

An Electrochemical Understanding of Extraction of Silver Picrate by Benzo-3*m*-Crown-*m* Ethers (*m* = 5, 6) into 1,2-Dichloroethane and Dichloromethane

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Abstract

Two extraction constants ($K_{\text{ex}\pm}$ and K_{ex}) for extraction of silver picrate (Ag^+Pic^-) by benzo-15-crown-5 ether (B15C5) and benzo-18-crown-6 one (B18C6) into 1,2-dichloroethane (DCE) and dichloromethane (DCM) were determined at 298 K and given values of ionic strength. Here, $K_{\text{ex}\pm}$ and K_{ex} were expressed as $[\text{AgL}^+]_{\text{o}}[\text{Pic}^-]_{\text{o}}/[\text{Ag}^+][\text{L}]_{\text{o}}[\text{Pic}^-]$ and $[\text{AgLPic}]_{\text{o}}/[\text{Ag}^+][\text{L}]_{\text{o}}[\text{Pic}^-]$, respectively: L symbolizes B15C5 or B18C6 and the subscript “o” denotes the organic phase composed of DCE or DCM. Individual distribution constants ($K_{\text{D,Pic}}$) of picrate ion, Pic^- , into the two diluents were also determined with the determination of K_{ex} . From comparison of these $K_{\text{D,Pic}}$ values with those standardized, interfacial potential differences ($\Delta\phi_{\text{eq}}$) at extraction equilibria were evaluated. Then, using these $\Delta\phi_{\text{eq}}$ values, relations of the experimentally-determined $\log K_{\text{ex}\pm}$ or $\log K_{\text{ex}}$ values with their electrochemically-standardized ones were precisely discussed. Consequently, it was indicated that $\log K_{\text{ex}\pm}$ should be expressed as a function of $\Delta\phi_{\text{eq}}$.

Keywords

Individual Distribution Constants, Interfacial Potential Differences, Standardized Extraction Constants, Silver Picrate, Benzo Crown Ethers, Dihaloalkanes

1. Introduction

Recently, individual distribution constants ($K_{\text{D,A}}$) of single anions (A^-), such as picrate ion (Pic^-) and MnO_4^- , into various diluents or organic (o) phases have been determined in course of determination of extraction constants (K_{ex}) for the extraction of some salts, $\text{M}^{\text{I}}\text{A}$ and $\text{M}^{\text{II}}\text{A}_2$, by crown compounds (L) [1]-[4]. Here, $K_{\text{D,A}}$ and

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K_{ex} have been defined as $[A^-]_{\text{o}}/[A^-]$ and $[MLA_z]_{\text{o}}/[M^{z+}][L]_{\text{o}}[A^-]^z$ with $z = 1$ or 2 , respectively. For example, the $\log K_{\text{D,Pic}}$ values were reported to be -2.9_1 for a benzene (Bz) system, -1.89 for 1,2-dichloroethane (DCE), and -0.94 for nitrobenzene (NB) by PbPic_2 extraction experiments with 18-crown-6 ether (18C6) [3]. Also, the values were -6.1_2 for Bz and -4.3_5 for DCE from CdPic_2 extraction experiments with 18C6 [2]. The $\log K_{\text{D,A}}$ values were -0.65 for $A^- = \text{Pic}^-$ and -2.137 for MnO_4^- in the CsA extraction by dibenzo-24-crown-8 ether derivatives into DCE [4]. Such differences in $\log K_{\text{D,Pic}}$ between these extraction experiments may be due to those between experimental conditions, such as kinds of the metal ion, M^{z+} , and L employed, the values of ionic strength (I) of the aqueous solutions and their pH values. Furthermore, the experimental $\log K_{\text{D,Pic}}$ values have been different from the values [5]–[8] standardized by electrochemical measurements at the water (w)/DCE and w/NB interfaces. These differences seemed to be beyond the range of experimental errors. The electrochemically standardized values, which should be compared to the above $\log K_{\text{D,Pic}}$ ones, were $\log K_{\text{D,Pic}}^{\text{S}} = -1.01_1$ [6] for the distribution into DCE and $+0.05$ for that into NB [6]. Similar results have been observed in NaMnO_4 extraction experiments with Benzo-15-crown-5 ether (B15C5) and benzo-18C6 (B18C6) into DCE and NB [1]; as examples, the $\log K_{\text{D,MnO}_4}$ values were -3.3 for the extraction system with B15C5 and -2.5 for that with B18C6 into DCE [1], while $\log K_{\text{D,MnO}_4}^{\text{S}}$ was -3.3_3 [6]. Why are the above $\log K_{\text{D,A}}$ values much different from the $\log K_{\text{D,A}}^{\text{S}}$ ones? Are the $\log K_{\text{ex}}$ values also different from their standardized ones? Does an extraction constant ($K_{\text{ex}\pm}$) for the extraction of ML^{z+} with A^- differ from its standardized value? Here, $K_{\text{ex}\pm}$ has been expressed as $[ML^+]_{\text{o}}[A^-]_{\text{o}}/[M^+][L]_{\text{o}}[A^-]$ [1].

In the present paper, we determined the $K_{\text{D,Pic}}$ and K_{ex} values by the silver picrate (AgPic) extraction-experiments with B15C5 and B18C6 into less-polar DCE and dichloromethane (DCM), in order to examine the deviations of the $\log K_{\text{D,Pic}}$ values from the $\log K_{\text{D,Pic}}^{\text{S}}$ ones. In course of this examination, the differences were discussed by introducing interfacial potential differences ($\Delta\phi_{\text{eq}}$) at extraction (and distribution) equilibria [9] in an extraction model. Also, it was considered how the extraction constants, K_{ex} and $K_{\text{ex}\pm}$, were expressed by these $\Delta\phi_{\text{eq}}$ values. Here, the $K_{\text{ex}\pm}$ values were calculated from the K_{ex} values and other equilibrium constants determined in this study.

2. Theory

2.1. Expression of Overall Extraction Processes by Potential Differences

The following two overall extraction-processes [1] were considered in this study:



and



Here, species with and without the subscript “o” denote those in the organic and w phases, respectively.

(A) To the process (1), ideas of electrochemical potentials ($\bar{\mu}_j$) can be applied as follows.

$$\bar{\mu}_{\text{M}} + \bar{\mu}_{\text{L,o}} + \bar{\mu}_{\text{A}} = \bar{\mu}_{\text{MLA,o}} \quad (3)$$

This equation was rearranged using the properties [10] of $\bar{\mu}_j$.

$$RT(\ln a_{\text{MLA,o}} - \ln a_{\text{M}} - \ln a_{\text{L,o}} - \ln a_{\text{A}}) + \mu_{\text{MLA,o}}^0 - \mu_{\text{M}}^0 - \mu_{\text{L,o}}^0 - \mu_{\text{A}}^0 = F(\phi_{\text{M}}' - \phi_{\text{A}}') = F\Delta\phi_{\text{eq}}' \quad (4)$$

Here, $a_{j,\alpha}$, $\mu_{j,\alpha}^0$ and ϕ_j (or ϕ_j') denote the activity of species j (M(I) , A(-I) , L , MLA), the standard chemical potential of j in a phase α ($=\text{o}$) and the inner potential of j , respectively; $\Delta\phi_{\text{eq}}'$ and $\Delta\phi_k^0$ (or $\Delta\phi_k^{0'}$) refer to the potential difference at an extraction equilibrium in the single phase or between the o and w phases and the potential difference for a process k , such as the overall extraction ($k = \text{ex}$, $\text{ex}\pm$) and an individual distribution $\{\text{A(-I)}$, M(I) , $\text{ML(I)}\}$, respectively. Then, we can obtain from Equation (4) the following equation

$$\Delta\phi_{\text{eq}}' = \Delta\phi_{\text{ex}}^0 + \frac{RT}{F} \ln K_{\text{ex}}^0 \quad (5)$$

with

$$\Delta\phi_{\text{ex}}^0 = \frac{\mu_{\text{MLA,o}}^0 - \mu_{\text{M}}^0 - \mu_{\text{L,o}}^0 - \mu_{\text{A}}^0}{F} \quad (6)$$

and

$$K_{\text{ex}}^0 = \frac{a_{\text{MLA},o}}{a_{\text{M}} a_{\text{L},o} a_{\text{A}}} \quad (7)$$

The symbols, $\Delta\phi_{\text{ex}}^0$ and K_{ex}^0 , in Equation (5) can be also expressed in a molar concentration unit, where the “ex” term in $\Delta\phi_{\text{ex}}^0$ shows the process corresponding to its potential difference.

$$\Delta'\phi_{\text{eq}} = \Delta\phi_{\text{ex}}^{0'} + \frac{2.3RT}{F} \log K_{\text{ex}} \quad (5a)$$

with $\Delta\phi_{\text{ex}}^{0'} = \Delta\phi_{\text{ex}}^0 - (2.3RT/F) \log y_{\text{M}} y_{\text{A}}$, where y_{M} and y_{A} refer to activity coefficients of M^+ and A^- in water, respectively, and both $y_{\text{L},o}$ and $y_{\text{MLA},o}$ were assumed to be unity. In Equations (5) and (5a), $\Delta'\phi_{\text{eq}}$ must equal zero [10], because M^+ and A^- are present in the same phase. Therefore, $\log K_{\text{ex}}$ (see Introduction) is expressed as follows and then becomes independent of $\Delta'\phi_{\text{eq}}$.

$$\log K_{\text{ex}} = -\frac{F}{2.3RT} \Delta\phi_{\text{ex}}^{0'} \quad (8)$$

(B) Similarly, the process (2) was treated with $\bar{\mu}_j$. Its results were

$$\Delta\phi_{\text{eq}} = \Delta\phi_{\text{ex}\pm}^{0'} + \frac{2.3RT}{F} \log K_{\text{ex}\pm} \quad (9)$$

with

$$\Delta\phi_{\text{eq}} = (\phi_{\text{M}} - \phi_{\text{ML},o}) - (\phi_{\text{A}} - \phi_{\text{A},o}), \quad (10)$$

$$\Delta\phi_{\text{ex}\pm}^{0'} = \Delta\phi_{\text{ex}\pm}^0 + \frac{2.3RT}{F} \log \frac{y_{\text{ML},o} y_{\text{A},o}}{y_{\text{M}} y_{\text{A}}} \quad (11)$$

and

$$\Delta\phi_{\text{ex}\pm}^0 = \frac{\mu_{\text{ML},o}^0 + \mu_{\text{A},o}^0 - \mu_{\text{M}}^0 - \mu_{\text{L},o}^0 - \mu_{\text{A}}^0}{F} \quad (12)$$

From Equation (10), we can easily see that this $\Delta\phi_{\text{eq}}$ value is an interfacial potential difference at an extraction equilibrium [9] and its form corresponds to a general definition, $\phi(\text{w phase}) - \phi(\text{o phase})$ [5] [8], for the ion-transfer potential difference occurred at the w/o interface. So, it was assumed that the $\Delta\phi_{\text{eq}}$ value in Equation (9) does not become zero, except for an accidental case (see Table 2 for these examples). Thus, the $\log K_{\text{ex}\pm}$ values determined by extraction experiments were expressed as

$$\log K_{\text{ex}\pm} = \frac{F}{2.3RT} (\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}) \quad (9a)$$

This equation clearly shows that $\log K_{\text{ex}\pm}$ is the function of $\Delta\phi_{\text{eq}}$.

2.2. Evaluation of $\Delta\phi_{\text{eq}}$

Such $\Delta\phi_{\text{eq}}$ values can be experimentally obtained as a result of the $K_{\text{D,A}}$ determination. In this study, we defined $K_{\text{ex}}^{\text{mix}} = ([\text{MLA}]_o + [\text{ML}^+]_o) / ([\text{M}^+][\text{L}]_o [\text{A}^-]) = K_{\text{ex}} + K_{\text{D,A}} / ([\text{M}^+][\text{L}]_o)$ as an extraction-constant parameter under the condition of $[\text{ML}^+]_o = [\text{A}^-]_o$ [1]. Regression analysis of the $\log K_{\text{ex}}^{\text{mix}}$ -versus- $\log([\text{M}^+][\text{L}]_o)^{-1}$ plot [1] gives the $K_{\text{D,A}}$ value which is dependent on experimental conditions, such as initial concentrations of AgNO_3 , HPic, and L, the ionic strength estimated from their concentrations and pH in the w phases.

According to our previous papers [2] [9], the $\log K_{\text{D,A}}$ value has been related to an interfacial potential difference, $\Delta\phi$, as

$$\Delta\phi = \Delta\phi_{\text{A}}^{0'} - \frac{2.3RT}{F} \log K_{\text{D,A}} \quad (13)$$

Putting $\Delta\phi = \Delta\phi_{\text{eq}}$ into this equation, we can immediately obtain the $\Delta\phi_{\text{eq}}$ value from a difference between the

$\log K_{D,A}^S$ value, the standardized one, and the experimental $\log K_{D,A}$ value, that is, $\log K_{D,A}^S = (F/2.3RT)\Delta\phi_A^{0'}$ (at $\Delta\phi_{eq} = 0$ V) and $\log K_{D,A} = -(F/2.3RT)(\Delta\phi_{eq} - \Delta\phi_A^{0'})$. This is due to the idea that the $\Delta\phi_{eq}$ value should be uniform on the interface of a given extraction system [9]. The $\Delta\phi_{Pic}^{0'}$ or $\log K_{D,Pic}^S$ values of the DCE and DCM systems were available from the references [5] [6] [11] (see Introduction and below). Also, the $K_{ex\pm}$ values were easily obtained from the relation [1] of

$$K_{ex\pm} = K_{ex}/K_{MLA,o}, \quad (14)$$

where a combination of $[ML^+]_o = (K_{ex}^{mix} - K_{ex})[M^+][L]_o[A^-]$ [1], $[A^-]_o = K_{D,A}[A^-]$ and $[MLA]_o = K_{ex}[M^+][L]_o[A^-]$ was used for the calculation of $K_{MLA,o}$ ($= [MLA]_o/[M^+]_o[A^-]_o$, see Appendix), namely, $K_{ex}/\{(K_{ex}^{mix} - K_{ex})K_{D,A}[A^-]\}$ under the condition of $K_{ex}^{mix} - K_{ex} > 0$.

2.3. For Expression of Component Equilibrium Constants by $\Delta\phi_{eq}$

As described in (A) and (B) of the Section 2.1, we can see that the $\Delta\phi_{eq}$ (or $\Delta'\phi_{eq}$) dependences of $\log K_{ex\pm}$ and $\log K_{ex}$ are different. So, the derivations of standard formal potentials corresponding to the extraction constants from thermodynamic cycles are tried. From the processes (1) and (2), the following cycles can be obtained as examples.

$$\log K_{ex} = \log K_{D,M} K_{D,A} K_{ML,o} K_{MLA,o} \quad (1a)$$

$$\log K_{ex\pm} = \log K_{D,M} K_{D,A} K_{ML,o} \quad [12]. \quad (2a)$$

Here, $K_{D,M}$ and $K_{ML,o}$ are defined as $[M^+]_o/[M^+]$ and $[ML^+]_o/[M^+][L]_o$, respectively; $K_{D,M}$ is called an individual distribution constant of a single M^+ into the o phase, $K_{ML,o}$ called a complex formation constant for ML^+ in the o phase and $K_{MLA,o}$ called an ion-pair formation constant for ML^+A^- in it.

We will derive the standard formal potentials for the complex formation and then the ion-pair formation in the single phase from the properties [10] of $\bar{\mu}_j$.

$$\bar{\mu}_{M,o} + \bar{\mu}_{L,o} = \bar{\mu}_{ML,o} \quad (15)$$

This equation can be rearranged in the same manner as that described in the Section 2.2.

$$RT(\ln a_{ML,o} - \ln a_{M,o} - \ln a_{L,o}) + \mu_{ML,o}^0 - \mu_{M,o}^0 - \mu_{L,o}^0 = F(\phi'_{ML,o} - \phi'_{M,o}) = F\Delta'\phi_{eq} \quad (16)$$

Similarly, the $\Delta'\phi_{eq}$ value equals zero [10], because all species are present in the same phase (see above). Therefore, $\log K_{ML,o}$ becomes

$$\log K_{ML,o} = -\frac{F}{2.3RT}\Delta\phi_{ML,o}^{0'}. \quad (17)$$

The same is true of the ion-pair formation for MLA in the o phase: $\log K_{MLA,o} = -(F/2.3RT)\Delta\phi_{MLA,o}^{0'}$ under the condition [10] of $\Delta'\phi_{eq} = 0 (= \phi'_{ML,o} - \phi'_{A,o})$. Additionally, from the handling similar to that for A^- , $\log K_{D,M}$ is transformed into $(F/2.3RT)(\Delta\phi_{eq} - \Delta\phi_M^{0'})$ with $\Delta\phi_{eq} = \phi_M - \phi_{M,o}$ [9].

2.4. Proofs of $\Delta\phi_{ex}^{0'}$ and $\Delta\phi_{ex\pm}^{0'}$ Based on Thermodynamic Cycles

Introducing Equations (8), (13), (17) and $\log K_{D,M} = (F/2.3RT)(\Delta\phi_{eq} - \Delta\phi_M^{0'})$ in Equation (1a), we can obtain

$$-\frac{F}{2.3RT}\Delta\phi_{ex}^{0'} = \frac{F}{2.3RT}(\Delta\phi_{eq} - \Delta\phi_M^{0'}) - \frac{F}{2.3RT}(\Delta\phi_{eq} - \Delta\phi_A^{0'}) - \frac{F}{2.3RT}\Delta\phi_{ML,o}^{0'} - \frac{F}{2.3RT}\Delta\phi_{MLA,o}^{0'} \quad (18)$$

and then rearrange it as

$$\Delta\phi_{ex}^{0'} = \phi_M^{0'} + \phi_{ML,o}^{0'} + \phi_{MLA,o}^{0'} - \phi_A^{0'}. \quad (19)$$

Thus, the interfacial potential differences, $\Delta\phi_{\text{eq}}$, were canceled out in the cycle (1a). The same is also true of the other cycle [13] of $\log K_{\text{ex}} = \log K_{\text{ML}}K_{\text{MLA}}K_{\text{D,MLA}}/K_{\text{D,L}}$ because of $\Delta'\phi_{\text{eq}} = 0$ and accordingly we can obtain

$$\Delta\phi_{\text{ex}}^{0'} = \phi_{\text{ML,w}}^{0'} + \phi_{\text{MLA,w}}^{0'} + \phi_{\text{MLA}}^{0'} - \phi_{\text{L}}^{0'}. \quad (19a)$$

The definition of the component equilibrium constants were $K_{\text{ML}} = [\text{ML}^+]/[\text{M}^+][\text{L}]$, $K_{\text{MLA}} = [\text{MLA}]/[\text{ML}^+][\text{A}^-]$, $K_{\text{D,MLA}} = [\text{MLA}]_{\text{o}}/[\text{MLA}]$, and $K_{\text{D,L}} = [\text{L}]_{\text{o}}/[\text{L}]$. As a result $\Delta'\phi_{\text{eq}} = 0$ in Equation (5a) was proved, because all species are either present in the same phase or neutral compounds [10].

For the cycle (2a), a similar treatment can be performed.

$$\frac{F}{2.3RT}(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}) = \frac{F}{2.3RT}(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'}) - \frac{F}{2.3RT}(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) - \frac{F}{2.3RT}\Delta\phi_{\text{ML,o}}^{0'} \quad (20)$$

Rearranging this equation, we easily obtain

$$\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'} = \phi_{\text{A}}^{0'} - \phi_{\text{M}}^{0'} - \phi_{\text{ML,o}}^{0'}. \quad (21)$$

Consequently, the interfacial potential difference, $\Delta\phi_{\text{eq}}$, was not canceled out in the cycle (2a). That is, in this cycle, the experimental potential difference, $\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}$, deviates from its standardized one, $-\Delta\phi_{\text{ex}\pm}^{0'}$, by $\Delta\phi_{\text{eq}}$. This difference should be considered to be that in numeral between electrochemically-standardized extraction or distribution data and extraction-experimental data. This is not in conflict with the consideration described in our previous paper [9].

3. Experimental

3.1. Chemicals

Concentrations of aqueous solutions of AgNO_3 (>99.8%, Kanto Chemical Co., Inc., Tokyo) were determined by a precipitation titration with NaCl (standard for the volumetric analysis, Wako Pure Chemical Industries, Tokyo); for example, 98.8% was obtained as a purity of AgNO_3 . Commercially-available B15C5 (>98%, Tokyo Chemical Industry Co. Ltd., Tokyo) and B18C6 (>96%, TCI Co. Ltd.) were dried at room temperature for more than 20 h under reduced pressures. Their purities were checked by measurements of the melting points: as examples, 79.0 - 80.5°C for B15C5 and 39.0 - 40.0 for B18C6. The concentrations of their solutions were obtained from weighed amounts. Although the melting-point range of B15C5 was a little larger than unity, its purity was calculated as 100%. Concentrations of aqueous solutions of picric acid {HPic, guaranteed pure reagent (GR): > 99.5% after drying, Wako P.C.I.} were determined by 0.1 mol·L⁻¹ NaOH solutions standardized by acid-base titrations with potassium hydrogen phthalate (GR: 99.8% - 100.2%, Wako P.C.I.). Commercially-available DCE (GR: 99.5%, Kanto C.C.) and DCM (GR: 99.5%, Kanto C.C.) were washed three-times with water and kept at water saturated conditions. Other chemicals were of GR grades and used without further purifications. A tap water was distilled once with a still of the stainless steel and then was purified by passing through the Autopure system (type WT101 UV, Yamato/Millipore). This water was employed for preparing all the aqueous solutions.

3.2. Instruments

Mixtures of the w phase with the o phase in stoppered glass tubes were agitated at 298 K for 2 h with an Iwaki shaker system, a water bath (type WTB-24) equipped with a driver unit (SHK driver) and a thermoregulator (type CTR-100). Then, the mixtures were centrifuged by a Kokusan centrifuge (type 7163 - 4.8.20). Total amounts of species with Ag(I) extracted into the o phase were also determined at 328.1 nm by a Hitachi polarized Zeeman atomic absorption spectrophotometer (type Z-6100) equipped with a hollow cathode lamp (type 139-3614, Mito-rika Co. under the license of Hitachi Ltd.) for Ag. The calibration-curve procedure was employed here for the determination of Ag(I) extracted. Besides, some pH values of the w phases centrifuged were measured at 298 K by using a Horiba pH/ion meter (type F-23) with a commercial glass electrode.

3.3. Extraction Experiments

Initial concentrations of the aqueous solutions of AgNO_3 , those of HPic and those of the organic solutions of L employed for the extraction into DCE were $(1.5 \text{ or } 9.8) \times 10^{-4}$ mol·L⁻¹, $(3.2 \text{ or } 3.3) \times 10^{-3}$ and $(0.3_2 - 6.4) \times 10^{-4}$ for L = B18C6; $(0.4_9 \text{ or } 3.0) \times 10^{-3}$, $(2.9 \text{ or } 3.1) \times 10^{-3}$ and $(0.5_4 - 3.8) \times 10^{-4}$ for B15C5, respectively. Also, the

concentrations employed for the extraction into DCM were 1.5×10^{-4} mol·L⁻¹ for the aqueous AgNO₃ solution, 3.2×10^{-3} for HPic and $(0.2_7 - 1.1) \times 10^{-4}$ for the organic solutions of B18C6; $(1.8, 4.9 \text{ or } 5.9) \times 10^{-3}$, $(1.8, 4.4 \text{ or } 5.9) \times 10^{-3}$ and $(0.5_4 - 3.6) \times 10^{-4}$ for those of B15C5, respectively.

The organic solutions containing L were mixed with aqueous ones containing AgNO₃ and HPic in the stoppered glass-tubes of about 30 mL, these tubes were vigorously shaken up for 1 minute with hand, and then agitated at 298 ± 0.2 K for 2 h in the water bath (see the Section 3.2). After these operations, the mixtures were centrifuged for 5 minutes. The o phases were separated from the w phases and then the pH values of the latter were measured. The o phases were transferred in part into the glass tubes, aqueous solutions of 0.1 mol·L⁻¹ HNO₃ were added in their tubes, and then their mixtures were mechanically agitated for 2 h in the bath. The w phases with HNO₃ were separated from the mixtures and then total amounts of Ag(I) in the separated w phases were determined by AAS (see the Section 3.2). The extraction of Ag(I) into the o phases was not detected in blank experiments without L in the both phases.

3.4. Data Analysis

Procedures were essentially the same as those reported previously [1] [14] except for an addition of the dissociation of MLA in the o phase: see Appendix. In computations of [Ag⁺], [L]_o and [Pic⁻] by the successive approximation [1] [14], K_{AgLPic} , K_{AgPic} [14] and K_{HPic} values [15] were evaluated as the functions of activity coefficients from the I values. Here, K_{AgPic} and K_{HPic} are defines as $[\text{AgPic}]/[\text{Ag}^+][\text{Pic}^-]$ and $[\text{HPic}]/[\text{H}^+][\text{Pic}^-]$, respectively. On the other hand, it was assumed that other component equilibrium-constants are independent of I or I_o , since experimental ranges of I and I_o were narrow in many cases or ratios of activity coefficients for K_{AgL} and $K_{\text{AgL},o}$ (see the Section 4.1 for the definition) were close to unity. The experimental data were $I = (3.4 - 5.8) \times 10^{-3}$ mol·L⁻¹ and $I_{\text{DCE}} = (1.0 - 1.1) \times 10^{-5}$ for L = B15C5, $(3.2 - 4.0) \times 10^{-3}$ and $I_{\text{DCE}} = (6.3 - 6.6) \times 10^{-6}$ for B18C6; $I = (0.3_5 - 1.2) \times 10^{-2}$ and $I_{\text{DCM}} = (2.1 - 6.9) \times 10^{-7}$ for B15C5 and 3.3×10^{-3} and $I_{\text{DCM}} = 1.9 \times 10^{-6}$ for B18C6. The symbols, I_{DCE} and I_{DCM} , denote ionic strength for the DCE phase and that for DCM, respectively. Also, the dissociation of HPic in the DCE or DCM phase was neglected. Namely, this means that a contribution of the distribution of H⁺ to the $\Delta\phi_{\text{eq}}$ value is negligible. Besides, the formation of AgLNO₃, HLNO₃ and HLPic and their distribution into the o phase were neglected.

4. Results and Discussion

4.1. Determination of $K_{\text{D,Pic}}$, K_{ex} and $K_{\text{ex}\pm}$

The experimental data of $[\text{AgLPic}]_o + [\text{AgL}^+]_o$, $[\text{Ag}^+]_o$, $[\text{L}]_o$ and $[\text{Pic}^-]_o$ were analyzed using a logarithmic form of the equation described in the Section 2.2: $\log K_{\text{ex}}^{\text{mix}} = \log \left\{ \left([\text{MLA}]_o + [\text{ML}^+]_o \right) / [\text{M}^+]_o [\text{L}]_o [\text{A}^-]_o \right\}$ [1]. An experimental plot analyzed by this equation is shown in Figure 1. Regression lines of the other systems were of a correlation coefficient (R) = 0.196 for the B15C5/DCM system, 0.969 for B18C6/DCM and 0.823 for B15C5/DCE. From these regression analyses [1], curve fittings of the plots, we obtained the $K_{\text{D,A}}$ and K_{ex} values. The $\log K_{\text{ex}\pm}$ values were also calculated from the logarithmic form of Equation (14). The thus-obtained values were listed in Table 1.

The experimental $\log K_{\text{D,Pic}}$ values in Table 1 were much smaller than those standardized on the extra-thermodynamic assumption of $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ [5] [7]. These facts enable us to examine a presence of the $\Delta\phi_{\text{eq}}$ values. So, it was assumed from Equation (2a) that the potential difference, $\Delta\phi_{\text{eq}}$, occurred at the w/o interface is the same for the distribution of Ag⁺, Pic⁻, and AgL⁺ into the o phase [9], because these ions are simultaneously present in the extraction process. Here, the distribution of H⁺ into the DCE or DCM phase was neglected (see the Section 3.4). Details for $\Delta\phi_{\text{eq}}$ are discussed in the next section.

Also, from the $\log K_{\text{Ag/AgL}}$ values in Table 1, we can see that the $K_{\text{AgL},o}$ ($= [\text{AgL}^+]_o / [\text{Ag}^+]_o [\text{L}]_o$) values satisfy the relation of B15C5 \leq B18C6, because the $K_{\text{D,Ag}}$ values are constants for given diluents. Here, $K_{\text{Ag/AgL}}$ is expressed as the product [16] of $K_{\text{AgL},o}$ and $K_{\text{D,Ag}}$. Moreover, the $\log K_{\text{AgLPic},o}$ values which are logarithmic equilibrium constants for the AgLPic formation in the o phases saturated with water were calculated from the relation, $K_{\text{ex}} / \left\{ \left(K_{\text{ex}}^{\text{mix}} - K_{\text{ex}} \right) K_{\text{D,Pic}} [\text{Pic}^-]_o \right\}$, described in the Section 2.2: $\log K_{\text{AgLPic},\text{DCM}} = 8.0_8 \pm 0.2_7$ at $I_{\text{DCM,av}} = 4.5 \times 10^{-7}$ mol·L⁻¹ for L = B15C5, $5.9_1 \pm 0.1_9$ at $I_{\text{DCM,av}} = 1.9 \times 10^{-6}$ for B18C6, $\log K_{\text{AgLPic},\text{DCE}} = 5.5_7 \pm 0.2_3$ at $I_{\text{DCE,av}} = 1.0$

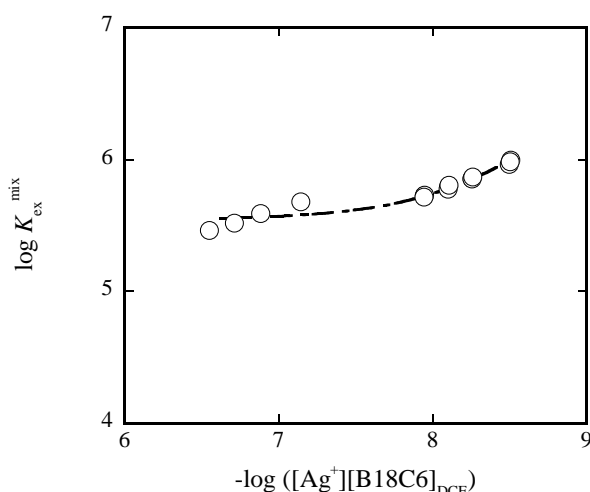


Figure 1. Plot of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log([M^+][L]_o)$ for the AgPic extraction by $L = \text{B18C6}$ into $o = \text{DCE}$. A broken line was a regression one which gave $(K_{\text{ex}}/\text{mol}^{-2}\cdot\text{L}^2) = (3.5_1 \pm 0.1_6) \times 10^5$ and $K_{\text{D,Pic}} = (1.9_9 \pm 0.1_5) \times 10^{-3}$ at $R = 0.968$.

Table 1. Individual distribution constants of $\text{Pic}^- (=A^-)$ and overall equilibrium constants for the extraction of AgPic by L into DCE and DCM at 298 K.

Diluents	L	$\log K_{\text{D,A}}^a$	$\log K_{\text{ex}\pm}^a$	$\log K_{\text{ex}}^a$	$\log K_{\text{Ag/AgL}}^b$
DCM	B15C5	-3.9 ± 1.0	$-3.97 \pm 0.2_8$	4.12 ± 0.05	-0.0 ± 1.0
	B18C6	-3.23 ± 0.04	$-0.87 \pm 0.1_9$	5.04 ± 0.03	$2.3_6 \pm 0.1_9$
DCE	B15C5	$-2.4_6 \pm 0.1_0$	$-0.57 \pm 0.2_4$	5.00 ± 0.03	$1.9_0 \pm 0.2_6$
	B18C6	-2.70 ± 0.03	$-0.5_1 \pm 0.6_7$	5.55 ± 0.02	$2.1_9 \pm 0.6_7$

^aAverage values and standard errors. ^bAverage values of $\log K_{\text{D,Ag}}K_{\text{AgL,o}}$ calculated from Equation (2a) and their estimated errors.

$\times 10^{-5}$ for B15C5, and $6.0_5 \pm 0.6_7$ at $I_{\text{DCE,av}} = 6.4 \times 10^{-6}$ for B18C6. Here, these $I_{\text{DCM,av}}$ and $I_{\text{DCE,av}}$ values show those on the average; see the Section 3.4 for their original values. The relation of $\log K_{\text{AgLPic,DCM}}$ between L is in agreement with that of $\log K_{\text{AgLPic}}$ at 298 K and $I \rightarrow 0$ in water [14]. Considering this agreement, the dielectric constant of pure DCM < that of pure DCE and a ring size of B15C5 < that of B18C6, these results show that a major interaction of $\text{Ag}(\text{B15C5})^+$ with Pic^- in the o phases or of AgL^+ in DCM saturated with water is coulombic force at least.

4.2. $\Delta\phi_{\text{eq}}$ Values Evaluated from Differences in $\log K_{\text{D,Pic}}$ between the Electrochemical and Extraction Experiments

As can be seen from Table 1, the experimental $\log K_{\text{D,Pic}}$ values deviate between the B15C5 and B18C6 systems for a fixed diluent. Also their values are different from the $\log K_{\text{D,Pic}}^S$ ones. Using Equation (13), the $\Delta\phi_{\text{eq}}$ values corresponding to the differences with $\log K_{\text{D,Pic}}^S$ were evaluated. Here, the $\Delta\phi_{\text{Pic}}^{0'}$ values employed for the $\Delta\phi_{\text{eq}}$ evaluation were -0.0598 V [6] for the w/DCE system and -0.040_2 [11] for the w/DCM one; these standard formal or ion transfer potentials [8] have been directly or indirectly determined based on the extra-thermodynamic assumption for $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ [5]–[7]. Table 2 lists these $\Delta\phi_{\text{eq}}$ and $\Delta\phi_{\text{Pic}}^{0'}$ values. Thus, the $\Delta\phi_{\text{eq}}$ values were different with each system.

Also, using Equation (9a) with the experimental $\log K_{\text{ex}\pm}$ values (Table 1) and the $\Delta\phi_{\text{eq}}$ ones, we reduced the experimental potentials $(= \Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'})$ to the standardized ones, $\Delta\phi_{\text{ex}\pm}^{0'}$. These values were 0.12 V for the B15C5/DCE system, 0.13 for B18C6/DCE, 0.4₃ for B15C5/DCM, and 0.20 for B18C6/DCM. At the same time,

Table 2. Interfacial potentials, $\Delta\phi_{\text{eq}}$, at equilibria and standardized formal potentials, $\Delta\phi_{\text{A}}^{0'}$ and $\Delta\phi_{\text{K}}^{0'}$, and $\log K_{\text{ex}\pm}$ values at 298 K.

Diluents	MA	L	$\Delta\phi_{\text{eq}}^{\text{a}}$	$\Delta\phi_{\text{A}}^{0'\text{a,b}}$	$\Delta\phi_{\text{ex}\pm}^{0'\text{a}}$	$\Delta\phi_{\text{ex}}^{0'\text{a}}$	$\log K_{\text{ex}\pm}$	
							Found	Stand. ^c
DCM	AgPic	B15C5	0.1 ₉	−0.040 ₂	0.4 ₃	−0.24	−3.9 ₇	−7.2
		B18C6	0.15 ₁		0.20	−0.30	−0.8 ₇	−3.4 ₂
DCE	AgPic	B15C5	0.08 ₆	−0.0598	0.12	−0.30	−0.5 ₇	−2.0 ₂
		B18C6	0.10 ₀		0.13	−0.33	−0.5 ₁	−2.2 ₀
	NaMnO ₄	B15C5	0.00	−0.020	0.22	−0.13	−3.7 ₅ ^d	−3.7 ₂
		B18C6	−0.04 ₉		0.08	−0.13	−2.2 ₃ ^d	−1.4 ₀
NB	NaMnO ₄	B15C5	0.00 ₂	−0.069	0.02	−0.22	−0.2 ₃ ^d	−0.2 ₇
		B18C6	0.03 ₂		0.00	−0.30	0.6 ₁ ^d	0.0 ₇
	NaPic ^e	B15C5	0.04 ₇ ^f	3.0×10^{-3}	−0.05 ₉ ^g	--- ^h	1.7 ₉ ^f	1.0
		B18C6	0.04 ₆ ^f		−0.1 ₂ ^g	--- ^h	2.7 ₈ ^f	2.0

^aV unit. Values were evaluated from the differences between the experimental and standardized $\log K_{\text{D,A}}$ values and essentially based on the extra-thermodynamic assumption of $\text{Ph}_4\text{As}^+\text{BPh}_4^-$. ^bRefs. [5]–[7]. ^cValues standardized with Equation (9). ^dRef. [1]. ^eRef. [12]. ^fValues estimated from Equations (21), (9a) and the relation of $\Delta\phi_{\text{Na}}^{0'} + \Delta\phi_{\text{NaL,NB}}^{0'} = -0.05916(\log K_{\text{D,Na}} + \log K_{\text{NaL,NB}})$. See Refs. [6] [16] & [17] for the $\log K_{\text{D,Na}}$ and $\log K_{\text{NaL,NB}}$ values. ^gValues calculated from the $\log K_{\text{ex}\pm}^{\text{S}}$ values. See Ref. [12]. ^hNot obtained.

their values yielded the standardized $\log K_{\text{ex}\pm}$ values: $\log K_{\text{ex}}^{\text{S}} \left\{ = -(F/2.3RT)\Delta\phi_{\text{ex}\pm}^{0'} \right\} = -2.0_2$ for the B15C5/DCE system; see Table 2 for the other values. The same calculations were also performed for the NaMnO₄ or NaPic extraction [1] by B15C5 and B18C6 into DCE and/or NB (see the Section 4.3 for the NaPic-L system).

On the other hand, the experimental $\log K_{\text{ex}}$ values are equal to the $\log K_{\text{ex}}^{\text{S}}$ ones, being based on Equation (8); $\Delta\phi_{\text{ex}}^{0'} = -(2.3RT/F)\log K_{\text{ex}} = -(2.3RT/F)\log K_{\text{ex}}^{\text{S}}$. This is due to the fact that Equation (19) does not contain $\Delta'\phi_{\text{eq}}$. These results for $\Delta\phi_{\text{ex}}^{0'}$ are also listed in Table 2.

4.3. Evaluation of the $\Delta\phi_{\text{eq}}$, $\Delta\phi_{\text{ex}\pm}^{0'}$ and $\log K_{\text{ex}\pm}$ Values for the MA Extraction by L into NB and DCE

The $\Delta\phi_{\text{eq}}$ and $\log K_{\text{ex}\pm}$ values (listed in Table 2) for the NaPic extraction by L into NB were evaluated from Equations (21) and (9a), using the $\log K_{\text{D,Na}}$ and $\log K_{\text{NaL,NB}}$ values: $\log K_{\text{D,Na}} = -5.18$ [6] and $\log K_{\text{NaL,NB}} = 6.9_2$ [16] for L = B15C5 and 7.91 [17] for B18C6. The $\log K_{\text{ex}\pm}$ values evaluated were larger than the $\log K_{\text{ex}\pm}^{\text{S}}$ ones (at $\Delta\phi_{\text{eq}} = 0$). The $\Delta\phi_{\text{eq}}$ values evaluated for the two Ls were in agreement with each other within calculation errors; we suppose this agreement to be other accidental cases. The validity of these evaluations will be examined in future.

Similarly, the above procedure was applied for the CsPic and CsMnO₄ extraction [4] by 4,5''-bis(*tert*-octylbenzo) dibenzo-24-crown-8 ether (TB24C8) into DCE. From Equation (13), the $\Delta\phi_{\text{eq}}$ values were evaluated to be −0.021 V for Pic^- and +0.067 for MnO_4^- ; see Introduction for the experimental $\log K_{\text{D,A}}$ values. Using these values, the $\Delta\phi_{\text{ex}\pm}^{0'}$ values were calculated to be −0.17 V for Pic^- and +0.010 for MnO_4^- from Equation (9a), where the experimental $\log K_{\text{ex}\pm}$ values were reported to be 2.45 and 0.96, respectively [4].

Then, we obtained $\log K_{\text{ex}\pm}^{\text{S}}(\text{CsLPic}) = 2.81$ and $\log K_{\text{ex}\pm}^{\text{S}}(\text{CsLMnO}_4) = -0.17$ at $\Delta\phi_{\text{eq}} = 0$ V for L = TB24C8. These relations between $\log K_{\text{ex}\pm}^{\text{S}}$ and $\log K_{\text{ex}\pm}$ were similar to those in Table 2; see Figure 2 for reference.

4.4. For Tendencies of $\Delta\phi_{\text{A}}^{0'}$, $\Delta\phi_{\text{eq}}$ and $\Delta\phi_{\text{ex}\pm}^{0'}$

An order of $\Delta\phi_{\text{Pic}}^{0'} \left\{ = (2.3RT/F)\log K_{\text{D,Pic}}^{\text{S}} : \text{Equation (13) at } \Delta\phi = 0 \right\}$ was DCE < DCM (<0 V) < NB (see

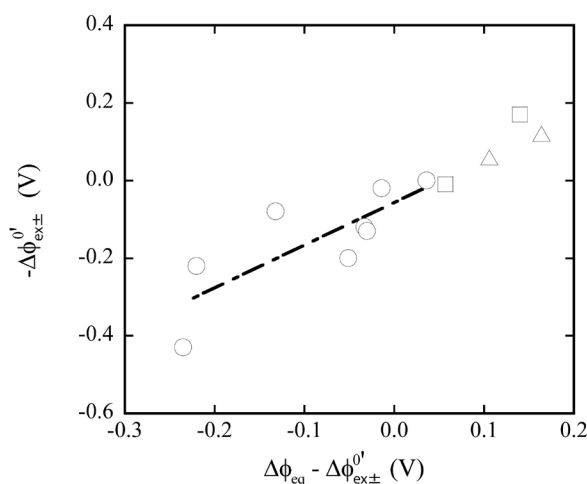


Figure 2. Plot of $-\Delta\phi_{\text{ex}\pm}^{0'}$ versus $\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}$ for the MA extraction by L into DCE, DCM and NB. The data listed in Table 2 were essentially used for preparing this plot. A broken line for the circles was a regression one with the slope of $1.1_0 \pm 0.3_3$ and the intercept of $-0.05_5 \pm 0.04_2$ at $R = 0.802$. The triangles and squares show the points for the NaPic extraction [1] by B15C5 and B18C6 into NB and those for the CsPic and CsMnO₄ extraction [4] by TB24C8 into DCE, respectively.

Table 2). This fact indicates that interactions of Pic^- with the diluent molecules increase with this order; namely Pic^- is easy to more transfer from water to NB than does to DCE. On the other hand, a relation of $\Delta\phi_{\text{MnO}_4}^{0'}$ was $\text{NB} < \text{DCE} (< 0)$. These findings suggest that these interfacial formal or ion transfer potentials reflect the interactions of the diluent molecules with A^- [8].

The $\Delta\phi_{\text{eq}}$ values were in the orders of $\text{NaMnO}_4/\text{DCE} (\approx 0 \text{ V}) \leq -/\text{NB}$ and $\text{NaPic}/\text{NB} < \text{AgPic}/\text{DCE} < -/\text{DCM}$ for $\text{L} = \text{B15C5}$ and $\text{NaMnO}_4/\text{DCE} < (0 \text{ V}) < -/\text{NB}$ and $\text{NaPic}/\text{NB} < \text{AgPic}/\text{DCE} < -/\text{DCM}$ for B18C6. There are tendencies of $\text{DCE} \leq \text{NB}$ for the NaMnO_4 system and $\text{NB} < \text{DCE} < \text{DCM}$ for MPic.

Also, the $\Delta\phi_{\text{ex}\pm}^{0'}$ values were in the orders of $(\text{NaPic}/\text{NB} < 0 \text{ V} <) \text{NaMnO}_4/\text{NB} < \text{AgPic}/\text{DCE} < \text{NaMnO}_4/\text{DCE} < \text{AgPic}/\text{DCM}$ for B15C5 and $(\text{NaPic}/\text{NB} < 0 \text{ V} <) \text{NaMnO}_4/\text{NB} < \text{NaMnO}_4/\text{DCE} < \text{AgPic}/\text{DCE} < \text{AgPic}/\text{DCM}$ for B18C6. We can easily see from these facts that there is a tendency of $\text{NB} < \text{DCE} < \text{DCM}$ in $\Delta\phi_{\text{ex}\pm}^{0'}$, irrespective of kinds of MA and L. In other word, these tendencies mean that MA is more-effectively extracted with L into NB or DCE than into DCM. In a potential scale, the more the formal (or ion transfer) potentials $\Delta\phi_j^{0'}$ are negative, the more cations transfer from water to an o phase, while the more they are positive, the more anions transfer to the o phase. Probably, the tendency of $\Delta\phi_{\text{ex}\pm}^{0'}$ corresponds to the former case, although the process corresponding to $\Delta\phi_{\text{ex}\pm}^{0'}$ is not the component equilibrium. While, that of $\Delta\phi_{\text{A}}^{0'}$ does to the latter case. There was partially a correlation between the $\Delta\phi_{\text{eq}}$ and $\Delta\phi_{\text{ex}\pm}^{0'}$ values at MPic.

4.5. For Tendencies of $\log K_{\text{ex}\pm}^{\text{S}}$ and $\log K_{\text{ex}\pm}^{\text{S}}$

Relations, $\text{L} = \text{B15C5} \geq \text{B18C6}$ for the AgPic/DCE system and $\text{B15C5} < \text{B18C6}$ for AgPic/DCM , in $\log K_{\text{ex}\pm}^{\text{S}}$ are a little difference from those, $\text{B15C5} < \text{B18C6}$ for AgPic/DCE and $-/\text{DCM}$, in $\log K_{\text{ex}\pm}$ determined experimentally (Table 2). Also, the relations, $\log K_{\text{ex}\pm}^{\text{S}} (\text{B15C5}) < \log K_{\text{ex}\pm}^{\text{S}} (\text{B18C6})$ for $\text{NaMnO}_4/\text{DCE}$ and $-/\text{NB}$, are the same as those in the experimentally-determined $\log K_{\text{ex}\pm}$ values. These results show that properties of the DCE system with AgPic and L are a little different with those of the others. The $\log K_{\text{ex}\pm}$ values in Table 2 (or Table 1) were in the orders of $\text{NaMnO}_4/\text{NB} > \text{AgPic}/\text{DCE} > \text{NaMnO}_4/\text{DCE} > \text{AgPic}/\text{DCM}$ for B15C5 and

$\text{NaMnO}_4/\text{NB} > \text{AgPic}/\text{DCE} \geq \text{AgPic}/\text{DCM} > \text{NaMnO}_4/\text{DCE}$ for B18C6. This reverse between the AgPic/DCM and NaMnO₄/DCE systems for B18C6 suggests that the $\log K_{\text{ex}\pm}$ value of the NaMnO₄/DCE system is so small or that of the AgPic/DCM one so large, although the authors cannot now show its cause, except for the differences of the $\Delta\phi_{\text{eq}}$ values related to their systems.

The $\log K_{\text{ex}\pm}^{\text{S}}$ values were in the orders of $\text{NaPic}/\text{NB} > \text{NaMnO}_4/\text{NB} > \text{AgPic}/\text{DCE} > \text{NaMnO}_4/\text{DCE} > \text{AgPic}/\text{DCM}$ for L = B15C5 and $\text{NaPic}/\text{NB} > \text{NaMnO}_4/\text{NB} > \text{NaMnO}_4/\text{DCE} > \text{AgPic}/\text{DCE} > \text{AgPic}/\text{DCM}$ for B18C6. Except for the NaMnO₄/DCE system with B18C6, these orders were in agreement with those (see above) of the experimental $\log K_{\text{ex}\pm}$ values. This fact indicates that the experimental $\log K_{\text{ex}\pm}$ values are usually reflected into the $\log K_{\text{ex}\pm}^{\text{S}}$ ones (at $\Delta\phi_{\text{eq}} = 0$). Therefore, in many cases, we can expect that a comparison among the $\log K_{\text{ex}\pm}$ values has the same meanings as that among the $\log K_{\text{ex}\pm}^{\text{S}}$ ones. This expectation is also shown in Figure 2, together with the data (see the Section 4.3) of the CsPic and CsMnO₄ extraction [4] by TB24C8 into DCE. A plot of $-\Delta\phi_{\text{ex}\pm}^{0'}$ against $\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}$, namely $\log K_{\text{ex}\pm}^{\text{S}}$ versus $\log K_{\text{ex}\pm}$, gave a positive correlation with $R = 0.802$. The potentials employed for the plot are essentially based on the $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ assumption [5] [7].

5. Conclusion

It was demonstrated that the $\Delta\phi_{\text{eq}}$ values of the MA extraction systems with L are not necessarily zero in some cases. The $\log K_{\text{ex}\pm}$ values determined by the solvent-extraction experiments fairly reflected the $\log K_{\text{ex}\pm}^{\text{S}}$ ones standardized on the electrochemical measure at the w/o interface. The $\Delta\phi_{\text{eq}}$ (or $\Delta'\phi_{\text{eq}}$) term disappeared in the extraction constant such as K_{ex} , namely, the constant expressing the system without apparently ion transfer at the w/o interface. The same was true of reactions occurred in the single phase. Also, the above results will be applied to the $\text{M}^{\text{II}}\text{A}_2$ extraction systems with L. Besides, the introduction of $\Delta\phi_{\text{eq}}$ in the extraction systems can solve problems with respect to deviations in $\log K_{\text{Dj}}$, $\Delta\phi_j^{0'}$ or $\Delta\phi_k^{0'}$ between extraction and electrochemical methods.

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Appendix

The extraction model employed here was essentially the same as that reported before [14]. However, the following component equilibrium in the o phase [1] [4] was added:



This introduction in the model is comparable with those of the individual distribution of ML^+ and that of A^- into the o phase [1] [18]. Therefore, the following equation similar to Equation (13) can be derived.

$$\Delta\phi_{\text{eq}} = \Delta\phi_{\text{ML}}^{0'} + \frac{2.3RT}{F} \log K_{\text{D,ML}} \quad (\text{A2})$$

with

$$\Delta\phi_{\text{eq}} = \phi_{\text{ML}} - \phi_{\text{ML,o}} , \quad (\text{A3})$$

$$\Delta\phi_{\text{ML}}^{0'} = \Delta\phi_{\text{ML}}^0 + \frac{2.3RT}{F} \log \frac{y_{\text{ML,o}}}{y_{\text{ML}}} , \quad (\text{A4})$$

$$\Delta\phi_{\text{ML}}^0 = \frac{\mu_{\text{ML,o}}^0 - \mu_{\text{ML}}^0}{F} \quad (\text{A5})$$

and $K_{\text{D,ML}} = [\text{ML}^+]_o / [\text{ML}^+]$. As described in the text, this $\Delta\phi_{\text{eq}}$ value becomes a common value with those of A^- and M^+ , in the extraction system in question.