Solvent Extraction of Cadmium Picrate by 18-Crown-6 Ether into Several Less-polar Diluents and Nitrobenzene: Re-evaluation of the Corresponding Overall Extraction Systems

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Abstract

TCadmium picrate (CdPic₂) in water was extracted at 25°C by 18-crown-6 ether (18C6) into o-dichlorobenzene (oDCBz), bromobenzene (BBz), dibutylether (DBE), and nitrobenzene (NB). Their extraction constants (Kₙ and Kₙ⁻) were determined, where Kₙ and Kₙ⁻ at L=18C6 were defined as (CdLPic)₀/(Cd²⁺)(L)₀(Pic⁻) and (CdLPic⁻)₀/(Pic⁻)(L)₀(Cd²⁺), respectively. The subscript “o” denotes an organic phase, such as oDCBz and BBz. The same extraction constants were re-determined for a system with benzene. Also, individual distribution constants (K₁(Pic⁻)₀(Pic⁻)₀) of picrate ion Pic⁻ into the above o phases were determined with the Kₙ determination. Properties for the CdPic₂ extraction with 18C6 were discussed by using the above constants and those available from the same extraction systems with other diluents. From comparing the experimental log Kₙ values with the log Kₙ₋ values for only the high-polar NB system, an interfacial potential difference (∆φo) at extraction equilibrium was evaluated, where the symbol, log Kₙ₋, shows the log Kₙ value standardized at ∆φo=0 V and 25°C. In this case, an extraction constant for an HPic extraction into DBE was determined spectrophotometrically at 25°C.

Keywords: Extraction constants; Individual distribution constant; Interfacial equilibrium potential; Solute-solvent interaction; At water/nitrobenzene interface; Cadmium picrate; 18-Crown-6 ether

Introduction

18-Crown-6 ether (18C6) extracts CdBr₂, cadmium picrate (CdPic₂), or alkaline-earth metal picrates into various diluents [1-3]. In the previous study [1], the authors clarified that the extracted ion-pair complex, Cd(18C6)Br, very weakly interacts with water molecules and also the diluents ones and they also suggested that another complex Cd(18C6)Pic, strongly interacts with water molecules. In addition to this, it has been suggested that the latter ion-pair complex has a more polar structure than the former does [1]. However, kinds of the diluents used for the CdPic₂ extraction experiments with 18C6 were fewer, compared with kinds of the diluents for the CdBr₂ extraction ones.

In the above studies, furthermore, component equilibria which constitute overall extraction equilibria have been considered to be at least 6-10 ones [1,3,4]. For example, the component equilibria are L⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻=-=-=-=-O

Materials and Methods

Chemicals

The preparation method of CdPic₂⋅nH₂O was essentially the same as that reported before [1] this n value was determined by a Karl-Fischer titration to be 5.67 ± 0.23 at number (N) of run of 3. This finding was in good agreement with that (n=5.65) obtained from an EDTA titration of Cd(II) in the aqueous solution which contains CdPic₂⋅nH₂O. Also, spectrophotometric analysis of Pic⁻ in the aqueous solution at 355.0 nm showed the molar ratio of Cd(II):Pic⁻=1:2.1 (see below). Water amount of used 18C6 (>98.0%, Wako) was determined by the Karl-Fischer titration to be 0.062 ± 0.029% at N=4. The H(I) amount of an aqueous solution prepared from a commercial HPic (>99.5%, Wako) was determined by an acid-base titration [7]. Other reagents were the same as or similar to those employed previously [1,4].

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Extraction procedures

The experimental procedures for the CdPic extraction by 18C6 were essentially the same as those described before [1,4] although the experiments were performed with the oDCBz (>99.0%, Kanto), DBE (>99.0%, Kanto), NB (>99.5%, Kanto), and Bz (>99.5%, Wako) systems and with mixtures of CdSO₄ (>99.0%: (3/8) hydrate, Kanto) with HPic for the BBz, (>99.5%, Kanto) systems. Here, the mixture was prepared by mixing an aqueous CdSO₄ solution with a mixture between Ba(OH)₂ (>98.0%: 8 hydrate, Wako) and an excess amount of HPic and then that with the precipitate was filtered. Total amounts of Cd(II) back-extracted from the o phases into aqueous solutions of the 0.1 mol dm⁻³ HNO₃ were determined at the wavelength of 228.8 nm by a Hitachi atomic absorption spectrophotometer (type Z-6100) equipped with a Hitachi hollow cathode lamp (Mitorika Co., under the license of Hitachi Ltd.) of CdSn an air-acetylene flame [1]. Total concentrations employed for the experiments were (0.79-1.7) × 10⁻³ mol dm⁻³ for the prepared CdPic, and 1.1 × 10⁻³-0.22 for 18C6 (0.79-1.5) × 10⁻³ mol dm⁻³ Cd(II), 0.012-0.030 Pic⁻(I), and 0.0017 SO₄²⁻ for the mixture and (0.051-5.1) × 10⁻³ for 18C6. Also, the procedures for the HPic extraction into DBE were the same as those reported before [7]. Total amounts of Pic⁻(I) extracted into DBE were back-extracted into aqueous solutions with 0.1 mol dm⁻³ NaOH from the DBE phases and then were determined at the wavelength of 355.0 nm spectrophotometrically [7]. Total concentrations of the aqueous HPic solutions employed were in the range of (0.50-3.4) × 10⁻³ mol dm⁻³.

Data analysis

Data analysis for the extraction experiments was essentially the same as that described before [1,3,4]. The extraction constant parameter, , has been introduced, where as defined as ([MLA]⁺+[MLA]⁻)/([M²⁺][L][A⁻]) by assuming that ML[A]⁻->[M]+[MLA]⁺+[M²⁺] [1,3,4]. Its numerators were determined by AAS measurements (see above) and were expressed as “Ab” here. Also, the [M²⁺], [L] and [A⁻] values were calculated from the following equations by a successive approximation method:

\[
\begin{align*}
[M²⁺] &= \frac{[M] - Ab}{1 + K_{ML} [A⁻] + K_{ML} K_{MLD} [L] [A⁻] + K_{ML} K_{MLD} K_{MLDA} [L]² [A⁻]²} \\
[L] &= \frac{[L] - Ab}{1 + K_{MLD} [L] + K_{MLD} K_{MLDA} [L] [A⁻] + K_{MLD} K_{MLDA} K_{MLDAA} [L]² [A⁻]²} \\
[A⁻] &= \frac{\sqrt{b^2 - 4ac} - b}{2a}
\end{align*}
\]

(1) (2) (3)

With \(a=2K_{MLA} K_{ML} [M²⁺][L]/K_{MLD}, \)
\(b=1+2K_{MLA} [M²⁺][K_{MLA} + K_{MLD}][H⁻], \)
and \(c=2Ab - [A⁻]. \)

Here, \(K_{MLA}, K_{MLD}, K_{MLDA}, \) and \(K_{MLDA} \) in the above equations denote an ion-pair formation constant (mol⁻¹ dm⁶ unit) for MA⁺ in water, a complex formation one (mol⁻¹ dm⁶) for ML²⁺ in water, overall ion-pair formation one (mol⁻¹ dm⁶) between ML²⁺ and 2A⁻ in water, an association one(mol⁻¹ dm³) for an acid, HA, in water, and an extraction one (mol⁻¹ dm⁶) for HA into the o phase, respectively. These values were either available from a reference [8] or evaluated from those [1,9,10] reported previously. Also, \(j \) shows the total concentration of species with \(j=M(II), \) or \(A⁻(I). \) In the computation, the \(K_{MLA}, K_{MLD}, \) and \(K_{MLDA} \) values were calculated taking account of the ionic strength (I) of ionic species in water: \(I=\frac{1}{2}(a[M²⁺]+[ML²⁺]+[ML⁺]+[MA⁺]+[A⁻]) \)

[3,4] which was changed into \(I=[M²⁺]+[ML²⁺]+[A⁻] \) fundamentally based on the charge balance equation, \([2M²⁺]+2[ML²⁺]+[ML⁺]+[MA⁺]+[M⁻]+[M⁻]=1 \) (see below).

Results and Discussion

On the determination of fundamental extraction data

Compositions of extracted complexes were determined by plotting \( \log (D/Pic⁻) \) against log (18C6) at \( \alpha=BBz, \) oDCBz, DBE, and NB [1-4,11]. Here, \( D \) refers to an experimental distribution ratio of Cd(II) into the o phases and the (Pic⁻) and (18C6), values were calculated from Equations (3) and (2), respectively. Regression lines of the plots were lines with slope \((a)=0.81 \) and intercept \((b)=3.90 \) at a correlation coefficient \((R)=0.976 \) and \(N=11\) for the BBz system, \(a=1.13\) and \(b=4.65\) at \(R=0.972 \) and \(N=7\) for oDCBz with the mixture, \(a=0.76 \) and \(b=3.39 \) at \(R=0.944 \) and \(N=18\) for oDCBz with the prepared CdPic, \(a=1.02\) and \(b=4.61 \) at \(R=0.712 \) and \(N=23\) for DBE, \(a=0.55 \) and \(b=4.80 \) at \(R=0.902 \) and \(N=15\) for NB, and \(a=0.95 \) and \(b=4.28 \) at \(R=0.995 \) and \(N=15\) for Bz. These results indicate that the species composed of MLA=1:1:2 are extracted into oDCBz from the mixture, DBE, and Bz, where the ratios of Pic⁻(I)=A are speculated from the charge balance to Cd(II) (see above) [1,3,4,11]. Also, the intercepts \(a,b\) of these systems approximately show their \(K_{ex} \) values, when \(a \) equals unity [11]. On the other hand, dissociations of the species extracted are suggested for the BBz, NB systems, and oDCBz one with the prepared salt. The difference in \(a\) between the two oDCBz systems is caused by that between the experimental log [18C6]DCBz ranges which were -3.02 to -2.53 for the mixture and -6.73 to -3.09 for the prepared salt. That is, Cd(18C6)Pic in the oDCBz phase dissociates in the lower log [18C6]DCBz range and its ion-pair formation is facilitated in the higher range: the former case causes \(a<1\), while the latter one does \(a \geq 1\). Therefore, further data analyses were performed by assuming the extraction of CdLPic into the three diluent-systems [3,4,11]. Next, we determined the \(K_{ex}, K_{mix}, \) and \(K_{mix} \) values in terms of the following equations:

\[
\log K_{ex} = \log K_{ex} + \log ([M²⁺][L][A⁻])
\]

(4)

and \(\log (K_{mix} + \log ([M²⁺][L][A⁻]) \)

(4a)

under the electroneutrality condition of \([MLA]⁺-[A⁻] \) [3,4,11]: see Data Analysis. The non-linear regression analyses of plots [1,3,4,11] of \(K_{mix} \) versus \(\log ([M²⁺][L][A⁻]) \) (from Equation (4)) and \(\log ([M²⁺][L][A⁻]) \) (from Equation (4a)) yielded these values. The latter plots were analyzed here by introducing the \(K_{ex} \) values, obtained from the former plots, in Equation (4a). As examples, Figures 1 and 2 show the plots for the extraction of the prepared CdPic, with 18C6 into oDCBz. Lastly, the log \(K_{mix} \) log \(K_{mix} \) and \(K_{mix} \) were evaluated from the following thermodynamic cycles: log \(K_{mix} \) log \(K_{mix} \) log \(K_{mix} \) (see the introduction for the \(K_{mix} \) definition), and log \(K_{mix} \) log \(K_{mix} \) (respectively [3,4]. Table 1 summarizes the thus determined fundamental values.

In Table 1, there were no large differences in log \(K \) values between the 18C6 extraction from the prepared salt, CdPic, 5.7H₂O, and that from the mixture into oDCBz, except for log \(K_{mix} \). These facts fundamentally show that the BBz system is comparable with the oDCBz, DBE, and NB systems. The difference in log \(K_{mix} \) can come from that in \(I_{DCBz} \), because its value is proportional to the log \((I_{DCBz}) \) one in some cases [4] see below for another detailed explanation.
The log $K_e$ values were in the order DBE < oDCBz < BBz < NB (Table 1). Similar tendencies were observed in the log $K_{ex}$, log $K_{DLPic}$, and log $K_{DLPic}$ values. The log $K_{mix}$ values were in the order DBE ≥ oDCBz ≥ BBz < NB. Although there are differences in $I_{ex}$ and amounts of water saturated into the diluents, these three orders seem to fundamentally reflect the diluent’s polarity except for the $K_{ex}$ order; the authors were not able to find the data of amount of water into DBE in references (H$_2$O)$_{nb}$=0.178 mol dm$^{-3}$ at 25°C [12] mole fractions of water in the o phases were 0.0025 for o=DCBz, 0.0021 for BBz, and 0.0149 for NB [13]. The log $K_{DLPic}$ order was DBE-oDCBz < BBz < NB. This order is strongly reflected into the log $K_e$ one, because the average log $K_e$ values are in the range of 8.68-7.04 (see Table 1); that is, differences in $K_e$ among the diluents employed are very small.

**Plot of log $K_{ex}$ versus log $K_{DLPic}$**

Figure 3 shows the plot of log $K_{ex}$ versus log $K_{DLPic}$ for the various diluent systems [1,14] at L=18C6. A point of the NB extraction system seemed to largely deviate from other points. Its regression line in Figure 3 was log $K_{ex}$=(0.80 ± 0.13) log $K_{DLPic}$ at R=0.894 and N=12 except for the NB system, where the two sets of data were employed for the oDCBz system in the calculation. In CdLX crystals at L=18C6 with $X_2$=Cl, Br, and I [1,15,16] and at B18C6 with Cl and Br [17] the two (X−I) bind directly to the central Cd(II) and their positions are perpendicular to the mean plane composed of the donor oxygen atoms in L. These complexes have the hexagonal bi pyramidal geometry. One can easily suppose its structure is kept in o phases with less polarities, except for the NB phase; see the caption in Figure 1 about the o phases. From comparing the log $K_{ex}$ versus log $K_{DLPic}$ plot of the Cd(18C6)Pic system with that of Cd(18C6)Br, one (log $K_{ex}$=1.16log $K_{DLPic}$+5.27 at R=0.993 and N=11 [1,4]) we can immediately see that the plots of the both systems largely differ from each other at the R and slope values. The $R$ value of the Pic system suggests that the extracted ion-pair complex Cd(18C6)Pic, has the higher polar structure, compared with Cd(18C6)Br, and also its slope ($=V_{mix}/V_1$) suggests that the complex with Pic(−) has relatively a compact shape [1,4]. Here, V denotes a molar volume (cm$^3$ mol$^{-1}$) of the species corresponding to the subscript, MLA, or L. The $V_{mix}/V_1$ value was estimated to be 1.7×10$^5$ cm$^3$ mol$^{-1}$ from $V_{mix}$=214 cm$^3$ mol$^{-1}$ [14]. This value is in accord with that ($=4$ about 200) reported before.

Since the intercept is expressed as log $K_eK_{ex}$/a term based on interactions between solutes and solvent molecules [1,14], we can immediately evaluate this latter term from the average log $K_eK_{ex}$ value among the extraction systems. This interaction term was calculated to be -2.7, when log $K_eK_{ex}$=6.68 was used. This negative sign suggests a...
strong interaction between water molecules and the ion-pair complex Cd(18C6)Pic, and/or a weak one between diluent molecules and the complex (see below), compared with the interaction of 18C6 with both the solvent molecules. This suggestion is in agreement with the finding speculated from the R value [1]. The same discussion can be satisfied for the plot of \( \log K_{D,L} \) versus \( \log K_{o,1} \) [1].

For the CdPic extraction by 18C6 into Bz, we easily obtained from the analysis described in the above section \( \log K_s = 4.3 \pm 0.04 \) (or \( 4.2 \pm 0.1 \) from Equation (4a)), \( \log K_{D,Pb} = -5.1 \pm 0.1 \), and \( \log K_{ex} = -2.9 \pm 0.1 \), or \( -2.3 \pm 0.2 \) from Equation (4a) without the fixed \( K_s \). These values also gave \( K_{o,1} = \log K_{ex} - \log K_{o,1} = 7.4 \pm 0.2 \) at \( I = 8.4 \times 10^{-4} \) mol dm\(^{-3} \) and \( \log K_{o,1} = -3.75 \) (or \( -3.74 \)) at \( 25^\circ C \) [1] (see above) [1,10,14].

The thus determined \( K_o,1 \) value was used for arc- calculation of \( K_{o,1} \) and \( K_{o,12} \) becomes 3.17 (evaluated from \( K_{o,1} \)). In this study, the authors correct the \( K_o,1 \) value from 1.98 reported in ref.1 to 4.39 and also do the logarithmic separation factor [4] (\( \log (K_{o,12}/K_{o,11}) \)) from 9.73 in ref. 4 to 7.32; the revised \( K_{o,1} \) value became 7.1. By there-determination of \( K_o \), the authors will eliminate a problem on the large deviation (1) of the Bz system from the plot of \( \log K_{o,1} \) versus \( \log K_{o,12} \).

Determination of equilibrium constants for the HPic extraction into DBE

Figure 4 shows a plot of \( \log D_s \) versus pH for the HPic extraction into DBE. A non-linear regression analysis of this plot gave the log \( K_{o,HPic} \) value from its intercept: \( K_{o,HPic} = [HA]_o/[H^+][A^-] \). Here, the relation of 

\[ \log D_o = \log K_{o,HPic} + \log (1 + K_{eq,AB}) + \log (1 + K_{eq,AB}) \]

(5) in which the \( K_{eq} \) value averaged in the experimental \( I \) range (=0.00043-0.022 mol dm\(^{-3} \)) at HA=HPic was introduced, was employed for the analysis [7]. The symbol \( D_s \) refers to the distribution ratio of species with \( A^- \); the line seems to be somewhat higher than the plots in the lower range of pH. This deviation may be due to that of the averaged \( K_{eq} \). The thus obtained value was \( \log K_{o,HPic} = 1.06 \pm 0.01 \) at 25°C with the regression line at \( R=0.997 \). This value was used for the \( K_s \) calculation (see Equations (3) and (3b)). Also, using the average \( \log K_{o,HPic} \) value (=0.55 ± 0.03) [8], we evaluated \( \log K_{o,HPic} \) to be 0.51 ± 0.03. This log \( K_{o,HPic} \) value was the smallest of those (=0.89-1.97) [7] reported previously by the authors on the HPic extraction into various diluents.

On the interfacial equilibrium-potential difference at extraction

According to our previous papers [3,18], a difference between \( \log K_{D,A} \) and \( \log K_{D,Pb} \) for the NB system shows the presence of an interfacial potential difference, \( \Delta \phi_{eq} \), at extraction equilibrium. From the relation [1,3,18]

\[ \Delta \phi_{eq} = \Delta \phi_{eq}^\circ - (2.303RT/F) \log K_{D,A} \] (6)

for the univalent anion \( A^- \), we can easily calculate the \( \Delta \phi_{eq}^\circ \) value. Here, the symbol, \( \Delta \phi_{eq}^\circ \), refers to the formal potential standardized at \( \Delta \phi_{eq} = 0 \) V based on the PbAs and PbPb\(^{2+} \) assumption [19] and is expressed as the function \( \log K_{eq} = \Delta \phi_{eq}^\circ (2.303RT/F) \) of \( \Delta \phi_{eq}^\circ \) [0.05916 (defined as \( \log K_{D,A} \) at 25°C [1,3,18,20]). Also, \( F, R, \) and \( T \) show usual meanings. From \( \Delta \phi_{eq}^\circ = 0.030 \) V [21] and the log \( K_{D,A} \) value of the NB extraction system in Table 1, the \( \Delta \phi_{eq} \) value was calculated to be 0.14 V. At the same time, this value indicates that \( \log K_{D,A} \) greater than \( \log K_{D,Bz} \) and \( \log K_{D,Bz,HL} \) values are expressed as \( 2(\Delta \phi_{eq} - \Delta \phi_{eq}^\circ) / 0.05916,2(\Delta \phi_{eq} - \Delta \phi_{eq}^\circ) / 0.05916 \) and \( (\Delta \phi_{eq} - \Delta \phi_{eq}^\circ) / 0.05916 \) at \( \Delta \phi_{eq} = 0.14 \) V, respectively [3,18]; +"2" of the former two terms refer to the formal charges of Cd\(^{2+} \) and CdL\(^{2+} \)(see Equation (7)). The same is essentially true of the other extraction systems, although their \( \Delta \phi_{eq}^\circ \) values have not been determined in many cases. For the 1,2-dichloroethane and dichloromethane systems, the \( s \) values are available from references [21,22].

The difference between \( \log K_{D,A} \) values (see Table 1) in the oDCBz extraction system can be explained in terms of those between their charge balance equations, namely the difference between the \( \Delta \phi_{eq} \) and \( \Delta \phi_{eq} \) is also relevant to the difference between the \( I_{18C6,HBz} \) values (see above). The experimental condition with the extraction of the prepared CdPic by L yields the charge balance equation of

\[ 2(Cd^{2+}) + 2(CdL^{2+}) + [CdPic]_o = [Pic]_o \] (7)

(or actually \( [CdPic]_o = [Pic]_o \); see above) in the o phase, while the other condition with the extraction of the mixture can yield the equation of \( 2(Cd^{2+}) + 2(CdL^{2+}) + [CdPic]_o + [H^+] \) \( + [HL^+] = [Pic]_o \) (8).

Figure 4: Plot of \( \log D_o \) versus pH for the HPic extraction into DBE. The dotted line shows a regression one based on Equation (5) (see text).
(or similarly [CdLPic]++[H]++[HL]+=[Pic]+). Probably, the [H]++[HL] term in Equation (8) contributes to an increase in \( I_e \) for the extraction of the mixture with L (see Table 1).

Applying Equation (6) to Equation (7) and the term in Equation (8), we can rewrite as

\[
2[CD^{2+}] \exp(2F(\Delta \phi_{o} - \Delta \phi_{CL}^{0}))/RT + 2[CD^{2+}] \exp(2F(\phi_{Pic} - \phi_{CL}^{0}))/RT + [CdLPic] \exp(-2F(\Delta \phi_{o} - \phi_{Pic}^{0}))/RT (7a)
\]

And \([H]^{+} \exp(F(\Delta \phi_{o} - \phi_{Pic}^{0}))/RT + [HL]^{+} \exp(F(\Delta \phi_{o} - \phi_{Pic}^{0}))/RT (8b)\) respectively [18,23]. The symbol \( \Delta \phi_{o}^{0} \) denotes the standard formal potential for the species \( j = \{ Cd(II), Cd(II), CdLPic\}, Pic(-), I(II), \) and \( HL(II) \).

Defining \( \exp(\Delta \phi_{o}^{0}/RT) \) in Equation (7a) or Equation (8a) that \( \exp(\Delta \phi_{o}^{0}/RT) \) was added to the left-hand side of Equation 7a, then we can easily obtain the cubic equations, and for \( \Delta \phi_{o} \) for the NB system, and \( \exp(-2F(\phi_{Pic} - \phi_{CL}^{0}))/RT \) in the case of Equation (7a).

One can easily see that this \( \Delta \phi_{o} \) value is constant for all processes of \( CD^{2+}, \) CdLPic, CdPic, CdLPic, and Pic or to those of Cd\( ^{2+} \), CdLPic, CdLPic, H\( ^{+} \), H\( ^{+} \), HL\( ^{+} \), HL\( ^{+} \), and Pic\( ^{-} \) [18] at \( o = \) oDCBz. Thus, these \( \Delta \phi_{o} \) values solved by the above-charge-balance equations are equivalent to those determined from \( \Delta \phi_{o} \) value [18,23].

The coextraction of water at 25°C was shown from the lower value (−4.2) and the increase in the lower value from Equation (7) can be caused by Equation (8b). Unfortunately, we were not able to find out the basic \( \Delta \phi_{o}^{0} \) data \( = \) [Cd(II), Pic(−), or (H)I] in respects with the oDCBz system.

**Estimate of ion-transfer formal potential of CdLPic at the water/NB interface**

On the basis of the above discussion, the \( \Delta \phi_{o}^{0} \) value at the water/NB interface was evaluated at 18°C. The [CdLPic]log values were evaluated from the relation [ML\( ^{2+} \)] = \( K_{eq}[K_{eq}][ML^{2+}][L][L][L][L][L][A]^{0} \) and then the [CdLPic]+ ones were calculated from [ML\( ^{2+} \)] = \( K_{eq}[K_{eq}][ML^{2+}][L][L][L][L][L][A]^{0} \).

Here, \( K_{eq} \) was evaluated from the relation \( K_{eq} = \log K_{eq}^0 \) \( = \log K_{eq}^0 \log (y_{y}/y_{y}) = \log K_{eq}^0 \log y_{y} \) with \( y = y_{y} \). The symbols, \( K_{eq}^0, y_{y}, y_{y}, \) and \( y_{y} \), denote that \( I > 0 \), an activity coefficient of ML\( ^{2+} \), of that of A, and that of ML\( ^{2+} \) at 25°C, respectively [10,24]. \( K_{eq}^0 = 3.4 \times 10^{-13} \) mol \( ^{-1} \) dm\( ^{3} \). From the above calculation, \( \Delta \phi_{o}^{0} \) was obtained as 0.14 V (see above), immediately we were able to calculate \( \Delta \phi_{o}^{0} \) to be 0.17 V at 25°C. This value is much larger than that of Pic\( ^{-} \) in the ion transfer at the water/NB interface. This fact suggests the stronger interaction of CdLPic than Pic with water molecules, as described above.

**Conclusion**

By adding the log \( K_{eq}^0 \) values for the three diluent systems except for the NB one, the plot of log \( K_{eq}^0 \) versus log \( K_{eq}^0 \) for the present CdPic18C6 extraction system was re-analyzed in the number of data comparable with the plot of CdBr218C6 extraction one. Although the extraction data for the Bz system were revised, the result for the interaction between Cd(18C6)\( ^{2+} \) (Pic\( ^{-} \)) and water molecules, obtained from the former plot, was in agreement with the previously-reported result [1]. Also, the presence of \( \Delta \phi_{o} \) in the CdII extraction system was shown from the \( K_{eq}^0 \) determination, as well as that in the M(I) extraction ones with L. Moreover, the authors were able to estimate the ion-transfer formal potential of Cd(18C6)Pic\( ^{-} \) at the water/NB interface.

**References**


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