) and the y_+y_- value in $K_{\text{ex}\pm}^{0'}$ was estimated on average ($N = 10$) to be 0.76 ± 0.14 . This product was calculated from the ion size parameters, $a(\text{Ag}^+) = 2.5$ and $a(\text{Pic}^-) = 7 \text{ \AA}$, in water [15]. A plot analysis gave $\log K_{\text{ex}\pm}^{0'} = -0.45 \pm 0.24$ and $A_{\text{DCE}} = 116 \pm 46 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$ at $r = 0.665$. Accordingly, introducing y_+y_- in $\log K_{\text{ex}\pm}^{0'} = \log y_+y_- + \log K_{\text{ex}\pm}^0$, the $\log K_{\text{ex}\pm}^0$ value became -0.36 ± 0.24 . The experimental A_{DCE} value was much larger than its theoretical one ($= 10.6 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$) for a pure DCE at 298 K. This difference between these A_{DCE} values may be due to simple errors caused by the narrow experimental I_{DCE} -range of $(0.097\text{--}2.2) \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ or to the condition where the diluent DCE was saturated with water.

3.3. I_{DCE} Dependences of $\text{Log}K_{1,\text{DCE}}$

The thermodynamic ion-pair formation constant ($K_{1,\text{org}}^0$) at $I_{\text{org}} \rightarrow 0$ is described as

$$\log K_{1,\text{org}}^0 = \log([\text{MLA}]_{\text{org}}/a_{\text{ML,org}}a_{\text{A,org}}) = \log K_{1,\text{org}} - \log(y_{\text{ML,org}}y_{-, \text{org}}) \quad (7)$$

Rearranging this equation at $\text{org} = \text{DCE}$ and $\text{ML}^+ = \text{AgB18C6}^+$ can give the following equation:

$$\log K_{1,\text{DCE}} = \log K_{1,\text{DCE}}^0 + \log(y_{\text{AgB18C6,DCE}}y_{-, \text{DCE}}) \approx \log K_{1,\text{DCE}}^0 - 2A_{\text{DCE}}\sqrt{I_{\text{DCE}}} \quad (7a)$$

A plot of $\log K_{1,\text{DCE}}$ versus I_{DCE} is shown in Figure 8. The plot analysis yielded the regression line with $\log K_{1,\text{DCE}}^0 = 5.89 \pm 0.19$ and $A_{\text{DCE}} = 152 \pm 37 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$ at $r = 0.821$ and $N = 10$. This A_{DCE} value overlaps with the value ($= 116$) determined above (see Section 3.2), within the calculation error ($= 46$) and much larger than the theoretical one too. The authors cannot clearly explain the larger experimental A_{DCE} values, as similar to Section 3.2.

The logarithmic value, $\log K_{1,\text{DCE}}^{\text{av}}$, of simple average- $K_{1,\text{DCE}}$ one was 5.36 ± 0.42 in the I_{DCE} range of $(0.097\text{--}2.2) \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ at $N = 10$ and was smaller than the $\log K_{1,\text{DCE}}^0$ value ($= 5.9$ at $I \rightarrow 0$). Although the experimental I_{DCE} values were adequately small ($I_{\text{DCE}} \ll 0.001$), the magnitude of $K_{1,\text{DCE}}$ decreased with an increase in I_{DCE} . Also, the $\log K_{1,\text{DCE}}^{\text{av}}$ value was smaller than the $\log K_{\text{AgPic,DCE}}$ one ($= 6.0$, see Section 2.1). From the $\log K_{\text{ex}\pm}^{0'}$ value ($= 0.6$) in Section 3.1 and the $\log K_{\text{ex}\pm}^0$ one ($= -0.36$) in 3.2, we obtained $\log(y_{\text{AgB18C6,DCE}}y_{-, \text{DCE}}) (= \log K_{\text{ex}\pm}^{0'} - \log K_{\text{ex}\pm}^0) = -0.96 \pm 0.27$. Hence, the $\log K_{1,\text{DCE}}$ value was estimated to be $4.93 (= \log K_{1,\text{DCE}}^0 + \log(y_{\text{AgB18C6,DCE}}y_{-, \text{DCE}}) = 5.89 - 0.96)$, being somewhat smaller than the $\log K_{1,\text{DCE}}^{\text{av}}$ value ($= 5.4$). These facts indicate that the $\log K_{1,\text{DCE}}^{\text{av}}$ value is not properly reflective of the $\log K_{1,\text{DCE}}$ one in Equation (7).

On the other hand, the $\log(K_{\text{AgB18C6,DCE}}/\text{mol}^{-1} \cdot \text{dm}^3)$ values were calculated from the relation $\log K_{\text{ML,org}} = \log K_{\text{ex}\pm} - \log K_{\text{D,M}}^{\text{S}} \cdot K_{\text{D,A}}^{\text{S}}$ for a given I_{DCE} . Here, we assumed that, considering the smaller I_{DCE} values, the ratio, $y_{\text{ML,DCE}}/y_{+, \text{DCE}}$, of the activity coefficients in the thermodynamic complex-formation constant, $K_{\text{ML,DCE}}^0$, equals unity. Accordingly, the approximation that an average value among the $K_{\text{AgB18C6,DCE}}$ ones equals the $K_{\text{AgB18C6,DCE}}^0$ value becomes valid. Consequently, as its logarithmic value, 7.77 ± 0.25 was obtained on average ($N = 12$) at 298 K.

3.4. A Trend between $\text{Log}K_{\text{D,Pic}}$ and $\text{Log}(I_{\text{DCE}}/I)$

From a plot of $\log K_{\text{D,Pic}}$ versus $\log(I_{\text{DCE}}/I)$, we obtained a theoretical line of $\log K_{\text{D,Pic}} = \log(I_{\text{DCE}}/I) - (0.09 \pm 0.12)$ at $r = 0.398$ (Figure 9) under the condition of the fixed slope of unity, except for the points in the I range of $0.024\text{--}0.26 \text{ mol} \cdot \text{dm}^{-3}$. This trend suggests that the $K_{\text{D,Pic}}$ values are basically proportional to the ratios of (I_{DCE}/I) , as reported before [16]. The deviation of the five points in Figure 9 can come from an effect of the higher I values in (I_{DCE}/I) . An answer to this deviation is explained as follows.

For the case of only MA (or mixture of MX with small excess organic acid, HA) in w phase with L, we can propose the following equation for I and I_{org} .

$$I = (1/2)([M^+] + [ML^+] + [A^-]) = [A^-] \quad (8)$$

with the charge balance equation of $[M^+] + [ML^+] = [A^-]$. Similarly, the authors can obtain

$$I_{\text{org}} = (1/2)([M^+]_{\text{org}} + [ML^+]_{\text{org}} + [A^-]_{\text{org}}) \approx [A^-]_{\text{org}} \quad (8a)$$

in the org phase. The assumption that $[AgB18C6^+]_{\text{DCE}}$ is much larger than $[Ag^+]_{\text{DCE}}$, namely $[AgB18C6^+]_{\text{DCE}} \approx [Pic^-]_{\text{DCE}}$, was employed for the experiments. From Equations (8) and (8a), one can see easily the experimental relation that (I_{DCE}/I) is basically proportional to $K_{\text{D,Pic}}$.

On the other hand, for the present case of mixture of MX with the small excess HA and excess HX (strong acid) in the w phase with L, the corresponding equations are

$$I = (1/2)([M^+] + [H^+] + [ML^+] + [HL^+] + [A^-] + [X^-]) \approx [A^-] + [X^-] \quad (9)$$

and

$$I_{\text{org}} = (1/2)([M^+]_{\text{org}} + [H^+]_{\text{org}} + [ML^+]_{\text{org}} + [HL^+]_{\text{org}} + [A^-]_{\text{org}} + [X^-]_{\text{org}}) \approx [A^-]_{\text{org}} \quad (9a)$$

with the assumptions that $[M^+] + [ML^+] + [H^+] \approx [A^-] + [X^-]$ and $[M^+]_{\text{org}} + [H^+]_{\text{org}} + [ML^+]_{\text{org}} + [HL^+]_{\text{org}} \approx [A^-]_{\text{org}} (>> [X^-]_{\text{org}})$, respectively. Therefore, Equations (9) and (9a) give the experimental relation of

$$(I_{\text{DCE}}/I) \approx [Pic^-]_{\text{DCE}} / ([Pic^-] + [NO_3^-]) = K_{\text{D,Pic}} / (1 + [NO_3^-]/[Pic^-]) \quad (9b)$$

and then its ratio becomes smaller than the $K_{\text{D,Pic}}$ value in the case of $[NO_3^-] >> [Pic^-]$. When $[NO_3^-]$ nearly equals $[Pic^-]$ in Equation (9b), the $\log(I_{\text{DCE}}/I)$ value deviates from the $\log K_{\text{D,Pic}}$ one by +0.3: that is, $(I_{\text{DCE}}/I) \approx K_{\text{D,Pic}}/2$. However, such a deviation is comparable to experimental errors. Thus, Equation (9b) explains well the deviation of the five points from the regression line in Figure 9. Obviously, the deviation becomes larger, when an excess of HX, such as HNO_3 , was added in the w phase and X^- less distribute into the org phase than A^- does (for example, see the $K_{\text{D,Pic}}^{\text{S}}$ & $K_{\text{D,NO}_3}^{\text{S}}$ values in Table 3).

Table 3. Log $K_{\text{ex}\pm}$ values evaluated from the $\log K_{\text{D,A}}^{\text{S}}$ and $\log K_{\text{Ag/AgL}}^{\text{S}}$ values at B18C6 (= L), DCE, and 298 K.

A^-	$\log K_{\text{D,A}}^{\text{S}1}$	$\log K_{\text{ex}\pm}$	
		Evaluated ²	Experimental
Cl^-	-7.99, -8.135 ³	-6.69	- ⁴
Br^-	-6.57, -6.74 ³	-5.27	- ⁴
N_3^-	-6.42	-5.12	- ⁴
NO_3^-	-5.91, -5.94 ³	-4.61, -4.64 ³	-4.40
I^-	-4.50, -4.62 ³	-3.20	- ⁴
SCN^-	-4.21, -4.47 ³	-2.91	- ⁴
MnO_4^-	-3.33	-2.03	- ⁵
ClO_4^-	-2.84, -3.00 ³	-1.54, -1.70 ³	-1.24
Pic^{-6}	-1.01 ₁	- ⁷	0.35 ± 0.12 ⁸ -0.36 ± 0.24 ⁹

¹ Ref. [12]; ² Values calculated from $\log K_{\text{ex}\pm} = 1.30 + \log K_{\text{D,A}}^{\text{S}}$ [see Equation (11)]. They have the error of 0.3 at least because of the standard deviation of $\log K_{\text{Ag/AgL}}^{\text{S}}$; ³ Ref. [17]; ⁴ Not determinable, probably because of precipitation etc. See the text; ⁵ Not determined here; ⁶ The $K_{\text{Ag/AgL}}^{\text{S}}$ value was determined, based on the data of the extraction experiments. See Table 1; ⁷ Not evaluated; ⁸ Average value in the I range of $(2.5\text{--}3.6) \times 10^{-3}$ mol·dm⁻³. See Table 1; ⁹ Value at $I_{\text{DCE}} \rightarrow 0$. See the text.

3.5. $\Delta\phi_{eq}$ Dependences of $\log K_{M/ML}$ and $\log K_{ex\pm}$

The $\log K_{M/ML}$, defined as $\log([ML^+]_{org}/[M^+][L]_{org})$ [8], can be resolved as follows and calculated from $\log K_{ex\pm} - \log K_{D,A}$.

$$\log K_{M/ML} = \log K_{D,M} + \log K_{ML,org} = 16.90\Delta\phi_{eq} + \log K_{D,M}^S \cdot K_{ML,org} \quad (10)$$

at 298 K with

$$\log K_{D,M} = (F/2.303RT)\Delta\phi_{eq} + \log K_{D,M}^S \quad (10a)$$

Here, the term of $\log(K_{D,M}^S \cdot K_{ML,org})$ has to be a constant, because these two equilibrium constants are independent of $\Delta\phi_{eq}$; $\log K_{ML,org} = -(F/2.303RT)$ (standard formal potential of the ML^+ formation in the org phase) [8]. The magnitude of the $K_{M/ML}$ (or $K_{M/ML}^S$) value shows an incorporation-ability into the org phase of L against M^+ . Then, the plot of $\log K_{M/ML}$ versus $\Delta\phi_{eq}$ based on Equation (10) can yield a straight line with the slope of 17 V^{-1} and the intercept of $\log K_{D,M}^S \cdot K_{ML,org}$.

Figure 10 shows its plot, of which the experimental regression line was $\log K_{M/ML} = (16.8 \pm 6.1)\Delta\phi_{eq,Pic} + (1.30 \pm 0.50)$ at $r = 0.775$ and $N = 7$. Here, the three data (the squares in Figure 10) were neglected from the calculation of the line, because their I values were much larger than the values of the extraction systems without the presence of excess HNO_3 in the w phase (see Tables 1 and 2). The $\Delta\phi_{eq,Pic}$ values show the $\Delta\phi_{eq}$ ones obtained from the experimental $\log K_{D,Pic}$ values. The predictable intercept value was calculated to be $1.30 (= \log K_{D,Ag}^S + \log K_{AgB18C6,DCE} = -6.47 + 7.77) \pm 0.25$, being in accord with the experimental value. Similarly, the slope value was in good agreement with its theoretical one ($= 17$). These facts indicate that the $\Delta\phi_{eq,Pic}$ values essentially correspond to the $\Delta\phi_{eq}$ ones in $\log K_{D,Ag}$ {see Equation (10a)}. In other words, the relation of $\log K_{Ag/AgB18C6} = (\text{slope}) \times \Delta\phi_{eq,Pic} + \log K_{D,Ag}^S \cdot K_{AgB18C6,DCE}$ is satisfied.

A plot of $\log K_{ex\pm}$ versus $\Delta\phi_{eq}$ for the $A^- = \text{Pic}^-$, ClO_4^- , and NO_3^- systems also gave a regression line with a slope of $19.3 \pm 2.0 \text{ V}^{-1}$ and an intercept of -1.23 ± 0.18 at $r = 0.974$ and $N = 7$ in the narrow I range (see Table 1 for their basic data). This slope was very close to the theoretical value ($= 17$). As similar to the previous results [11], these results indicate that the plot satisfies the relation of $\log K_{ex\pm} = 16.90\Delta\phi_{eq} + \log K_{D,A} + \log K_{D,Ag}^S \cdot K_{AgB18C6,DCE} (= 16.90\Delta\phi_{eq} + \log K_{D,A} + 1.30)$. The $(\log K_{D,A} + 1.3)$ term corresponds to the intercept [11] within ± 0.3 at least.

3.6. Evaluation of $\log K_{ex\pm}$ Based on $\log K_{D,A}^S$

Using the $\log K_{M/ML}^S$ and $\log K_{D,A}^S$ values, we can immediately evaluate the $\log K_{ex\pm}$ value as follows. A thermodynamic cycle gives

$$\log K_{ex\pm} = \log K_{M/ML}^S + \log K_{D,A}^S = \log K_{M/ML} + \log K_{D,A} \quad (11)$$

by using Equations (10a) and (4). It is difficult to accurately determine the $K_{D,M}^S$ (or $K_{D,M}(\Delta\phi_{eq})$: the function of $\Delta\phi_{eq}$, see Equation (10a)) and $K_{ML,org}$ values. On the other hand, it is comparatively easy to determine the $K_{M/ML}^S$ value. So, if the $\log K_{M/ML}^S$ {or $\log K_{M/ML}(\Delta\phi_{eq})$ } value is determined for given ML^+ and diluent, then the $\log K_{ex\pm}$ values can be calculated from Equation (11) with the $\log K_{D,A}^S$ {or $\log K_{D,A}(\Delta\phi_{eq})$ } ones. In this study, we determined the $\log K_{Ag/AgL}^S$ value to be 1.30 from the data (see Table 1) of the AgPic-B18C6 extraction systems with DCE. Calculated $\log K_{ex\pm}$ values for some A^- are listed in Table 3, together with several experimental values.

The determination of the $K_{ex\pm}$ values will be experimentally difficult for the Cl^- to I^- extraction systems, because of the precipitation [18] of their silver salts. The same is true of the SCN^- extraction system, because of its low solubility product ($= 1.0 \times 10^{-12} \text{ mol}^2 \cdot \text{dm}^{-6}$ [18]) against Ag^+ in water. Also, AgN_3 , which is a white insoluble crystal, is explosive [19]. Therefore, the experimental $K_{ex\pm}$ values were determined at 298 K for the ClO_4^- and NO_3^- extraction systems (see Table 1). Considering the differences (0.03–0.26) between the $\log K_{D,A}^S$ values at a fixed A^- in Table 3 and the standard deviation

(= 0.3) of the $\log K_{\text{Ag}/\text{AgB18C6}}^{\text{S}}$ value, these experimentally-obtained $\log K_{\text{ex}\pm}$ values are very close to the values evaluated here.

Similar results were obtained for the NaA-B18C6 extraction into DCE. Their $\log K_{\text{ex}\pm}$ values evaluated from $\log K_{\text{Na}/\text{NaB18C6}}^{\text{S}} = 0.53$, which were calculated here, were -2.8 for $\text{A}^- = \text{MnO}_4^-$ and -2.3 for ClO_4^- . Their experimental $\log K_{\text{ex}\pm}$ values were -2.23 [13] at $I = 0.0077 \text{ mol}\cdot\text{dm}^{-3}$ for MnO_4^- and -3.65 ± 0.07 at 0.074 for ClO_4^- of which the value was re-calculated from the data reported before [8]. These differences, $\leq |1.4|$, between the evaluated and experimental values were larger than those for the AgA-B18C6 extraction systems.

The above fact indicates that the $\log K_{\text{ex}\pm}$ values can be evaluated from a sum of the $\log K_{\text{Ag}/\text{AgB18C6}}^{\text{S}}$ and $\log K_{\text{D,A}}^{\text{S}}$ (or $\log K_{\text{Ag}/\text{AgB18C6}}$ & $\log K_{\text{D,A}}$) ones. Namely, the order, $\text{A}^- = \text{NO}_3^- < \text{ClO}_4^- \ll \text{Pic}^-$, in $\log K_{\text{ex}\pm}$ for a given extraction system at fixed AgB18C6^+ and DCE is fundamentally predicted from that of $\log K_{\text{D,A}}^{\text{S}}$ (see Table 3). Thus, for the systems where the extraction experiments are difficult, the present procedure becomes easy to evaluate the $\log K_{\text{ex}\pm}$ values. Also, the experimental intercepts ($\approx \log K_{\text{ex}\pm}$ [13]) of the straight lines in Figure 2 support this order: the intercepts were -4.05 for $\text{A}^- = \text{NO}_3^-$, -0.92 for ClO_4^- , and 2.20 for Pic^- .

4. Materials and Methods

4.1. Materials

An aqueous solution of a commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ($\geq 98\%$, Wako Pure Chemical Industries, Tokyo, Japan) and a solution with 2 equivalents of $\text{HPic} \cdot n\text{H}_2\text{O}$ ($\geq 99.5\%$, Wako Pure Chemical Industries, Tokyo, Japan) were mixed, that of Ag_2SO_4 ($\geq 99.5\%$, Kanto Chemicals Co. Ltd., Tokyo, Japan) was added in the mixture, and immediately BaSO_4 precipitated. After standing the mixture overnight, the thus-obtained yellow solution with the precipitate was filtered and then its filtrate was evaporated by a rotary evaporator (type RE1-N, Iwaki, Japan) in order to deposit a fine yellow crystal. The crystal obtained was filtered and dried in vacuo for 21 h. Found: 97.29% for Ag by the AAS measurements at 328.1 nm; 101% for Pic^- by spectrophotometric measurements at 355.0 nm. An amount of water in the AgPic crystal was not detected by a Karl-Fischer titration. This crystal was employed only for the AgPic extraction experiments without B18C6.

Concentrations of the aqueous solution with AgNO_3 ($\geq 99.8\%$, Kanto Chemicals Co. Ltd., Tokyo, Japan) and that with AgClO_4 (97%, Aldrich, Missouri, MO, USA) were determined by a precipitation titration with NaCl ($99.98\% \pm 0.01\%$, Wako: standard reagent for volumetric analysis, Wako Pure Chemical Industries, Tokyo, Japan). A commercial DCE (guaranteed-pure reagent, Kanto Chemicals Co. Ltd., Tokyo, Japan) was treated with the same procedure as that described previously [13,16]. All other chemicals used in this study were of guaranteed-pure reagent grade.

4.2. Extraction Experiments

Procedures for both the AgPic extraction experiments and the AgA extraction ones with B18C6 into DCE were essentially the same as those [8,20] reported before. The latter experiments were performed by using mixtures of AgNO_3 with HPic in the w phases. The total concentration range of Ag(I) was 0.00041 to $0.043 \text{ mol}\cdot\text{dm}^{-3}$ for the AgPic extraction and the ranges of AgNO_3 , HPic , and B18C6 were $(1.5 \text{ or } 5.0) \times 10^{-4}$, $(3.3 \text{ or } 3.4) \times 10^{-3}$, and $(0.4\text{--}7.5) \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, respectively, for the Ag(I) extraction with B18C6. The extraction of AgB18C6^+ with NO_3^- or $\text{Ag}(\text{B18C6})\text{NO}_3$ was negligible, compared with that of AgB18C6^+ with Pic^- or $\text{Ag}(\text{B18C6})\text{Pic}$ (see Figure 2 or the $\log K_{\text{ex}\pm}$ and $\log K_{\text{ex}}$ values in Table 1). After the extraction operations, the w phases were in the pH ranges of 2.68–2.74 at the system of $I = 0.0025 \text{ mol}\cdot\text{dm}^{-3}$ and 2.70–3.37 at that of 0.0031 (see Table 1).

For the AgPic extraction by B18C6 into DCE in the presence of “excess HNO_3 ” in the w phases, the total concentrations of AgNO_3 and HPic were fixed at 1.5×10^{-4} and 0.0033 or $0.0034 \text{ mol}\cdot\text{dm}^{-3}$, respectively. Under this condition, the total concentration, $[\text{HNO}_3]_{\text{t}}$, of HNO_3 in the w phase was changed in the range of 0.025 to $0.25 \text{ mol}\cdot\text{dm}^{-3}$. After the extraction operations, the w phases were

in the pH ranges of 1.64 and 1.65 at $[\text{HNO}_3]_t = 0.025 \text{ mol}\cdot\text{dm}^{-3}$, 1.34–1.38 at 0.050, 1.06 at 0.10, and 0.62–0.68 at 0.25.

Used apparatus, such as the atomic absorption spectrophotometer, UV-V, centrifuge, mechanical shaker, and pH meter with the glass electrode, were the same as those [8,16] described previously.

5. Conclusions

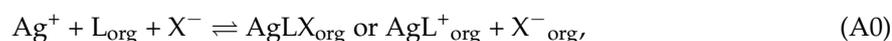
The I or I_{DCE} dependences of the $\log K_{\text{ex}\pm}$ and $\log K_{\text{ex}}$ values for the present extraction systems were clarified experimentally. Their experimental equations were $\log K_{\text{ex}} = 5.3 - 2 \times 0.51 \sqrt{I} / (1 + 44 \sqrt{I})$ and $\log K_{\text{ex}\pm} = 0.6 - 2 \times 2.0 \left\{ \sqrt{I} / (1 + \sqrt{I}) - 0.3I \right\} = -0.5 + 2 \times 116 \sqrt{I_{\text{DCE}}}$. However, the magnitudes of these changes in $\log K_{\text{ex}\pm}$ or $\log K_{\text{ex}}$ with I or I_{DCE} were insignificant in practical separation. It was also suggested that the style of M(I) employed in the extraction experiments with L, either the simple salt MPic or the mixture of MX with HPic and excess HX, largely control whether the $\log K_{\text{D,Pic}}$ values are dependent on the $\log(I_{\text{DCE}}/I)$ ones or not. The $\log K_{\text{ex}\pm}$ -versus- $\Delta\phi_{\text{eq}}$ plot for the Pic^- , ClO_4^- , and NO_3^- systems yielded the good positive correlation. On the basis of the plot of $\log K_{\text{Ag/AgB18C6}}$ versus $\Delta\phi_{\text{eq,Pic}}$, it was indirectly proved that the $\Delta\phi_{\text{eq}}$ values obtained from the $K_{\text{D,Pic}}$ ones is common to those from the $K_{\text{D,Ag}}$ values. Moreover, the $\log K_{\text{ex}\pm}$ values were predicted from the sum of the $\log K_{\text{D,A}}^{\text{S}}$ and $\log K_{\text{Ag/AgB18C6}}^{\text{S}}$ ones for given MB18C6^+ and DCE at least. At the same time, the order in $K_{\text{ex}\pm}$ reflected that in $K_{\text{D,A}}^{\text{S}}$.

Author Contributions: Yoshihiro Kudo and Satoshi Ikeda conceived and designed the experiments; Saya Morioka, Shuntaro Tomokata, and Satoshi Ikeda performed the experiments; Yoshihiro Kudo and Satoshi Ikeda analyzed the data; Yoshihiro Kudo wrote the paper.

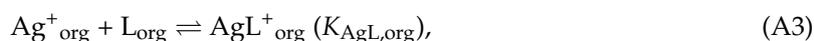
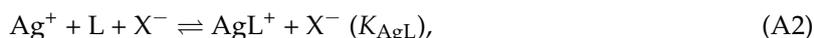
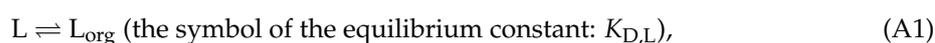
Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

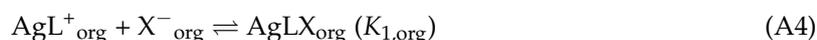
The extraction of AgX by L into the org phase was analyzed at $X^- = \text{ClO}_4^-$ or NO_3^- , $L = \text{B18C6}$, and org = DCE as follows. The component equilibria constituting the overall extraction equilibrium,



were considered to be



and



From the reactions (A2)–(A4), the following equilibria, $\text{Ag}^+ \rightleftharpoons \text{Ag}^+_{\text{org}}$ ($K_{\text{D,Ag}}$), $\text{X}^- \rightleftharpoons \text{X}^-_{\text{org}}$ ($K_{\text{D,X}}$), and $\text{AgL}^+ \rightleftharpoons \text{AgL}^+_{\text{org}}$ ($K_{\text{D,AgL}}$), necessarily appear in the component equilibria. Apparently, these three distribution constants are the conditional distribution ones (see the Introduction). The mass balance equations based on the processes (A1)–(A4) became

$$[\text{Ag}]_t = [\text{Ag}^+] + [\text{AgL}^+] + [\text{Ag}^+]_{\text{org}} + [\text{AgL}^+]_{\text{org}} + [\text{AgLX}]_{\text{org}}, \quad (\text{A5})$$

$$[\text{L}]_t = [\text{L}] + [\text{AgL}^+] + [\text{L}]_{\text{org}} + [\text{AgL}^+]_{\text{org}} + [\text{AgLX}]_{\text{org}},$$

and

$$[\text{X}]_t = [\text{X}^-] + [\text{X}^-]_{\text{org}} + [\text{AgLX}]_{\text{org}}$$

$$(\text{=} [\text{X}^-] + [\text{Ag}^+]_{\text{org}} + [\text{AgL}^+]_{\text{org}} + [\text{AgLX}]_{\text{org}}, \text{ based on a charge balance equation}).$$

Rearranging these three equations for $[Ag]_t$, $[L]_t$, and $[X]_t$, we can obtain easily

$$[Ag^+] = \frac{[Ag]_t - Ab}{1 + K_{AgL}[L]} \quad (A6)$$

$$[L]_{org} \approx \frac{K_{D,L}([L]_t - Ab)}{1 + K_{D,L} + K_{AgL}[Ag^+]}$$

and

$$[X^-] (= I) = [X]_t - Ab \quad (A7)$$

Here, K_{AgL} , Ab , and $K_{D,L}$ denote the complex formation constant ($\text{mol}^{-1} \cdot \text{dm}^3$) for AgL^+ in water, the analytical concentration ($= [Ag^+]_{org} + [AgL^+]_{org} + [AgLX]_{org}$) of Ag(I) in the org phase, and the distribution constant of L into the org phase, respectively. Especially, the Ab values were directly determined in terms of AAS measurements. Also, the I_{org} value can be expressed as $([Ag^+]_{org} + [AgL^+]_{org} + [X^-]_{org})/2 = [X^-]_{org}$. In Equation (A6), the Ab term was approximately expressed as $[AgL^+]_{org} + [AgLX]_{org} (>> [Ag^+]_{org})$. Using Equations (A5) and (A6), we determined the $[Ag^+]$ and $[L]_{org}$ values by the successive approximation computation [2,13,21] and then obtained K_{ex}^{mix} values from the relation of

$$K_{ex}^{mix} = Ab / ([Ag^+][L]_{org}[X^-]) \quad (A8)$$

After the above handlings, we determined the $K_{D,A}$ and $K_{ex\pm}$ values, together with the K_{ex} value(s), by the plots (see Section 2.3) reported before [7,8,11,13]. The above extraction model can be essentially applied for systems with another diluent, M(I), or L.

References

1. Danesi, P.R.; Meider-Gorican, H.; Chiarizia, R.; Scibona, G. Extraction selectivity of organic solutions of a cyclic polyether with respect to the alkali cations. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1479–1483. [CrossRef]
2. Takeda, Y. Extraction of alkali metal picrates with 18-crown-6, benzo-18-crown-6, and dibenzo-18-crown-6 into various organic solvents. Elucidation of fundamental equilibria governing the extraction-ability and -selectivity. *Bunseki Kagaku* **2002**, *51*, 515–525. [CrossRef]
3. Jawaid, M.; Ingman, F. Ion-pair extraction of Na^+ , K^+ , and Ca^{2+} with some organic counter-ions and dicyclohexyl-18-crown-6 as adduct-forming reagents. *Talanta* **1978**, *25*, 91–95. [CrossRef]
4. Kikuchi, Y.; Sakamoto, Y. Complex formation of alkali metal ions with 18-crown-6 and its derivatives in 1,2-dichloroethane. *Anal. Chim. Acta* **2000**, *403*, 325–332. [CrossRef]
5. Kudo, Y.; Takeuchi, T. On the interfacial potential differences for the extraction of alkaline-earth metal picrates by 18-crown-6 ether derivatives into nitrobenzene. *J. Thermodyn. Catal.* **2014**, *5*. [CrossRef]
6. Kudo, Y.; Katsuta, S. On an expression of extraction constants without the interfacial equilibrium-potential differences for the extraction of univalent and divalent metal picrates by crown ethers into 1,2-dichloroethane and nitrobenzene. *Am. J. Anal. Chem.* **2015**, *6*, 350–363. [CrossRef]
7. Kudo, Y.; Nakamori, T.; Numako, C. Extraction of sodium picrate by 3*m*-crown-*m* ether and their monobenzo derivatives ($m = 5, 6$) into benzene: Estimation of their equilibrium-potential differences at the less-polar diluent/water interface by an extraction method. *J. Chem.* **2016**, 2016. [CrossRef]
8. Kudo, Y.; Ogihara, M.; Katsuta, S. An electrochemical understanding of extraction of silver picrate by benzo-3*m*-crown-*m* ethers ($m = 5, 6$) into 1,2-dichloroethane and nitrobenzene. *Am. J. Anal. Chem.* **2015**, *5*, 433–444. [CrossRef]
9. Sladkov, V.; Guillou, V.; Peulon, S.; L'Her, M. Voltammerty of tetraalkylammonium picrates at water/nitrobenzene and water/dichloroethane microinterfaces; influences of distribution phenomena. *J. Electroanal. Chem.* **2004**, *573*, 129–138.
10. Kakiuchi, T. *Liquid-Liquid Interfaces: Theory and Methods*; Volkov, A.G., Deamer, D.W., Eds.; CRC Press: Boca Raton, FL, USA, 1996; Chapter 1.

11. Kudo, Y.; Kaminagayoshi, A.; Ikeda, S.; Yamada, H.; Katsuta, S. Brief determination of standard formal potentials for the transfer of several pairing anions across the nitrobenzene/water interface by Na(I) extraction with 18-crown-6 ether. *J. Anal. Bioanal. Tech.* **2016**, *7*. [[CrossRef](#)]
12. Kudo, Y.; Harashima, K.; Hiyoshi, K.; Takagi, J.; Katsuta, S.; Takeda, Y. Extraction of some univalent salts into 1,2-dichloroethane and nitrobenzene: Analysis of overall extraction equilibrium based on elucidating ion-pair formation and evaluation of standard potentials for ion transfer at the interfaces between their diluents and water. *Anal. Sci.* **2011**, *27*, 913–919. [[PubMed](#)]
13. Kudo, Y.; Harashima, K.; Katsuta, S.; Takeda, Y. Solvent extraction of sodium permanganate by mono-benzo 3*m*-crown-*m* ethers (*m* = 5, 6) into 1,2-dichloroethane and nitrobenzene: A method which analyzes the extraction system with the polar diluents. *Inter. J. Chem.* **2011**, *3*, 99–107. [[CrossRef](#)]
14. De Levie, R. *Oxford Chemistry Primers: Aqueous Acid-Base Equilibria and Titrations*; Oxford University Press: Oxford, UK, 1999.
15. Kielland, J. Individual activity coefficients of ions in aqueous solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678. [[CrossRef](#)]
16. Kudo, Y.; Takahashi, Y.; Numako, C.; Katsuta, S. Extraction of lead picrate by 18-crown-6 ether into various diluents: Examples of sub-analysis of overall extraction equilibrium based on component equilibria. *J. Mol. Liq.* **2014**, *194*, 121–129. [[CrossRef](#)]
17. Czapkiewicz, J.; Czapkiewicz-Tutaj, B. Relative scale of free energy of transfer of anions from water to 1,2-dichloroethane. *J. Chem. Soc. Faraday Trans.* **1980**, *76*, 1663–1668. [[CrossRef](#)]
18. Griest, G.D. *Analytical Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, NY, USA, 1994.
19. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*, 4th ed.; John Wiley & Sons, Inc.: New York, NY, USA, 1980.
20. Kudo, Y.; Usami, J.; Katsuta, S.; Takeda, Y. Solvent extraction of silver picrate by 3*m*-crown-*m* ethers (*m* = 5, 6) and its mono-benzo-derivatives from water to benzene or chloroform: Elucidation of an extraction equilibrium using component equilibrium constants. *Talanta* **2004**, *62*, 701–706. [[CrossRef](#)] [[PubMed](#)]
21. Takeda, Y.; Yasui, A.; Morita, M.; Katsuta, S. Extraction of sodium and potassium perchlorates with benzo-18-crown-6 into various organic solvents. Quantitative elucidation of anion effects on the extraction-ability and -selectivity for Na⁺ and K⁺. *Talanta* **2002**, *56*, 505–513. [[CrossRef](#)]



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