On the Interfacial Potential Differences for the Extraction of Alkaline-Earth Metal Picrates by 18-Crown-6 Ether Derivatives into Nitrobenzene

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Abstract

Individual distribution constants (\( K_{\text{ex}} \)) of picrate ion (Pic\(^{−}\)) into nitrobenzene (NB) were determined at 298 K and given values of ionic strength, together with the determination of an extraction constant (\( K_{\text{ex}} \)) for the extraction of alkaline-earth metal picrates, MPic\(_2\), by 18-crown-6 ether (18C6) and benzo-18C6 (B18C6). Here, \( K_{\text{ex}} \) and \( K_{\text{D,Pic}} \) were defined as \([\text{MLA}^{2+}][\text{L}]_0/([\text{M}^{2+}][\text{A}^{−}])\) and \([\text{MLA}^{2+}][\text{L}]_0/([\text{M}^{2+}][\text{A}^{−}])\), respectively. A* shows Pic\(^{−}\)L does either 18C6 or B18C6 and the subscript “NB” refers to the NB phase. Interfacial potential differences (\( \Delta \phi_{\text{ex}} \)) at unit extraction equilibria were evaluated from differences between the experimental \( K_{\text{D,Pic}} \) and its standardized values (log \( K_{\text{ex}} \)) which can be determined by electrochemical measurements at a water/NB interface. By a combination with the \( K_{\text{ex}} \) values, other extraction constants, \( K_{\text{ex}} = \text{[MLPic}^{−}\text{]}_0/([\text{M}^{2+}][\text{L}]_0[\text{Pic}^{−}]) \), were also determined. Electrochemically-standardized log \( K_{\text{ex}} \) values, log \( K_{\text{ex}} \) values were calculated from the relation of log \( K_{\text{ex}} \) = (\( \Delta \phi_{\text{ex}} / 0.05916 \)) at 298 K. Using the log \( K_{\text{ex}} \) values, their correlation with the log \( K_{\text{ex}} \) ones was discussed. Additionally, ion-pair formation constants (\( K_{\text{D,Pic}} \) and \( K_{\text{D,Pic}} \)) of the stepwise reactions of ML\(^n\) with Pic\(^{−}\) in the NB phase were evaluated from \( K_{\text{ex}} \) and another constant (\( K_{\text{ex}} \)) reported before at \( \Delta \phi_{\text{ex}} = 0 \). Here, \( K_{\text{ex}} \) was extracted from \( K_{\text{ex}} \) and \( K_{\text{ex}} \), which was defined as \([\text{MLPic}^{−}\text{]}_0/([\text{M}^{2+}][\text{L}]_0[\text{Pic}^{−}]) \). Moreover, reproductions of the electrochemically-standardized \( K_{\text{ex}} \) and \( K_{\text{ex}} \) values were tried, using the \( \Delta \phi_{\text{ex}} \) and relations between \( K_{\text{ex}} \) or \( K_{\text{ex}} \) and component equilibrium constants constituting their extraction ones. Consequently, a functional expression of \( K_{\text{ex}} \) with \( \Delta \phi_{\text{ex}} \) was extended into the MPic\(_2\)-L extraction systems, in addition to the AgPic\(_2\)-L extraction ones reported previously.

Keywords: Interfacial potential differences; Individual distribution constants of ions; Extraction into nitrobenzene; Alkaline-earth metal picrates; 18-Crown-6 ether derivatives

Introduction

Recently one of the authors has reported an expression by an interfacial potential difference (\( \Delta \phi_{\text{ex}} \)) as an extraction constant on silver picrate extraction with crown ethers (L) into 1,2-dichloroethane (DCE) or dichloromethane (DCM), and picrate ion, respectively. An introduction of \( \Delta \phi_{\text{ex}} \) was evaluated in the NB phase were evaluated from \( K_{\text{ex}} \) and \( K_{\text{ex}} \) in the NB phase were evaluated from \( K_{\text{ex}} \) and \( K_{\text{ex}} \). Here, the symbol \( K_{\text{ex}} \) refers to an individual distribution constant (= \([\text{A}^{−}\_0]/[\text{A}^{−}]\)) of \( \text{A}^{−}\) into the NB phase during the difference between the \( K_{\text{ex}} \) values electrochemically-determined and those determined by the present extraction experiments. Here, the electrochemically-determined constant was expressed as \( K_{\text{ex}} \), showing the equilibrium constant standardized at \( \Delta \phi_{\text{ex}} = 0 \) [1,6]. Moreover, the functional expression of \( K_{\text{ex}} \), \( K_{\text{ex}} \) and \( K_{\text{ex}} \) by \( \Delta \phi_{\text{ex}} \) were examined; the symbols, \( K_{\text{ex}} \), \( K_{\text{ex}} \) and \( K_{\text{ex}} \), refer to \([\text{MLA}^{2+}][\text{L}]_0/([\text{M}^{2+}][\text{A}^{−}])\), \([\text{MLA}^{2+}][\text{L}]_0/([\text{M}^{2+}][\text{A}^{−}])\), respectively [3,4,8]. On the basis of the above values determined, the M\(^{2+}\) picrate extraction system with L into NB was characterized.

Keywords: Interfacial potential differences; Individual distribution constants of ions; Extraction into nitrobenzene; Alkaline-earth metal picrates; 18-Crown-6 ether derivatives

Theory

Derivation of a potential difference at the water/o interface

Using properties of electrochemical potentials \( \mu \), [9,10], we have reported relations between \( \Delta \phi_{\text{ex}} \) and the constants expressing overall extraction equilibria, such as \( \text{M}^{2+} + \text{L}^{−} + \text{A}^{−} \rightleftharpoons \text{MLA}^{2+} + \text{M}^{2+} + \text{L}^{−} + \text{A}^{−} \rightleftharpoons \text{ML}^{−} + \text{A}^{−} \rightleftharpoons \text{M}^{2+} + \text{L}^{−} + \text{A}^{−} \rightleftharpoons \text{ML}^{−} + \text{A}^{−} \) [1]. The same handling [1,11] was applied for the present extraction equilibria. For example, the authors will apply it to the process:

\[
\text{M}^{2+} + \text{L}^{−} + 2\text{A}^{−} \rightleftharpoons \text{MLA}^{2+} + \text{A}^{−} \quad (1)
\]

This process was expressed by \( \Delta \phi_{\text{ex}} \) as

\[
\Delta \phi_{\text{ex}} = \Delta \mu_{\text{ex}} = \Delta \mu + \Delta \phi_{\text{ex}} = \Delta \mu + \Delta \phi_{\text{ex}} \quad (2)
\]

\[
\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

Rearranging this equation for the \( \Delta \phi_{\text{ex}} \) definition, then we obtained

\[
\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

\[
\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

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\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

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\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

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\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]

\[
\Delta \phi_{\text{ex}} = \mu_{\text{ex}} + \mu_{\text{L}} + \mu_{\text{A}} - (\mu_{\text{M}} + \mu_{\text{L}} + \mu_{\text{A}})
\]
Therefore, the following equations were derived:

\[ \Delta \phi_{eq} = \Delta \phi_{ext}^{0} + (2.3RT/F)\log K_{ex}^{0} \tag{3} \]

with \( \Delta \phi_{eq} = (\Delta \phi_{M2+}^{0} + \Delta \phi_{L,o}^{0}) - (\Delta \phi_{A}^{0} + \Delta \phi_{a}^{0}) \), \( \Delta \phi_{ext}^{0} = (\mu_{ML2+}^{0} + \mu_{M2+}^{0} - \mu_{M}^{0} - \mu_{L,o}^{0} - 2\mu_{A}^{0})/F \) and \( K_{ex}^{0} = a_{ML2+}/a_{M2+}(a_{L,o}/a_{A})^{2} \). Here, \( \phi_{eq} \) and \( \phi_{ext}^{0} \) denote an inner potential for species \( j \) in the phase \( a \) (or \( o \)) and an activity of \( j \) in the \( o \) phase, respectively; the symbols without \( a \) mean those to the water (w) phase, although there is an exception to this rule. From Equation (3), the interfacial potential difference \( \Delta \phi_{ext}^{0} \) at an equilibrium was defined \[1,11]\; in principle, \( \Delta \phi_{eq}^{0} \) was defined as \( \phi(w) - \phi(o) \). Then, rearranging Equation (3) in a molar concentration unit, we immediately obtain

\[ \Delta \phi_{eq}^{0} = \Delta \phi_{ext}^{0} + (2.3RT/F)\log K_{ex}^{0} \tag{3a} \]

with \( \Delta \phi_{ext}^{0} = \Delta \phi_{ext}^{0} + (2.3RT/F)\log [y_{M2+}y_{L,o}]/[y_{A}y_{o}] \) and \( K_{ex}^{0} = [ML^{2+}][A]^{2}/([M^{2+}][L][A])^{2} \). Here, \( y_{y} \) refers to an activity coefficient of the ionic species \( j \) (\( = MLA^{+}, A^{2-} \)) in the \( o \) phase; the symbol \( y \) without \( a \) shows the coefficient for the \( w \) phase; \( \Delta \phi_{eq}^{0} \) is a standard formal potential. Similarly, equilibrium constants of other processes were expressed as functions of potential differences. These results are listed in Table 1. The condition of \( \Delta \phi_{eq}^{0} = 0 \) V was applied for some processes from their properties: namely, \( \Delta \phi_{eq}^{0} \) essentially becomes zero, when all species relevant to the inner potentials are present in a single phase \[1,9\].

Using thermodynamic cycles and the various equilibrium constants in Table 1, we can express the overall extraction processes \[1\]. Thereby, it becomes possible that we express the overall extraction constants as functions of some formal potentials with \( \Delta \phi_{eq}^{0} \). As an example, \( K_{ex}^{0} \) (see Introduction for its definition) is expressed as \( K_{ex}^{0} = (K_{ex}^{0})(K_{ex}^{0})^{N} \). Taking logarithms of both sides in this equation and rearranging it based on the corresponding relations in Table 1, we easily obtain

\[ \Delta \phi_{ext}^{0} = \Delta \phi_{eq}^{0} + \Delta \phi_{ext}^{0} + \Delta \phi_{ext,log}^{0} + \Delta \phi_{eq}^{0} \tag{4} \]

from \( \Delta \phi_{eq}^{0} = \Delta \phi_{ext}^{0} - \Delta \phi_{ext,log}^{0} - (\Delta \phi_{eq}^{0} - \Delta \phi_{ext,log}^{0} - \Delta \phi_{ext,log}^{0} = \Delta \phi_{eq}^{0} \).

The same was true of \( K_{ex}^{0} \) and \( K_{ex}^{0} \), where the condition of \( \Delta \phi_{eq}^{0} = 0 \) V was satisfied for \( K_{ex}^{0} \), since all species relevant to the inner potentials were present in the single phase \[1,9\]. Table 2 summarizes these results. According to the previous paper \[1\], when the \( K_{ex}^{0} \) values are determined experimentally and the \( \Delta \phi_{eq}^{0} \) ones are available, we immediately calculate the \( \Delta \phi_{eq}^{0} \) values from the relation in Table 1.

For an analytical handling of extraction processes

The extraction-constant parameter, \( K_{ex}^{0} \), has been employed for the determination of \( K_{ex}^{0} \) and \( K_{ex}^{0} \) [3-5]:

\[ \log K_{ex}^{0} = \log \left[ ([MLA^{+}] + [M^{2+}])/([M^{2+}][L][A]) \right] \]

\[ = \log \left[ K_{ex}^{0} + K_{ex}^{0}/([M^{2+}][L][A]) \right] \tag{5} \]

under the condition of \( [A] = [MLA^{+}] + [M^{2+}]/[M^{2+}]+[ML^{2+}] \). A regression analysis to the plot of \( \log K_{ex}^{0} \) versus \( \log ([M^{2+}][L][A]) \) yields the \( K_{ex}^{0} \) and \( K_{ex}^{0} \) values [3-5]. Equation (5) can be also rearranged as

\[ \log K_{ex}^{0} = \log \left[ K_{ex}^{0} + (K_{ex}^{0}/([M^{2+}][L][A]) \right] \tag{5a} \]

Then, this equation makes it possible that one obtains the \( K_{ex}^{0} \) value from the plot of \( \log K_{ex}^{0} \) versus \( \log ([M^{2+}][L][A]) \). In this study, the regression analyses with Equation (5a) were performed at a fixed condition of the \( K_{ex}^{0} \) value which was determined in terms of the analysis of Equation (5) and accordingly the thus-obtained \( K_{ex}^{0} \) value was checked by calculating it from each experimental point (Table 3).

Evaluation of stepwise ion-pair formation constants for \( MLA^{+} \) in the \( o \) phase

Stepwise ion-pair formation constants for \( MLA^{+} \) in the water-saturated \( o \) phase for given \( I_{eq,org} \) values were evaluated from the following relations.

\[ K_{ex}^{0} = [MLA^{+}]/([MLA^{+}][A]_{eq}^{0} = K_{ex}^{0} \tag{6} \]

\[ K_{ex}^{0} = [MLA^{+}]/([MLA^{+}][A]_{eq}^{0} = K_{ex}^{0} \tag{7} \]

Here, the symbol, \( I_{eq,org} \) was defined as \( (I_{eq,org})_{N} \) with a number (\( N \)) of run and ion strength (\( I_{eq} \)) for the \( o \) phase. Table 3 lists the five equilibrium constants determined with the above procedures. The \( K_{ex}^{0} \) values which were available from references [8] were actually used as \( K_{ex}^{0} \) in the \( K_{ex}^{0} \) calculation with Equation (6). Strictly speaking, there

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**Table 1:** Relations between the potential differences, \( \Delta \phi_{eq}^{0} \), \( \Delta \phi_{ext}^{0} \), and \( \log K_{eq}^{0} \) values in an extraction system.

| Process | Symbol | Relation |
|---------|--------|----------|
| Overall | M2+ + L + 2A | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
| Component | M2+ | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | M2+ + A | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | L | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | MLA2+ + A | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | L | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | MLA2+ | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |
|   | L | MLA2+ | \( K_{eq}^{0} = \log \left[ 2(M_{2+}L_{o})/(A_{eq}^{0}) \right] \) |

* A thermodynamic cycle of an extraction constant expressed by the component equilibrium constants. \( \Delta \phi_{eq}^{0} = \phi(o) - \phi(w) \; \text{or} \; \phi^{0}(w) - \phi^{0}(o) \).

**Table 2:** Some examples on relations between the \( \Delta \phi_{eq}^{0} \) values and the potential differences based on component equilibrium constants.
Materials and Methods

**Chemicals**

Purities of commercial Ca(NO$_3$)$_2$·4H$_2$O (Kanto Chemical Co. (Kanto), guaranteed reagent (GR)), Sr(NO$_3$)$_2$ (Kanto, GR) and Ba(NO$_3$)$_2$ (Wako Pure Chemical Industries (Wako), GR) were checked by a Karl-Fischer titration with disodium of EDTA. Also, a purity of commercially-available picric acid, HPic, with amount of 10-15% (w/w) water (Wako, GR) was checked by an acid-base titration [1,5]. Commercial crown ethers, 18C$_6$ (99%, Acros) and B18C$_6$ (98%, Aldrich), were dried at room temperature for 20 h under a reduced pressure. Their purities were checked by measurements of the melting points: 39.7-40.1 or 37.2-39.9 °C for 18C$_6$; 42.3-42.8 for B18C$_6$.

Additionally, their water contents were determined by a Karl-Fischer titration: 0.462% (w/w) for 18C$_6$ and 0.410, for B18C$_6$. Nitrobenzene (Kanto, GR) was washed three-times with water and then kept at a water-saturated condition. Other chemicals were of GR grades and (Kanto, GR) was washed three-times with water and then kept at a reduced pressure. Their purities were checked by measurements of the melting points: 39.7-40.1 or 37.2-39.9 °C for 18C$_6$; 42.3-42.8 for B18C$_6$.

**Extraction procedures**

Alkaline-earth metal nitrates M(NO$_3$)$_2$·4H$_2$O, HPic and L were mixed with 0.002 mol dm$^{-3}$ HNO$_3$ in a stoppered glass-tube of about 30 cm$^3$ and then the same volume of NB was added in its solution. Their total concentrations were [Ca(NO$_3$)$_2$]$_t$ = 0.0012 mol dm$^{-3}$, [HPic]$_t$ = 0.0024 mol dm$^{-3}$, [Sr(NO$_3$)$_2$]$_t$ = 0.0014 mol dm$^{-3}$, and [Ba(NO$_3$)$_2$]$_t$ = 0.0018 mol dm$^{-3}$, [18C$_6$]$_t$ = 0.071 mol dm$^{-3}$, [B18C$_6$]$_t$ = 0.071 mol dm$^{-3}$, [Sr(NO$_3$)$_2$]$_t$ = 4.1 mol dm$^{-3}$, [HPic]$_t$ = 7.1 mol dm$^{-3}$ and [B18C$_6$]$_t$ = 0.071 mol dm$^{-3}$. The thus-prepared glass tube was shaken for 1 minute by hand and was agitated at 298 ± 0.2 K for 2 h in a water bath (Iwaki, type WTE-24) equipped with a water pump (Iwaki, type SHK driver) and a thermoregulator (Iwaki, type CTR-100). After this operation, its mixture was centrifuged with a Koksuzen centrifuge (type 7163-4.8.20) for 7 minutes.

A portion of the separated NB phase was transferred into another stoppered glass-tube and then 0.1 mol dm$^{-3}$ HNO$_3$ was added in this tube. By shaking the tube, all M(II) species in the NB phase were back-extracted into the HNO$_3$ solution. If necessary, the operation for this back extraction was repeated. An amount of all the M(II) species in the aqueous HNO$_3$ solution was determined by a Hitachi polarized Zeeman atomic absorption spectrophotometer (type Z-6100) with a hollow cathode lamp of Ca (type 10-020, Mito-rika Co. under the license of Hitachi, Ltd.; measured wavelength: 422.7 nm) or Sr (type 10-038, Mito-rika Co.; 460.7 nm). A calibration-curve method was employed for the determination of the M(II) concentration by AAS. For the Ba(II) determination, a >0.1 mol dm$^{-3}$ NaOH solution was added in the back-extracted solution with Pic$^-$ and then its Ba(II) solution was measured at 355 nm based on the Pic$^-$ absorption and 298 K by a spectrophotometer (Hitachi, type U-2001). The Ba(II) concentration was determined with a calibration curve which was prepared at 355 nm. On the other hand, the pH value in the separated NB phase was measured at 298 K with the same electrode and pH/ion meter [1,4,5].

### Table 3: Fundamental equilibrium constants for the extraction of alkaline-earth metal picrates by L into nitrobenzene at 298 K.

| L | M   | $\log K_{ex}^{\text{mix}}$ | $\log K_{ex}^{\text{mix}}$ | $n_{\text{eq}}$ |
|---|-----|--------------------------|--------------------------|----------------|---|
| 18C$_6$ | Ca | $-1.43 \pm 0.03$ | $9.82 \pm 0.02$ | 0.0014 | 0.86-6.4 |
| | Sr | $-0.98 \pm 0.07$ | $11.44 \pm 0.03$ | 0.80-5.9 |
| Ba | $-0.69 \pm 0.04$ | $10.75 \pm 0.08$ | 3.60-10$^3$ | 0.80-5.9 |
| B18C$_6$ | Ca | $-1.92 \pm 0.04$ | $7.35 \pm 0.08$ | 3.60-10$^3$ | 0.80-5.9 |
| | Sr | $-1.34 \pm 0.04$ | $9.41 \pm 0.04$ | 4.00-10$^3$ | 0.80-5.9 |
| Ba | $-1.17 \pm 0.02$ | $9.51 \pm 0.02$ | 4.70-10$^3$ | 0.80-5.9 |

$^a$Average values of $n$ in the w phase. $^b$Average values of $n$ in the NB phase.

$^c$Logarithms of average values calculated from each value of $K_{ex}$ and their propagation errors simultaneously-calculated. Number, $n$, of water molecules coextracted with ML$^2^+$ into the NB phase. See ref. [17]
Rearranging this equation and adding $2[Ba\text{Pic}^2]_{NB}$ in its both sides, we can immediately obtain

$$[\text{Pic}^-]_{NB} + 2[Ba\text{Pic}^2]_{NB} = [\text{Pic}^-]_{NB}$$

$$= 2[Ba^+]_{NB} + 2[Ba\text{L}^2+]_{NB} + [Ba\text{LPic}^+]_{NB} + 2[Ba\text{LPic}^2]_{NB} \quad (8a)$$

Hence, when the condition of $2[Ba\text{Pic}^2]_{NB} > [Ba\text{Pic}^+]_{NB} (> 2[Ba^+]_{NB} + 2[Ba\text{L}^2+]_{NB})$ holds, the half of the left hand side of Equation (8a) approximately becomes $[Ba^+]_{NB} + [Ba\text{L}^2+]_{NB} + [Ba\text{Pic}^-]_{NB} + [Ba\text{LPic}^+]_{NB}$ namely $[Ba(\text{II})]_{NB}$. We were able to determine spectrophotometrically the $([\text{Pic}^-]_{NB} + 2[Ba\text{Pic}^2]_{NB})$ value at least by the back extraction experiments.

**Results and Discussion**

**Tendencies of $K_{D,Pic}$, $K_{ex^+,}$ and $K_{ex^-,}$ at $n = 1, 2$**

As can be seen from Table 3, the log $K_{D,Pic}$ values are different from each other in spite of the same definition. These are in the orders of Ca $<$ Sr $<$ Ba for a given L. Also, the orders are B18C6 $<$ 18C6 for a given M(II). Thus, these $K_{D,Pic}$ orders are influenced by sizes $[14,15]$ of $M^{2+}$ and $L$, not cavity sizes of $L$; molar volumes of L were reported to be 214 cm$^3$/mol$^{-1}$ for L = 18C6 and 252 for B18C6 $[15]$.

The values of both log $K_{ex^+}$ and log $K_{ex^-}$ were in the orders of Ca $<$ Sr $<$ Ba (Table 3). These tendencies are similar to those for log $K_{ML,C}$ and log $K_{ML,NB}$ (see below for these values). Such facts suggest the presence of these equilibrium constants in the thermodynamic cycles (Table 2). Also, two procedures for evaluating the log $K_{ex}$ values in Table 3 well agreed with consideration errors. These facts support that the regression analyses based on Equation (5a) are essentially valid under the conditions of constant $K_{ex}$ values.

Orders of the log $K_{ex}$ values were Ca $>$ Sr $>$ Ba for the both L, when we neglected differences in $K_{ex}$ among the extraction systems (see Table 3 for $I_{1,NB}$). On the other hand, the log $K_{ex}$ values were Ca $<$ Sr $>$ Ba. These differences suggest that sizes of M(II) are more-effectively reflected to stability of the 1st-step ion-pair formation than to that of the 2nd-step formation. In other words, these results seem to be due to differences in a size and/or charges, such as the formal and net charges, between $ML^{2+}$ and $ML\text{Pic}^-$ as reaction species in NB saturated with water. Also, such effects may be reduced in the more-bulky SrPic$^-$ and BaPic$^-$-18C6 systems.

As another explanation for the $K_{ex}$ orders, it can be considered that the $I_{ex}$ values of the Ca(II) system are largest of all the systems. The $I_{ex}$ orders were of $M = Ca > Sr > Ba$ for L = 18C6 and Ca $>$ Sr $\geq$ Ba for B18C6 (Table 3). The highest $I_{ex}$ values for the Ca(II) systems may cause the lowest $K_{ex}$ values. While their values were less effective for the $K_{ex}$ values, because $K_{ex}$ is constituted by the concentrations of all the ionic species.

If the 1st-step ion-pair formation is assumed to be

$$ML^{2+} \cdot H_2O_{NB} + \text{Pic}^- \rightleftharpoons ML\text{Pic}^- \cdot mH_2O_{NB} + pH_2O_{NB} \quad (9)$$

with $p = h - m$, then $K_{ex}$ can be expressed as $K_{ex} = [ML\text{Pic}^-]_{NB}/[H_2O_{NB}]^h$ with $K_{ex} = [ML\text{Pic}^-]_{NB}/[H_2O_{NB}]^h$ (as an expression without a hydrated $H_2O$). Here, the hydration of Pic$^-$ in the NB phase was neglected $[16]$. From Table 3, the larger the $h$ values $[17]$ are, the larger the $K_{ex}$ values become. These facts suggest that the $m$ values are about a constant and thereby the $p$ values are proportional to the $h$ ones. Taking logarithms of the both sides of the equation, $K_{ex} = K_{ex} / [H_2O_{NB}]^h$, we can immediately obtain the equation, log $K_{ex} = \log K_{ex} - p \times \log [H_2O_{NB}]^h$. Under the conditions of $[H_2O_{NB}]_{NB} = 0.178$ mol...
thermodynamic cycle, \( \log K_{\text{ex}^2}\pm = \log K_{\text{D},\text{M}} \) potentials.

\[ \Delta K_{\text{1,NB}} = -\Delta K_{\text{eq}} \]

As can be seen from Table 4, the \( \log K_{\text{ex}^2\pm} \) values calculated from the relation in Table 2 are very small, compared to those [8] reported [20]. Also, the \( \Delta K_{\text{1,NB}} \) values were in the range of 1.2 to 3.9 (Table 4). (i) These differences can be due to experimental errors of data, because estimated fractions, [ML\textsuperscript{2+}]\textsubscript{NB} [AAS-analyzed (MII)\textsubscript{ML}]+ were in the ranges of 0.001 - 0.043% for M = Ca, 0.02 - 0.33 for Sr and 0.0 - 3.1 for Ba. That is, these values indicate that the amounts of ML\textsuperscript{2+} in the NB phases are negligible, compared to those of all species with M(II) in the phases and accordingly the \( K_{\text{ex}^2\pm} \) evaluations may cause the larger errors. (ii) Or the difference can come from the fact that the original extraction model does not take account of the overall process, \( \text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightarrow \text{ML}_{\text{NB}} + 2\text{Pic}^- \). While the overall process, \( \text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightarrow \text{ML}_{\text{NB}} + 2\text{Pic}^- \) might be included in the model [3-5] (see Equation (5a)). However, it is unclear whether the two above facts, (i) and (ii), cause the negative errors of \( K_{\text{ex}^2\pm} \) or not.

Determination of the \( K_{\text{ex}^2\pm} \) and \( K_{\text{ex}^2\pm} \) values

The \( \Delta K_{\text{1,NB}} \) values were evaluated from the \( \Delta \phi_{\text{eq}} \) and \( K_{\text{ex}^2\pm} \) values (Tables 3&4) using \( K_{\text{ex}^2\pm} = (\Delta \phi_{\text{eq}} - \Delta \phi_{\text{D,M}})/0.05916 \) listed in Table 1. After these evaluations, the \( K_{\text{ex}^2\pm} \) values were calculated from the same equation at \( \Delta \phi_{\text{eq}} = 0 \) V. The same values were evaluated from \( \Delta \phi_{\text{eq}} = 2\Delta \phi_{\text{D,M}} + 2\Delta \phi_{\text{org}}^0 + \Delta \phi_{\text{H}^+} + \Delta \phi_{\text{A}} \)

\[ \Delta \phi_{\text{D,M}} \] in Table 2 and then \( K_{\text{ex}^2\pm} = (\Delta \phi_{\text{eq}} - 0.05916) \). Here, we calculated the \( \Delta \phi_{\text{eq}} \) values from \( \log K_{\text{ex}^2\pm} = -11.799 \) for M = Ca, -11.562 for Sr and -10.818 for Ba [19] and similarly the \( \Delta \phi_{\text{org}}^0 \) values from \( K_{\text{ex}^2\pm} = 11.2 \) for ML\textsuperscript{2+} = Ca(18C6)\textsuperscript{2+}, 13.1 for Sr(18C6)\textsuperscript{2+}, 13.4 for Ba(18C6)\textsuperscript{2+}, \( \log K_{\text{ex}^2\pm} = 9.43 \) for Ca(B18C6)\textsuperscript{2+} and 11.1 for Sr(B18C6)\textsuperscript{2+} and 11.6 and for Ba(B18C6)\textsuperscript{2+} [20]. Also, the \( \Delta \phi_{\text{A}} \) values were calculated from the relation of \( \log K_{\text{ex}^2\pm} = 0.05916(1) \) and the \( K_{\text{ex}^2\pm} \) values in Table 3. Similar evaluations were performed for the \( K_{\text{ex}^2\pm} \) values using the relation among the potentials listed in Table 2.

As can be seen from Table 4, the \( K_{\text{ex}^2\pm} \) values calculated from the relation in Table 1 are equal or close to those calculated from that in Table 2. Especially, a little larger deviations for the BaPic\textsubscript{L} systems may be due to the approximation of \( [\text{Ba}][\text{Pic}]^0 \) (see Materials and Methods). On the other hand, the \( K_{\text{ex}^2\pm} \) values calculated from the relation in Table 2 are very small, compared to those [8] reported before, although the order in magnitude of the calculated values is the same as that of the reported ones [8]. A correlation between these two orders was expressed by the following equation: \( K_{\text{ex}^2\pm} \) (calcd) = (1.54 ± 0.05)\( K_{\text{ex}^2\pm} \) (found) - (2.62 ± 0.07) at \( R = 0.998 \). Also, differences between the \( K_{\text{ex}^2\pm} \) (calcd) and \( K_{\text{ex}^2\pm} \) (found) values were in the range of 1.2 to 3.9 (Table 4). (i) These differences can be due to experimental errors of data, because estimated fractions, [ML\textsuperscript{2+}]\textsubscript{NB} [AAS-analyzed (MII)\textsubscript{ML}]+ were in the ranges of 0.001 - 0.043% for M = Ca, 0.02 - 0.33 for Sr and 0.0 - 3.1 for Ba. That is, these values indicate that the amounts of ML\textsuperscript{2+} in the NB phases are negligible, compared to those of all species with M(II) in the phases and accordingly the \( K_{\text{ex}^2\pm} \) evaluations may cause the larger errors. (ii) Or the difference can come from the fact that the original extraction model does not take account of the overall process, \( \text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightarrow \text{ML}_{\text{NB}} + 2\text{Pic}^- \). While the overall process, \( \text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightarrow \text{ML}_{\text{NB}} + 2\text{Pic}^- \) might be included in the model [3-5] (see Equation (5a)). However, it is unclear whether the two above facts, (i) and (ii), cause the negative errors of \( K_{\text{ex}^2\pm} \) or not.

Figure 3 shows a plot of \( K_{\text{ex}^2\pm} \) versus \( K_{\text{ex}^2\pm} \) (found) for all the MPic\textsubscript{L} systems. Here, the former logarithmic values are listed in Table 3, while the latter values in Table 4. The plot gave a good correlation between both the values: \( \log K_{\text{ex}^2\pm} = (0.81 \pm 0.03)\log K_{\text{ex}^2\pm} \) (found) + (2.0, ± 0.1) at \( R = 0.998 \). This fact indicates that the experimental \( K_{\text{ex}^2\pm} \) values clearly reflect the \( K_{\text{ex}^2\pm} \) ones at \( \Delta \phi_{\text{eq}} = 0 \). The result is the same as that [1] reported before for the AgPic extraction by B15C6 and B18C6 into DCE or DCM. On the other hand, in this study, we were not able to obtain the \( K_{\text{ex}^2\pm} \) values which are comparable to the above \( K_{\text{ex}^2\pm} \) ones.

Accordance of \( \Delta \phi_{\text{eq}} \) with the distribution of ML\textsuperscript{2+} into NB

The individual distribution constants (\( K_{\text{DML}} \)) of ML\textsuperscript{2+} into the NB phase can be evaluated from the other thermodynamic cycle, \( \text{K}_{\text{ML,org}} = \text{K}_{\text{DML}}\text{K}_{\text{ML,org}}/\text{K}_{\text{D,L}} \) (Table 2). Here, \( \text{K}_{\text{ML,org}} \) and \( \text{K}_{\text{D,L}} \) (Table 1) are defined as [ML\textsuperscript{2+}]/[M\textsuperscript{2+}][L] and [L]/[L] [15], respectively, and these values at 298 K were available from references; \( \log K_{\text{D,L}} = 0.48 \) for M = Ca, 2.72 for Sr and 3.87 for Ba [4]; \( \log K_{\text{D,ML}} \) was 0.48 for M = Ca, 2.41 for Sr and 2.90 for Ba [21,22]; \( \log K_{\text{ML,org}} = -1.00 \) for L = 18C6 and 1.57 [20] for B18C6. Using the logarithmic form of the above equation, we obtained \( \log K_{\text{D,M18C6}} = 0.8 \) for M = Ca, -0.1 for Sr and -0.9 for Ba and \( \log K_{\text{D,B18C6}} = 2.6 \) for M = Ca, 1.4 for Sr and 1.6 for Ba. There was a tendency that these values increase with an increase in the log \( K_{\text{D,L}} \) ones: \( \log K_{\text{D,18C6}} = (1.6, 0.5)\log K_{\text{D,M18C6}} + (3.6, 0.9) \) at \( R = 0.848 \). Here, the log \( K_{\text{D,M18C6}} \) values [20] determined in terms of ion-transfer...
Conclusion

Expressions of the extraction constants by $\Delta \phi_{eq}$ were extended into $K_{ex}$, $K_{ex}^{2,NB}$, and $K_{eq}$ of the MPic extraction systems with L in addition to $K_{ex}$ and $K_{ex}^{2,NB}$ of the AgPic-L systems [1]. These expressions were summarized in Tables 1 and 2. However, the matters for precision of the values in the analyses have been present for the determination of $K_{ex}^{2,NB}$. Also, there may be self-inconsistency for the estimation of the $K_{SNB}$ values. It was demonstrated that the log $K_{ex}$ values well reflect the log $K_{ex}^{2,NB}$ values for the SrPic 2-B18C6 system and the coextraction of water into nitrobenzene with alkali and alkaline-earth metal waters. So, one can see markedly the relation between $K_{ex}$ obtained from an extraction experiment and $K_{ex}^{2,NB}$ from an electrochemical one. This result fundamentally enables us to discuss the extraction-ability and -selectivity of L against M from both the values. Moreover, it was shown that the expressions of $K_{ex}$, $K_{ex}^{2,NB}$ and $K_{ex}^{2,NB}$ by $\Delta \phi_{eq}$ do not conflict with data obtained from the electrochemical measurements.

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Appendix

In practice, we have calculated the values of

$$\log K_{\text{eq}} = \log K_{\text{eq}}^{2} + \log K_{\text{eq}}^{2,NB}$$

from Equation (6) and the relation in Table 1. Rearranging this equation, the following equation can be easily obtained

$$\log K_{\text{eq}}^{2} = \log K_{\text{eq}}^{2} + \log K_{\text{eq}}^{2,NB}$$

Also, Equation (7) gave

$$\log K_{\text{eq}}^{2} = \log K_{\text{eq}}^{2} + \log K_{\text{eq}}^{2,NB} = R \Delta \phi_{ex}$$

$$\log K_{\text{eq}}^{2} = \log K_{\text{eq}}^{2} + \log K_{\text{eq}}^{2,NB}$$

$\log K_{\text{eq}}^{2}$ and $\log K_{\text{eq}}^{2,NB}$ in Table 3 are equal to Equations (2A) and (A3), respectively. As examples, the log $K_{\text{eq}}^{2}$ and log $K_{\text{eq}}^{2,NB}$ values for the SrPic-B18C6 system were calculated from these equations to be 4.7 and 6.0, respectively. These values were in good accord with those listed in Table 3.

Why do Equations (A2) and (A3), the functions expressing log $K_{\text{eq}}^{2}$ and log $K_{\text{eq}}^{2,NB}$ contain $\Delta \phi_{ex}$? This question comes from the fact that log $K_{\text{eq}}^{2}$ (n = 1, 2) in Table 1 were derived from the condition of $\Delta \phi_{ex} = 0$.V. Also, the above results are self-consistent to the fact that all the log $K_{\text{eq}}^{2,NB}$ values in Table 3 are conditional equilibrium-constants, such as $K_{SNB}$ fixed in an $\text{lub}$ value. Unfortunately, the authors now can explain these inconsistencies.

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