



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 ($K_{D,A}$) 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_{ex}) for the extraction of alkaline-earth metal picrates, MPic_2 , by 18-crown-6 ether (18C6) and benzo-18C6 (B18C6). Here, $K_{D,A}$ and K_{ex} were defined as $[\text{A}^-]_{\text{NB}}/[\text{A}^-]$ and $[\text{MLA}_2]_{\text{NB}}/([\text{M}^{2+}][\text{L}]_{\text{NB}}[\text{A}^-]^2)$, respectively: A⁻ shows Pic^- , L does either 18C6 or B18C6 and the subscript “NB” refers to the NB phase. Interfacial potential differences ($\Delta\phi_{\text{eq}}$ in a V unit) at extraction equilibria were evaluated from differences between the experimental $\log K_{D,\text{Pic}}$ and its standardized values ($\log K_{D,\text{Pic}}^{\text{S}}$) which have been determined by electrochemical measurements at a water/NB interface. By a combination with the K_{ex} values, other extraction constants, $K_{\text{ex}\pm} = [\text{MLPic}^+]_{\text{NB}}/([\text{M}^{2+}][\text{Pic}^-]_{\text{NB}})$, were also determined. Electrochemically-standardized $\log K_{\text{ex}\pm}$ values, $\log K_{\text{ex}\pm}^{\text{S}}$ ones, were calculated from the relation of $\log K_{\text{ex}\pm} = (\Delta\phi_{\text{eq}}/0.05916) + \log K_{\text{ex}\pm}^{\text{S}}$ at 298 K. Using the $\log K_{\text{ex}\pm}^{\text{S}}$ values, their correlation with the $\log K_{\text{ex}\pm}$ ones was discussed. Additionally, ion-pair formation constants ($K_{1,\text{NB}}$ & $K_{2,\text{NB}}$) for the stepwise reactions of ML^{2+} with Pic^- in the NB phase were evaluated from K_{ex}^{\pm} , $K_{\text{ex}\pm}$ and another constant ($K_{\text{ex}2\pm}$) reported before at $\Delta\phi_{\text{eq}} = 0$. Here, $K_{2,\text{NB}}$ was evaluated from $K_{\text{ex}}/K_{\text{ex}\pm}$ and $K_{1,\text{NB}}$ is defined as $[\text{MLPic}^+]_{\text{NB}}/([\text{ML}^{2+}]_{\text{NB}}[\text{Pic}^-]_{\text{NB}})$, which was evaluated from the relation of $K_{1,\text{NB}} = K_{\text{ex}\pm}/K_{\text{ex}2\pm}$. Moreover, reproductions of the electrochemically-standardized $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$ values were tried, using the $\Delta\phi_{\text{eq}}$ values and relations between $K_{\text{ex}\pm}$ or $K_{\text{ex}2\pm}$ and component equilibrium constants constituting their extraction ones. Consequently, a functional expression of $K_{\text{ex}\pm}$ with $\Delta\phi_{\text{eq}}$ was extended into the MPic_2 -L extraction systems, in addition to the AgPic -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 ($\Delta\phi_{\text{eq}}$) of an extraction constant on silver picrate extraction with crown ethers (L) into 1,2-dichloroethane (DCE) or dichloromethane (DCM) [1]. In this study, its extraction constant has been defined as $[\text{AgL}^+]_{\text{o}}[\text{Pic}^-]_{\text{o}}/([\text{Ag}^+][\text{L}]_{\text{o}}[\text{Pic}^-])$, in addition to the well-known definition of $K_{\text{ex}} = [\text{AgL}^+\text{Pic}^-]_{\text{o}}/([\text{Ag}^+][\text{L}]_{\text{o}}[\text{Pic}^-])$, where the subscript “o” and Pic^- denote an organic (o) phase, such as DCE and DCM, and picrate ion, respectively. An introduction of $\Delta\phi_{\text{eq}}$ in extraction experiments also gave an answer for a problem of the deviation between the electrochemically-determined $K_{D,A}$ values and extraction-experimentally-determined values [1,2]. Here, the symbol $K_{D,A}$ refers to an individual distribution constant ($= [\text{A}^-]_{\text{o}}/[\text{A}^-]$) of A^- into the o phase. Similar problems have been observed in the extraction of divalent metal salts, such as CdPic_2 , PbPic_2 and CaPic_2 , by L into various diluents [3-5].

In the present paper, we determined at 298 K the $K_{D,\text{Pic}}$ values for the extraction of alkaline-earth metal picrates (MPic_2 ; M = Ca, Sr, Ba) by 18-crown-6 ether (18C6) or benzo-18C6 (B18C6) into nitrobenzene (NB) which shows the higher polarity. Then, the $\Delta\phi_{\text{eq}}$ values were evaluated from differences between the $K_{D,\text{Pic}}$ values electrochemically-determined and those determined by the present extraction-experiments. Here, the electrochemically-determined constant was expressed as $K_{D,\text{Pic}}^{\text{S}}$, showing the equilibrium constant standardized at $\Delta\phi_{\text{eq}} = 0$ V [1,6,7]. Moreover, the functional expressions of $K_{\text{ex}\pm}$, $K_{\text{ex}2\pm}$ and K_{ex} by $\Delta\phi_{\text{eq}}$ were examined; the symbols, $K_{\text{ex}\pm}$, $K_{\text{ex}2\pm}$ and K_{ex} , refer to $[\text{MLA}^+]_{\text{o}}/([\text{M}^{2+}][\text{L}]_{\text{o}}[\text{A}^-]^2)$, $[\text{ML}^{2+}]_{\text{o}}/([\text{M}^{2+}][\text{L}]_{\text{o}}[\text{A}^-]^2)$ and $[\text{MLA}_2]_{\text{o}}/([\text{M}^{2+}][\text{L}]_{\text{o}}[\text{A}^-]^2)$, respectively [3,4,8]. On the basis of the above values determined, the $\text{M}^{\text{II}}\text{Pic}_2$ extraction system with L into NB was characterized.

Theory

Derivation of a potential difference at the water/o interface

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



This process was expressed by $\bar{\mu}_i$ as

$$\begin{aligned} \bar{\mu}_M + \bar{\mu}_{L,o} + 2\bar{\mu}_A &= \bar{\mu}_{\text{MLA},o} + \bar{\mu}_{A,o} \quad (2) \\ \mu_M^o + RT \ln a_M + 2F\phi_M + \mu_{L,o}^o + RT \ln a_{L,o} + 2(\mu_A^o + RT \ln a_A - F\phi_A) \\ &= \mu_{\text{MLA},o}^o + RT \ln a_{\text{MLA},o} + F\phi_{\text{MLA},o} + \mu_{A,o}^o + RT \ln a_{A,o} - F\phi_{A,o} \quad (2a) \end{aligned}$$

Rearranging this equation for the $K_{\text{ex}\pm}$ definition, then we obtained

$$\begin{aligned} RT \ln K_{\text{ex}\pm}^o + \mu_{\text{MLA},o}^o + \mu_{A,o}^o - \mu_M^o - \mu_{L,o}^o - 2\mu_A^o \\ = F\{(2\phi_M - \phi_{\text{MLA},o}) - (2\phi_A - \phi_{A,o})\}. \end{aligned}$$

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Therefore, the following equations were derived:

$$\Delta\phi_{\text{eq}} = \Delta\phi_{\text{ex}\pm}^0 + (2.3RT/F)\log K_{\text{ex}\pm}^0 \quad (3)$$

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

$$\Delta\phi_{\text{eq}} = \Delta\phi_{\text{ex}\pm}^{0'} + (2.3RT/F)\log K_{\text{ex}\pm}^{0'} \quad (3a)$$

with $\Delta\phi_{\text{ex}\pm}^{0'} = \Delta\phi_{\text{ex}\pm}^0 + (2.3RT/F)\log [y_{\text{MLA},o} y_{A,o} / \{y_M (y_A)^2\}]$ and $K_{\text{ex}\pm}^{0'} = [\text{MLA}^+]_o [\text{A}^-]_o / ([\text{M}^{2+}]_o [\text{L}]_o [\text{A}^-]_o^2)$. Here, $y_{j,\alpha}$ refers to an activity coefficient of the ionic species j ($= \text{MLA}(\text{I}), \text{A}(-\text{I}), \text{M}(\text{II})$) in the α phase; the symbol y without α shows the coefficient for the w phase; $\Delta\phi_k^{0'}$ means 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 $\Delta\phi_{\text{eq}} = 0 \text{ V}$ was applied for some processes from their properties: namely, $\Delta\phi_{\text{eq}}$ 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

Process	Symbol	Relation ^a
Overall		
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{MLA}_{2,o}$	K_{ex}	$\log K_{\text{ex}} = -2f\Delta\phi_{\text{ex}}^{0'}$
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{MLA}_o^+ + \text{A}_o^-$	$K_{\text{ex}\pm}$	$\log K_{\text{ex}\pm} = f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'})$
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{ML}_{2,o}^{2+} + 2\text{A}_o^-$	$K_{\text{ex}2\pm}$	$\log K_{\text{ex}2\pm} = 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}2\pm}^{0'})$
Component		
$\text{M}^{2+} \rightleftharpoons \text{M}_o^{2+}$	$K_{\text{D},\text{M}}$	$\log K_{\text{D},\text{M}} = 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'})$
$\text{ML}^{2+} \rightleftharpoons \text{ML}_o^{2+}$	$K_{\text{D},\text{ML}}$	$\log K_{\text{D},\text{ML}} = 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ML}}^{0'})$
$\text{A}^- \rightleftharpoons \text{A}_o^-$	$K_{\text{D},\text{A}}$	$\log K_{\text{D},\text{A}} = -f(\Delta\phi_{\text{eq}} - \phi_A^{0'})$
$\text{M}_o^{2+} + \text{L}_o \rightleftharpoons \text{ML}_o^{2+}$	$K_{\text{ML,org}}$	$\log K_{\text{ML,org}} = -2f\Delta\phi_{\text{ML,org}}^{0'}$
$\text{M}^{2+} + \text{L} \rightleftharpoons \text{ML}^{2+}$	K_{ML}	$\log K_{\text{ML}} = -2f\Delta\phi_{\text{ML,w}}^{0' \text{ b}}$
$\text{L} \rightleftharpoons \text{L}_o$	$K_{\text{D},\text{L}}$	$\log K_{\text{D},\text{L}} = -f\Delta\phi_{\text{L}}^{0'}$
$\text{ML}_o^{2+} + \text{A}_o^- \rightleftharpoons \text{MLA}_o^+$	$K_{1,\text{org}}$	$\log K_{1,\text{org}} = -f\Delta\phi_{1,\text{org}}^{0'}$
$\text{MLA}_o^+ + \text{A}_o^- \rightleftharpoons \text{MLA}_{2,o}$	$K_{2,\text{org}}$	$\log K_{2,\text{org}} = -f\Delta\phi_{2,\text{org}}^{0'}$
$\text{ML}_o^{2+} + 2\text{A}_o^- \rightleftharpoons \text{MLA}_{2,o}$	$\beta_{\text{ip,org}}^{\text{c}}$	$\log \beta_{\text{ip,org}} = -2f\Delta\phi_{\text{ip,org}}^{0'}$

^a $f = F/2.3RT$. Hence, $1/f = 0.05916 \text{ V}$ at 298 K. ^b $\Delta\phi_{\text{ML,w}}^{0'}$ shows a standard formal potential for the ML^{2+} formation in the w phase. ^c $\beta_{\text{ip,org}} = K_{1,\text{org}} K_{2,\text{org}}$. Accordingly, the relation of $2\Delta\phi_{\text{ip,org}}^{0'} = \Delta\phi_{1,\text{org}}^{0'} + \Delta\phi_{2,\text{org}}^{0'}$ holds

Table 1: Relations between the potential differences, $\Delta\phi_{\text{eq}}$, $\Delta\phi_k^{0'}$ or $\Delta\phi_j^{0'}$, and $\log K_k$ values in an extraction system.

Overall process & its cycle ^a	Relation ^b
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{MLA}_{2,o}$ $K_{\text{ex}} = K_{\text{D},\text{M}}(K_{\text{D},\text{A}})^2 K_{\text{ML,org}} \beta_{\text{ip,org}}$	$\Delta\phi_{\text{ex}}^{0'} = \Delta\phi_{\text{M}}^{0'} - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML,org}}^{0'} + \Delta\phi_{\text{ip,org}}^{0'}$
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{MLA}_o^+ + \text{A}_o^-$	(a) $\Delta\phi_{\text{ex}\pm}^{0'} = 2\Delta\phi_{\text{M}}^{0'} - 2\Delta\phi_{\text{A}}^{0'} + 2\Delta\phi_{\text{ML,org}}^{0'} + \Delta\phi_{1,\text{org}}^{0'} + \Delta\phi_{\text{eq}}$ (b) $\Delta\phi_{\text{ex}2\pm}^{0'} = 2\Delta\phi_{\text{ML,w}}^{0'} + 2\Delta\phi_{\text{ML}}^{0'} + \Delta\phi_{1,\text{org}}^{0'} - 2\Delta\phi_{\text{A}}^{0'} - \Delta\phi_{\text{L}}^{0'} + \Delta\phi_{\text{eq}}$
(a) $K_{\text{ex}\pm} = K_{\text{D},\text{M}}(K_{\text{D},\text{A}})^2 K_{\text{ML,org}} K_{1,\text{org}}$ (b) $K_{\text{ex}2\pm} = K_{\text{ML}} K_{\text{D},\text{ML}} K_{1,\text{org}} (K_{\text{D},\text{A}})^2 / K_{\text{D},\text{L}}$	
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{ML}_{2,o}^{2+} + 2\text{A}_o^-$ $K_{\text{ex}2\pm} = K_{\text{D},\text{M}}(K_{\text{D},\text{A}})^2 K_{\text{ML,org}}$	$\Delta\phi_{\text{ex}2\pm}^{0'} = \Delta\phi_{\text{M}}^{0'} - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML,org}}^{0'} + \Delta\phi_{\text{eq}}$

^aA thermodynamic cycle of an extraction constant expressed by the component equilibrium constants. ^b $\Delta\phi_{\text{ip,org}}^{0'} = (\Delta\phi_{1,\text{org}}^{0'} + \Delta\phi_{2,\text{org}}^{0'})/2$

Table 2: Some examples on relations between the $\Delta\phi_k^{0'}$ values and the potential differences based on component 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 $\Delta\phi_{\text{eq}}$. As an example, $K_{\text{ex}2\pm}$ (see Introduction for its definition) is expressed as $K_{\text{D},\text{M}}(K_{\text{D},\text{A}})^2 K_{\text{ML,org}}$. Taking logarithms of both sides in this equation and rearranging it based on the corresponding relations in Table 1, we easily obtain

$$\Delta\phi_{\text{ex}2\pm}^{0'} = \Delta\phi_{\text{M}}^{0'} - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML,org}}^{0'} + \Delta\phi_{\text{eq}} \quad (4)$$

from $\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}2\pm}^{0'} = (\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'}) - (\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) - \Delta\phi_{\text{ML,org}}^{0'}$. The same was true of K_{ex} and $K_{\text{ex}\pm}$, where the condition of $\Delta\phi_{\text{eq}} = 0 \text{ V}$ was satisfied for K_{ex} , 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 $\log K_{\text{D},\text{A}}$ values are determined experimentally and the $\Delta\phi_{\text{A}}^{0'}$ ones are available, we immediately can calculate the $\Delta\phi_{\text{eq}}$ values from the relation in Table 1.

For an analytical handling of extraction processes

The extraction-constant parameter, $K_{\text{ex}}^{\text{mix}}$, has been employed for the determination of $K_{\text{D},\text{A}}$ and K_{ex} [3-5]:

$$\log K_{\text{ex}}^{\text{mix}} = \log \{([\text{MLA}_2]_o + [\text{MLA}^+]_o) / ([\text{M}^{2+}]_o [\text{L}]_o [\text{A}^-]_o^2)\} \\ = \log \{K_{\text{ex}} + K_{\text{D},\text{A}} / ([\text{M}^{2+}]_o [\text{L}]_o [\text{A}^-]_o)\} \quad (5)$$

under the condition of $[\text{A}^-]_o \approx [\text{MLA}^+]_o (>> 2[\text{M}^{2+}]_o + 2[\text{ML}^{2+}]_o)$. A regression analysis to the plot of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log ([\text{M}^{2+}]_o [\text{L}]_o [\text{A}^-]_o^2)$ yielded the $K_{\text{D},\text{A}}$ and K_{ex} values [3-5]. Equation (5) can be also rearranged as

$$\log K_{\text{ex}}^{\text{mix}} = \log \{K_{\text{ex}} + (K_{\text{ex}} / [\text{M}^{2+}]_o [\text{L}]_o)^{1/2} [\text{A}^-]_o^{-1}\}. \quad (5a)$$

Then, this equation makes it possible that one obtains the $K_{\text{ex}\pm}$ value from the plot of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log \{([\text{M}^{2+}]_o [\text{L}]_o)^{1/2} [\text{A}^-]_o\}$. In this study, the regression analyses with Equation (5a) were performed at a fixed condition of the K_{ex} value which was determined in terms of the analysis of Equation (5) and accordingly the thus-obtained $K_{\text{ex}\pm}$ value was checked by calculating it from each experimental point (Table 3).

Evaluation of stepwise ion-pair formation constants for MLA_2 in the o phase

Stepwise ion-pair formation constants for MLA_2 in the water-saturated o phase for given $I_{\text{org,av}}$ values were evaluated from the following relations.

$$K_{1,\text{org}} = [\text{MLA}^+]_o / [\text{ML}^{2+}]_o [\text{A}^-]_o = K_{\text{ex}\pm} / K_{\text{ex}2\pm} \quad (6)$$

$$K_{2,\text{org}} = [\text{MLA}_2]_o / [\text{MLA}^+]_o [\text{A}^-]_o = K_{\text{ex}} / K_{\text{ex}\pm} \quad (7)$$

Here, the symbol, $I_{\text{org,av}}$, was defined as $(\sum I_{\text{org}}) / N$ with a number (N) of run and ionic strength (I_{org}) for the o phase. Table 3 lists the five equilibrium constants determined with the above procedures. The $K_{\text{ex}2\pm}^{\text{S}}$ values which were available from references [8] were actually used as $K_{\text{ex}2\pm}$ in the $K_{1,\text{NB}}$ -calculation with Equation (6). Strictly speaking, there

L	M	log $K_{D,A}$	log K_{ex} () ^a	log K_{ext}	log $K_{n,NB}$ () ^b	
					n=1	2
18C6	Ca	-1.43 ± 0.03	9.82 ± 0.02 (5.3×10 ⁻³)	5.44 ± 0.07 5.4 ₃ ± 0.1 ₈ ^c	5.9 [4.7] ^d	4.38 ± 0.08 (8.9×10 ⁻⁴)
	Sr	-0.98 ± 0.07	11.44 ± 0.03 (3.1×10 ⁻³)	6.9 ₂ ± 0.1 ₂ ^c 6.9 ₁ ± 0.1 ₃ ^c	5.3 [4.6] ^d	4.5 ₂ ± 0.1 ₂ (4.8×10 ⁻⁴)
	Ba	-0.69 ± 0.04	10.75 ± 0.08 (4.5×10 ⁻³)	7.3 ₅ ± 0.1 ₁ ^c 7.4 ₁ ± 0.3 ₃ ^c	4.9 [3.4] ^d	3.4 ₁ ± 0.1 ₁ (5.9×10 ⁻⁴)
B18C6	Ca	-1.92 ± 0.04	7.35 ± 0.08 (3.6×10 ⁻³)	2.7 ₁ ± 0.1 ₀ ^c 2.8 ₀ ± 0.2 ₉ ^c	5.0 [5.5] ^d	4.6 ₂ ± 0.1 ₁ (6.9×10 ⁻⁴)
	Sr	-1.34 ± 0.04	9.41 ± 0.02 (4.0×10 ⁻³)	4.34 ± 0.08 4.3 ₃ ± 0.1 ₃ ^c	4.7 [4.6] ^d	5.07 ± 0.08 (2.3×10 ⁻⁴)
	Ba	-1.17 ± 0.02	9.51 ± 0.02 (4.7×10 ⁻³)	5.0 ₁ ± 0.1 ₁ ^c 5.0 ₀ ± 0.4 ₂ ^c	4.1 [4.2] ^d	4.5 ₀ ± 0.1 ₁ (2.1×10 ⁻⁴)

^aAverage values of I in the w phase. ^bAverage values of I_{NB} in the NB phase. ^cLogarithms of average values calculated from each values of K_{ext} and their propagation errors simultaneously-calculated. ^dNumber, h , of water molecules coextracted with ML^{2+} into the NB phase. See ref. [17]

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

is a difference between actual contents calculated from Equations (6) and (7). See Appendix for this details.

Materials and Methods

Chemicals

Purities of commercial Ca(NO₃)₂·4H₂O {Kanto Chemical Co. (Kanto), guaranteed reagent (GR)}, Sr(NO₃)₂ (Kanto, GR) and Ba(NO₃)₂ {Wako Pure Chemical Industries (Wako), GR} were checked by a chelatometric titration with disodium salt 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, 18C6 (99%, Acros) and B18C6 (98%, Aldrich), were dried at room temperature for >20 h under a reduced pressure. Their purities were checked by measurements of the melting points: 39₇-40₁ or 37₂-39₉ °C for 18C6; 42₃-42₈ for B18C6. Additionally, their water contents were determined by a Karl-Fischer titration: 0.462₈%(w/w) for 18C6 and 0.410₇ for B18C6. Nitrobenzene (Kanto, GR) was washed three-times with water and then kept at a water-saturated condition. 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 purified by passing through the Autopure system (type WT101 UV, Yamato/Millipore). Thus purified water was employed for the present work.

Extraction procedures

Alkaline-earth metal nitrates M(NO₃)₂, HPic and L were mixed with 0.002 mol dm⁻³ HNO₃ in a stoppered glass-tube of about 30cm³ and then the same volume of NB was added in its solution. Their total concentrations were [Ca(NO₃)₂]_t = 0.0012 mol dm⁻³, [HPic]_t = 0.0024 and [18C6]_t = (0.70-7.0) × 10⁻⁴; [Sr(NO₃)₂]_t = 6.8 × 10⁻⁴, [HPic]_t = 0.0014 and [18C6]_t = (0.86-6.4) × 10⁻⁴; [Ba(NO₃)₂]_t = 8.8 × 10⁻⁴, [HPic]_t = 0.0018 and [18C6]_t = (0.071-2.6) × 10⁻³ and [Ca(NO₃)₂]_t = 8.0 × 10⁻⁴, [HPic]_t = 1.6 × 10⁻³ and [B18C6]_t = (0.080-2.4) × 10⁻³; [Sr(NO₃)₂]_t = 4.1 × 10⁻⁴, [HPic]_t = 8.2 × 10⁻⁴ and [B18C6]_t = (0.082-2.5) × 10⁻³; [Ba(NO₃)₂]_t = 3.5 × 10⁻⁴, [HPic]_t = 7.1 × 10⁻⁴ and [B18C6]_t = (0.032-2.0) × 10⁻³. 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 driver unit (Iwaki, SHK driver) and a thermoregulator (Iwaki, type CTR-100). After this operation, its mixture was centrifuged with a Kokusan centrifuge (type 7163-4.8.20) for 7 minutes.

A portion of the separated NB phase was transferred into another

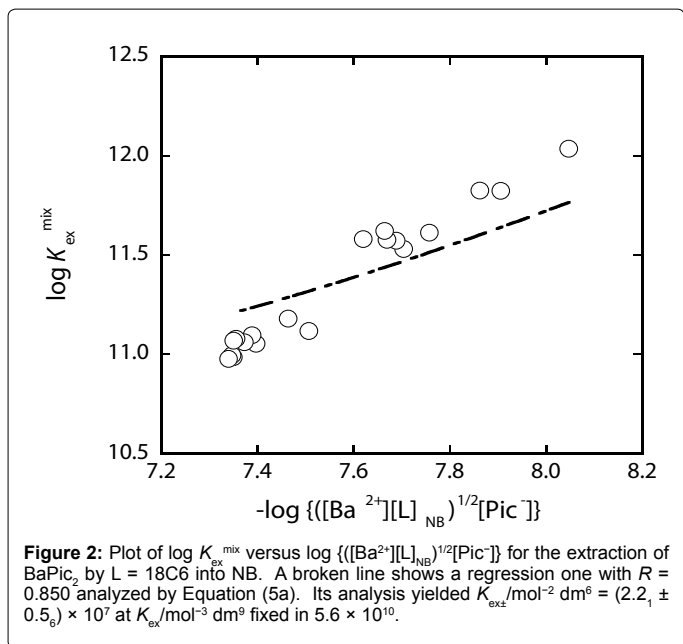
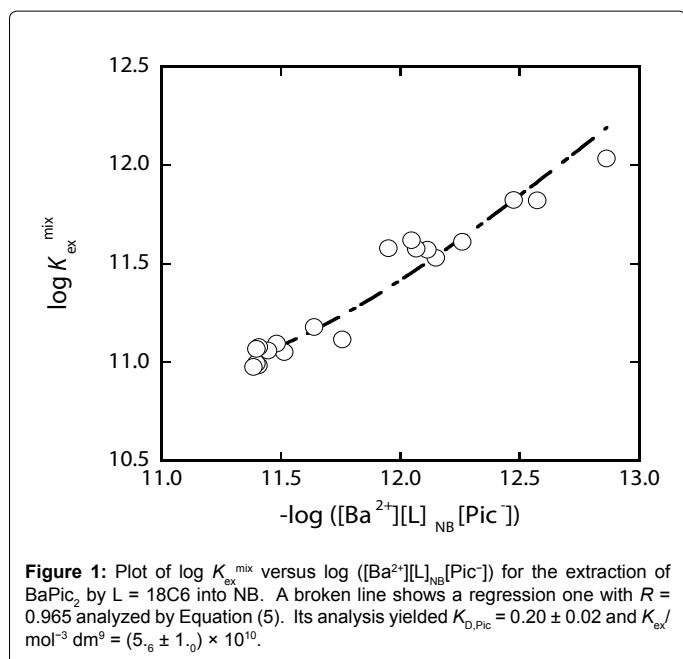
stoppered glass-tube and then 0.1 mol dm⁻³ HNO₃ was added in this tube. By shaking the tube, all M(II) species in the NB phase were back-extracted into the HNO₃ solution. If necessary, the operation for this back extraction was repeated. An amount of all the M(II) species in the aqueous HNO₃ solution 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 had been prepared at 355 nm. On the other hand, the pH value in the separated w phase was measured at 298 K with the same electrode and pH/ion meter [1,4,5].

Determination of K_{ex}^{mix}

We used here the same extraction model as that [5] for sub-analysis described previously. Its component equilibria are 1) $M^{2+} + A^- \rightleftharpoons MA^+$ [12], 2) $A^- \rightleftharpoons A^-$, 3) $M^{2+} \rightleftharpoons M^{2+}$, 4) $MLA^+ + A^- \rightleftharpoons MLA_{2,0}$, 5) $ML^{2+} \rightleftharpoons ML^{2+}$, 6) $L \rightleftharpoons L$, 7) $M^{2+} + L \rightleftharpoons ML^{2+}$, 8) $M^{2+} + L \rightleftharpoons ML^{2+}$, 9) $H^+ + A^- \rightleftharpoons HA$ [4], 10) $HA \rightleftharpoons HA$ [4], 11) $HA \rightleftharpoons H^+ + A^-$ [13], 12) $H^+ \rightleftharpoons H^+$ [6], 13) $X^- \rightleftharpoons X^-$ [11] and 14) $H^+ + X^- \rightleftharpoons HX$ [11], where the symbol HX shows a strong acid, such as HNO₃ and HCl, in water. In particular, the two reactions, 7) and 8), indirectly yielded the process 5). Also, the parentheses with the asterisks show that their equilibrium constants at 298 K have been already determined by several methods (see below for some values).

The equilibrium constants for the reactions 1) and 9) were estimated taking account of the ionic strength, I , for the w phases in a successive approximation [3,5]. Here, the formation constants (K_{MA}) for $MA^+ = MPic^+$ ($M = Sr, Ba$) in the w phase were determined by the same method as that [4] reported before: as the log K_{MPic} values at 298 K and $I \rightarrow 0$ mol dm⁻³, 2.1₈ for $M = Sr$ and 2.0₈ for Ba were obtained. While the K_{CaPic} value was estimated with the value available from reference [12].

The procedure for the calculation of K_{ex}^{mix} values by the successive approximation was essentially the same as that [3] described previously (see the theoretical section). Plots of log ($D_{expl}/[Pic^-]^2$) versus log [L]_{NB} gave a straight line with a slope of 0.56 and an intercept of 7.9 for the CaPic₂-18C6 system, 0.91 and 11.1 (≈ log K_{ex}) for SrPic₂-18C6, 0.62 and 9.4 for BaPic₂-18C6, 0.38 and 5.9 for CaPic₂-B18C6, 0.65 and 8.5 for SrPic₂-B18C6 and 0.44 and 7.9 for BaPic₂-B18C6. Here, the distribution ratio D_{expl} is defined as [AAS-analyzed M(II)]_{NB}/([M(NO₃)₂]_t - [AAS-analyzed M(II)]_{NB}) and the intercept corresponds to the log K_{ex} value only when the slope is about unity [3-5]. Except for the SrPic₂-18C6 system, the compositions of M(II):L:Pic(-) were assumed to be 1:1:2 in the determination of $K_{D,Pic}$, K_{ex} and K_{ext} [3-5]. The slope's values less than unity indicate dissociations of $MLPic_2$ in the NB phases [4]. Figures 1 and 2 show the plots for the BaPic₂-18C6 extraction system based on Equations (5) and (5a), respectively, yielding the $K_{D,Pic}$, K_{ex} and K_{ext} values (Table 3). The less correlation coefficient (R) of the plot in Figure 2 may reflect the defect in the sub-analytical extraction model}



[4,5], that is, the absence of the ion-pair formation for MLPic_2 in the w phase. Also, the other extraction systems yielded similar plots, from which we got similarly these three kinds of values (Tables 3).

In the determination of $K_{\text{D,Pic}}$, K_{ex} and $K_{\text{ex}\pm}$ for the BaPic_2 -L extraction system, it was assumed that a total amount, $[\text{Ba(II)}]_{\text{NB,t}}$ of Ba(II) in the NB phase nearly equals the half of that, $[\text{Pic}^-]_{\text{NB,t}}$ of Pic^- in the NB one. This assumption was derived as follows. A charge balance equation for the NB phase was essentially

$$2[\text{Ba}^{2+}]_{\text{NB}} + 2[\text{BaL}^{2+}]_{\text{NB}} + [\text{BaLPic}^+]_{\text{NB}} + [\text{H}^+]_{\text{NB}} = [\text{Pic}^-]_{\text{NB}} + [\text{X}^-]_{\text{NB}} \quad (8)$$

where the distribution of BaPic^+ into the NB phase was neglected, because its data were not available. When $[\text{H}^+]_{\text{NB}} \approx [\text{X}^-]_{\text{NB}}$ holds, Equation (8) becomes $2[\text{Ba}^{2+}]_{\text{NB}} + 2[\text{BaL}^{2+}]_{\text{NB}} + [\text{BaLPic}^+]_{\text{NB}} \approx [\text{Pic}^-]_{\text{NB}}$.

Rearranging this equation and adding $2[\text{BaLPic}_2]_{\text{NB}}$ in its both sides, we can immediately obtain

$$\begin{aligned} [\text{Pic}^-]_{\text{NB}} + 2[\text{BaLPic}_2]_{\text{NB}} &= [\text{Pic}^-]_{\text{NB,t}} \\ &\approx 2[\text{Ba}^{2+}]_{\text{NB}} + 2[\text{BaL}^{2+}]_{\text{NB}} + [\text{BaLPic}^+]_{\text{NB}} + 2[\text{BaLPic}_2]_{\text{NB}} \quad (8a) \end{aligned}$$

Hence, when the condition of $2[\text{BaLPic}_2]_{\text{NB}} > [\text{BaLPic}^+]_{\text{NB}} (> 2[\text{BaL}^{2+}]_{\text{NB}} + 2[\text{Ba}^{2+}]_{\text{NB}})$ holds, the half of the left hand side of Equation (8a) approximately becomes $[\text{Ba}^{2+}]_{\text{NB}} + [\text{BaL}^{2+}]_{\text{NB}} + [\text{BaLPic}^+]_{\text{NB}} + [\text{BaLPic}_2]_{\text{NB}}$, namely $[\text{Ba(II)}]_{\text{NB,t}}$. We were able to determine spectrophotometrically the $([\text{Pic}^-]_{\text{NB}} + 2[\text{BaLPic}_2]_{\text{NB}})$ value at least by the back extraction experiments.

Results and Discussion

Tendencies of $K_{\text{D,Pic}}$, K_{ex} , $K_{\text{ex}\pm}$ and $K_{\text{n,NB}}$ at $n = 1, 2$

As can be seen from Table 3, the $\log K_{\text{D,Pic}}$ values are different from each other in spite of the same definition. These are in the orders of $\text{Ca} < \text{Sr} < \text{Ba}$ for a given L. Also, the orders are $\text{B18C6} < \text{18C6}$ for a given M(II). Thus, these $K_{\text{D,Pic}}$ 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 $214 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{L} = 18\text{C6}$ and 252 for B18C6 [15].

The values of both $\log K_{\text{ex}}$ and $\log K_{\text{ex}\pm}$ were in the orders of $\text{Ca} < \text{Sr} < \text{Ba}$ (Table 3). These tendencies are similar to those for $\log K_{\text{D,M}}^{\text{s}}$ and $\log K_{\text{ML,NB}}$ (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 $\log K_{\text{ex}\pm}$ values in Table 3 well agreed within calculation 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 $\log K_{\text{1,NB}}$ values were $\text{Ca} > \text{Sr} > \text{Ba}$ for the both L, when we neglected differences in I_{NB} among the extraction systems (see Table 3 for I_{NB}). On the other hand, the $\log K_{\text{2,NB}}$ values were $\text{Ca} < \text{Sr} > \text{Ba}$. 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 MLPic^+ as reaction species in NB saturated with water. Also, such effects may be reduced in the more-bulky SrPic_2 - and BaPic_2 - B18C6 systems.

As another explanation for the $K_{\text{2,NB}}$ orders, it can be considered that the I_{NB} values of the Ca(II) system are largest of all the systems. The I_{NB} orders were of $\text{M} = \text{Ca} > \text{Sr} < \text{Ba}$ for $\text{L} = 18\text{C6}$ and $\text{Ca} > \text{Sr} \geq \text{Ba}$ for B18C6 (Table 3). The highest I_{NB} values for the Ca(II) systems may cause the lowest $K_{\text{2,NB}}$ values. While their values were less effective for the $K_{\text{1,NB}}$ values, because $K_{\text{1,NB}}$ is constituted by the concentrations of all the ionic species.

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



with $p = h - m$, then $K_{\text{1,NB}}$ can be expressed as $K_{\text{1,NB}} / ([\text{H}_2\text{O}]_{\text{NB}})^p$ with $K_{\text{1,NB}}' = [\text{MLPic}^+]_{\text{NB}} ([\text{H}_2\text{O}]_{\text{NB}})^p / [\text{ML}^{2+}]_{\text{NB}} [\text{Pic}^-]_{\text{NB}}$ (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 $K_{\text{1,NB}}$ 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, $K_{\text{1,NB}} = K_{\text{1,NB}}' / ([\text{H}_2\text{O}]_{\text{NB}})^p$, we can immediately obtain the equation, $\log K_{\text{1,NB}} = \log K_{\text{1,NB}}' - p \times \log [\text{H}_2\text{O}]_{\text{NB}}$. Under the conditions of $[\text{H}_2\text{O}]_{\text{NB}} (= 0.178 \text{ mol}$

dm^{-3} at 298 K [17,18]) < 1 and $p > 0$, the equation becomes $\log K_{1,\text{NB}} = \log K_{1,\text{NB}}' + 0.750p$. Therefore, the $\log K_{1,\text{NB}}$ values basically increase with an increase in p and consequently can increase with that in h (Table 3). The above results suggest the existence of the reaction (9) with H_2O molecules in NB phase, as reported before on the process of $\text{M}^+ + \text{L}_{\text{NB}} + \text{A}^- \rightleftharpoons \text{ML}_{\text{NB}}^+ + \text{A}^-_{\text{NB}}$ [8].

Calculation of the $\Delta\phi_{\text{eq}}$ values from the experimental $\log K_{\text{D,Pic}}$ values

Using the relation of $\log K_{\text{D,A}} = -(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^0)/0.05916$ at 298 K (Table 1), we calculated the $\Delta\phi_{\text{eq}}$ values from the $\log K_{\text{D,Pic}}$ and $\Delta\phi_{\text{Pic}}^0$ ones, where the $\Delta\phi_{\text{Pic}}^0$ value of 3.0×10^{-3} V [6] at the w/NB interface was employed. Thus obtained values are summarized in Table 4. The $\Delta\phi_{\text{eq}}$ range for the 18C6 system was a little smaller than that for B18C6 one. From a comparison with the $\log K_{\text{ex}\pm}$ values in Table 3, the smaller the $\Delta\phi_{\text{eq}}$ values are, the larger the $\log K_{\text{ex}\pm}$ ones become. This trend is similar to that reported previously for the extraction of AgPic by B18C6 and benzo-15-crown-5 ether B15C5 into DCE or DCM [1].

Determination of the $\log K_{\text{ex}\pm}^{\text{s}}$ and $\log K_{\text{ex}\pm}^{\text{s}}$ values

The $\Delta\phi_{\text{ex}\pm}^0$ values were evaluated from the $\Delta\phi_{\text{eq}}$ and $\log K_{\text{ex}\pm}$ values (Tables 3&4) using $\log K_{\text{ex}\pm} = (\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^0)/0.05916$ listed in Table 1. After these evaluations, the $\log K_{\text{ex}\pm}^{\text{s}}$ values were calculated from the same equation at the condition of $\Delta\phi_{\text{eq}} = 0$ V. The same values were evaluated from $\Delta\phi_{\text{ex}}^0 = 2\phi_{\text{M}}^0 - 2\Delta\phi_{\text{A}}^0 + 2\Delta\phi_{\text{ML,org}}^0 + \Delta\phi_{\text{1,org}}^0 + \Delta\phi_{\text{eq}}$ in Table 2 and then $\log K_{\text{ex}\pm}^{\text{s}} = -\Delta\phi_{\text{ex}\pm}^0/0.05916$. Here, we calculated the $\Delta\phi_{\text{M}}^0$ values from $\log K_{\text{D,M}}^{\text{s}} = -11.799$ for M = Ca, -11.562 for Sr and -10.818 for Ba [19] and similarly the $\Delta\phi_{\text{ML,NB}}^0$ values from $\log K_{\text{ML,NB}} = 11.2$ for $\text{ML}^{2+} = \text{Ca}(\text{18C6})^{2+}$, 13.1 for $\text{Sr}(\text{18C6})^{2+}$, 13.4 for $\text{Ba}(\text{18C6})^{2+}$, $\log K_{\text{ML,NB}} = 9.43$ for $\text{Ca}(\text{B18C6})^{2+}$, 11.1 for $\text{Sr}(\text{B18C6})^{2+}$ and 11.6 for $\text{Ba}(\text{B18C6})^{2+}$ [20]. Also, the $\Delta\phi_{1,\text{NB}}^0$ values were calculated from the relation of $\log K_{1,\text{NB}} = -\Delta\phi_{1,\text{NB}}^0/0.05916$ (Table 1) and the $\log K_{1,\text{NB}}^{\text{s}}$ values in Table 3. Similar evaluations were performed for the $\log K_{\text{ex}\pm}^{\text{s}}$ values using the relation among the potentials listed in Table 2.

As can be seen from Table 4, the $\log K_{\text{ex}\pm}^{\text{s}}$ 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 BaPic₂-L systems may be due to the approximation of $[\text{Ba}(\text{II})]_{\text{NB},\text{t}} \approx [\text{Pic}^-]_{\text{NB},\text{t}}$ (see Materials and Methods). On the other hand, the $\log K_{\text{ex}\pm}^{\text{s}}$ 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: $\log K_{\text{ex}\pm}^{\text{s}}(\text{calcd}) = (1.54 \pm 0.05)\log K_{\text{ex}\pm}^{\text{s}}(\text{found}) - (2.62 \pm 0.07)$ at $R = 0.998$. Also, differences between the $\log K_{\text{ex}\pm}^{\text{s}}(\text{calcd})$ and $\log K_{\text{ex}\pm}^{\text{s}}(\text{found})$ values

L	M	$\Delta\phi_{\text{eq}}/\text{V}^{\text{b}}$	$\log K_{\text{ex}\pm}^{\text{s}}$		$\log K_{\text{ex}\pm}^{\text{s}}$	
			Found ^b	Calcd ^c	Found ^d	Calcd ^e
18C6	Ca	0.088	3.96	3.9 ₆	-0.5	-3.4 ₆
	Sr	0.061	5.89	5.9 ₃	1.6	-0.4 ₂
	Ba	0.044	6.61	6.8 ₉	2.4	1.2 ₁
B18C6	Ca	0.12	0.75	0.7 ₈	-2.3	-6.20
	Sr	0.082	2.95	2.9 ₉	-0.4	-3.1 ₄
	Ba	0.072	3.79	4.0 ₇	0.6	-1.5 ₆

^aEssentially based on $\Delta\phi/\text{V}$ versus $\text{Ph}_2\text{As}^+\text{BPh}_4^-$ electrode. ^bCalculated from the relation of $\log K_{\text{ex}\pm} = f(\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^0)$ in Table 1. ^cCalculated from the relation of $\Delta\phi_{\text{ex}\pm}^0 = 2(\Delta\phi_{\text{M}}^0 - \Delta\phi_{\text{A}}^0 + \Delta\phi_{\text{ML,org}}^0) + \Delta\phi_{\text{1,org}}^0 + \Delta\phi_{\text{eq}}$ in Table 2. ^dCalculated from the thermodynamic cycle, $\log K_{\text{ex}\pm}^{\text{s}} = \log K_{\text{D,M}}^{\text{s}} + 2\log K_{\text{D,Pic}}^{\text{s}} + \log K_{\text{ML,NB}}^{\text{s}}$. See ref. [8]. ^eCalculated from the relation of $\Delta\phi_{\text{ex}\pm}^0 = \Delta\phi_{\text{M}}^0 - \Delta\phi_{\text{A}}^0 + \Delta\phi_{\text{ML,org}}^0 + \Delta\phi_{\text{eq}}$ in Table 2
Table 4: $\Delta\phi_{\text{eq}}$ and the $\log K_{\text{ex}\pm}$ and $\log K_{\text{ex}\pm}^{\text{s}}$ values at 298 K standardized by their potentials.

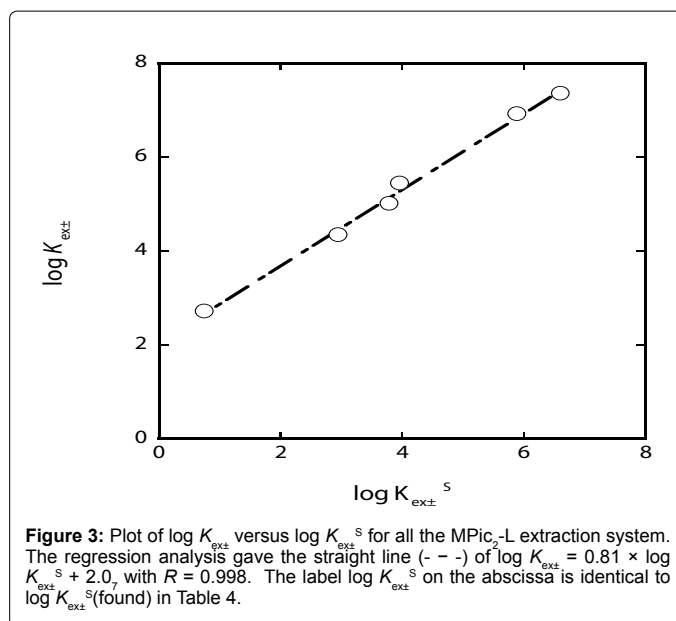


Figure 3: Plot of $\log K_{\text{ex}\pm}$ versus $\log K_{\text{ex}\pm}^{\text{s}}$ for all the MPic₂-L extraction system. The regression analysis gave the straight line (---) of $\log K_{\text{ex}\pm} = 0.81 \times \log K_{\text{ex}\pm}^{\text{s}} + 2.07$, with $R = 0.998$. The label $\log K_{\text{ex}\pm}^{\text{s}}$ on the abscissa is identical to $\log K_{\text{ex}\pm}^{\text{s}}(\text{found})$ in Table 4.

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, $[\text{ML}^{2+}]_{\text{NB}}/[\text{AAS-analyzed M(II)}]_{\text{NB}}$, were in the ranges of 0.001₂-0.043% for M = Ca, 0.02₄-0.33 for Sr and 0.0₅-3.1 for Ba. That is, these values indicate that the amounts of ML^{2+} in the NB phases are negligible, compared to those of all species with M(II) in the phases and accordingly the $K_{\text{ex}\pm}$ 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, $\text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightleftharpoons \text{ML}_{\text{NB}}^{2+} + 2\text{Pic}^-_{\text{NB}}$. While the overall process, $\text{M}^{2+} + \text{L}_{\text{NB}} + 2\text{Pic}^- \rightleftharpoons \text{MLPic}_{\text{NB}}^+ + \text{Pic}^-_{\text{NB}}$, has been 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 $\log K_{\text{ex}\pm}^{\text{s}}$ or not.

Figure 3 shows a plot of $\log K_{\text{ex}\pm}$ versus $\log K_{\text{ex}\pm}^{\text{s}}$ for all the MPic₂-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: $\log K_{\text{ex}\pm} = (0.81 \pm 0.03)\log K_{\text{ex}\pm}^{\text{s}}(\text{found}) + (2.0, \pm 0.1)$, at $R = 0.998$. This fact indicates that the experimental $\log K_{\text{ex}\pm}$ values clearly reflect the $\log K_{\text{ex}\pm}^{\text{s}}$ ones at $\Delta\phi_{\text{eq}} = 0$. The result is the same as that [1] reported before for the AgPic extraction by B15C5 and B18C6 into DCE or DCM. On the other hand, in this study, we were not able to obtain the $\log K_{\text{ex}\pm}$ values which are comparable to the above $\log K_{\text{ex}\pm}^{\text{s}}$ ones.

Accordance of $\Delta\phi_{\text{eq}}$ with the distribution of ML^{2+} into NB

The individual distribution constants ($K_{\text{D,ML}}$) of ML^{2+} into the NB phase can be evaluated from the other thermodynamic cycle, $K_{\text{ex}\pm} = K_{\text{ML}}K_{\text{D,ML}}K_{\text{1,org}}(K_{\text{D,A}})^2/K_{\text{D,L}}$ (Table 2). Here, K_{ML} and $K_{\text{D,L}}$ (Table 1) are defined as $[\text{ML}^{2+}]/[\text{M}^{2+}][\text{L}]$ and $[\text{L}]_0/[\text{L}]$ [15], respectively, and these values at 298 K were available from references; $\log K_{\text{M18C6}} = 0.48$ for M = Ca, 2.72 for Sr and 3.87 for Ba [4]; $\log K_{\text{MB18C6}} = 0.48$ for M = Ca, 2.41 for Sr and 2.90 for Ba [21,22]; $\log K_{\text{D,L}} = -1.00$ [18] for L = 18C6 and 1.57 [20] for B18C6. Using the logarithmic form of the above equation, we obtained $\log K_{\text{D,M18C6}} = 0.8_8$ for M = Ca, -0.1_7 for Sr and -0.9_9 for Ba and $\log K_{\text{D,MB18C6}} = 2.6_3$ for M = Ca, 1.4_3 for Sr and 1.6_1 for Ba. There was a tendency that these values increase with an increase in the $\log K_{\text{D,ML}}^{\text{s}}$ ones: $\log K_{\text{D,ML}} = (1.6_1 \ 0.5_0)\log K_{\text{D,ML}}^{\text{s}} + (3.6_7 \pm 0.9_2)$ at $R = 0.848$. Here, the $\log K_{\text{D,ML}}$ values [20] determined in terms of ion-transfer

polarography were employed as $\log K_{D,ML}^s$. Also, the $\Delta\phi_{eq}$ values can be easily evaluated from a modified form, $\log K_{D,ML}^s = 2(\Delta\phi_{eq}/0.05916) + \log K_{D,ML}^s$, of the relation in Table 1: $\Delta\phi_{eq} = 0.088$ V for the $CaPic_2$ -18C6 system, 0.06₀ for $SrPic_2$ -18C6, 0.04₇ for $BaPic_2$ -18C6, 0.1₂ for $CaPic_2$ -B18C6, 0.08₁ for $SrPic_2$ -B18C6 and 0.07₁ for $BaPic_2$ -B18C6 at 298 K. These $\Delta\phi_{eq}$ values were in good agreement with those listed in Table 4. This fact indicates that the expression of $K_{ex\pm}$ and $K_{D,Pic}$ by $\Delta\phi_{eq}$ in the $MPic_2$ extraction systems with L into NB does not conflict with the data [20] obtained from the electrochemical measurements. Additionally, the $\Delta\phi_{ex\pm}^0$ values calculated from the relation in Table 1 were well reproduced by the $\Delta\phi$ -relation (b) in Table 2.

Conclusion

Expressions of the extraction constants by $\Delta\phi_{eq}$ were extended into $K_{ex\pm}$, $K_{ex2\pm}$ and K_{ex} of the $M^{II}Pic_2$ extraction systems with L, in addition to $K_{ex\pm}$ and K_{ex} 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 $K_{ex2\pm}^s$. Also, there may be self-inconsistency for the estimation of the $K_{n,NB}$ values. It was demonstrated that the $\log K_{ex\pm}$ values well reflect the $\log K_{ex\pm}^s$ ones. So, one can see markedly the relation between $K_{ex\pm}$ obtained from an extraction experiment and $K_{ex\pm}^s$ from an electrochemical one. This result fundamentally enables us to discuss the extraction-ability and -selectivity of L against M^{2+} from both the values. Moreover, it was shown that the expressions of $K_{ex\pm}$, $K_{D,ML}$ and $K_{D,Pic}$ 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

$$\log K_{ex\pm} - \log K_{ex2\pm}^s = f(\Delta\phi_{eq} - \Delta\phi_{ex\pm}^0) - \log K_{ex2\pm}^s \quad (A1)$$

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

$$\log K_{ex\pm} - \log K_{ex2\pm}^s = \log K_{ex\pm}^s - \log K_{ex2\pm}^s + f\Delta\phi_{eq} \quad (A2)$$

Also, Equation (7) gave

$$\begin{aligned} \log K_{ex} - \log K_{ex\pm} &= \log K_{ex}^s - \log K_{ex\pm} = \log K_{ex}^s - f(\Delta\phi_{eq} - \Delta\phi_{ex\pm}^0) \\ &= \log K_{ex}^s - \log K_{ex\pm}^s - f\Delta\phi_{eq} \quad (A3) \end{aligned}$$

$\log K_{1,NB}$ and $\log K_{2,NB}$ in Table 3 are equal to Equations (A2) and (A3), respectively. As examples, the $\log K_{1,NB}$ and $\log K_{2,NB}$ values for the $SrPic_2$ -B18C6 system were calculated from these equations to be 4.7₃ and 5.0₇, respectively. These values were in good accord with those listed in Table 3.

Why do Equations (A2) and (A3), the functions expressing $\log K_{1,NB}$ and $\log K_{2,NB}$, contain $\Delta\phi_{eq}$? This question comes from the fact that $\log K_{n,NB}$ ($n = 1, 2$) in Table 1 were derived from the condition of $\Delta\phi_{eq} = 0$ V. Also, the above results are self-consistent to the fact that all the $\log K_{n,NB}$ values in Table 3 are conditional equilibrium-constants, such as $K_{n,NB}$ fixed in an I_{NB} value. Unfortunately, the authors cannot now explain these inconsistencies.

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