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Research Article

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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 $[A^-]_{NB}/[A^-]$ and $[MLA_2]_{NB}/[M^{2+}][L]_{NB}[A^-]^2$, respectively: A^- shows Pic^-, L does either 18C6 or B18C6 and the subscript "NB" refers to the NB phase. Interfacial potential differences ($\Delta\phi_{eq}$ in a V unit) at extraction equilibria were evaluated from differences between the experimental log $K_{D,Pic}$ and its standardized values (log $_{KD'Pic}{}^{S}$) which have been determined by electrochemical measurements at a water/NB interface. By a combination with the K_{ex} values, other extraction constants, $K_{ex\pm}=[MLPic^+]_{NB}[Pic^-]_{NB}/[M^{2+}][L]_{NB}[Pic^-]^2$, were also determined. Electrochemically-standardized log $K_{ex\pm}$ values, log $K_{ex\pm}{}^S$ ones, were calculated from the relation of log $K_{ex\pm} = (\Delta\phi_{eq}/0.05916) + \log K_{ex\pm}{}^S$ at 298 K. Using the log $K_{ex\pm}{}^S$ values, their correlation with the log $K_{ex\pm}$ ones was discussed. Additionally, ion-pair formation constants ($K_{1,NB}$ & $K_{2,NB}$) for the stepwise reactions of ML^{2+} with Pic^- in the NB phase were evaluated from K_{ex}, $K_{ex\pm}$ and another constant ($K_{ex2\pm}$) reported before at $\Delta\phi_{eq} = 0$. Here, $K_{2,NB}$ was evaluated from $K_{ex}/K_{ex\pm}$ and $K_{1,NB}$ is defined as $[MLPic^+]_{NB}/[ML^{2+}]_{NB}[Pic^-]_{NB}$, which was evaluated from the relation of $K_{1,NB} = K_{ex\pm}/K_{ex2\pm}$. Moreover, reproductions of the electrochemically-standardized $K_{ex\pm}$ and $K_{ex2\pm}$ values were tried, using the $\Delta\phi_{eq}$ values and relations between $K_{ex\pm}$ or $K_{ex2\pm}$ and component equilibrium constants constituting their extraction ones. Consequently, a functional expression of $K_{ex\pm}$ with $\Delta\phi_{eq}$ 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 ($\Delta\phi_{eq}$) 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 $[AgL^+]_o[Pic^-]_o/([Ag^+][L]_o[Pic^-])$, in addition to the well-known definition of $K_{ex} = [AgL^+Pic^-]_o/([Ag^+][L]_o[Pic^-])$, where the subscript "o" and Pic^- denote an organic (o) phase, such as DCE and DCM, and picrate ion, respectively. An introduction of $\Delta\phi_{eq}$ 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 ($= [A^-]_o/[A^-]$) 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 $K_{D,Pic}$ 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 $\Delta\phi_{eq}$ values were evaluated from differences between the $K_{D,Pic}$ values electrochemically-determined and those determined by the present extraction-experiments. Here, the electrochemically-determined constant was expressed as $K_{D,Pic}{}^S$, showing the equilibrium constant standardized at $\Delta\phi_{eq} = 0$ V [1,6,7]. Moreover, the functional expressions of $K_{ex\pm}$, $K_{ex2\pm}$ and K_{ex} by $\Delta\phi_{eq}$ were examined; the symbols, $K_{ex\pm}$, $K_{ex2\pm}$ and K_{ex}, refer to $[MLA^+]_o[A^-]_o/([M^{2+}][L]_o[A^-]^2)$, $[ML^{2+}]_o[A^-]_o{}^2/([M^{2+}][L]_o[A^-]^2)$ and $[MLA_2]_o/([M^{2+}][L]_o[A^-]^2)$, respectively [3,4,8]. On the basis of the above values determined, the $M^{II}Pic_2$ extraction system with L into NB was characterized.

Theory

Derivation of a potential difference at the water/o interface

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

$$M^{2+} + L_o + 2A^- \rightleftharpoons MLA^+{}_o + A^-{}_o. \quad (1)$$

This process was expressed by $\overline{\mu_j}$ as

$$\bar{\mu}_{M} + \bar{\mu}_{L,O} + 2\bar{\mu}_{A} = \bar{\mu}_{MLA,O} + \bar{\mu}_{A,O} \quad (2)$$

$$\mu_M{}^0 + RT\ln a_M + 2F\phi_M + \mu_{L,o}{}^0 + RT\ln a_{L,o} + 2(\mu_A{}^0 + RT\ln a_A - F\phi_A)$$

$$= \mu_{MLA,o}{}^0 + RT\ln a_{MLA,o} + F\phi_{MLA,o} + \mu_{A,o}{}^0 + RT\ln a_{A,o} - F\phi_{A,o}. \quad (2a)$$

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

$$RT\ln K_{ex\pm}{}^0 + \mu_{MLA,o}{}^0 + \mu_{A,o}{}^0 - \mu_M{}^0 - \mu_{L,o}{}^0 - 2\mu_A{}^0$$

$$= F\{(2\phi_M - \phi_{MLA,o}) - (2\phi_A - \phi_{A,o})\}.$$

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Therefore, the following equations were derived:

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

with $\Delta\phi_{eq} = (2\phi_{M} - \phi_{MLA,o}) - (2\phi_{A} - \phi_{A,o})$, $\Delta\phi_{ex\pm}^{0} = (\mu_{MLA,o}^{0} + \mu_{A,o}^{0} - \mu_{M}^{0} - \mu_{L,o}^{0} - 2\mu_{A}^{0})/F$ and $K_{ex\pm}^{0} = a_{MLA,o}a_{A,o}/\{a_{M}a_{L,o}(a_{A})^{2}\}$. 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 $\Delta\phi_{eq}$ at an equilibrium was defined [1,11]; in principle, $\Delta\phi_{eq}$ has been defined as ϕ(w phase) − ϕ(o phase). Then, rearranging Equation (3) in a molar concentration unit, we immediately obtain

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

with $\Delta\phi_{ex\pm}^{0'} = \Delta\phi_{ex\pm}^{0} + (2.3RT/F)\log [y_{MLA,o}y_{A,o}/\{y_{M}(y_{A})^{2}\}]$ and $K_{ex\pm} = [MLA^{+}]_{o}[A^{-}]_{o}/([M^{2+}][L]_{o}[A^{-}]^{2})$. Here, $y_{j,\alpha}$ refers to an activity coefficient of the ionic species j {= MLA(I), A(−I), M(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 $\Delta\phi_{eq} = 0$ V was applied for some processes from their properties: namely, $\Delta\phi_{eq}$ essentially becomes zero, when all species relevant to the inner potentials are present in a single phase [1,9].

Process	Symbol	Relation[a]
Overall		
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons MLA_{2,o}$	K_{ex}	$\log K_{ex} = -2f\Delta\phi_{ex}^{0'}$
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons MLA^{+}_{o} + A^{-}_{o}$	$K_{ex\pm}$	$\log K_{ex\pm} = f(\Delta\phi_{eq} - \Delta\phi_{ex\pm}^{0'})$
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons ML^{2+}_{o} + 2A^{-}_{o}$	$K_{ex2\pm}$	$\log K_{ex2\pm} = 2f(\Delta\phi_{eq} - \Delta\phi_{ex2\pm}^{0'})$
Component		
$M^{2+} \rightleftharpoons M^{2+}_{o}$	$K_{D,M}$	$\log K_{D,M} = 2f(\Delta_{eq} - \Delta\phi_{M}^{0'})$
$ML^{2+} \rightleftharpoons ML^{2+}_{o}$	$K_{D,ML}$	$\log K_{D,ML} = 2f(\Delta\phi_{eq} - \Delta\phi_{ML}^{0'})$
$A^{-} \rightleftharpoons A^{-}_{o}$	$K_{D,A}$	$\log K_{D,A} = -f(\Delta\phi_{eq} - \phi_{A}^{0'})$
$M^{2+}_{o} + L_{o} \rightleftharpoons ML^{2+}_{o}$	$K_{ML.org}$	$\log K_{ML,org} = -2f\Delta\phi_{ML,org}^{0'}$
$M^{2+} + L \rightleftharpoons ML^{2+}$	K_{ML}	$\log K_{ML} = -2f\Delta\phi_{ML,w}^{0'\,b}$
$L \rightleftharpoons L_{o}$	$K_{D,L}$	$\log K_{D,L} = -f\Delta\phi_{L}^{0'}$
$ML^{2+}_{o} + A^{-}_{o} \rightleftharpoons MLA^{+}_{o}$	$K_{1,org}$	$\log K_{1,org} = -f\Delta\phi_{1,org}^{0'}$
$MLA^{+}_{o} + A^{-}_{o} \rightleftharpoons MLA_{2,o}$	$K_{2,org}$	$\log K_{2,org} = -f\Delta\phi_{2,org}^{0'}$
$ML^{2+}_{o} + 2A^{-}_{o} \rightleftharpoons MLA_{2,o}$	$\beta_{ip,org}^{\ c}$	$\log \beta_{ip,org} = -2f\Delta\phi_{ip,org}^{0'}$

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

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

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 $\Delta\phi_{eq}$. As an example, $K_{ex2\pm}$ (see Introduction for its definition) is expressed as $K_{D,M}(K_{D,A})^{2}K_{ML,org}$. Taking logarithms of both sides in this equation and rearranging it based on the corresponding relations in Table 1, we easily obtain

$$\Delta\phi_{ex2\pm}^{0'} = \Delta\phi_{M}^{0'} - \Delta\phi_{A}^{0'} + \Delta\phi_{ML,org}^{0'} + \Delta\phi_{eq} \quad (4)$$

from $\Delta\phi_{eq} - \Delta\phi_{ex2\pm}^{0'} = (\Delta\phi_{eq} - \Delta\phi_{M}^{0'}) - (\Delta\phi_{eq} - \Delta\phi_{A}^{0'}) - \Delta\phi_{ML,org}^{0'}$. The same was true of K_{ex} and $K_{ex\pm}$, where the condition of $\Delta\phi_{eq} = 0$ 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 $K_{D,A}$ values are determined experimentally and the $\Delta\phi_{A}^{0'}$ ones are available, we immediately can calculate the $\Delta\phi_{eq}$ values from the relation in Table 1.

For an analytical handling of extraction processes

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

$$\log K_{ex}^{mix} = \log \{([MLA_{2}]_{o} + [MLA^{+}]_{o})/([M^{2+}][L]_{o}[A^{-}]^{2})\}$$

$$= \log \{K_{ex} + K_{D,A}/([M^{2+}][L]_{o}[A^{-}])\} \quad (5)$$

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

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

Then, this equation makes it possible that one obtains the $K_{ex\pm}$ value from the plot of log K_{ex}^{mix} versus −log $\{([M^{2+}][L]_{o})^{1/2}[A^{-}]\}$. 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 $K_{ex\pm}$ 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 $I_{org,av}$ values were evaluated from the following relations.

$$K_{1,org} = [MLA^{+}]_{o}/[ML^{2+}]_{o}[A^{-}]_{o} = K_{ex\pm}/K_{ex2\pm} \quad (6)$$

$$K_{2,org} = [MLA_{2}]_{o}/[MLA^{+}]_{o}[A^{-}]_{o} = K_{ex}/K_{ex\pm} \quad (7)$$

Here, the symbol, $I_{org,av}$, was defined as $(\Sigma I_{org})/N$ 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 $K_{ex2\pm}^{S}$ values which were available from references [8] were actually used as $K_{ex2\pm}$ in the $K_{1,NB}$-calculation with Equation (6). Strictly speaking, there

Overall process & Its cycle[a]	Relation[b]
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons MLA_{2,o}$ $K_{ex} = K_{D,M}(K_{D,A})^{2}K_{ML,org}\beta_{ip,org}$	$\Delta\phi_{ex}^{0'} = \Delta\phi_{M}^{0'} - \Delta\phi_{A}^{0'} + \Delta\phi_{ML,org}^{0'} + \Delta\phi_{ip,org}^{0'}$
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons MLA^{+}_{o} + A^{-}_{o}$ (a) $K_{ex\pm} = K_{D,M}(K_{D,A})^{2}K_{ML,org}K_{1,org}$ (b) $K_{ex\pm} = K_{ML}K_{D,ML}K_{1,org}(K_{D,A})^{2}/K_{D,L}$	(a) $\Delta\phi_{ex\pm}^{0'} = 2\Delta\phi_{M}^{0'} - 2\Delta\phi_{A}^{0'} + 2\Delta\phi_{ML,org}^{0'} + \Delta\phi_{1,org}^{0'} + \Delta\phi_{eq}$ (b) $\Delta\phi_{ex\pm}^{0'} = 2\Delta\phi_{ML,w}^{0'} + 2\Delta\phi_{ML}^{0'} + \Delta\phi_{1,org}^{0'} - 2\Delta\phi_{A}^{0'} - \Delta\phi_{L}^{0'} + \Delta\phi_{eq}$
$M^{2+} + L_{o} + 2A^{-} \rightleftharpoons ML^{2+}_{o} + 2A^{-}_{o}$ $K_{ex2\pm} = K_{D,M}(K_{D,A})^{2}K_{ML,org}$	$\Delta\phi_{ex2\pm}^{0'} = \Delta\phi_{M}^{0'} - \Delta\phi_{A}^{0'} + \Delta\phi_{ML,org}^{0'} + \Delta\phi_{eq}$

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

Table 2: Some examples on relations between the $\Delta\varphi_{k}^{0'}$ values and the potential differences based on component equilibrium constants.

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L	M	log $K_{D,A}$	log K_{ex} ( )[a]	log $K_{ex\pm}$	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 $5.4_3 \pm 0.1_8$[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 $6.9_1 \pm 0.1_3$[c]	5.3 [4.6][d]	$4.5_2 \pm 0.1_2$ (4.8×10^{-4})
	Ba	−0.69 ± 0.04	10.75 ± 0.08 (4.5×10^{-3})	7.3_5 0.1_1 $7.4_4 \pm 0.3_3$[c]	4.9 [3.4][d]	$3.4_1 \pm 0.1_4$ (5.9×10^{-4})
B18C6	Ca	−1.92 ± 0.04	7.35 ± 0.08 (3.6×10^{-3})	$2.7_1 \pm 0.1_0$ $2.8_0 \pm 0.2_9$[c]	5.0 [5.5][d]	$4.6_4 \pm 0.1_3$ (6.9×10^{-4})
	Sr	−1.34 ± 0.04	9.41 ± 0.02 (4.0×10^{-3})	4.34 ± 0.08 $4.3_3 \pm 0.1_3$[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})	$5.0_1 \pm 0.1_1$ $5.0_8 \pm 0.4_2$[c]	4.1 [4.2][d]	$4.5_0 \pm 0.1_1$ (2.1×10^{-4})

[a] Average values of I in the w phase. [b] Average values of I_{NB} in the NB phase. [c] Logarithms of average values calculated from each values of $K_{ex\pm}$ and their propagation errors simultaneously-calculated. [d] Number, 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 $Ca(NO_3)_2{\cdot}4H_2O$ {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 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: $39._7$-$40._1$ or $37._2$-$39._9$ °C for 18C6; $42._3$-$42._8$ for B18C6. Additionally, their water contents were determined by a Karl-Fischer titration: 0.462_8%(w/w) for 18C6 and 0.410_7 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 $M(NO_3)_2$, HPic and L were mixed with 0.002 mol dm^{-3} HNO_3 in a stoppered glass-tube of about 30cm^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}, $[HPic]_t = 0.0024$ and $[18C6]_t = (0.70\text{-}7.0) \times 10^{-4}$; $[Sr(NO_3)_2]_t = 6.8 \times 10^{-4}$, $[HPic]_t = 0.0014$ and $[18C6]_t = (0.86\text{-}6.4) \times 10^{-4}$; $[Ba(NO_3)_2]_t = 8.8 \times 10^{-4}$, $[HPic]_t = 0.0018$ and $[18C6]_t = (0.071\text{-}2.6) \times 10^{-3}$ and $[Ca(NO_3)_2]_t = 8.0 \times 10^{-4}$, $[HPic]_t = 1.6 \times 10^{-3}$ and $[B18C6]_t = (0.080\text{-}2.4) \times 10^{-3}$; $[Sr(NO_3)_2]_t = 4.1 \times 10^{-4}$, $[HPic]_t = 8.2 \times 10^{-4}$ and $[B18C6]_t = (0.082\text{-}2.5) \times 10^{-3}$; $[Ba(NO_3)_2]_t = 3.5 \times 10^{-4}$, $[HPic]_t = 7.1 \times 10^{-4}$ and $[B18C6]_t = (0.032\text{-}2.0) \times 10^{-3}$. 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 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 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)* $A^- \rightleftharpoons A^-_o$, 3)* $M^{2+} \rightleftharpoons M^{2+}_o$, 4) $MLA^+_o + A^-_o \rightleftharpoons MLA_{2,o}$, 5) $ML^{2+} \rightleftharpoons ML^{2+}_o$, 6)* $L \rightleftharpoons L_o$, 7)* $M^{2+} + L \rightleftharpoons ML^{2+}$, 8)* $M^{2+}_o + L_o \rightleftharpoons ML^{2+}_o$, 9)* $H^+ + A^- \rightleftharpoons HA$ [4], 10)* $HA \rightleftharpoons HA_o$ [4], 11)* $HA_o \rightleftharpoons H^+_o + A^-_o$ [13], 12)* $H^+ \rightleftharpoons H^+_o$ [6], 13)* $X^- \rightleftharpoons X^-_o$ [11] and 14)* $H^+_o + X^-_o \rightleftharpoons HX_o$ [11], where the symbol HX shows a strong acid, such as HNO_3 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}, 2.1_8 for M = Sr and 2.0_8 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 $CaPic_2$-18C6 system, 0.91 and 11.1 (≈ log K_{ex}) for $SrPic_2$-18C6, 0.62 and 9.4 for $BaPic_2$-18C6, 0.38 and 5.9 for $CaPic_2$-B18C6, 0.65 and 8.5 for $SrPic_2$-B18C6 and 0.44 and 7.9 for $BaPic_2$-B18C6. Here, the distribution ratio $D_{expl.}$ is defined as $[\text{AAS-analyzed M(II)}]_{NB}/\{[M(NO_3)_2]_t - [\text{AAS-analyzed M(II)}]_{NB}\}$ and the intercept corresponds to the log K_{ex} value only when the slope is about unity [3-5]. Except for the $SrPic_2$-18C6 system, the compositions of M(II):L:Pic(−I) were assumed to be 1:1:2 in the determination of $K_{D,Pic}$, K_{ex} and $K_{ex\pm}$ [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 $BaPic_2$-18C6 extraction system based on Equations (5) and (5a), respectively, yielding the $K_{D,Pic}$, K_{ex} and $K_{ex\pm}$ values (Table 3). The less correlation coefficient (R) of the plot in Figure 2 may reflect the defect in the sub-analytical extraction model

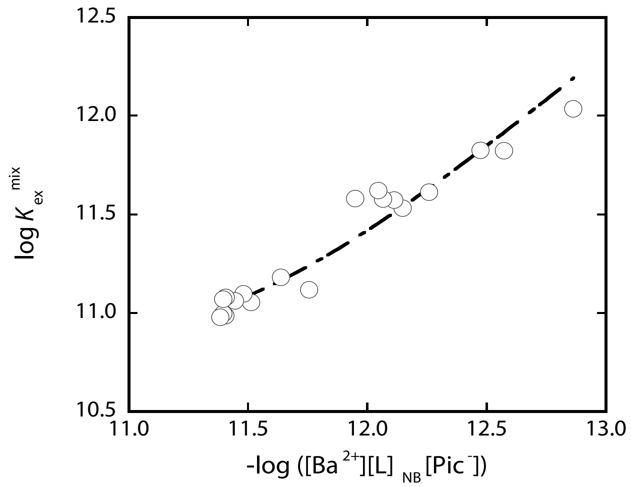

Figure 1: Plot of log K_{ex}^{mix} versus log ($[Ba^{2+}][L]_{NB}[Pic^{-}]$) for the extraction of $BaPic_2$ by L = 18C6 into NB. A broken line shows a regression one with R = 0.965 analyzed by Equation (5). Its analysis yielded $K_{D,Pic}$ = 0.20 ± 0.02 and K_{ex}/mol^{-3} dm^9 = ($5._6 \pm 1._0$) × 10^{10}.

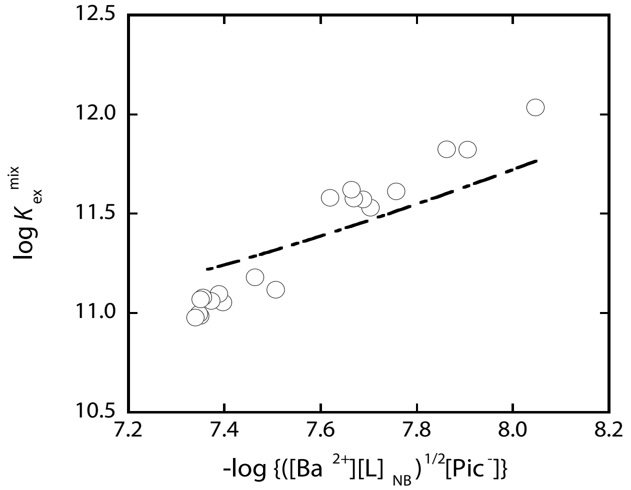

Figure 2: Plot of log K_{ex}^{mix} versus log $\{([Ba^{2+}][L]_{NB})^{1/2}[Pic^{-}]\}$ for the extraction of $BaPic_2$ by L = 18C6 into NB. A broken line shows a regression one with R = 0.850 analyzed by Equation (5a). Its analysis yielded $K_{ex\pm}$/mol^{-2} dm^6 = ($2.2_1 \pm 0.5_6$) × 10^7 at K_{ex}/mol^{-3} dm^9 fixed in 5.6 × 10^{10}.

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

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

where the distribution of $BaPic^+$ into the NB phase was neglected, because its data were not available. When $[H^+]_{NB} \approx [X^-]_{NB}$ holds, Equation (8) becomes $2[Ba^{2+}]_{NB} + 2[BaL^{2+}]_{NB} + [BaLPic^{+}]_{NB} \approx [Pic^{-}]_{NB}$. Rearranging this equation and adding $2[BaLPic_2]_{NB}$ in its both sides, we can immediately obtain

$$[Pic^{-}]_{NB} + 2[BaLPic_2]_{NB} = [Pic^{-}]_{NB,t}$$
$$\approx 2[Ba^{2+}]_{NB} + 2[BaL^{2+}]_{NB} + [BaLPic^{+}]_{NB} + 2[BaLPic_2]_{NB}. \quad (8a)$$

Hence, when the condition of $2[BaLPic_2]_{NB} > [BaLPic^+]_{NB}$ ($> 2[BaL^{2+}]_{NB} + 2[Ba^{2+}]_{NB}$) holds, the half of the left hand side of Equation (8a) approximately becomes $[Ba^{2+}]_{NB} + [BaL^{2+}]_{NB} + [BaLPic^{+}]_{NB} + [BaLPic_2]_{NB}$, namely $[Ba(II)]_{NB,t}$. We were able to determine spectrophotometrically the ($[Pic^-]_{NB} + 2[BaLPic_2]_{NB}$) value at least by the back extraction experiments.

Results and Discussion

Tendencies of $K_{D,Pic}$, K_{ex}, $K_{ex\pm}$ and $K_{n,NB}$ 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 $K_{ex\pm}$ were in the orders of Ca < Sr < Ba (Table 3). These tendencies are similar to those for log $K_{D,M}^{S}$ 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 $K_{ex\pm}$ 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 $K_{1,NB}$ values were Ca > Sr > 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 $K_{2,NB}$ 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 $MLPic^+$ 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 $K_{2,NB}$ 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 M = Ca > Sr < Ba for L = 18C6 and Ca > Sr ≥ Ba for B18C6 (Table 3). The highest I_{NB} values for the Ca(II) systems may cause the lowest $K_{2,NB}$ values. While their values were less effective for the $K_{1,NB}$ values, because $K_{1,NB}$ is constituted by the concentrations of all the ionic species.

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

$$ML^{2+}\cdot hH_2O_{NB} + Pic^{-}_{NB} \rightleftharpoons MLPic^{+}\cdot mH_2O_{NB} + pH_2O_{NB} \quad (9)$$

with $p = h - m$, then $K_{1,NB}$ can be expressed as $K_{1,NB}'/([H_2O]_{NB})^p$ with $K_{1,NB}' = [MLPic^+]_{NB}([H_2O]_{NB})^p/[ML^{2+}]_{NB}[Pic^-]_{NB}$ (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 $K_{1,NB}$ 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, $K_{1,NB} = K_{1,NB}'/([H_2O]_{NB})^p$, we can immediately obtain the equation, log $K_{1,NB}$ = log $K_{1,NB}' - p \times \log [H_2O]_{NB}$. Under the conditions of $[H_2O]_{NB}$ (= 0.178 mol dm^{-3} at 298 K [17,18]) < 1 and $p > 0$, the equation becomes log $K_{1,\mathrm{NB}}$ = log $K_{1,\mathrm{NB}}'$ + 0.750p. Therefore, the log $K_{1,\mathrm{NB}}$ 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 $M^+ + L_{\mathrm{NB}} + A^- \rightleftharpoons ML^+_{\mathrm{NB}} + A^-_{\mathrm{NB}}$ [8].

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

Using the relation of log $K_{\mathrm{D,A}} = -(\Delta\phi_{\mathrm{eq}} - \Delta\phi_{\mathrm{A}}{}^{0})/0.05916$ at 298 K (Table 1), we calculated the $\Delta\varphi_{\mathrm{eq}}$ values from the log $K_{\mathrm{D,Pic}}$ and $\Delta\phi_{\mathrm{Pic}}{}^{0\prime}$ones, where the $\Delta\phi_{\mathrm{Pic}}{}^{0\prime}$ value of 3.0 × 10^{-3} V [6] at the w/NB interface was employed. Thus obtained values are summarized in Table 4. The $\Delta\phi_{\mathrm{eq}}$ range for the 18C6 system was a little smaller than that for B18C6 one. From a comparison with the log $K_{\mathrm{ex}\pm}$ values in Table 3, the smaller the $\Delta\phi_{\mathrm{eq}}$ values are, the larger the log $K_{\mathrm{ex}\pm}$ 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 $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ and log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$ values

The $\Delta\phi_{\mathrm{ex}\pm}{}^{0\prime}$ values were evaluated from the $\Delta\phi_{\mathrm{eq}}$ and log $K_{\mathrm{ex}\pm}$ values (Tables 3&4) using log $K_{\mathrm{ex}\pm} = (\Delta\phi_{\mathrm{eq}} - \Delta\phi_{\mathrm{ex}\pm}{}^{0\prime})/0.05916$ listed in Table 1. After these evaluations, the log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ values were calculated from the same equation at the condition of $\Delta\phi_{\mathrm{eq}} = 0$ V. The same values were evaluated from $\Delta\phi_{\mathrm{ex}}{}^{0\prime} = 2\phi_{\mathrm{M}}{}^{0\prime} - 2\Delta\phi_{\mathrm{A}}{}^{0\prime} + 2\Delta\phi_{\mathrm{ML,org}}{}^{0\prime} + \Delta\phi_{1,\mathrm{org}}{}^{0\prime} + \Delta\phi_{\mathrm{eq}}$ in Table 2 and then log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}} = -\Delta\phi_{\mathrm{ex}\pm}{}^{0\prime}/0.05916$. Here, we calculated the $\Delta\phi_{\mathrm{M}}{}^{0\prime}$ values from log $K_{\mathrm{D,M}}{}^{\mathrm{S}} = -11.799$ for M = Ca, −11.562 for Sr and −10.818 for Ba [19] and similarly the $\Delta\phi_{\mathrm{ML,NB}}{}^{0\prime}$ values from log $K_{\mathrm{ML,NB}}$ = 11.2 for ML^{2+} = Ca(18C6)$^{2+}$, 13.1 for Sr(18C6)$^{2+}$, 13.4 for Ba(18C6)$^{2+}$, log $K_{\mathrm{ML,NB}}$ = 9.43 for Ca(B18C6)$^{2+}$, 11.1 for Sr(B18C6)$^{2+}$ and 11.6 for Ba(B18C6)$^{2+}$ [20]. Also, the $\Delta\phi_{1,\mathrm{NB}}{}^{0\prime}$ values were calculated from the relation of log $K_{1,\mathrm{NB}} = -\Delta\phi_{1,\mathrm{NB}}{}^{0\prime}/0.05916$ (Table 1) and the log $K_{1,\mathrm{NB}}$ values in Table 3. Similar evaluations were performed for the log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$ values using the relation among the potentials listed in Table 2.

As can be seen from Table 4, the log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ 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 BaPic$_2$-L systems may be due to the approximation of $[\mathrm{Ba(II)}]_{\mathrm{NB,t}} \approx [\mathrm{Pic}^-]_{\mathrm{NB,t}}$ (see Materials and Methods). On the other hand, the log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$ 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 $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$(calcd) = (1.54 ± 0.05)log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$(found) − (2.62 ± 0.07) at R = 0.998. Also, differences between the log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$(calcd) and log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$(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, $[ML^{2+}]_{\mathrm{NB}}$/[AAS-analyzed M(II)]$_{\mathrm{NB}}$, were in the ranges of 0.001$_2$-0.043% for M = Ca, 0.02$_4$-0.33 for Sr and 0.0$_5$-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 $K_{\mathrm{ex2}\pm}$ 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, $M^{2+} + L_{\mathrm{NB}} + 2\mathrm{Pic}^- \rightleftharpoons ML^{2+}{}_{\mathrm{NB}} + 2\mathrm{Pic}^-{}_{\mathrm{NB}}$. While the overall process, $M^{2+} + L_{\mathrm{NB}} + 2\mathrm{Pic}^- \rightleftharpoons \mathrm{MLPic}^+{}_{\mathrm{NB}} + \mathrm{Pic}^-{}_{\mathrm{NB}}$, 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 $K_{\mathrm{ex2}}{}^{\mathrm{S}}$ or not.

L	M	$\Delta\phi_{\mathrm{eq}}$/V^{a}	log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$		log $K_{\mathrm{ex2}\pm}{}^{\mathrm{S}}$	
			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

^{a}Essentially based on $\Delta\phi$/V versus $\mathrm{Ph_4As^+BPh_4^-}$ electrode. ^{b}Calculated from the relation of log $K_{\mathrm{ex}\pm} = f(\phi_{\mathrm{eq}} - \Delta\phi_{\mathrm{ex}\pm}{}^{0\prime})$ in Table 1. ^{c}Calculated from the relation of $\Delta\phi_{\mathrm{ex}\pm}{}^{0\prime} = 2(\Delta\phi_{\mathrm{M}}{}^{0\prime} - \Delta\phi_{\mathrm{A}}{}^{0\prime} + \Delta\phi_{\mathrm{ML,org}}{}^{0\prime}) + \Delta\phi_{1,\mathrm{org}}{}^{0\prime} + \Delta\phi_{\mathrm{eq}}$ in Table 2. ^{d}Calculated from the thermodynamic cycle, log $K_{\mathrm{ex2}\pm}$ = log $K_{\mathrm{D,M}}{}^{\mathrm{S}}$ + 2log $K_{\mathrm{D,Pic}}{}^{\mathrm{S}}$ + log $K_{\mathrm{ML,NB}}$. See ref. [8]. ^{e}Calculated from the relation of $\Delta\phi_{\mathrm{ex2}\pm}{}^{0\prime} = \Delta\phi_{\mathrm{M}}{}^{0\prime} - \Delta\phi_{\mathrm{A}}{}^{0\prime} + \Delta\phi_{\mathrm{ML,org}}{}^{0\prime} + \Delta\phi_{\mathrm{eq}}$ in Table 2

Table 4: $\Delta\varphi_{\mathrm{eq}}$ and the log $K_{\mathrm{ex}\pm}$ and log $K_{\mathrm{ex2}\pm}$ values at 298 K standardized by their potentials.

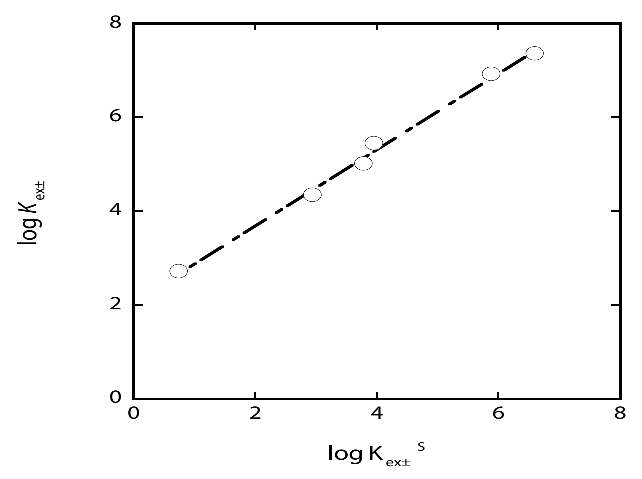

Figure 3: Plot of log $K_{\mathrm{ex}\pm}$ versus log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ for all the MPic$_2$-L extraction system. The regression analysis gave the straight line (- − -) of log $K_{\mathrm{ex}\pm}$ = 0.81 × log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ + 2.0$_7$ with R = 0.998. The label log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ on the abscissa is identical to log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$(found) in Table 4.

Figure 3 shows a plot of log $K_{\mathrm{ex}\pm}$ versus log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$(found) for all the MPic$_2$-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 $K_{\mathrm{ex}\pm}$ = (0.81 ± 0.03)log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$(found) + (2.0$_7$ ± 0.1$_3$) at R = 0.998. This fact indicates that the experimental log $K_{\mathrm{ex}\pm}$ values clearly reflect the log $K_{\mathrm{ex}\pm}{}^{\mathrm{S}}$ ones at $\Delta\phi_{\mathrm{eq}} = 0$. 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 $K_{\mathrm{ex2}\pm}$ values which are comparable to the above log $K_{\mathrm{ex}\pm}$ ones.

Accordance of Δφeq with the distribution of ML2+ into NB

The individual distribution constants ($K_{\mathrm{D,ML}}$) of ML^{2+} into the NB phase can be evaluated from the other thermodynamic cycle, $K_{\mathrm{ex}\pm} = K_{\mathrm{ML}}K_{\mathrm{D,ML}}K_{1,\mathrm{org}}(K_{\mathrm{D,A}})^2/K_{\mathrm{D,L}}$ (Table 2). Here, K_{ML} and $K_{\mathrm{D,L}}$ (Table 1) are defined as $[ML^{2+}]/[M^{2+}][L]$ and $[L]_o/[L]$ [15], respectively, and these values at 298 K were available from references; log K_{M18C6} = 0.48 for M = Ca, 2.72 for Sr and 3.87 for Ba [4]; log K_{MB18C6} = 0.48 for M = Ca, 2.41 for Sr and 2.90 for Ba [21,22]; log $K_{\mathrm{D,L}}$ = −1.00 [18] for L = 18C6 and 1.57 [20] for B18C6. Using the logarithmic form of the above equation, we obtained log $K_{\mathrm{D,M18C6}}$ = 0.8$_8$ for M = Ca, −0.1$_7$ for Sr and −0.9$_9$ for Ba and log $K_{\mathrm{D,MB18C6}}$ = 2.6$_2$ for M = Ca, 1.4$_4$ for Sr and 1.6$_1$ for Ba. There was a tendency that these values increase with an increase in the log $K_{\mathrm{D,ML}}{}^{\mathrm{S}}$ ones: log $K_{\mathrm{D,ML}}$ = (1.6$_1$ 0.5$_0$)log $K_{\mathrm{D,ML}}{}^{\mathrm{S}}$ + (3.6$_7$ ± 0.9$_2$) at R = 0.848. Here, the log $K_{\mathrm{D,ML}}$ values [20] determined in terms of ion-transfer

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polarography were employed as log $K_{D,ML}^{S}$. Also, the $\Delta\varphi_{eq}$ values can be easily evaluated from a modified form, log $K_{D,ML} = 2(\Delta\varphi_{eq}/0.05916)$ + log $K_{D,ML}^{S}$, of the relation in Table 1: $\Delta\phi_{eq} = 0.08_8$ V for the CaPic$_2$-18C6 system, 0.06_0 for SrPic$_2$-18C6, 0.04_7 for BaPic$_2$-18C6, 0.1_2 for CaPic$_2$-B18C6, 0.08_1 for SrPic$_2$-B18C6 and 0.07_1 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 $\Delta\phi_{ex\pm}^{0\prime}$ 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.

Acknowledgement

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Appendix

In practice, we have calculated the values of

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

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

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

Also, Equation (7) gave

$$\log K_{ex} - \log K_{ex\pm} = \log K_{ex}^{S} - \log K_{ex\pm} = \log K_{ex}^{S} - f(\Delta\phi_{eq} - \Delta\phi_{ex\pm}^{0\prime})$$

$$= \log K_{ex}^{S} - \log K_{ex\pm}^{S} - f\Delta\phi_{eq} \quad (A3)$$

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 4.7_3 and 5.0_7, 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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