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Extraction of lead picrate by 18-crown-6 ether into various diluents: Examples of sub-analysis of overall extraction equilibrium based on component equilibria

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ABSTRACT

Extraction constants for lead picrate, $PbPic_2$, with 18-crown-6 ether (L) from aqueous solutions at a narrow range of ionic strength (I) into eleven diluents were determined at 298 K by AAS measurements. These constants were defined as $K_{ex} = [PbLPic_2]_o/([Pb^{2+}][L]_o[Pic^-]^2)$ and $K_{ex\pm} = [PbLPic^+]_o[Pic^-]_o/([Pb^{2+}][L]_o[Pic^-]^2)$, where the subscript "o" denotes the organic phase (or diluent). The ratio, $K_{ex}/K_{ex\pm}$, gave an ion-pair formation constant for $PbLPic^+{}_o + Pic^-{}_o \rightleftharpoons PbLPic_{2,o}$ at the averaged value of ionic strength (I_o) of the organic phase. A plot of log $K_{ex\pm}$ versus log $K_{D,Pic}$ yielded a straight line with the slope of 2.1 in a series of the diluents employed; $K_{D,Pic}$ refers to an apparent distribution constant of Pic^- between the aqueous and organic phases and its values were experimentally determined. The slope indicated that $K_{ex\pm}$ is mainly controlled by the square of $K_{D,Pic}$ when a thermodynamic cycle is assumed. The extraction constant based on the cycle was expressed as $K_{ex\pm} = (K_{D,Pic})^2 K_{D,M} K_{ML,org} K_{1,org}$, where $K_{D,M} K_{ML,org} K_{1,org}$ denotes the product of other component equilibrium-constants. Moreover, the relation of log $K_{D,Pic} = a\log(I_o/I) + b$ was experimentally found at $a \approx 1$ and then an example of b was expressed theoretically. It was shown that Pb(II) can be separated from mixtures with Cd(II) in unit operation.

1. Introduction

It is known that crown compounds (L) extract divalent metal ions (M^{2+}), such as alkaline-earth metal ions, Pb^{2+}, Cd^{2+}, and Hg^{2+}, with picrate ion (Pic^-), SCN^-, or NO_3^- into various diluents [1–11]. Recently, the authors have reported in this journal an extraction of $CdBr_2$ and $CdPic_2$ by 18-crown-6 ether (18C6) into various diluents, such as 1,2-dichloroethane (DCE), dichloromethane (DCM), chlorobenzene (CBz), and *m*-xylene (mX) [6]. In this study, the following component equilibria, (i)–(v), were introduced in analysis of an overall extraction equilibrium: (i) a first-step ion-pair formation of $Cd(18C6)^{2+}$ with Br^- or an overall ion-pair formation of $Cd(18C6)^{2+}$ with Pic^- in water, (ii) a distribution of A^- between water and the diluent at $A^- = Br^-$ and Pic^-, (iii) that of $Cd(18C6)Br^+$ or the distribution of $Cd(18C6)Pic_2$ between them, (iv) a second-step ion-pair formation of $Cd(18C6)A^+$ with A^- in the diluent phases, and (v) the first-step ion-pair formation of a free Cd^{2+} with A^- in water.

By the determination of equilibrium constants corresponding to these component equilibria, more detailed analysis of the overall extraction equilibrium has been performed [5,6]. For example, the second-step ion-pair formation constant ($K_{2,org}$) for the benzene (Bz) saturated with water was largest of those for the other diluents employed [6] {see process (iv) above}. Also, it was demonstrated that extraction-abilities, expressed as $K_{ex\pm}$ (see below), for $Cd(18C6)Br^+$ are actually controlled by the distribution-abilities, expressed as $K_{D,A}$, for Br^- among the diluents [6] {see process (ii)}. However, such studies have not been major for the extraction of M^{2+} by L into the diluents; the extraction of $CdPic_2$ by benzo-18C6 into benzene (Bz) has been reported in ref. [5].

In the present paper, in order to expand this kind of extraction study to other M(II) system, we determined overall extraction constants, such as K_{ex} and $K_{ex\pm}$, for the $PbPic_2$–18C6 system and the apparent distribution ones, $K_{D,Pic}$, of Pic^- into various diluents which contain nitrobenzene (NB) with a high polarity. Here, these constants have been defined as $K_{ex} = [PbLPic_2]_o/([Pb^{2+}][L]_o[Pic^-]^2)$, $K_{ex\pm} = [PbLPic^+]_o[Pic^-]_o/([Pb^{2+}][L]_o[Pic^-]^2)$ [6,12] at L = 18C6, and $K_{D,Pic} = [Pic^-]_o/[Pic^-]$ [6,12] and the subscript "o" denotes an organic phase composed of a diluent saturated with water. By using the equilibrium constants thus determined, characteristics of the Pb(II) extraction systems with 18C6 were discussed, compared to those [6] of the Cd(II) systems. Unfortunately, the equilibrium constants for the component equilibria, (i) and (iii), were not experimentally determined here.

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2. Theory

2.1. Model for sub-analysis of overall extraction equilibrium

We employed here the following model for analyzing overall extraction equilibrium which is fundamentally expressed by the two extraction constants, K_{ex} and $K_{ex\pm}$ [6,12]:

$$L \rightleftharpoons L_o : K_{D,L} \text{ is defined as a corresponding equilibrium constant,} \tag{1}$$

$$M^{2+} + L \rightleftharpoons ML^{2+} : K_{ML}, \tag{2}$$

$$ML^{2+} + 2A^- \rightleftharpoons MLA_2 : K_1K_2, \tag{3}$$

$$MLA_2 \rightleftharpoons MLA_{2,o} : K_{D,MLA2}, \tag{4}$$

$$MLA_{2,o} \rightleftharpoons MLA^+{}_o + A^-{}_o : \left(K_{2,org}\right)^{-1} \tag{5}$$

$$MLA^+ \rightleftharpoons MLA^+{}_o : K_{D,MLA}, \tag{6}$$

$$A^- \rightleftharpoons A^-{}_o : K_{D,A}, \tag{7}$$

$$H^+ + A^- \rightleftharpoons HA : K_{HA}\left(\text{means } K_a{}^{-1} \text{ of HA}\right), \tag{8}$$

$$HA \rightleftharpoons HA_o : K_{D,HA}, \tag{9}$$

and

$$M^{2+} + A^- \rightleftharpoons MA^+ : K_{MA}. \tag{10}$$

However, we could not determine in this study the equilibrium constants of Processes (3) and (4) and, instead of them, used $K_{ex,ip} = [MLA_2]_o/[ML^{2+}][A^-]^2$ ($=K_1K_2K_{D,MLA2}$) for discussion, where $K_{ex,ip}$ is ordinarily called an ion-pair extraction constant [2–4] and K_1K_2 equals $[MLA_2]/[ML^{2+}][A^-]^2$ [6,12]. This means lack of processes (i) and (iii) in the Introduction. Also, the $K_{D,MLA}$ value of Process (6) was not determined. Because of such lack, we expressed here the analysis of the present overall extraction equilibria as "the sub-analysis", compared with that of the Cd(II) system [6].

For the extraction into nitrobenzene, NB, besides, the following component equilibria [8,13,14] were added in the above model:

$$H^+{}_{NB} + A^-{}_{NB} \rightleftharpoons HA_{NB} : K_{HA,NB} \tag{11}$$

$$H^+ \rightleftharpoons H^+{}_{NB} : K_{D,H}, \tag{12}$$

$$X^- \rightleftharpoons X^-{}_{NB} : K_{D,X}, \tag{7a}$$

and

$$H^+{}_{NB} + X^-{}_{NB} \rightleftharpoons HX_{NB} : K_{HX,NB}. \tag{13}$$

Here, HX denotes a strong acid, such as HNO_3 and HCl, and $K_{D,HPic}$ was estimated from the relation $K_{D,H}K_{D,Pic}K_{HPic,NB} = K_{HPic}K_{D,HPic}$.

Details of the derivation of $[M^{2+}]$, $[L]_o$, and $[A^-]$, which are expressed as functions [6,12] of the component equilibrium constants corresponding to Processes (1) to (13), are described in Appendix A.

2.2. For determination of the extraction constants for mixture with M(II)

According to our previous papers [6,12], the extraction constant for mixture of MLA_2 and MLA^+ in the diluent has been actually defined as

$$K_{ex}{}^{mix} = \left([MLA_2]_o + \left[MLA^+\right]_o\right)/\left(\left[M^{2+}\right][L]_o[A^-]^2\right), \tag{14}$$

where the presence of ML^{2+} and ML_2A_2 in the organic phase was neglected: that is, $[MLA_2]_o + [MLA^+]_o \gg [ML^{2+}]_o + [ML_2A_2]_o$. This equation is rearranged into the two forms:

$$K_{ex}{}^{mix} = K_{ex} + K_{D,A}/\left(\left[M^{2+}\right][L]_o[A^-]\right) \tag{14a}$$

$$= K_{ex} + \sqrt{K_{ex\pm}}/\left([A^-]\sqrt{\left[M^{2+}\right][L]_o}\right). \tag{14b}$$

Since the $[M^{2+}]$, $[L]_o$, $[A^-]$, and K_{ex}^{mix} values are calculated from experimental data by a successive approximation, one can determine the K_{ex} and $K_{D,A}$ or $K_{ex\pm}$ values in terms of a regression analysis of the plots of $\log K_{ex}^{mix}$ versus $-\log([M^{2+}][L]_o[A^-])$ or $-\log\{[A^-]([M^{2+}][L]_o)^{1/2}\}$, respectively [6,12].

3. Results and discussion

3.1. For the composition-determination of species extracted into the diluents

Compositions of the species extracted into the diluents were determined in terms of plots of $\log(D/[A^-]^2)$ versus $\log [L]_o$, as described previously [2–6,10,12]. Here, D was experimentally obtained from [analyzed total-concentration of Pb(II)]$_o$/{[initial concentration of Pb(II)] − [analyzed total-concentration of Pb(II)]$_o$}. Thus, [the analyzed total-concentrations of Pb(II)]$_o$ can mean mixtures of the species with Pb(II), because their total concentrations of Pb(II) were determined by AAS measurements. If the ratio of Pb^{2+}:L is 1:1, then the slope of the plot should be close to unity. A ratio of A^- to Pb^{2+}:L (=1:1) also can be supported by a counterbalance in charge between Pb^{2+} and A^-, and is accordingly reflected to the exponent of $[A^-]$ in $D/[A^-]^2$. This has been verified experimentally [2,12]. In addition, the conditions of $1 \gg r$ and $1 \gg s$ were assumed in the equation of $\log(D/[A^-]^2) = \log\{[(1+r)/(1+s)] \times D_M/[A^-]^2\} = \log [L]_o + \log K_{ex}^{mix}$ with $r = ([MLA^+]_o + [ML^{2+}]_o + [ML_2A_2]_o + \cdots)/[MLA_2]_o$, $s = ([ML^{2+}] + [MA^+] + [MLA^+] + \cdots)/[M^{2+}]$, and $D_M = [MLA_2]_o/[M^{2+}]$ [2–4,12]. As a first diagnosis, hence, one can estimate extraction-abilities and -selectivities of L, A^-, or diluents against M^{2+} from the $\log K_{ex}^{mix}$ values, which are intercepts for the plots of $\log(D/[A^-]^2)$ versus $\log [L]_o$.

The experimentally obtained slopes of the above plots were 0.67 for the extraction into NB, 1.05 for 1,2-dichloroethane, DCE, 0.91 for *o*-dichlorobenzene (oDCBz), 1.18 for dichloromethane, DCM, 0.80 for 1-chlorobutane (CBu), 0.96 for chlorobenzene, CBz, 0.95 for bromobenzene (BBz), 1.06 for chloroform (CF), 0.93 for benzene, Bz, 0.98 for toluene (TE), and 0.92 for *m*-xylene, mX. These diluent systems, except for the NB, DCM, and CBu ones, indicated the extraction of $Pb(18C6)Pic_2$ as the major species.

As examples, Fig. 1 shows the plots for the Pb(II) extraction into NB, DCM, CBu, and Bz, together with the calculated straight lines which have the hypothetical slope of unity for the NB, DCM, and CBu systems. The value of the slope for the NB system reflects a dissociation of $Pb(18C6)Pic_2$ into $Pb(18C6)Pic^+$ (and Pic^-) in the lower $[18C6]_{NB}$ range [6,12]. The fractions of $Pb(18C6)Pic^+$ against the total amounts of the Pb(II) species extracted into the NB phases were in the range of 0.37 to 0.73 {see Eq. (A10) in Appendix A}. As shown in Fig. 1, the value for the DCM system suggests a formation of $Pb(18C6)_2Pic_2$ or $[Pb(18C6)Pic_2]_2$ in the higher $[18C6]_{DCM}$ range [5,15], while that for CBu does a dimerization of 18C6 itself in the higher $[18C6]_{CBu}$ range from its shape of the plot [16]. The former was predicted from a gradual increase in the slope (>1), while the latter was done from a gradual decrease in the slope (<1). In the determination of K_{ex} and $K_{ex\pm}$ for the NB, CBu, and DCM systems, the formation of $Pb(18C6)Pic_2$ and $Pb(18C6)Pic^+$ with Pic^- was assumed and then their data were curve-fitted using Eqs. (14a) and (14b).

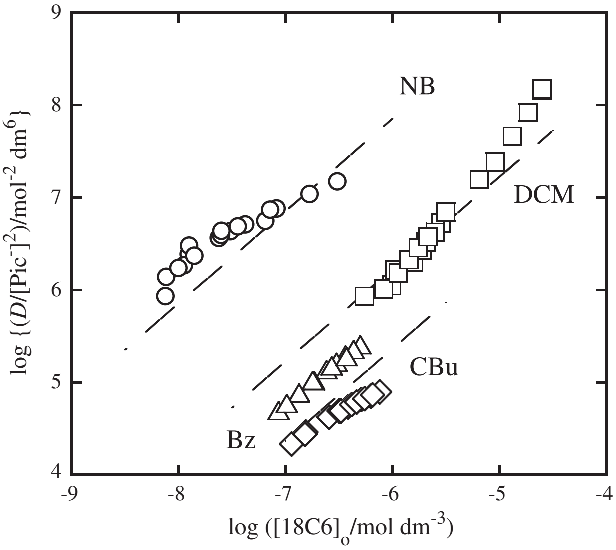

Fig. 1. Plots for the Pb(II) extraction into NB, DCM, CBu, and Bz. Log (D/[Pic^-]^2) were plotted against log [18C6]$_o$ for the extraction into NB (circle), DCM (square), Bz (triangle), and CBu (diamond). Broken lines are ones calculated from the slope of unity and the intercept of log K_{ex} (see Table 1) for the NB, DCM, and CBu extraction systems.

3.2. Determination of K_{ex}, $K_{ex\pm}$, and $K_{D,Pic}$ and that of component equilibrium constants

Figs. 2 and 3 show the plots based on Eqs. (14a) and (14b) for the extraction into NB, respectively. Similar plots were also obtained for the other extraction systems. Only the plots for the NB and TE systems gave the positive $K_{D,Pic}$ values by their regression analyses based on Eq. (14a). When the plots did not yield the positive $K_{D,Pic}$ values, their values were evaluated from the relation of $(K_{ex\pm}[\text{Pb}^{2+}][\text{L}]_o)^{1/2} \approx K_{D,Pic}$ under the condition of $[\text{Pb}(18\text{C}6)\text{Pic}^+]_o \approx [\text{Pic}^-]_o$ (see Appendix A).

These results are listed in Table 1, together with several component equilibrium-constants, such as $K_{D,A}$ and $K_{2,org}$. The K_{ex} and $K_{ex\pm}$ values were larger than those [6] for the CdPic$_2$–18C6 extraction system by a factor of 10^6 to 10^{15} (see Section 3.8). The $K_{ex,Bz}$ value was not largely different from that ($=10^{11.75}$ mol^{-3} dm^9 [2]) reported before without introducing K_{PbPic} and calculating K_{HPic} at given I values. Here, the symbol, I, denotes an ionic strength for ionic species in the aqueous phase. The K_{ex} values determined by Eq. (14a) were in good agreement with those done by Eq. (14b) for the DCE, DCM, CBu, CBz, BBz, Bz, and TE systems. On the other hand, differences in K_{ex} between both the equations were observed for the other four diluent systems. It is to be desired that the plots based on Eq. (14b) are performed in the wider range of the $-\log\{[\text{A}^-]([\text{M}^{2+}][\text{L}]_o)^{1/2}\}$ values because of keeping experimental errors as low as possible. In the following discussion, therefore, the values determined by Eq. (14a) were predominantly used, because the K_{ex} values were determined in the wider ranges of the $-\log([\text{M}^{2+}][\text{L}]_o[\text{A}^-])$ values, compared to those determined by Eq. (14b) (see the x-axes in Figs. 2 & 3). The $K_{ex,ip}$ values and the values of some component equilibrium-constants obtained as a result of the computation of [Pb^{2+}], [18C6]$_o$, and [Pic^-] are listed in Table 2.

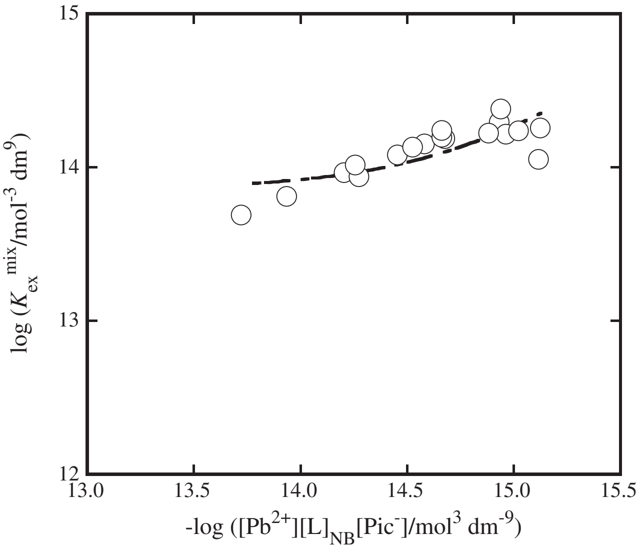

Fig. 2. Plot of log K_{ex}^{mix} versus $-\log([\text{Pb}^{2+}][\text{L}]_{NB}[\text{Pic}^-])$ at L = 18C6 for the NB extraction system. A curve is a regression line at $R = 0.744$ based on Eq. (14a).

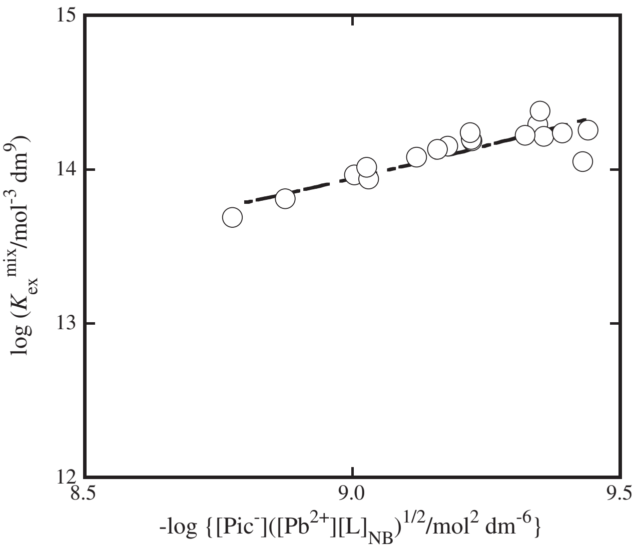

Fig. 3. Plot of log K_{ex}^{mix} versus $-\log\{[\text{Pic}^-]([\text{Pb}^{2+}][\text{L}]_{NB})^{1/2}\}$ at L = 18C6 for the NB extraction system. A curve is a regression line at $R = 0.859$ based on Eq. (14b).

3.3. Sampled analyses of extraction-abilities by diluents for the PbPic$_2$–18C6 extraction systems

We mainly compare the extraction into Bz with that into NB, CBz, oDCBz, or mX, as compared in the following Section 3.5. There was a difference ($=2.14$) in log K_{ex} between Bz and NB, as can be seen from Table 1. According to the thermodynamic cycle of

$$K_{ex} = K_{ML}K_{ex,ip}/K_{D,L}, \tag{I}$$

the log K_{ex}-difference is mainly caused by that ($=2.41$) in log $K_{ex,ip}$ (Table 2), where K_{Pb18C6} is a common value ($=10^{4.27}$ mol^{-1} dm^3 at 298 K in water [18]) and is independent of kinds of the diluents. A similar result was observed in the log K_{ex}-difference ($=0.69$) between CBz and Bz: log $K_{ex,ip}$(CBz) − log $K_{ex,ip}$(Bz) = 0.89 (see Table 2). The same is true of the K_{ex}-difference ($=0.625$) between oDCBz and Bz; that in log $K_{ex,ip}$ was 0.77. On the other hand, the difference ($=0.56$) in log K_{ex} between Bz and mX is primarily caused by that ($=|0.68|$) in log $K_{D,18C6}$ (Table 1). In comparison of Bz with mX, the log $K_{ex,ip}$-difference ($=-0.12$) negatively contributes the log K_{ex} one. Thus, the thermodynamic cycle shows whether there are possibilities or not that the component equilibrium constants positively contribute K_{ex}. Its cycle cannot answer actual effects of their component equilibrium constants on K_{ex}.

Similarly, there was difference ($=5.6$) in log $K_{ex\pm}$ between Bz and NB (Table 1). The cycle [6,12],

$$K_{ex\pm} = K_{ML}K_{ex,ip}/K_{D,L}K_{2,org}, \tag{II}$$

Table 1
Overall extraction constants and their several component equilibrium-constants for the extraction of $MA_2 = PbPic_2$ by L = 18C6 into various diluents at 298 K.

Diluents[a]	$\log K_{D,L}$[b]	$\log K_{ex}$	$\log K_{ex\pm}$	$\log K_{D,A}$[c]	$\log K_{2,org}$ (I_o)[d]
NB	−1.00	13.86 ± 0.07,[e] $13.2_0 \pm 0.3_6$[f]	$9.7_1 \pm 0.1_2$	-0.94 ± 0.09[e]	$4.1_5 \pm 0.1_4$ (1.9×10^{-4})
DCE	0.03	12.44 ± 0.03,[e] 12.39 ± 0.08[f]	$5._5 \pm 3._1$	-1.89 ± 0.09	$7._0 \pm 3._1$ (2.2×10^{-6})
oDCBz	−1.13	12.337 ± 0.007,[e] 12.29 ± 0.03[f]	$5.4_3 \pm 0.7_6$	$-2.1_0 \pm 0.1_5$	$6.9_0 \pm 0.7_6$ (2.3×10^{-6})
DCM	0.60	12.23 ± 0.04,[e] $12.1_8 \pm 0.1_3$[f]	ND[g]	-6.06 ± 0.09	ND[g] (1.6×10^{-10})
CBu	−1.93	11.364 ± 0.004,[e] 11.352 ± 0.009[f]	$2._7 \pm 1._0$	-3.57 ± 0.07	$8._6 \pm 1._0$ (1.5×10^{-7})
CBz	−1.07	12.40 ± 0.01,[e] 12.36 ± 0.03[f]	$5._0 \pm 1._4$	$-2.3_8 \pm 0.1_2$	$7._4 \pm 1._4$ (1.1×10^{-6})
BBz	−1.12	12.474 ± 0.009,[e] 12.45 ± 0.02[f]	$4._8 \pm 1._8$	$-2.4_5 \pm 0.1_3$	$7._7 \pm 1._8$ (8.7×10^{-7})
CF	0.786	11.38 ± 0.01,[e] 11.31 ± 0.05[f]	$4._3 \pm 1._6$	$-2.3_6 \pm 0.1_2$	$7._1 \pm 1._6$ (1.6×10^{-6})
Bz	−1.27	11.712 ± 0.006,[e] 11.70 ± 0.01[f], 11.75[h], 11.6[h]	$4.0_9 \pm 0.8_2$, 6.4[h]	$-2.9_1 \pm 0.1_0$, −1.60[h]	$7.6_2 \pm 0.8_2$ (8.2×10^{-7}), 5.3[h]
TE	−1.59	12.37 ± 0.09,[e] $12.3_7 \pm 0.1_7$[f]	ND[g]	$-3._2 \pm 4._0$[e]	ND[g] (1.6×10^{-7})
mX	−1.95	12.268 ± 0.008,[e] 12.22 ± 0.02[f]	$4.8_7 \pm 0.5_0$	-2.63 ± 0.07	$7.3_9 \pm 0.5_0$ (4.8×10^{-7})

[a] Diluents were arranged in the sequence that polarities of their pure diluents decrease from the top to the bottom in the table. See Section 3.1 in the text for the abbreviation of the diluents.
[b] Refs. [20,17] for NB.
[c] Values calculated from $K_{D,Pic} = (K_{ex\pm}[Pb^{2+}][L]_o)^{1/2}$. See Section 3.2.
[d] The average values of ionic strength for species in the organic phases.
[e] Values determined by the analysis based on Eq. (14a).
[f] Values determined by the analysis based on Eq. (14b).
[g] Not determinable because of large experimental errors.
[h] Ref. [2]. The value of 11.6 was determined from the experimental data of ref. [2] by introducing K_{PbPic} and $K_{2,Bz}$ in the extraction model and accordingly $I = 0.0030$ and $I_{Bz} = 7.6 \times 10^{-6}$ mol dm^{-3} were estimated. See ref. [12].

indicates the larger contribution of the log $K_{2,org}$-difference (=|3.5|) than that of the log $K_{ex,ip}$ one (=2.41) to the log $K_{ex\pm}$-difference. On the other hand, major contribution to the log $K_{ex\pm}$-difference between Bz and mX or CBz was essentially the same as contribution to the log K_{ex}-difference. Also, the contribution (=|0.7$_2$|) of log $K_{2,org}$ to the log $K_{ex\pm}$-difference (=1.3$_4$) between Bz and oDCBz was comparable to that (=0.7$_7$) of log $K_{ex,ip}$ (see Tables 1 & 2). It can be easily observed that the increased $K_{ex\pm}$ value for the NB system is due to the contribution of the much smaller $K_{2,org}$ value of NB than those of mX, oDCBz, and CBz. That is, $Pb(18C6)Pic_2$ dissociates much larger into $Pb(18C6)Pic^+$ in the NB phase (its mole fractions = 0.37 to 0.73) than it does in the mX, oDCBz, and CBz phases. The mole fractions were 0.06 to 0.10 for mX, 0.04 to 0.09 for oDCBz, and 0.03 to 0.06 for CBz {see Eq. (A10) in Appendix}.

A difference in log K_{ex} between maximum and minimum values was 1.07$_6$ (=log $K_{ex,DCE}$ − log $K_{ex,CBu}$) for the eight diluents or 2.50 (=log $K_{ex,NB}$ − log $K_{ex,CBu}$) for the eleven diluents (see Table 1). These values are less than that (=log $K_{ex,CBz}$ − log $K_{ex,Bz}$ = 3.28 [6]) for the $CdPic_2$–18C6 systems. When NB is contained in discussion, the difference (=7.0 = log $K_{ex\pm,NB}$ − log $K_{ex\pm,CBu}$) in log $K_{ex\pm}$ between both the values was comparable to that (≈7 [6]) of the $CdPic_2$–18C6 system. On the other hand, when NB is not contained, the difference (=2.3 = log $K_{ex\pm,CBz}$ − log $K_{ex\pm,CBu}$) was much smaller than about 7. These results indicate that the extraction-selectivity of 18C6 to $PbPic_2$ is less than that to $CdPic_2$ into the diluents employed.

Table 2
Ion-pair extraction constants, $K_{ex,ip}$, and component equilibrium constants for averaged I values at 298 K.

Diluents[a]	I[b]$/10^{-3}$	$\log K_{ex,ip}$[c]	$\log K_{MA}$[b,d]	$\log K_{HA}$[b,e]	$\log K_{D,HA}$[f]
NB	2.7	8.59	1.91	0.42	2.4, 2.2[g]
DCE	4.9	8.20	1.88	0.41	1.90
oDCBz	5.1	6.94	1.88	0.41	1.59
DCM	4.9	8.56	1.88	0.41	1.88
CBu	5.7	5.16	1.87	0.40	0.89
CBz	5.1	7.06	1.88	0.41	1.72
BBz	5.0	7.08	1.88	0.41	1.72
CF	5.3	7.89	1.87	0.40	1.347, 1.65$_0$[h]
Bz	5.9	6.17	1.87	0.40	1.81, 2.10$_3$[i]
TE	5.0	6.51	1.88	0.41	1.88
mX	5.0	6.05	1.88	0.41	1.97

[a] See Section 3.1 in the text for the abbreviation of the diluents.
[b] Values averaged: mol dm^{-3}. Or KMA and KHA values at I averaged.
[c] Values calculated from the relation log ($K_{ex,ip}$/mol^{-2} dm^6) = log K_{ex} + log $K_{D,18C6}$ − log K_{Pb18C6}. Log K_{Pb18C6} = 4.27: see ref. [18].
[d] Values evaluated from the extended Debye–Hückel equation, using 4.5 Å as the ion-size parameter [27] of Pb^{2+} and assuming that the activity coefficient of Pic^- equals that of $PbPic^+$. Here, 2.00 [12] was used as the log K_{PbPic} value at $I \to 0$ and 298 K.
[e] Values evaluated from the extended Debye–Hückel equation, using 9 Å as the ion-size parameter of H^+ and 7 as that of Pic^- [27]. Here, 1.9$_5$ [28] which is the K_{HPic} value at $I = 0.1$ and 298 K was used as a basic value in calculation and the activity coefficient of HPic in water was assumed to be unity.
[f] Ref. [19].
[g] Value estimated from log $K_{D,HPic}$ = log $K_{D,H}$ + log $K_{D,Pic}$ + log $K_{HPic,NB}$ − log K_{HPic} (=−5.0 + 0.05 + 7.6 − log K_{HPic}). See refs. [14,26,29].
[h] Ref. [4].
[i] Ref. [2].

3.4. Component equilibrium constant controlling $K_{ex\pm}$

The plot of log $K_{ex\pm}$ versus log $K_{D,Pic}$ yielded a straight line with a slope of 2.1 ± 0.1 and a constant intercept of 9.8 ± 0.6 at a correlation coefficient (R) = 0.989, except for the extraction into NB, suggesting the thermodynamic cycle of

$$K_{ex\pm} = K_{D,M}\left(K_{D,A}\right)^2 K_{ML,org} K_{1,org} \tag{IIa}$$

with $K_{D,M} = [M^{2+}]_o/[M^{2+}]$, $K_{ML,org} = [ML^{2+}]_o/[M^{2+}]_o[L]_o$, and $K_{1,org} = [MLA^+]_o/[ML^{2+}]_o[A^-]_o$. The plot shows that there are few differences in $K_{D,Pb}K_{PbL,org}K_{1,org}$ (=9.8) at L = 18C6 among the diluents employed. In other words, it indicates that the $K_{\mathrm{D,Pic}}$ values are sensitive to kinds of the diluents, while the products of the other three constants are not sensitive to them, although the equilibrium constants in the right hand side of the cycle (IIa) can depend on interactions with the diluent molecules employed. Unfortunately, no $K_{\mathrm{D,Pb}}$, $K_{\mathrm{Pb18C6,org}}$ and $K_{\mathrm{1,org}}$ values at 298 K were available.

The plot of log $K_{\mathrm{ex\pm}}$ versus − log $K_{\mathrm{2,org}}$ also yielded a straight line with a slope of 1.52 ± 0.05 and an intercept of 16.0 ± 0.3 (≈log K_{ex} on average) at $R = 0.978$, indicating a good linearity except for the extraction into DCM and TE on which lack of log $K_{\mathrm{ex\pm}}$ is present. However, the plot showed a deviation from the cycle [6,12] of

$$K_{\mathrm{ex\pm}} = K_{\mathrm{ML}} K_1 K_2 K_{\mathrm{D,MLA2}} / K_{\mathrm{D,L}} K_{\mathrm{2,org}} \left(= K_{\mathrm{ex}} / K_{\mathrm{2,org}} \right). \tag{IIb}$$

From the slope of the plot, it is difficult to conclude the presence of a correlation based on the cycle (IIb) for all the diluents employed. However, the good linearity and the deviation of the slope from unity on the cycle (IIb) can suggest that the $K_{\mathrm{ex\pm}}$ values are controlled by the $K_{\mathrm{2,org}}$ ones for "some" diluents employed. For example, plots except for the TE, DCM, CBu, and NB systems yielded the relation of log $K_{\mathrm{ex\pm}} \approx (-0.9_8 \pm 0.2_2)$ log $K_{\mathrm{2,org}} + (12._0 \pm 1._0)$ at $R = 0.587$, although the R value was low.

The plot of log $K_{\mathrm{ex\pm}}$ versus log $K_{\mathrm{D,Pic}}$ did not yield a straight line with a slope of unity {see the cycle (IIa)}. This finding shows the less dependence of the plot on the thermodynamic cycle [6] of

$$K_{\mathrm{ex\pm}} = K_{\mathrm{ML}} K_1 K_{\mathrm{D,MLA}} K_{\mathrm{D,A}} / K_{\mathrm{D,L}}. \tag{IIc}$$

Since the condition of $K_{\mathrm{D,MLA}}\ (= [\mathrm{MLA}^+]_{\mathrm{o}}/[\mathrm{MLA}^+]) = K_{\mathrm{D,A}}$ is not held for the MA_2-L extraction systems [6] in general, the cycle (IIc) cannot be approximated to $K_{\mathrm{ex\pm}} = K_{\mathrm{ML}} K_1 (K_{\mathrm{D,A}})^2 / K_{\mathrm{D,L}}$. Therefore, the finding indicates that there are differences in $K_{\mathrm{D,PbLPic}}/K_{\mathrm{D,L}}$ at L = 18C6 among the diluents employed. In other words, the distribution properties of 18C6 do not directly reflect those of ionic Pb(18C6)Pic^+, although the 18C6 properties directly reflect the distribution properties of neutral Pb(18C6)Pic_2 (see Section 3.9). On the other hand, the Cd(II) extraction systems showed dependences to the cycle (IIc): log $K_{\mathrm{ex\pm,Br}} \approx$ log $K_{\mathrm{D,Br}}$ + constant and log $K_{\mathrm{ex\pm,Pic}} \approx$ log $K_{\mathrm{D,Cd18C6Pic}}$ + constant [6]. From the A^--distribution-point of view, the $PbPic_2$ systems with 18C6 may be close to the $CdBr_2$ ones with it.

It is expected in the cycle (IIa) that increases in all the component equilibrium constants contribute that in $K_{\mathrm{ex\pm}}$. The present Pb(II) extraction systems correspond to this cycle. In the cycle (IIb) {or (II)}, it is also expected that increases in the component equilibrium constants, K_{ML}, K_1, K_2, and $K_{\mathrm{D,MLA2}}$, contribute that in $K_{\mathrm{ex\pm}}$, while increases in $K_{\mathrm{D,L}}$ and $K_{\mathrm{2,org}}$ do its decrease. Moreover, it is expected in the cycle (IIc) that increases in the component equilibrium constants, K_{ML}, K_1, $K_{\mathrm{D,MLA}}$, and $K_{\mathrm{D,A}}$, contribute that in $K_{\mathrm{ex\pm}}$, while increases in $K_{\mathrm{D,L}}$ do its decrease. This cycle corresponded to the Cd(II) extraction systems [6]. Thus, the above results indicate that all the component equilibrium constants which are concerned with the distribution of species into the diluents employed are not necessarily reflected into the increase of $K_{\mathrm{ex\pm}}$. As shown above, from the thermodynamic cycles, it is very difficult to predict a common property in $K_{\mathrm{ex\pm}}$ or K_{ex} even among the diluents employed.

Of course, the above results simply indicate that $K_{\mathrm{ex\pm}}$ has the common dependence on the square of $K_{\mathrm{D,Pic}}$ in a series of the diluents employed. As readers know, the cycle (IIa) does not mean a so-called reaction mechanism, because the process expressed as $K_{\mathrm{D,Pic}}$ does not necessarily show an elementary reaction.

3.5. For tendency of the interaction between diluent molecules and Pic^- or 18C6

The log $K_{\mathrm{D,Pic}}$ values listed in Table 1 were in the orders NB (−0.94) > oDCBz ≥ CBz ≥ BBz ≥ mX ≥ Bz > TE $(-3._2)$ and DCE (−1.89) ≥ CF > CBu > > DCM (−6.06). The former order for the aromatic diluents shows that the substitution of –H in a benzene ring by –NO_2, –Cl, or –Br contributes an increase in the interaction between the diluent molecules and Pic^- [19]. On the other hand, the latter order for halo-alkane diluents shows that the substitutions of –H by –Cl and –Cl by –CH_2Cl or –$CH_2CH_2CH_3$ increase in the interaction with Pic^-. From the above, the substitution effect of these functional groups on $K_{\mathrm{D,Pic}}$ can be in the order –H < −Br, –Cl < −CH_2Cl, –$CH_2CH_2CH_3$ < −NO_2, although the relation in the aromatic diluents between –CH_3 and –H is unclear. Of course, one must see that such orders are limited with the simultaneous distribution of Pb(18C6)Pic^+ into the diluents [6,12].

Similarly, the log $K_{\mathrm{D,18C6}}$ order for the aromatic diluents has been NB (−1.00) > CBz > BBz ≥ oDCBz > Bz > TE > mX (−1.95) and that for the halo-alkane diluents CF (0.786) > DCM > DCE > > CBu (−1.93) (see Table 1) [20]. The former order indicates that the substitution of –H by –Cl, –Br or –NO_2 increases the interaction of the aromatic diluent-molecules with 18C6, while that of –H by –CH_3 decreases its interaction. On the other hand, the latter shows that the substitution of –H by –Cl and –CH_2Cl, or –$CH_2CH_2CH_3$ by –H increases the interactions of the halo-alkane diluents with 18C6: **H**–$CHCl_2$ < **Cl**–$CHCl_2$ and **$CH_3CH_2CH_2$**–CH_2Cl ≪ **$ClCH_2$**–CH_2Cl < **Cl**–CH_2Cl.

Considering electronegativities (χ_{X}) [21] of the functional groups, X = −O– ($\chi_{\mathrm{O}} = 3.44$ [21]) and –CH_2– (estimated $\chi_{\mathrm{CH2}} = 2.2_9$), in 18C6, these results suggest any interactions of the –CH_2– site in 18C6 with the –Cl, –Br, or –NO_2 group in the diluent molecules. The reported and estimated group electronegativities [22] in Pauling unit were also in the order of –Cl ($\chi_{\mathrm{X}} = 3.16$ [21]) > –Br (2.96 [21]) > –NO_2 (estimated: 2.7_2) > –CH_2Cl (estimated: 2.4_7; 2.47 [22]) > –$CH_2CH_2CH_3$ (estimated: 2.2_8), –CH_3 (estimated: 2.2_7; 2.27 [22]) > –H (2.20 [21]). This order seems to be reflected to the log $K_{\mathrm{D,18C6}}$ one. Especially, its log $K_{\mathrm{D,18C6}}$ order for the halo-alkane diluents reflects well the χ_{X} one: **Cl**–$CHCl_2$ > **H**–$CHCl_2$ and/or **Cl**–CH_2Cl > **$ClCH_2$**–CH_2Cl > **$CH_3CH_2CH_2$**–CH_2Cl. In spite of a difference between 18C6 and Pic^- in the fundamental interaction, dipole–dipole one for the former and ion–dipole one for the latter, with the aromatic diluent molecules, it is also interesting to us that the log $K_{\mathrm{D,Pic}}$ order is similar to the log $K_{\mathrm{D,18C6}}$ one. This fact can support delocalization of electrons in Pic^-. In other words, Pic^- may be behaving as a neutral molecule in the distribution into the organic phases.

It is interesting to compare these log $K_{\mathrm{D,Pic}}$ orders with those for the $CdPic_2$–18C6 extraction system. The latter orders are CBz (log $K_{\mathrm{D,Pic}} = -4.8_7$) > TE, mX > Bz (-4.6_1) and DCM (−3.60) > DCE, CF > CBu (−5.6) [6,19]. It may be suggested that the $PbPic_2$–18C6 system weakens the interaction of Pic^- with DCM or TE molecules, compared to the $CdPic_2$–18C6 system.

3.6. For tendency of stabilization of Pb(18C6)Pic_2 in the diluents

The log $K_{\mathrm{2,org}}$ values listed in Table 1 were in the orders org = BBz $(7._7)$ ≥ Bz ≥ mX, CBz ≥ oDCBz > NB (4.1_5) and CBu $(8._6)$ ≥ CF ≥ DCE $(7._0)$ in the I_{o} range of 1.5×10^{-7} to 1.9×10^{-4} mol dm^{-3}, where I_{o} denotes the ionic strength for ionic species in the organic phase. Both orders seem to roughly depend on magnitudes of the dielectric constants of the pure diluents (see the sequence of the diluents in Table 1). It is also suggested that the Pb(18C6)Pic_2 ion pairs are stabilized in the BBz and CBu phases. The log $K_{\mathrm{2,org}}$ orders of the $CdPic_2$–18C6 system are Bz (log $K_{\mathrm{2,org}} = 9._5$) ≥ mX ≥ TE ≥ CBz (6.0) and CBu $(7._1)$ ≥ DCE ≥ CF ≥ DCM (5.4) in the I_{o} range of 8.2×10^{-9} to 6.2×10^{-7} mol dm^{-3} [6]. These orders are similar to those for the $PbPic_2$–18C6 system. The stabilization of the Bz and CBu systems is greater than those of the other systems, although the data of the $CdPic_2$–18C6 extraction system with BBz was not available.

3.7. For a correlation between log $K_{D,Pic}$ and log (I_{o}/I)

The plot of log $K_{\mathrm{D,Pic}}$ versus log (I_{o}/I) for the employed diluents yielded the straight line of log $K_{\mathrm{D,Pic}} = (0.96_8 \pm 0.05_0)\log (I_{\mathrm{o}}/I) + (1.1_2 \pm 0.1_6)$

at $R = 0.991$ (Fig. 4), where I_o and I refer to averaged values in each phase and are listed in Tables 1 and 2, respectively. Similar results for the $CdBr_2$- and $CdPic_2$–18C6 extraction systems were obtained from using their data [6]. These regression lines were $\log K_{D,Br} = (0.96_0 \pm 0.04_7)\log (I_o/I) + (0.1_8 \pm 0.2_2)$ at $R = 0.989$ and $\log K_{D,Pic} = (1.03_0 \pm 0.03_0)\log (I_o/I) + (0.2_7 \pm 0.1_5)$ at $R = 0.998$ (see Fig. 4). The R values of these three plots clearly indicate good correlations between $\log K_{D,A}$ and $\log (I_o/I)$ for the diluent systems employed. A similar relation has been suggested by the equation, $\log K_{D,\pm} = \log (I_{DCE}/I) +$ constant with $K^2_{D,\pm} = K_{D,M}K_{D,Pic}$, reported previously for the MPic single extraction system at M = Li–Cs [23].

For example, the following equations hold for the present $PbPic_2$–18C6 extraction system: $I_o = (1/N)\sum([A^-]_o + [X^-]_o)$ and $I = (1/N)\sum([M^{2+}] + [ML^{2+}] + [A^-] + [X^-])$ {see Eqs. (A5a) or (A5) and (A9) in Appendix A} in the presence of HNO_3 (=HX) in the aqueous phase, where N means a number of data. Therefore, the ratio I_o/I becomes $\sum[A^-]_o(1 + \sum[X^-]_o/\sum[A^-]_o)/[\sum[A^-]\{1 + \sum([M^{2+}] + [ML^{2+}] + [X^-])/\sum[A^-]\}] \approx K_{D,A}(1 + \sum[X^-]_o/\sum[A^-]_o)/\{1 + \sum([M^{2+}] + [ML^{2+}] + [X^-])/\sum[A^-]\}$, by assuming that $\sum[A^-]_o/\sum[A^-] = K_{D,A}$. In calculation, the $K_{D,A}$ values evaluated from $\sum[A^-]_o/\sum[A^-]$ were in agreement with those done from $(1/N)\sum K_{D,A}$ $\{=(1/N)\sum([A^-]_o/[A^-])\}$ within errors of calculation, except for the Pic^- distribution into NB. Then, from taking logarithms of both sides in this equation and rearranging it, we can immediately obtain

$$\log\ K_{D,A} = \log (I_o/I) + \log\ I_A \tag{15}$$

with

$$I_A = \left\{1 + \sum\left(\left[M^{2+}\right] + \left[ML^{2+}\right] + [X^-]\right)/\sum[A^-]\right\}/\left(1 + \sum[X^-]_o/\sum[A^-]_o\right). \tag{16}$$

Eq. (15) indicates that the slope and intercept of the plot for the $PbPic_2$–18C6 extraction system are unity and the $\log I_A$ value, respectively. The same can be true of the results for the CdA_2–18C6 extraction systems without HX [6].

Differences in intercept between the Pb(II) and Cd(II) extraction systems should come from whether HNO_3 is present in the aqueous phase or not. For the latter Cd(II) systems, the conditions of $\Sigma[NO_3^-]/\Sigma[A^-] = 0$ and $\Sigma[NO_3^-]_o/\Sigma[A^-]_o = 0$ hold [6], so that their $\log I_A$ terms can become smaller than those for the Pb(II) system at $[NO_3^-] = 0.002$ mol dm^{-3}, because the minimum $I_A = 1 + \sum([Cd^{2+}] + [Cd(18C6)^{2+}])/\sum[A^-] \approx (4/3)$ (see Appendix B). So, we can easily see that the $\log K_{D,A}$ value is estimated from the experimental ratio of $\log (I_o/I)$ within the experimental errors of less than unity (<1.1). In particular, when the aqueous phase does not contain any ionic strength adjusters (or supporting electrolytes), such as HNO_3, $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$, this estimate will improve its precision (<0.3).

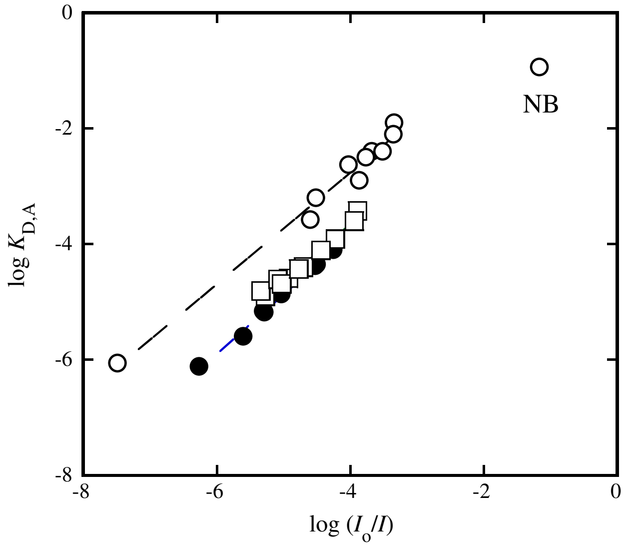

Fig. 4. Plots of $\log K_{D,A}$ versus $\log (I_o/I)$ for the $PbPic_2$–, $CdPic_2$–, and $CdBr_2$–18C6 extraction systems. Circles and square denote the Pic^- and Br^- systems, respectively: Pb(II) (open circle) and Cd(II) (full one). Broken lines are regression lines; the regression line of the Pb(II) system was calculated without a point of the NB system, because of lack of the NB system for the Cd(II) data.

The $\log K_{D,Pic}$ value was estimated to be −1.4 $\{=0.96_8\log (7.6 \times 10^{-6}/0.0030) + 1.1_2\}$ (see above) from the I and I_{Bz} values of the footnote g in Table 1. This value was close to −1.60 [12] (see Table 1) determined previously for the $PbPic_2$–18C6 extraction into Bz, when its calculation error was assumed to be about 0.2 ($\geq 0.1_6$). From this estimate, one can see also that the ratio between I and I_o values is reflected to the $K_{D,A}$ value.

3.8. For separation of Pb(II) from mixtures with Cd(II)

From the $\log K_{ex}$ values in Table 1 and ref. [6], $\log (K_{ex,Pb}/K_{ex,Cd})$ values were calculated to be 8.08 for the DCE system, 8.4_2 for DCM, 7.9_5 for CBu, 7.14 for CBz, 7.86 for CF, 9.73_2 for Bz, 8.67 for TE, and 7.46_8 for mX. These values indicate that a separation of Pb(II) from mixtures with Cd(II) by the use of 18C6 and HPic is possible in unit operation, because the ratios, $K_{ex,Pb}/K_{ex,Cd}$, are nearly equal to the separation factors, $(D_{Pb}/D_{Cd})_{expl.}$, and are over 10^4 [24]. Here, the following relation with a corrected factor (a) holds: $(D_{Pb}/D_{Cd})_{expl.} = a(D_{Pb}/D_{Cd}) = a(K_{ex,Pb}/K_{ex,Cd})$, where $a = (1 + r_{Pb})(1 + s_{Cd})/\{(1 + s_{Pb})(1 + r_{Cd})\}$, (see Section 3.1). In particular, the extraction into Bz is most effective of those into the other diluents for the Pb(II) separation. The same is true of $\log (K_{ex\pm,Pb}/K_{ex\pm,Cd})$ values: $6._8$ for the DCE system, 5.6 for CBu, 6.0 for CBz, 6.8 for CF, 15.1 for Bz, and 7.0 for mX. Similarly, Bz is the most effective diluent for the Pb(II) separation.

3.9. Plot of log $K_{ex,ip}$ versus log $K_{D,18C6}$

Fig. 5 shows the plot of $\log K_{ex,ip}$ versus $\log K_{D,18C6}$ based on the regular solution theory modified by Takeda et al. [5,6,20]. The plot yielded a straight line with a slope of $0.9_6 \pm 0.1_6$ and an intercept of $7.7_9 \pm 0.2_0$ at $R = 0.909$ and $N = 10$, except for the extraction into NB. Here, the data for the extraction into CF was not neglected for a comparison with the Cd(II) system [6]. From this slope $(=V_{MLA2}/V_L$ [5,6,20]), the molar volume of $Pb(18C6)Pic_2$ was estimated to be about 205 cm^3 mol^{-1}, using $V_{18C6} = 214$ cm^3 mol^{-1} [20]. This value is close to that (=about 200 cm^3 mol^{-1} [6]) of $Cd(18C6)Pic_2$, although there is a difference between the Pb(II) and Cd(II) extraction systems in N of the diluents employed for the plots. These values for $M(18C6)Pic_2$ were smaller than those [20] for the M(18C6)Pic at M = Li, Na, and K; $(V_{Li(18C6)Pic}/\text{cm}^3\ \text{mol}^{-1}) = 326$ or 235 [25], $V_{Na(18C6)Pic} = 294$ or 229 [25], $V_{K(18C6)Pic} = 248$ or 255 [25]. These facts suggest that $Pb(18C6)Pic_2$ and $Cd(18C6)Pic_2$ have a more tight (or a more compact) structure than M(18C6)Pic does.

A comparison of the R value with that (=0.692 at $N = 8$ [6]) of the Cd(II) extraction system also suggests that $PbLPic_2$ has a less polar structure than $CdLPic_2$ does at L = 18C6. The same is true of the R value (=0.993, after 0.901 for Fig. 6 in ref. [6] was revised) of the plot for the $CdBr_2$–18C6 system at $N = 11$. Namely, the polarity of their structures can increase in the order $Cd(18C6)Br_2$ ($R = 0.993$) < $Pb(18C6)Pic_2$ (0.909) < $Cd(18C6)Pic_2$ (0.692), because linearity of the plots is due to the limitation of the regular solution theory; as an example, the system does not contain an interaction like hydrogen bonding between solute and solvent [20].

According to our previous studies [5,6], it is also suggested that the overall ion-pair formation constant, K_1K_2, for $Pb(18C6)^{2+} + 2Pic^- \rightleftharpoons Pb(18C6)Pic_2$ in the aqueous phase is less than about eight

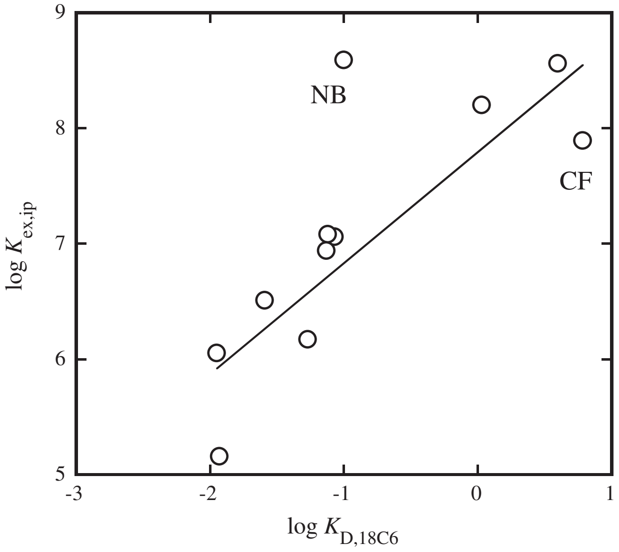

Fig. 5. Plot of log $K_{ex,ip}$ versus log $K_{D,18C6}$ for the $PbPic_2$–18C6 extraction system. A straight line shows a regression one calculated without a point of the NB system.

(≈the intercept), because terms of cohesive energy densities (C) for mixtures of water or a diluent with L or MLA_2 cannot be neglected in the system with 18C6 [6]: namely, an equation responsible for the plot is log $K_{ex,ip} = (V_{MLA2}/V_L)$log $K_{D,L}$ + log K_1K_2 + (the function of C) [5]. If the log K_1K_2 values are constant or show few deviations among the diluents employed, then the plot can mean that log $K_{D,PbLPic2}$ is proportional to log $K_{D,L}$ at L = 18C6 (see Section 3.4).

Another handling for Fig. 5 is as follows. If the plot correspond to the cycle $K_{ex} = K_{ML}K_{ex,ip}/K_{D,L}$ {see the thermodynamic cycle (I) in Section 3.3}, then Fig. 5 can become the plot based on

$$\log\ K_{ex,ip} = \log\ K_{D,L} + \log(K_{ex}/K_{ML}). \quad \text{(Ia)}$$

For this case, the slope can approach unity too. Besides, the average log (K_{ex}/K_{ML}) value for the ten diluents employed was calculated to be 7.8 ± 0.4. However, the log K_{ex}-versus-log K_{Pb18C6} plot does not obviously yield the slope of unity, because log K_{Pb18C6} is assumed to be the constant [18]: the regression analysis gave log $K_{ex} \approx 0.6_7$log K_{Pb18C6} + 5.3 at $R = 10^{-7}$. We obtained an equation log $K_{ex,ip}$ = log $K_{D,18C6}$ + log $\{K_{ex}/(K_{Pb18C6})^{0.67}\}$ + 5.3, but this equation was obviously different from Eq. (Ia). From the R value, moreover, the authors could not recognize a correlation between log K_{ex} and log K_{Pb18C6}. Thus, there are some questions for the above handling. Further, the handling is a backward movement to the detailed analysis of K_{ex} and thereby the direct consideration of K_1K_2 (and then $K_{D,MLA2}$) from the intercept does not occur. Therefore, we lay aside such a discussion to go around in circles.

4. Conclusion

A) The extraction-abilities, symbolized by $K_{ex\pm}$, of 18C6 against $PbLPic^+$ into a series of the diluents were directly proportional to the square of $K_{D,Pic}$. It should be stressed that, in a series of the diluents employed, the cycle (IIa) shows the common dependence on the component equilibrium constant, when compared the other cycles, (I), (IIb), and (IIc), with (IIa).

B) We experimentally verified the good correlations between the log $K_{D,Pic}$ and log (I_o/I) values for the extraction systems with a series of the diluents. This result makes an estimate of the log (I_o/I) values from the log $K_{D,Pic}$ ones in any extraction systems possible; however, we now have no answer to what kinds of applications are possible.

C) The order of log $K_{D,Pic}$ for the $PbPic_2$–18C6 system was close to that for the $CdPic_2$–18C6 one, except for the DCM and TE systems. This fact supports the presence of the individual distribution constant of single Pic^- into each diluent, in addition to the previously-reported result that the individual distribution constant for Bz is present [12].

D) The apparent separation factors between the Pb(II) and Cd(II) extraction systems were larger than 10^5. One can see that Pb(II) is most-effectively separated at unit operation from the mixtures with Cd(II) by using 18C6, HPic, and Bz.

E) It was demonstrated that $Pb(18C6)Pic_2$ has a more tight structure than $Cd(18C6)Pic_2$ or M(18C6)Pic does, in comparison with the $V_{M(18C6)Picn}$ values (n = 1, 2) for the $CdPic_2$–18C6 system or for the MPic–18C6 ones with M of the lighter alkali metal. Also, the polarity of $M(18C6)A_2$ was in the order $Cd(18C6)Br_2 < Pb(18C6)Pic_2 < Cd(18C6)Pic_2$.

The above results, A) and E), are similar to those reported previously in ref. [6] and also show that the analytical procedure [6] was expanded to the Pb(II) systems, although the analysis by the Pb(II) extraction model becomes the sub-handling comparing with that by the Cd(II) extraction one [6]. Further, the effectiveness of the model for the sub-analysis was clarified experimentally with the other results, B) to D).

5. Experimental

5.1. Chemicals

Lead nitrate (guaranteed reagent: GR, 99.5%, Kanto Chemical Co. Ltd.) was titrated by an aqueous solution of disodium salt of EDTA, in order to check the amount of lead in its nitrate. Commercially-available 18C6 (99%, Kanto Chemical Co. Ltd.) was recrystallized from acetonitrile, which was of GR (99.5%, Wako Pure Chemical Industries) and distilled once before use, and then its colorless-needle obtained was dried for 20 h in vacuo at room temperature [6]. Aqueous solution of picric acid ($HPic \cdot xH_2O$, 99.5%, Wako Pure Chemical Industries) was titrated with that of NaOH. Commercially-available diluents were of GR; NB, DCE, DCM, mX, BBz, and oDCBz were purchased from Kanto Chemical Co. Ltd. and the others from Wako Pure Chemical Industries. These diluents were washed three-times with water and kept at the condition saturated with water. Other chemicals were of GR and used without further purification.

A tap water was distilled once with the still of a stainless steel and then deionized by passing through the Autopure system (Yamato/Millipore, type WT101 UV). This pure water was used for preparing all the aqueous solutions.

5.2. Extraction procedures

A solution A: an aqueous solution (4 cm^3) of 0.036 mol dm^{-3} $Pb(NO_3)_2$, that (5 cm^3) of 0.034 HPic, and that (25 cm^3) of 0.02 nitric acid were mixed in a volumetric flask with 250 cm^3 mark. A solution B: an aqueous solution (8 cm^3) of 0.006 mol dm^{-3} 18C6, the solution (5 cm^3) of 0.034 mol dm^{-3} HPic, and that (25 cm^3) of 0.02 mol dm^{-3} nitric acid were mixed in the volumetric flask. The solutions A and B (see the x-axes in Fig. 1) were mixed at various volume ratios in a stoppered glass tube of about 30 cm^3 and then their total volume was adjusted to 12 cm^3. Besides, the solutions thus-obtained were mixed with the same volume of the diluent and then shaken for 1 min by hand. These solutions were agitated at 298 K for 2 h with an Iwaki shaker system (a driving unit: SHK driver; a thermoregulator: type CTR-100; water-bath: WTB-24). After the mixtures in the tube reached equilibrium, they were centrifuged with a Kokusan centrifuge (type 7163-4.8.20) for 7 min in order to separate the two phases.

A portion (10 cm^3) of the organic phase separated was dispensed with a transfer pipette, was transferred into the tube of about 30 cm^3, and then an aqueous solution (20 cm^3) of 0.07 mol dm^{-3} HNO_3 was added in it. Similarly, Pb(II) species extracted into the organic phase were back-extracted into the aqueous HNO_3 solution. Operations of equilibrating and separating the two phases were the same as those described above. A portion of the acidic aqueous phase was dispensed with a transfer pipette and then was used as a test solution for an atomic absorption analysis.

Amounts of Pb(II) back-extracted into the acidic aqueous solutions were determined at 283.3 nm by using a Hitachi polarized Zeeman atomic absorption spectrophotometer (type Z-6100) equipped with a hollow cathode lamp (type 208-2023, Hitachi High-Technologies). Amounts of Pb(II) by blank experiments were subtracted from those of Pb(II) extracted by 18C6. Calibration curves were employed here for the determination of total concentrations, [analyzed total-concentration of Pb(II)]$_o$, of Pb(II) extracted into the organic phases. The pH values of the separated aqueous phases were also measured at 298 K by a Horiba pH/ion meter (type F-23) equipped with a Horiba electrode (LAQUA, type 9615-10D) [19].

Appendix A

For Processes (1) to (10), mass balance equations were

$$[\mathrm{M}]_t = \left[\mathrm{M}^{2+}\right] + \left[\mathrm{ML}^{2+}\right] + \left[\mathrm{MA}^{+}\right] + [\mathrm{MLA}_2] + \left[\mathrm{MLA}^{+}\right]_o + [\mathrm{MLA}_2]_o, \tag{A1}$$

$$[\mathrm{L}]_t = [\mathrm{L}] + [\mathrm{L}]_o + \left[\mathrm{ML}^{2+}\right] + [\mathrm{MLA}_2] + \left[\mathrm{MLA}^{+}\right]_o + [\mathrm{MLA}_2]_o, \tag{A2}$$

and

$$\begin{aligned}[\mathrm{A}]_t = {} & [\mathrm{A}^-] + \left[\mathrm{MA}^{+}\right] + 2[\mathrm{MLA}_2] + [\mathrm{A}^-]_o + \left[\mathrm{MLA}^{+}\right]_o + 2[\mathrm{MLA}_2]_o \\ & + [\mathrm{HA}] + [\mathrm{HA}]_o.\end{aligned} \tag{A3}$$

Using $[\mathrm{MLA}^+]_o = [\mathrm{A}^-]_o$ (as a charge balance equation in the organic phase), assuming that $[\mathrm{M}^{2+}] + [\mathrm{ML}^{2+}] + [\mathrm{MA}^+] \gg [\mathrm{MLA}_2]$, $[\mathrm{L}] + [\mathrm{L}]_o + [\mathrm{ML}^{2+}] \gg [\mathrm{MLA}_2]$ [2], and $[\mathrm{A}^-] + [\mathrm{MA}^+] + [\mathrm{HA}] + [\mathrm{HA}]_o \gg 2[\mathrm{MLA}_2]$, and expressing $([\mathrm{MLA}^+]_o + [\mathrm{MLA}_2]_o)$ as *Ab*, then we obtain

$$\begin{aligned}[\mathrm{M}]_t - Ab & \approx \left[\mathrm{M}^{2+}\right] + \left[\mathrm{ML}^{2+}\right] + \left[\mathrm{MA}^{+}\right] \\ & = \left[\mathrm{M}^{2+}\right]\left(1 + K_{\mathrm{ML}}[\mathrm{L}]_o/K_{\mathrm{D,L}} + K_{\mathrm{MA}}[\mathrm{A}^-]\right),\end{aligned} \tag{A1a}$$

$$\begin{aligned}[\mathrm{L}]_t - Ab & \approx [\mathrm{L}] + [\mathrm{L}]_o + \left[\mathrm{ML}^{2+}\right] \\ & = [\mathrm{L}]_o\left(1 + {K_{\mathrm{D,L}}}^{-1} + K_{\mathrm{ML}}\left[\mathrm{M}^{2+}\right]/K_{\mathrm{D,L}}\right),\end{aligned} \tag{A2a}$$

and

$$\begin{aligned}[\mathrm{A}]_t - 2Ab & \approx [\mathrm{A}^-] + \left[\mathrm{MA}^{+}\right] + [\mathrm{HA}] + [\mathrm{HA}]_o \\ & = [\mathrm{A}^-]\left\{1 + K_{\mathrm{MA}}\left[\mathrm{M}^{2+}\right] + \left(K_{\mathrm{HA}} + K_{\mathrm{ex,HA}}\right)\left[\mathrm{H}^{+}\right]\right\}\end{aligned} \tag{A3a}$$

$$\text{with } K_{\mathrm{ex,HA}} = [\mathrm{HA}]_o/\left[\mathrm{H}^{+}\right][\mathrm{A}^-] = K_{\mathrm{HA}}K_{\mathrm{D,HA}}. \tag{A4}$$

Here, we can fix the $[\mathrm{M}]_t$, $[\mathrm{L}]_t$, and $[\mathrm{A}]_t$ values and then determine the *Ab* values by AAS measurements. Then, the above equations were rearranged into

$$\left[\mathrm{M}^{2+}\right] \approx ([\mathrm{M}]_t - Ab)/\left\{1 + K_{\mathrm{ML}}[\mathrm{L}]_o/K_{\mathrm{D,L}} + K_{\mathrm{MA}}[\mathrm{A}^-]\right\}, \tag{A1b}$$

$$[\mathrm{L}]_o \approx ([\mathrm{L}]_t - Ab)/\left\{1 + {K_{\mathrm{D,L}}}^{-1} + K_{\mathrm{ML}}\left[\mathrm{M}^{2+}\right]/K_{\mathrm{D,L}}\right\}, \tag{A2b}$$

and

$$[\mathrm{A}^-] \approx ([\mathrm{A}]_t - 2Ab)/\left\{1 + K_{\mathrm{MA}}\left[\mathrm{M}^{2+}\right] + K_{\mathrm{HA}}\left(1 + K_{\mathrm{D,HA}}\right)\left[\mathrm{H}^{+}\right]\right\}, \tag{A3b}$$

where K_{ML}, K_{MA}, $K_{\mathrm{D,L}}$, and K_{HA} are defined as $[\mathrm{ML}^{2+}]/[\mathrm{M}^{2+}][\mathrm{L}]$, $[\mathrm{MA}^+]/[\mathrm{M}^{2+}][\mathrm{A}^-]$, $[\mathrm{L}]_o/[\mathrm{L}]$, and $[\mathrm{HA}]/[\mathrm{H}^+][\mathrm{A}^-]$, respectively. Hence, computing K_{MA} and K_{HA} for given *I* values of the aqueous phases, we can obtain the $[\mathrm{M}^{2+}]$, $[\mathrm{L}]_o$, and $[\mathrm{A}^-]$ values from Eq. (A1b) to (A3b) by successive approximation and consequently evaluate the $K_{\mathrm{ex}}^{\mathrm{mix}}$ values from Eq. (14) in Section 2.2. The $K_{\mathrm{D,HPic}}$ (=$[\mathrm{HPic}]_o/[\mathrm{HPic}]$) values (see the footnote g in Table 2) were also treated as constants for given diluents [2,19]. Here, the *I* and I_o values for both the phases were calculated from

$$\begin{aligned} I & = (1/2)\left(4\left[\mathrm{M}^{2+}\right] + 4\left[\mathrm{ML}^{2+}\right] + \left[\mathrm{MA}^{+}\right] + \left[\mathrm{H}^{+}\right] + [\mathrm{A}^-] + [X^-]\right) \\ & = \left[\mathrm{M}^{2+}\right] + \left[\mathrm{ML}^{2+}\right] + [\mathrm{A}^-] + [\mathrm{HX}]_t = \left[\mathrm{M}^{2+}\right]\left(1 + K_{\mathrm{ML}}[\mathrm{L}]_o/K_{\mathrm{D,L}}\right) \\ & \quad + [\mathrm{A}^-] + [\mathrm{HX}]_t \end{aligned} \tag{A5}$$

and

$$I_o = (1/2)\left(\left[\mathrm{MLA}^{+}\right]_o + [\mathrm{A}^-]_o\right) = \left[\mathrm{MLA}^{+}\right]_o = [\mathrm{A}^-]_o = K_{\mathrm{D,A}}[\mathrm{A}^-]. \tag{A6}$$

In order to rearrange Eqs. (A5) and (A6), respective charge-balance equations were used: $2[\mathrm{M}^{2+}] + 2[\mathrm{ML}^{2+}] + [\mathrm{MA}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{X}^-]$ and $[\mathrm{MLA}^+]_o = [\mathrm{A}^-]_o$.

For the extraction into NB, the mass- and charge-balance equations were Eqs. (A1), (A2), and (A3); $2[\mathrm{M}^{2+}] + 2[\mathrm{ML}^{2+}] + [\mathrm{MA}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{X}^-]$ and $[\mathrm{MLA}^+]_{\mathrm{NB}} + [\mathrm{H}^+]_{\mathrm{NB}} = [\mathrm{A}^-]_{\mathrm{NB}} + [\mathrm{X}^-]_{\mathrm{NB}}$.

Also, we can obtain a mass-balance equation for the strong acid, HX, as follows:

$$\begin{aligned}[\mathrm{HX}]_t & = [\mathrm{X}^-] + [\mathrm{HX}] + [\mathrm{X}^-]_{\mathrm{NB}} + [\mathrm{HX}]_{\mathrm{NB}} \\ & \approx [\mathrm{X}^-] + [\mathrm{X}^-]_{\mathrm{NB}} + [\mathrm{HX}]_{\mathrm{NB}},\end{aligned} \tag{A7}$$

where the formation of HL^+, HLA, HLX, MLX^+, and MLX_2 was neglected. Rearranging Eq. (A7), the following equation was derived:

$$[\mathrm{X}^-] = [\mathrm{HX}]_t/\left\{1 + K_{\mathrm{D,X}}\left(1 + K_{\mathrm{HX,NB}}K_{\mathrm{D,H}}\left[\mathrm{H}^{+}\right]\right)\right\}. \tag{A8}$$

Here, as $K_{\mathrm{D,X}}$ (=$[\mathrm{X}^-]_{\mathrm{NB}}/[\mathrm{X}^-]$), $K_{\mathrm{HX,NB}}$ (=$[\mathrm{HX}]_{\mathrm{NB}}/[\mathrm{H}^+]_{\mathrm{NB}}[\mathrm{X}^-]_{\mathrm{NB}}$), and $K_{\mathrm{D,H}}$ (=$[\mathrm{H}^+]_{\mathrm{NB}}/[\mathrm{H}^+]$), reported values at $\mathrm{X}^- = \mathrm{NO}_3^-$ were employed and were treated as constants being independent of the *I* and I_{NB} values. Considering $\log K_{\mathrm{D,X}} = -5.63$ [14]. $\log K_{\mathrm{HX,NB}} = 8.08$ [14], and $\log K_{\mathrm{D,H}} = -5.0$ [26] at 298 K, we can actually approximate Eq. (A8) to $[\mathrm{X}^-] = [\mathrm{HX}]_t$. Hence, the *I* values for both the phases become

$$\begin{aligned} I & = \left[\mathrm{M}^{2+}\right] + \left[\mathrm{ML}^{2+}\right] + [\mathrm{A}^-] + [\mathrm{X}^-] = \left[\mathrm{M}^{2+}\right]\left(1 + K_{\mathrm{ML}}[\mathrm{L}]_{\mathrm{NB}}/K_{\mathrm{D,L}}\right) \\ & \quad + [\mathrm{A}^-] + [\mathrm{HX}]_t \end{aligned} \tag{A5a}$$

and

$$I_{\mathrm{NB}} = [\mathrm{A}^-]_{\mathrm{NB}} + [\mathrm{X}^-]_{\mathrm{NB}} = K_{\mathrm{D,A}}[\mathrm{A}^-] + K_{\mathrm{D,X}}[\mathrm{HX}]_t. \tag{A9}$$

Similarly, the $K_{\mathrm{D,Pic}}$ value [26] and the $K_{\mathrm{D,18C6}}$ one [17] were available and were used as constants. The mole fraction of $[\mathrm{Pb(18C6)Pic}^+]_o$ was calculated from the relation

$$\left[\mathrm{MLA}^{+}\right]_o/Ab = K_{\mathrm{ex\pm}}/\left(K_{\mathrm{ex\pm}} + K_{\mathrm{ex}}K_{\mathrm{D,A}}[\mathrm{A}^-]\right), \tag{A10}$$

where the $K_{\mathrm{ex}\pm}$, K_{ex}, $K_{\mathrm{D,A}}$, and $[\mathrm{A}^-]$ values at $\mathrm{A}^- = \mathrm{Pic}^-$ can be determined experimentally.

Appendix B

The relation,

$$I_{\mathrm{A,mini}} = 1 + \sum\left(\left[\mathrm{Cd}^{2+}\right] + \left[\mathrm{Cd(18C6)}^{2+}\right]\right) \bigg/ \sum[\mathrm{A}^-] \approx (4/3), \tag{A11}$$

in Section 3.7 was derived from the charge-balance equation, $2[\mathrm{M}^{2+}] + 2[\mathrm{ML}^{2+}] + [\mathrm{MA}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{X}^-]$, as follows. This equation can be rearranged into

$$[\mathrm{A}^-] \approx 2\left(\left[\mathrm{M}^{2+}\right] + \left[\mathrm{ML}^{2+}\right]\right) + \left[\mathrm{MA}^+\right] \tag{A12}$$

by assuming $2[\mathrm{M}^{2+}] + 2[\mathrm{ML}^{2+}] + [\mathrm{MA}^+] \gg [\mathrm{H}^+]$ and introducing $[\mathrm{X}^-] = 0$ in it. Then, the term $\sum([\mathrm{Cd}^{2+}] + [\mathrm{Cd(18C6)}^{2+}])/\sum[\mathrm{A}^-]$ in Eq. (A11) is changed into

$$\begin{aligned}\sum\left(\left[\mathrm{Cd}^{2+}\right] + \left[\mathrm{CdL}^{2+}\right]\right) \bigg/ \left\{2\sum\left(\left[\mathrm{Cd}^{2+}\right] + \left[\mathrm{CdL}^{2+}\right]\right) + \sum\left[\mathrm{CdA}^+\right]\right\} \\ = \left\{2 + \sum\left[\mathrm{CdA}^+\right] \bigg/ \sum\left(\left[\mathrm{Cd}^{2+}\right] + \left[\mathrm{CdL}^{2+}\right]\right)\right\}^{-1}\end{aligned} \tag{A13}$$

at L = 18C6. If the term, $\sum[\mathrm{CdA}^+]/\sum([\mathrm{Cd}^{2+}] + [\mathrm{CdL}^{2+}])$, is less than unity, then minimum of I_{A} can equal $(4/3)\ \{= 1 + (2 + 1)^{-1}\}$. Hence, $\log I_{\mathrm{A}}$ is estimated to be 0.12. The experimental values for the CdBr_2- and CdPic_2–18C6 extraction systems were somewhat larger than this value.

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