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Determination of Some Component Equilibrium-Constants by Cd(II) Picrate Extraction with Benzo-18-crown-6 Ether into Various Diluents and their Evaluation

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Abstract

Using benzo-18-crown-6 ether (B18C6), extraction experiments of cadmium picrate ($CdPic_2$) into various diluents were performed at 298 K. Thereby, three kinds of extraction constants, $K_{Cd/CdL}$, $K_{ex\pm}$ and K_{ex}, four kinds of distribution constants, $K_{D,j}$ ($=[j]_{org}/[j]$), with j=Pic$^-$, CdLPic$_2$, CdLPic$^+$ and CdL^{2+} and two kinds of ion-pair formation constants, $K_{1,org}$ $\{=K_{ex\pm}/K_{Cd/CdL}(K_{D,Pic})^2\}$ and $K_{2,org}$ ($=K_{ex}/K_{ex\pm}$), for L=B18C6 were determined. Here, $K_{Cd/CdL}$, $K_{ex\pm}$ and K_{ex} were defined as $[CdL^{2+}]_{org}/[Cd^{2+}][L]_{org}$, $[CdLPic^+]_{org}[Pic^-]_{org}/P$ and $[CdLPic_2]_{org}/P$, respectively, with $P=[Cd^{2+}][L]_{org}[Pic^-]^2$ and the subscript "org" denotes an organic phase. Based on these equilibrium constants, distribution properties of the species j between the water (w) and org phases and reactivity of CdL^{2+} or CdLPic$^+$ in the org phases were compared. Additionally, some Pb^{2+} selectivity coefficients, $k^{pot}_{PbCd}(=K_{Cd/CdL}/K_{Pb/PbL})$, against Cd^{2+} with L=18-crown-6 ether at the nitrobenzene/w, 1,2-dichloroethane/w, o-dichlorobenzene/w and dichloromethane/w interfaces.

Keywords: Conditional distribution constants; Ion-pair formation constants in organic phases; Distribution equilibrium-potential differences; Extraction constants; Potentiometric selectivity coefficients; Cadmium picrate; Benzo-18-crown-6 ether

Introduction

Crown compounds (L), such as 18-crown-6 ether (18C6) and benzo-18C6 (B18C6), have extracted Cd^{2+} and Pb^{2+} (= M^{2+}) with Cl$^-$, Br$^-$ and picrate ion (Pic$^-$) into various diluents [1-6]. In such M^{2+} extraction systems with L, four component equilibrium-constants, $K_{D,A}$, $K_{D,MLA}$, $K_{D,MLA2}$ and $K_{2,org}$, have been determined so far [1-5]. Here, the symbols, $K_{D,A}$, $K_{D,MLA}$, $K_{D,MLA2}$ and $K_{2,org}$, refer to the conditional distribution constant ($=[A^-]_{org}/[A^-]$) of A$^-$ (=Cl$^-$, Br$^-$ and Pic$^-$), that ($=[MLA^+]_{org}/[MLA^+]$) of MLA$^+$ with the distribution equilibrium-potential difference (dep; $\Delta\varphi_{eq}$ as its symbol employed for equations), the distribution constant ($=[MLA_2]_{org}/[MLA_2]$) of MLA$_2$ with dep=0 V into an organic (org) phase or diluent and the ion-pair formation one $\{=[MLA_2]_{org}/[MLA^+]_{org}[A^-]_{org}$, see Eq. (4)$\}$ for MLA$_2$ in the org phase, respectively [1-5]. Recently, the approximate determination method for the 5th component equilibrium-constant, that is $K_{1,org}=[MLA^+]_{org}/[ML^{2+}]_{org}[A^-]_{org}$ {see Eq. (9)}, was developed [6,7]. So, these five-component equilibrium-constants let us expect an evaluation of general characteristics for the above overall extraction-systems.

In order to evaluate the possibility as the method studying such extraction systems, we examined the present extraction experiments of CdPic$_2$ with B18C6 by using various diluents, as which nitrobenzene (NB), 1,2-dichloroethane (DCE), o-dichlorobenzene (oDCBz), dichloromethane (DCM), chlorobutane (CBu), chlorobenzene (CBz), bromobenzene (BBz), chloroform (CF), dibutylether (DBE), toluene (TE) and m-xylene (mX) were used. These diluents were selected as the group of the high polarity, NB, that of the medium one, DCE to BBz, and that of the low one, CF to mX with benzene (Bz). In course of such evaluations, the $K_{1,org}$ values were determined more precisely than those [6] reported previously and also comparisons among the $K_{D,Pic}$, $K_{D,CdLPic2}$, $K_{D,CdLPic}$ and $K_{D,CdL}$ values were performed. In addition to the above evaluations, standard distribution constants ($K_{D,j}^{s}$) of

j=Pic$^-$, CdLPic$^+$ and CdL^{2+} into the NB, DCE, oDCBz and DCM phases under the condition of dep=0 V were calculated from their conditional distribution constants, $K_{D,j}$, with dep [6,7]. Besides, the regular-solution theory (RST) plot [3-6,8] based on the data of the $K_{D,L}$ and $K_{ex,ip}$ values was examined, where the symbols $K_{D,L}$ and $K_{ex,ip}$ denote a distribution constant ($=[L]_{org}/[L]$) of L between the water and org phases and an ion-pair extraction constant ($=[CdLPic_2]_{org}/[CdL^{2+}][Pic^-]^2$) for CdLPic$_2$ into the org phase, respectively [8]. Application to the estimation of the potentiometric selectivity coefficient for ISE [9,10] based on $K_{M/ML}$ $[=ML^{2+}]_{org}/[M^{2+}][L]_{org}$, see Eq. (8)} was tried by using 18C6 as L.

Results and Discussion

Determination of the Cd(II):L composition of extracted species

In the present systems, slopes of the plots of log (D/[Pic$^-$]^2) *versus* log [L]$_{org}$ give compositions of Cd(II):L for species extracted into the various diluents [1-7]. Here, the symbol D refers to an experimental distribution ratio {see Eq. (5)}. Figure 1 shows some examples for such plots. The obtained slope values were 0.92 for the NB system, 1.0_6 for DCE, 1.0_0 for oDCBz (Figure 1), 0.93 for DCM, 0.99_8 for CBu (Figure 1), 0.95 for CBz (Figure 1), 0.96 for BBz (Figure 1), 1.0_4 for CF, 0.08 for DBE (Figure 1), 1.0_2 for TE (Figure 1) and 0.99 for mX. Except for the DBE system, we concluded the compositions of the mainly extracted species

to be Cd(II):L=1:1 on the basis of these values which are about unity. Also, the compositions of Cd(II):Pic($-$I)=1:2 for the extracted species were speculated by considering the principle of electroneutrality in the org phases [3-7].

The slope being less than unity in the experimental $[B18C6]_{DBE}$ range suggested the dissociation [3-7] of $Cd(B18C6)Pic_2$ or $Cd(B18C6)Pic^+$ in the DBE phases. So, the following analyses of this system were performed by essentially assuming the extraction of the species composed of Cd(II):B18C6:Pic($-$I)=1:1:2 into the DBE phase.

Determination of K_{ex}, $K_{ex\pm}$, $K_{D,Pic}$, $K_{2,org}$, $K_{Cd/CdL}$ and $K_{1,org}$

For the determination of $K_{D,Pic}$, K_{ex} and $K_{ex\pm}$, the extraction constant parameter (K_{ex}^{mix}) has been used [3-7].

$$\log K_{ex}^{mix}=\log ([CdLPic_2]_{org}+[CdLPic^+]_{org}+[CdL^{2+}]_{org}+...)/P \quad (1)$$

Here, assuming $[CdLPic_2]_{org}+[CdLPic^+]_{org} \gg [CdL^{2+}]_{org}+...$, this equation changes into

$$\log K_{ex}^{mix} \approx \log \{K_{ex}+(K_{D,Pic}/[Cd^{2+}][L]_{org}[Pic^-])\} \quad (2)$$

with $[CdLPic^+]_{org}/[Pic^-] \approx K_{D,Pic}$ at the approximation $[Pic^-]_{org} \approx [CdLPic^+]_{org}$ ($\gg 2[CdL^{2+}]_{org}+2[Cd^{2+}]_{org}+...$) on the charge balance equation, $[Pic^-]_{org}=2[Cd^{2+}]_{org}+2[CdL^{2+}]_{org}+[CdLPic^+]_{org}+[CdPic^+]_{org}$ for the org phase. Also, the following equation has been derived [3-7].

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

Hence, Eq. (2) gives $K_{D,Pic}$ and K_{ex} from the plot of log K_{ex}^{mix} *versus* $-\log ([Cd^{2+}][L]_{org}[Pic^-])$ and Eq. (3) does $K_{ex\pm}$ and K_{ex} from that of log K_{ex}^{mix} *versus* $-\log P^{1/2}$ [3-7]. Examples of these plots are shown in Figures 2 and 3. A regression line was log $K_{ex}^{mix}=\log [(1.7_1 \pm 0.2_1) \times 10^3+\{(1.0_9 \pm 0.2_5) \times 10^{-5}/[Cd^{2+}][L]_{mX}[Pic^-]\}]$ at the square of correlation coefficient (R)=0.521 in Figure 2, while a line was log $K_{ex}^{mix}=\log [(6._5 \pm 4._2) \times 10^2+\{(1.1_5 \pm 0.5_1) \times 10^{-3}/P\}^{1/2}]$ at R^2=0.520 in Figure 3. In this mX system, the analyses of both Eqs. (2) and (3) yielded somewhat different K_{ex} values over the experimental errors. Similar results were obtained for the other ten diluent systems. As log K_{ex} values, the analyses based on Eq. (3) gave 4.48 ± 0.03 for the NB system, $2.4_5 \pm 0.1_0$ for DCE, $2.4_8 \pm 0.1_5$ for oDCBz, 2.26 ± 0.08 for DCM, 3.05 ± 0.04 for CBz, 2.54 ± 0.09 for BBz and $2.8_2 \pm 0.2_8$ for mX (Figure 3).

The ($K_{2,org}$/mol^{-1} dm^3) values for given ionic-strength ones (I_{org}/mol dm^{-3}) of the org phases were calculated from the relation.

$$K_{2,org}=K_{ex}/K_{ex\pm} \quad (4)$$

Here, I_{org} was derived approximately to be $[Pic^-]_{org}$ $\{=(1/2)(4[Cd^{2+}]_{org}+4[CdL^{2+}]_{org}+[CdLPic^+]_{org}+[CdPic^+]_{org}+[Pic^-]_{org})=(1/2)(2[Cd^{2+}]_{org}+2[CdL^{2+}]_{org}+2[Pic^-]_{org})=[Cd^{2+}]_{org}+[CdL^{2+}]_{org}+[Pic^-]_{org}\}$ from the charge balance equation for the org phase (see above) under the condition of $[Pic^-]_{org} \gg$ (obviously $2[CdL^{2+}]_{org} >$) $[Cd^{2+}]_{org}+[CdL^+]_{org}$ {see the derivation of Eq. (2)}. The four basic constants determined above are listed as common logarithmic values in Table 1.

According to our previous papers [6,7], moreover, $K_{Cd/CdL}$ has been defined as $[CdL^{2+}]_{org}/[Cd^{2+}][L]_{org}$ (see Introduction) and the first-approximately equals $D/[L]_{org}$. Of course, this constant can be reflected to be the 3rd extraction constant [6,7], $K_{ex2\pm}=[CdL^{2+}]_{org}([Pic^-]_{org})^2/P=K_{Cd/CdL}(K_{D,Pic})^2$. Here, the experimental distribution ratio D is exactly expressed as:

$$D=[CdL^{2+}]_{org} \{1+([CdLPic^+]_{org}+[CdLPic_2]_{org}+[CdPic^+]_{org}+...)/[CdL^{2+}]_{org}\}/[Cd^{2+}]\{1+([CdL^{2+}]+[CdLPic^+]+[CdLPic_2]+[CdPic^+]+...)/[Cd^{2+}]\}=f \times [CdL^{2+}]_{org}/[Cd^{2+}] \quad (5)$$
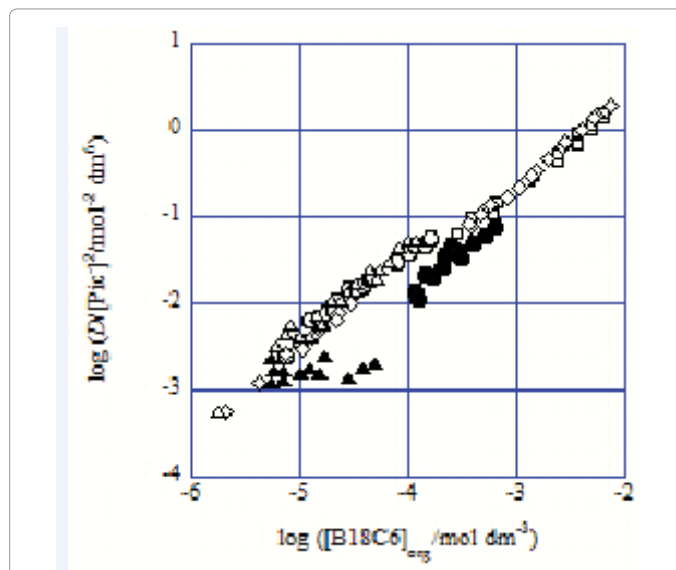

Figure 1: Plots of log (D/[Pic$^-$]^2) *vs.* log [B18C6]$_{org}$ for the CdPic$_2$ extraction with B18C6 into some diluents. Org=oDCBz (square), CBu (full circle), CBz (circle), BBz (diamond), DBE (full triangle) and TE (triangle).
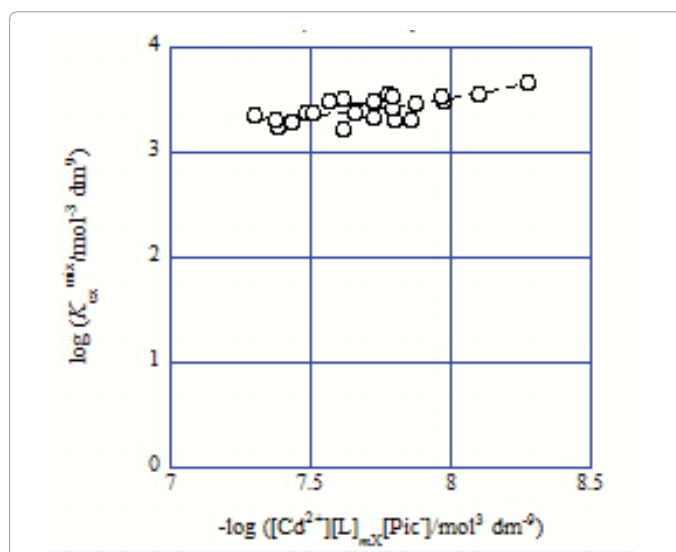

Figure 2: Plot of log K_{ex}^{mix} *vs.* -log ([Cd^{2+}][L]$_{mX}$[Pic$^-$]) for the mX extraction system with L=B18C6.

Rearranging this f term, we can easily obtain

$$f=\{1+K_{1,org}K_{D,Pic}[Pic^-](1+K_{2,org}K_{D,Pic}[Pic^-])+(K_{ex,CdPic}K_{D,L}/K_{D,CdL}K_{CdL})([Pic^-]/[L]_{org})+...\}/$$

$$[1+[Pic^-]\{(K_{CdL}/K_{D,L})[L]_{org}(K_1+K_1K_2[Pic^-])+K_{CdPic}\}+...] \quad (6)$$

with $K_{ex,CdPic}=[CdPic^+]_{org}/[Cd^{2+}][Pic^-]$ and $K_{CdL}/K_{D,L}=[CdL^{2+}]/[Cd^{2+}][L]_{org}$. Then, this equation was approximately expressed as:

$$f \approx \{1+K_{1,org}K_{D,Pic}[Pic^-](1+K_{2,org}K_{D,Pic}[Pic^-])\}/[1+[Pic^-]\{(K_{CdL}/K_{D,L})[L]_{org}(K_1+K_1K_2[Pic^-])+K_{CdPic}\}], \quad (7)$$

because of a lack of the $K_{ex,CdPic}$ value. For the symbols, K_{CdL}, $K_{D,CdL}$, K_1 and K_2, see Eq. (12) to (15). The f values for all the systems were

evaluated. The average values of the evaluated f were in the range of 1.2 to 2.6 for the present diluent systems and the the $K_{Cd/CdL}$ values were corrected with the f terms.

$$K_{Cd/CdL} \approx D/f[L]_{org}. \tag{8}$$

So, this equation becomes the second approximation. In the f calculation with Eq. (7), we assumed that $K_{2,org}$ is independent of I_{org}, while we calculated K_1, K_2 and K_{CdPic} as functions of I (see below). Also, $K_{D,Pic}$ and $K_{D,CdL}$ terms were used as constant values which consist of their averaged values in the f calculation. Besides, we can calculate easily $K_{1,org}$ from the thermodynamic relation of

$$K_{1,org} = K_{ex\pm}/K_{Cd/CdL}(K_{D,Pic})^2 = K_{ex\pm}/K_{ex2\pm} \text{ [11]} \tag{9}$$

These $K_{Cd/CdL}$ and $K_{1,org}$ values are summarized in Table 1, as well as the above four constants.

On amounts of dominant species distributed into org phases

Considering differences among the extraction constants, K_{ex}, $K_{ex\pm}$ and $K_{Cd/CdL}$, we can compare distribution (or population) of $CdLPic_2^0$, $CdLPic^+$ and CdL^{2+} in the org phases [6,7]. The D_0, D_+ and D_{2+} values can be calculated from the following equations:

$$D_0 = [CdLPic_2^0]_{org}/[Cd^{2+}] = K_{ex}[L]_{org}[Pic^-]^2 \tag{2a}$$

$$D_+ = [CdLPic^+]_{org}/[Cd^{2+}] = (K_{ex\pm}/K_{D,Pic})[L]_{org}[Pic^-] \tag{3a}$$

and

$$D_{2+} = [CdL^{2+}]_{org}/[Cd^{2+}] = K_{Cd/CdL}[L]_{org}. \tag{8a}$$

Figure 4 shows the representative example of the log D_0, log D_+ and log D_{2+} plots against log $[B18C6]_{CF}$ for the CF (=org) extraction system. Obviously, the distribution or population profiles were in the order $[CdLPic_2^0]_{CF} > [CdLPic^+]_{CF} \geq [CdL^{2+}]_{CF}$ at L=B18C6. Similar profiles were obtained for the other ten diluent systems. Their profiles were +>0>2+ for the NB system, $0 \geq 2+ = + = +$ for DCE, +≥ 0>2+ for oDCBz, 0 >+> 2+ for DCM, +≥ 0 ≥ 2+ for CBu, 0>+>2+ for CBz, +>0>2+ for BBz, +>2+≥0 for DBE, 0>2+ >+for TE and +>0>2+ for mX. Here, the symbols 0, + and 2+ denote the concentrations at equilibrium of the extracted species $CdLPic_2^0$, $CdLPic^+$ and CdL^{2+}, respectively. There is no diluent system that CdL^{2+} is most extractable. These profiles can be classified to two cases that $CdLPic_2^0$ is most extractable, while $CdLPic^+$ is most extractable. The DCE, DCM, CBz, CF and TE systems belong to the former cases and the NB, oDCBz, CBu, BBz, DBE and mX systems do to the latter ones. Except for TE, the former diluents contain the Cl group in their molecules. On the other hand, the diluent molecules without the Cl group are major in the latter [8-11].

Comparison of distribution properties of the complexes

The three distribution constants, $K_{D,MLA2}$, $K_{D,MLA}$ and $K_{D,ML}$, for the complexes can be calculated from the following thermodynamic cycles:

$$K_{D,MLA2} = [MLA_2^0]_{org}/[MLA_2^0] = K_{ex}K_{D,L}/K_{ML}K_1K_2, \tag{10}$$

$$K_{D,MLA} = [MLA^+]_{org}/[MLA^+] = K_{ex\pm}K_{D,L}/K_{ML}K_1K_{D,A} \tag{11}$$

and

$$K_{D,ML} = [ML^{2+}]_{org}/[ML^{2+}] = K_{M/ML}K_{D,L}/K_{ML} \tag{12}$$

with

$$K_{ML} = [ML^{2+}]/[M^{2+}][L] \tag{13}$$

$$K_1 = [MLA^+]/[ML^{2+}][A^-] \tag{14}$$

and

$$K_2 = [MLA_2]/[MLA^+][A^-] \tag{15}$$

Here, the two distribution constants, $K_{D,MLA}$ and $K_{D,ML}$, are the conditional equilibrium constants with dep and the evaluations of K_1 and K_2 were performed from the I-dependence of the K_1^0 and K_2^0 values [2] (the values at $I \to 0$ mol dm^{-3}), respectively. Thus calculated constants are listed in Table 2, with log $K_{D,Pic}$.

Figure 5 shows a general tendency for their distribution properties. The log $K_{D,Pic}$ values were smallest of these log K_{Dj} values. There was the order of $K_{D,CdLPic2} < K_{D,CdLPic} < K_{D,CdL}$, except for the TE system (No. 10 in Figure 5). For meanings of the order, the attention should be needed, because its order does not necessarily reflect amounts of the species extracted into the org phase (Figure 4).

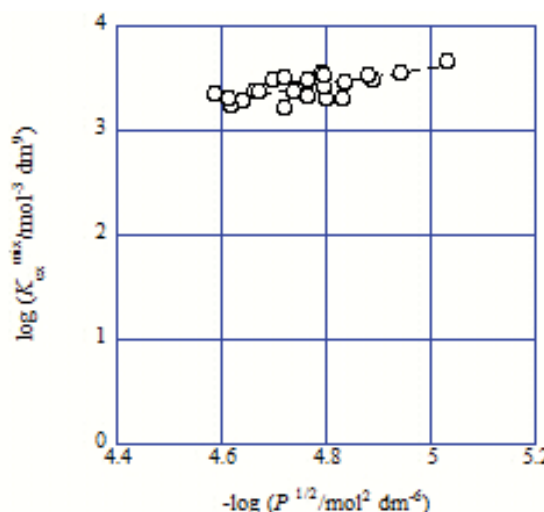The log $K_{D,CdL}$ values were positive for the NB (No. 1), DCE (2),

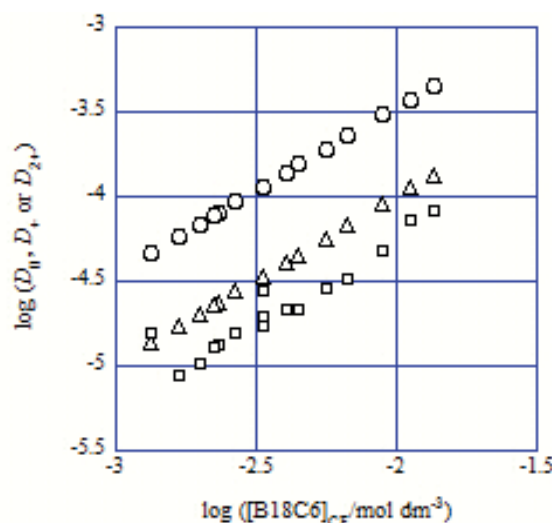**Figure 3:** Plot of log K_{ex}^{mix} vs. $-$log $P^{1/2}$ for the mX extraction system with L=B18C6.

Figure 4: Relative concentration profiles of $CdPic_2^0$ (circle and D_0), $CdLPic^+$ (triangle & D_+) and CdL^{2+} (square and D_{2+}) for the CF extraction with L=B18C6.

No. Diluent[a]	log K_{ex}[b]	log $K_{ex\pm}$[c]	log $K_{Cd/CdL}$[d]	log $K_{D,Pic}$[b] (I[e])	log $K_{1,org}$[f] (I_{org}[e]/10^{-7})	log $K_{2,org}$[g]
1. NB	4.622 ± 0.008	0.18 ± 0.07	0.63 ± 0.08	-2.88 ± 0.02 (0.02_8)	$5.3_0 ± 0.1_1$ ($2._9 × 10^2$)	4.44 ± 0.07
2. DCE	2.47 ± 0.07	$-4.5_5 ± 0.7_0$	$-1.5_2 ± 0.1_5$	$-4.7_0 ± 0.2_9$ (0.02_2)	$6.3_5 ± 0.8_2$ ($3._3$)	$7.0_3 ± 0.7_0$
3. oDCBz	2.61 ± 0.05	$-4.0_1 ± 0.4_4$	-1.31 ± 0.09	$-5.0_7 ± 0.2_1$ (0.02_9)	$7.4_3 ± 0.5_4$ ($2._0$)	$6.6_3 ± 0.4_5$
4. DCM	2.33 ± 0.04	$-4.1_6 ± 0.3_7$	$-1.4_8 ± 0.1_1$	$-4.7_4 ± 0.1_6$ (0.03_1)	$6.8_2 ± 0.4_5$ ($4._3$)	$6.4_9 ± 0.3_8$
5. CBu	2.50 ± 0.08	$-4.1_9 ± 0.1_7$	$-0.8_7 ± 0.3_3$	$-5.1_8 ± 0.1_0$ (0.03_3)	$7.0_3 ± 0.5_5$ ($1._8$)	$6.6_8 ± 0.1_8$
6. CBz	3.11 ± 0.02	$-4.0_0 ± 0.2_4$	-0.21 ± 0.06	$-5.5_2 ± 0.1_2$ (0.05_9)	$7.2_6 ± 0.3_0$ ($1._5$)	$7.1_0 ± 0.2_4$
7. BBz	2.76 ± 0.03	$-3.8_4 ± 0.1_5$	$-0.8_7 ± 0.2_6$	-5.53 ± 0.08 (0.04_3)	$8.1_0 ± 0.3_2$ ($1._0$)	$6.6_0 ± 0.1_5$
8. CF	1.78 ± 0.05	$-5.7_1 ± 0.7_3$	$-2.2_2 ± 0.1_2$	$-5.3_4 ± 0.3_0$ (0.03_1)	$7.1_9 ± 0.8_5$ ($1._1$)	$7.4_9 ± 0.7_4$
9. DBE	$2.0_5 ± 0.4_6$	$-5.0_3 ± 0.1_0$	$-0.9_2 ± 0.1_7$	$-6.1_4 ± 0.1_2$ (0.03_4)	$8.1_7 ± 0.2_6$ (0.2_0)	$7.0_8 ± 0.4_7$
Bz[h]	2.36, 2.3_7	---[i]	---[i]	---[i] (0.095)	---[i] (---[i])	---[i]
10. TE	3.23 ± 0.03	$-6._5 ± 2._4$	-0.04 ± 0.07	$-6._6 ± 1._5$ (0.05_9)	$6._7 ± 3._2$ (0.1_3)	$9._7 ± 2._4$
11. mX	3.23 ± 0.05	$-2.9_4 ± 0.1_9$	$-0.6_8 ± 0.1_2$	$-4.9_6 ± 0.1_0$ (0.02_9)	$7.6_6 ± 0.2_7$ ($2._5$)	$6.1_7 ± 0.2_0$

Table 1: Fundamental data of CdPic$_2$ extraction with B18C6 into various diluents at 298 K.

[a]Polarity of the diluents decreases in going from No. 1 to 11, where especially Nos. 10 and 11 with Bz show almost the same values. [b]Obtained from Eq. (2). $K_{D,Pic}$ is a conditional distribution constant with dep. [c]From Eq. (3). [d]From Eq. (8). This is the conditional constant with dep. [e]Unit: mol dm^{-3}. [f]Obtained from Eq. (9). [g]From Eq. (4). [h]See [3]. [i]Not determined.

DCM (4), CBz (6), BBz (7), CF (8) and TE (10) systems, indicating that interactions of CdB18C6^{2+} with the diluent molecules are larger than those with water molecules. Interestingly, the order, $K_{D,Pic} < K_{CdLPic2} < K_{D,CdLPic} < K_{D,CdL}$, holds except for the TE system (No. 10), being dependent on the formal charges (−1, 0, +1 and +2) of their species.

On the standardized distribution constants of the complex ions

Generally the dep value is related to the conditional distribution constant $K_{D,j}$ of an ion (j) as follows [6,7]:

$$\log K_{D,j} = (z_j F/2.303RT)(\Delta\varphi_{eq} - \Delta\varphi_j^{0\prime}) = 16.90z_j(\Delta\varphi_{eq} - \Delta\varphi_j^{0\prime}), \qquad (16)$$

where the symbols z_j and $\Delta\varphi_j^{0\prime}$ denote the formal charge of the ion j with its sign and the standard formal potential (V unit) for the j-ion transfer across the org/water (w) interface, respectively. Also, the following relation with the standard distribution constant $K_{D,j}^S$ holds: $\log K_{D,j}^S = -z_j F\Delta\varphi_j^{0\prime}/2.303RT = -16.90z_j\Delta\varphi_j^{0\prime}$ at $\Delta\varphi_{eq} = 0$ V (& 298 K) [4]. The $\log K_{D,Pic}^S$ values have been reported to be 0.05 [12] for the NB/w system, -1.01_1 [12] for DCE/w, -2.278 [13] for oDCBz/w and -0.68 [14] for DCM/w at 298 K. From these values, we were immediately able to calculate the φ_{eq} values (Table 2) using the modified form of Eq. (16) or the Nernst-Donnan equation [15]:

$$\Delta\varphi_{eq} = (2.303RT/z_jF)(\log K_{D,j} - \log K_{D,j}^S) = (0.05916/z_j)(\log K_{D,j} - \log K_{D,j}^S) \qquad (16a)$$

at 298 K.

Similarly, the $\log K_{D,CdLPic}^S$ and $\log K_{D,CdL}^S$ values were calculated from the experimentally-obtained $\log K_{D,j}$ (j=CdLPic$^+$ & CdL^{2+}) and $\Delta\varphi_{eq}$ values. As can be seen from Table 2, the actual (or conditional) $K_{D,CdLPic}$ and $K_{D,CdL}$ orders were NB>DCM>oDCBz>DCE and NB>DCM>DCE>oDCBz, respectively. On the other hand, the calculated $\log K_D^S$ orders were NB>oDCBz>DCM>DCE for j=CdLPic$^+$ and NB>oDCBz>DCE>DCM for CdL^{2+} (Table 2). These orders indicate those standardized at dep=0 V, namely, the orders that the dep effects on $\log K_{D,j}$ was lost. So, this fact shows that the occurrences of dep based on the extraction systems affect the more negative effects on CdLPic$^+$ and CdL^{2+} in interactions with oDCBz molecules than in those with the other molecules at the present time. On the other hand, DCM molecules have positive effects.

Comparison of $K_{1,org}$ with $K_{2,org}$

There was the relation of $K_{1,org} > K_{2,org}$ for the NB, oDCBz, DCM, CBu, CBz, BBz, DBE and mX systems. The authors think that this is a formal case [6,16]. On the other hand, the relation, $K_{1,org} \leq K_{2,org}$, holds for the other three diluent systems. This relation suggests a structural chance around Cd(II) in the reaction of Cd(B18C6)Pic$^+_{org}$+Pic$^-_{org} \rightleftharpoons$ Cd(B18C6)Pic$_{2,org}$. Relevantly, it has been reported that the crystals of Cd(B18C6)X$_2$ at X=Cl(−I) and Br(−I) have a hexagonal bipyramidal structure [17] {although these examples are not ones in solution and of X=Pic(−I)}.

The $\log K_{1,org}$ values were in the order org=NB ($\log K_{1,org}$=5.3)<DCE (6.4) $\leq$ TE $\leq$ DCM $\leq$ CBu (7.0) $\leq$ CF $\leq$ CBz $\leq$ oDCBz $\leq$ mX $\leq$ BBz (8.1) $\leq$ DBE (Table 1). Also, the $\log K_{2,org}$ values were in the order NB ($\log K_{2,org}$=4.44)<mX (6.2) $\leq$ DCM $\leq$ BBz $\leq$ oDCBz $\leq$ CBu $\leq$ DCE (7.0) $\leq$ DBE $\leq$ CBz $\leq$ CF $\leq$ TE ($9._7$) (Table 1). The NB and DCM systems were relatively in the lower range, while the CBz, CF and DBE ones in the higher range. The orders were independent of polarities of the diluents (see the footnote a described in Table 1).

RST plot for the CdPic$_2$-B18C6 system

The RST plot can be obtained from the data (Table 2) of $\log K_{ex,ip}$ (or $\log K_{D,CdLPic2}$) and $\log K_{D,B18C6}$, where the $\log K_{ex,ip}$ values were calculated

No. diluent	log $K_{D,Pic}$ [a] (dep[b]/V)	log $K_{D,CdLPic2}$ [c]	log $K_{D,CdLPic}$ [d,e] [ ][f]	log $K_{D,CdL}$ [e,g] [ ][h]	log $K_{D,L}$ [i]	log $K_{ex,ip}$ [j]
1. NB	-2.88 (0.17)	-0.88$_2$	-0.05 [-2.98]	2.09 [-3.76]	1.57[k]	6.08$_2$
2. DCE	-4.7$_0$ (0.2$_2$)	-2.64	-2.5$_6$ [-6.2$_5$]	0.3$_8$ [-6.9$_9$]	2.009	4.37
3. oDCBz	-5.0$_7$ (0.1$_7$)	-3.22	-2.3$_9$ [-5.1$_9$]	-0.19 [-5.78]	1.225	3.73
4. DCM	-4.7$_4$ (0.2$_4$)	-2.21	-1.5$_6$ [-5.6$_3$]	0.9$_3$ [-7.2$_0$]	2.52	4.74
5. CBu	-5.1$_8$	-4.18	-3.3$_0$	-0.6$_1$	0.37	2.76
6. CBz	-5.5$_2$	-2.69	-1.9$_2$	0.84	1.155	4.15
7. BBz	-5.53	-3.12	-1.8$_2$	0.1$_5$	1.130	3.78
8. CF	-5.3$_4$	-2.71	-2.4$_7$	0.2$_4$	2.57	4.24
9. DBE	-6.1$_4$	-5.6$_8$	-4.2$_3$	-1.7$_1$	-0.68	1.2$_6$
Bz[l]	---[m]	-3.56	---[m]	---[m]	0.943	3.19
10. TE	-6.$_6$	-3.08	-3.$_9$	0.49	0.64	3.76
11. mX	-4.9$_6$	-3.53	-2.3$_5$	-0.4$_9$	0.30	3.43

Table 2: Data derived from the distribution of some species into the various diluents at 298 K.

[a]See Table 1. [b]Calculated from Eq. (16a). [c]From Eq. (10). [d]From Eq. (11). [e]This is the conditional constant with dep. [f]Log $K_{D,CdLPic}$ ^{S} value. [g]From Eq. (12). [h]Log $K_{D,CdL}$ ^{S} value. [i]See [8]. [j]Calculated from log $K_{ex,ip}$=log K_{ex}-log ($K_{D,L}/K_{CdL}$) with $K_{CdB18C6}$=10$^{0.11}$ mol^{-1} dm^3 in water at 298 K [1]. See [18]. [k]See [23]. [l]See [1,2]. [m]Not determined

from the thermodynamic relation [1,18] of log $K_{ex,ip}$=log K_{ex}+log ($K_{D,L}/K_{CdL}$). The data set, reported before [2], of the Bz system was added in the plot (Table 2). Figure 6 shows its plot for the CdPic$_2$-B18C6 extraction system. The regression analysis of the plot gave the straight line of log $K_{ex,ip}$=(0.9$_9$ ± 0.1$_6$)log $K_{D,B18C6}$+(2.5$_6$ ± 0.2$_1$) at R^2=0.825. In this equation, the slope means a molar volume ratio ($V_{CdLPic2}/V_L$) of CdLPic$_2$ against L [3-6,8]. The points of the NB and CF extraction systems in Figure 6 were neglected from the calculation of the regression line, because of its high polarity [6] and its hydrogen-bonding ability [6,8], respectively. From the data [18] of V_{B18C6}=252 ± 28 cm^3 mol^{-1}, we were able to calculate to be $V_{CdLPic2}$=249 ± 49 at L=B18C6. The V_j values were in the order j=Cd(18C6)Pic$_2$ (about 200 cm^3 mol^{-1} [4]) ≤ 18C6 (214 [8]) ≤ Cd(B18C6)Pic$_2$ ≤ B18C6. At least, the V_j relation, Cd(18C6) Pic$_2$ ≤ Cd(B18C6)Pic$_2$, seems to be reasonable, as well as 18C6 ≤ B18C6.

On the other hand, the intercept generally means the term expressing solute-solvent interactions with the ion-pair formation in the w phase [6,8]: that is, (intercept)=(solute-solvent interaction term)+log K_1K_2. The common logarithmic values of the averaged K_1K_2 were in the range of 6.84-7.01. Obtaining K_1K_2=10$^{6.93}$ mol^{-2} dm^6 as average K_1K_2 value, we estimated −4.4 as the interaction term from the intercept. This negative sign indicates that the interaction between water molecules and Cd(B18C6)Pic$_2$ is larger than that between those and B18C6, assuming that there are little differences between B18C6 and Cd(B18C6)Pic$_2$ in the interaction with the diluent molecules employed [6]. This result is in good agreement with that in the log $K_{D,CdLPic2}$ values of which all are smaller than zero (namely $K_{D,CdLPic2}$<1, Table 2 and Figure 5).

Possibility for estimation of potentiometric selectivity coefficients

According to previous papers [9,10], a potentiometric selectivity coefficient of M^{z+} against M'$^{z+}$ at an org/w interface for ISE had been expressed as:

$$\log k^{pot}_{MM'}=\log K_{M'/M'L} - \log K_{M/ML} \quad (17)$$

where M'$^{z+}$ shows an interfering cation in a test solution. From the extraction data [3-5] of the MPic$_2$-18C6 systems with M=Cd(II) and Pb(II) reported by us and Eq. (8) without the f correction, we can immediately calculate the log $K_{Cd/Cd18C6}$ and log $K_{Pb/Pb18C6}$ values.

The log $K_{Cd/Cd18C6}$ values were calculated here to be 2.95 for the NB/w extraction system, −0.1$_3$ for DCE/w, −0.2$_5$ for oDCBz/w and −0.6$_8$ for DCM/w [6], while the log $K_{Pb/Pb18C6}$ values were 6.6$_0$ ± 0.1$_7$ for NB/w, 4.92 ± 0.06 for DCE/w, 6.309 ± 0.009 for oDCBz/w and 4.74 ± 0.05 for DCM/w. Therefore, the log k^{pot}_{PbCd} values based on 18C6 were obtained to be −3.7 for the NB/w interface, −5.1 for DCE/w, −6.6 for oDCBz/w and −5.4 for DCM/w. The oDCBz/w interface shows the highest Pb^{2+} selectivity of the four diluent/w interfaces. Similarly, if the $K_{Pb/PbB18C6}$ values are determined, then one can easily estimate the k^{pot}_{PbCd} values based on L=B18C6.

On the other hand, the logarithmic ratios of $K_{ex,Cd}/K_{ex,Pb}$ with L=18C6 were calculated to be −7.5 for the NB system, −7.3 for DCE and −8.5 for oDCBz based on the data [3-5] reported before and its selectivity order is oDCBz >> NB>DCE. Similarly the log ($K_{ex,Cd}/K_{ex,Pb}$) were −7.72 for NB (calculated here from the data [4,5]), −8.08 for DCE, −8.03 for oDCBz and −8.4 for DCM [5] and its order is DCM>DCE>oDCBz>NB. These both orders are not accord with the k^{pot}_{PbCd} order, oDCBz >> DCM>DCE >> NB (see above for the evaluated values). This fact indicates that the k^{pot}_{PbCd} values are not simply predicted by the ratios of the experimental $K_{ex±}$ or K_{ex} values without dep. So, this emphasizes the effect of the conditional $K_{M/ML}$ value on the estimation of $k^{pot}_{MM'}$ for ISE, because the relation, log $K_{M/ML}$=log $K_{D,M}$+log $K_{ML,org}$=(2F/2.303RT)($\Delta\varphi_{eq}-\Delta\varphi_M^{0'}$)+log $K_{ML,org}$, is derived from Eq. (16). In other words, $K_{M/ML}$ or $K_{M'/M'L}$ is the function of dep [6,7].

Experimental

Materials and reagents

Preparation procedures of CdPic$_2$·xH$_2$O, B18C6 and the 11 diluents were the same as those reported before [3].

Extraction experiments

Operational procedures and analytical methods of the Cd(II) species extracted into the org phases were the same as those reported before [2-4,6]. Experimental initial concentrations were [Cd(II)]$_0$=0.015 mol dm^{-3}, [Pic(−I)]$_0$=0.031 mol dm^{-3} and [B18C6]$_0$=0.00070-0.0074 mol dm^{-3} for the NB system, 0.0053 and 0.012, 0.011 & 0.024 and 0.0017-0.013 for DCE, 0.017, 0.034 and 0.00077-0.0051 for oDCBz, 0.017, 0.034 and 0.00077-0.015 for DCM, 0.020, 0.041 and 0.043 and 0.00074-
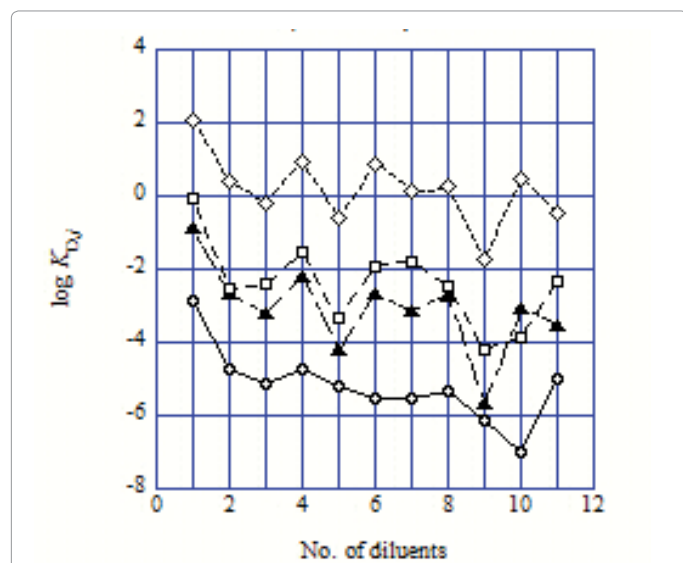
Figure 5: Comparison among the log $K_{D,Pic}$ (circle), log $K_{D,CdLPic2}$ (full triangle), log $K_{D,CdLPic}$ (square) and log $K_{D,CdL}$ (diamond) values in the various diluents. See Table 1 or 2 for the numbering of the diluents.
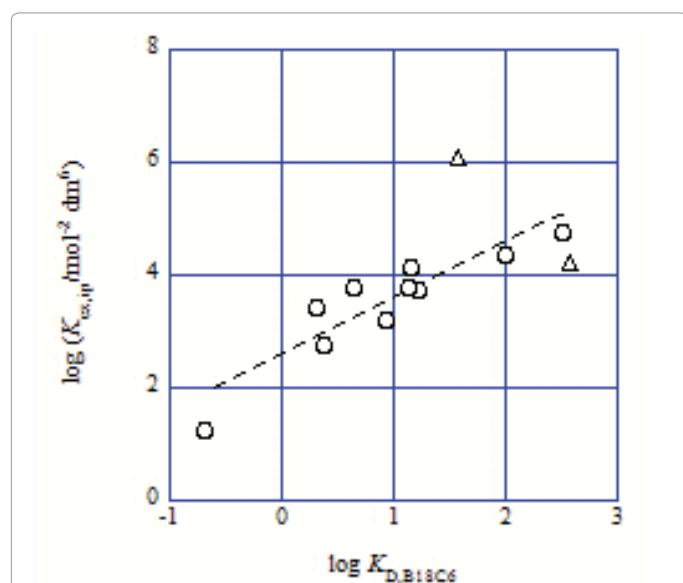
Figure 6: RST plot based on log $K_{ex,ip}$ and log $K_{D,B18C6}$ for the 12 diluent systems with Bz (Table 2). The symbols with triangle show the NB and CF systems which were neglected from the regression analyses of the plots. See the text for their reasons.

0.0095 for CBu, 0.037, 0.075 and 0.00024-0.0028 for CBz, 0.016&0.034, 0.034&0.072 and 0.00013-0.047 for BBz, 0.017, 0.034 and 0.0015-0.015 for CF, 0.020, 0.040 and 0.0018-0.0046 for DBE, 0.037, 0.075 and 0.00042-0.0056 for TE and 0.017, 0.034 and 0.00060-0.0053 for mX. Some results in the extraction experiments obtained from these initial concentrations are shown in Figure 1. The pH values for the w phases after the extraction operations were in the range of 5.34 to 6.87, except for the DBE system of which the lowest value was 4.26. Even such pH value shows that its [Pic$^-$]/[HPic] ratio was about $10^{3.8}$ ($=10^{-pKa}/10^{-pH}=10^{-0.49}/10^{-4.26}$), because p$K_{a,HPic}$=0.4$_9$ [19] at I=0.03$_4$ mol dm^{-3} (Table 1) for the DBE extraction system.

Data analyses

The data analyses were essentially the same as those reported before [6,7]. In the present study, the following component equilibria were basically employed for the analyses:

(i) Cd^{2+}+L $\rightleftharpoons$ CdL^{2+} [1], CdL^{2+}+Pic$^-$ $\rightleftharpoons$ CdLPic$^+$ [2,20], CdLPic$^+$+Pic$^-$ $\rightleftharpoons$ CdLPic$_2$ [2,20], Cd^{2+}+Pic$^-$ $\rightleftharpoons$ CdPic$^+$ [20] and H$^+$+Pic$^-$ $\rightleftharpoons$ HPic [19] in the w phase;

(ii) Pic$^-$ $\rightleftharpoons$ Pic$^-_{org}$, CdLPic$_2$ $\rightleftharpoons$ CdLPic$_{2,org}$, CdLPic$^+$ $\rightleftharpoons$ CdLPic$^+_{org}$, CdL^{2+} $\rightleftharpoons$ CdL$^{2+}_{org}$, L $\rightleftharpoons$ L$_{org}$ [8] and HPic $\rightleftharpoons$ HPic$_{org}$ [4,21] between the two phases;

(iii) CdL$^{2+}_{org}$+Pic$^-_{org}$ $\rightleftharpoons$ CdLPic$^+_{org}$ and CdLPic$^+_{org}$+Pic$^-_{org}$ $\rightleftharpoons$ CdLPic$_{2,org}$ in the org phase at L=B18C6. In order to avoid the unnecessary complexity in the overall extraction equilibrium, the equilibria of H$^+$ $\rightleftharpoons$ H$^+_{NB}$ and Cd^{2+} $\rightleftharpoons$ Cd$^{2+}_{NB}$ were neglected, because their distribution data had been reported so far [11,22,23].

Conclusion

The $K_{1,org}$ values were determined precisely in terms of evaluating the f coefficients. By comparing these values with the $K_{2,org}$ ones, the structural changes around Cd(II) in the ion-pair complexes were speculated, as well as the CdA$_2$-18C6 extraction systems with A=Cl($-$I), Br($-$I) and Pic($-$I). The conditional $K_{D,CdL}$ values were smoothly estimated from the thermodynamic cycle, in addition to the $K_{D,Pic}$, $K_{D,CdLPic2}$ and $K_{D,CdLPic}$ determination at L=B18C6. So, the determination of these actual distribution constants made a systematic study of their distribution properties possible. The results in such a study were not in conflict with those based on the RST plot. Moreover, it was suggested that the evaluation of the $K_{Cd/CdL}$ values with dep has a possibility in the prediction of the k^{pot}_{PbCd} values for ISE. The above results promise us a systematic procedure for the study of the actual M(II) extraction with L.

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