An Approximation Method for Determining Key Extraction Constants in the Equilibrium-Analysis of Cd(II) Extraction with 18-Crown-6 Ether into Some Diluents

Abstract
Three key extraction-constants, $K_{ex}$, $K_{ex+}$, and $K_{Cd/CdL}$, were determined at 298K with an approximate method. Here, $K_{ex}$, $K_{ex+}$, and $K_{Cd/CdL}$ were defined as

$$
\left(\frac{[CdLa^+]}{[Cd^{2+}][La^-]}\right)_{org} = \left(\frac{[CdLa^2^+]}{[Cd^{2+}][La^-]}\right)_{org}
$$

and

$$
\left(\frac{[CdLa^2^+]}{[Cd^{2+}][La^-]}\right)_{org} = \left(\frac{[CdLa^+]}{[Cd^{2+}][La^-]}\right)_{org},
$$

respectively. $L$ shows 18-crown-6 ether, $A^-$ does picrate ion, and the subscript "org" denotes an organic phase. Diluents employed as the org phases were o-dichlorobenzene, bromobenzene, dibutylether, and nitrobenzene. In order to determine briefly these key constants, the following approximate equations were used: $K_{ex} \approx D / \left[La^-\right]_{org} \left[A^+\right]_{org}^2$, $K_{ex+} \approx D / \left[La^-\right]_{org} \left[A^+\right]_{org}$, and $K_{Cd/CdL} \approx D / \left[L\right]_{org}$, where $D$ refers to an experimental distribution ratio of Cd(II) between water and the org phases. The former two constants were compared with the corresponding values previously-determined. By comparing other many values, validity of the method was also examined and it was consequently clarified.

Keywords: Extraction constants; Distribution ratio; Ion-pair formation constants; Primary diagnosis; Distribution constant of picrate ion; Cadmium picrate, 18-Crown-6 ether

Abbreviations: org: Organic; oDCBz: o-Dichlorobenzene; BBz: Bromobenzene; DBE: Dibutylether; NB: Nitrobenzene; Cd: Cadmium; 18C6: 18-Crown-6 Ether; Pic: Picrate Ion

Introduction
There are many studies for the metal extraction by crown compounds (L) and other extractants similar to L into various diluents, such as benzene, chloroform, 1,2-dichloroethane, and NB [1-17]. In these studies, procedures of equilibrium analyses have become more difficult for primary users or outsiders of the field year by year. The authors have also studied so far for the improvements of such procedures [9,15-17]. However, such improvements seem to reduce the convenience of the procedures especially for the users.

So, one of the authors will report here a user-friendly procedure for analyzing the overall extraction equilibrium. As examples, the results of our previous paper [17] reported for the CdPic₂ extraction with 18C6 into oDCBz, BBz, DBE, and NB were handled.

Case Presentation
Simplification of the convoluted procedures [3,4,10,12-17] for the divalent-metal, M(II), extraction systems can stimulate an estimate of L functions by many workers. The overall M(II) extraction system with a univalent pairing anion ($A^-$) can be expressed as the following three extraction equilibria:

$$
Cd^{2+} + 2A^- \rightleftharpoons CdLa_{2,org} \quad [3,4],
$$

$$
Cd^{2+} + 2A^- \rightleftharpoons CdLa_{org}^+ + A^-_{org} \quad [3,15],
$$

and

$$
Cd^{2+} + 2A^- \rightleftharpoons CdLa_{org}^{2+} + 2A^-_{org} \quad [3,14].
$$

The expressions of these equilibria as equilibrium constants are

$$
K_{ex} = \left(\frac{[CdLa^2^+]}{[Cd^{2+}][La^-]}\right)_{org},
$$

and

$$
K_{ex+} = \left(\frac{[CdLa^+]}{[Cd^{2+}][La^-]}\right)_{org}.
$$

for the divalent-metal, M(II), extraction systems can stimulate an estimate of L functions by many workers. The overall M(II) extraction system with a univalent pairing anion ($A^-$) can be expressed as the following three extraction equilibria:
An Approximation Method for Determining Key Extraction Constants in the Equilibrium-Analysis of Cd(II) Extraction with 18-Crown-6 Ether into Some Diluents

K_{ex2s} = \left[ \frac{\text{CdL}^{2+}}{\text{org}} \right]_{\text{org}} \left[ \frac{A^-}{\text{org}} \right]_D \left[ \frac{\text{Cd}^{2+}}{\text{org}} \right]_L \left[ \frac{A^-}{\text{org}} \right]_L \cdot (3a)

When one defines conditional distribution ratios, \( D_0 \), \( D_s \), and \( D_{2s} \), as \( \left[ \text{CdL}A^- \right]_{\text{org}} / \left[ \text{Cd}^{2+} \right]_{\text{org}} \), \( \left[ \text{CdLA}^+ \right]_{\text{org}} / \left[ \text{Cd}^{2+} \right]_{\text{org}} \), and \( \left[ \text{CdL}^{2+} \right]_{\text{org}} / \left[ \text{Cd}^{2+} \right]_{\text{org}} \) respectively, Eqs. (1a), (2a), and (3a) become

\[ K_{ex} = D_0 \left[ \frac{L}{\text{org}} \right] \left[ \frac{A^-}{\text{org}} \right]^2, \quad \text{(1b)} \]

\[ K_{ex2} = D_s \left[ \frac{A^-}{\text{org}} \right]_{\text{org}} \left[ \frac{L}{\text{org}} \right] \left[ A^- \right]^2 = D_s K_{D, A} \left[ \frac{L}{\text{org}} \right] \left[ A^- \right], \quad \text{(2b)} \]

and

\[ K_{ex2s} = D_{2s} \left[ \frac{A^-}{\text{org}} \right]_{\text{org}} \left[ \frac{L}{\text{org}} \right] \left[ A^- \right]^2 = D_{2s} (K_{D, A})^2 \left[ \frac{L}{\text{org}} \right]. \quad \text{(3b)} \]

Moreover, expressing as

\[ K_{ex2} \left( \frac{K_{D, A}}{K_{ex}} \right) = K_{ex} \left( \frac{\text{CdLA}^+}{\text{org}} \right) \left[ \frac{\text{Cd}^{2+}}{\text{org}} \right] \left[ \frac{L}{\text{org}} \right] \left[ A^- \right], \quad \text{Eqs. (2b) and (3b)} \]

(2b) and (3b) become

\[ K_{ex} = D_0 \left[ \frac{L}{\text{org}} \right] \left[ A^- \right]^2, \quad \text{(2c)} \]

\[ K_{ex2} = D_s \left[ \frac{A^-}{\text{org}} \right]_{\text{org}} \left[ \frac{L}{\text{org}} \right] \left[ A^- \right]^2 = D_s K_{D, A} \left[ \frac{L}{\text{org}} \right] \left[ A^- \right], \quad \text{(3c)} \]

respectively. Here, although it was a rough handling, we assumed that the \( D_0 \), \( D_s \), and \( D_{2s} \) values equal the experimental distribution ratio (D).

So, these assumptions were examined experimentally by comparison in \( K_{ex} \), \( K_{ex2} \), and \( K_{ex2s} \) between the procedures. The \( K_{ex} \) values can be directly compared with each other. The \( K_{ex}, K_{ex2} \), and \( K_{ex2s} \) values can be also compared with those calculated from the relation \( K_{ex} = K_{ex2} / (K_{D, A})^2 \) [15,17]. Furthermore, the \( K_{ex}, K_{ex2} \) values calculated from \( K_{ex} / K_{ex2} \) of \( (K_{D, A})^2 \) can be compared with those done from \( K_{ex}, K_{ex2} \) of \( (K_{D, A})^2 \) [15-17]. Here, the symbols \( K \) with the asterisks denote the equilibrium constants determined with the other procedure reported in the previous papers [15,17] and \( K_{D, A} \) denotes a distribution constant, \( \left[ \frac{A^-}{\text{org}} \right] \left[ \frac{A^-}{\text{org}} \right] \) of single \( A^- \) ion into the org phase. In this report, the author calls this procedure [15,17] reported before “the formal procedure”. In all calculations, the data [17] reported before were re-used.

In the previous paper [17], the plot of \( D \left[ \frac{\pi c^-}{2} \right] \) versus \( \log [L]_{\text{org}} \) for \( L = 18 \text{C6} \) and \( A^- = \pi c^- \) has given the straight line with the slope (a) of 0.81 and the intercept (b) of 3.90, the value corresponding to \( \log D \) versus \( \log [L]_{\text{org}} \) (circle in Figure 1). Here, \( [L]_{\text{org}}, [\pi c^-] \) and \( [\text{Cd}^{2+}] \) have been calculated in terms of a successive approximation [10,15-17]. The same is true of the extraction systems with the other diluents. The slope less than unity shows the dissociation of \( \text{CdLPic}_2 \) in the \( \text{BBz} \) phase [17].

The plot of \( \log D \left[ \frac{\pi c^-}{2} \right] \) versus \( \log [L]_{\text{org}} \) yielded a straight line with \( a = 0.93 \) and \( b = 1.17 \), the b value to \( \log K_{ex} \) (Figure 1).

This \( a \) value shows the extraction of \( \text{CdLPic}^- \) into the \( \text{BBz} \) phase. The plot of \( \log D \) versus \( \log [L]_{\text{org}} \) gave a straight line with \( a = 1.08 \) and \( b = -0.97 \), the b value to \( \log K_{D, A} \) (Figure 1). This \( a \) value shows the extraction of \( \text{CdL}^{2+} \) into the \( \text{BBz} \) phase. From these results, one can easily see the co-extraction of \( \text{CdLPic}^- \) and \( \text{CdL}^{2+} \) into the \( \text{BBz} \) phase. Here, we call the \( \log [L]_{\text{org}} \) (x-axis) plots of \( \log D \left[ \frac{\pi c^-}{2} \right] \), \( \log D \left[ \frac{\text{Cd}^{2+}}{2} \right] \), and \( \log D \) the plots (1B), (2C), and (3C), respectively. Similar data calculated for other systems are summarized in Table 1. The plots (1B) clearly indicate the dissociation of \( \text{CdLPic}_2 \) in the \( \text{oDCBz} \) and \( \text{NB} \) phases.

In discussing the data obtained from the above plots, it is important to examine the overlap of the \( [L]_{\text{org}} \) or ionic strength (I) values used for the data analyses; especially, the I values of \( [I]_{\text{org}} \) of the org phases are important for the latter case. The larger overlaps among the data make comparisons among them possible. Figure 2 shows the overlap of \( [L]_{\text{org}} \) among the plots for the extraction system with \( \text{org} = \text{BBz} \). On the other hand, Figure
3 shows an example of a minimum $I_{\text{opt}}$ overlap in the report. The BBz system indicates the better overlap, while the NB one does the less one. The latter suggests the larger deviation of the data determined with the present approximate procedure from the data with "the formal one". A degree of the $I_{\text{opt}}$ overlap increased with the order, $\text{org} = \text{NB} < o\text{DCBz} < \text{BBz} < \text{DBE}$. Table 2 lists the data of mainly $\log K_{\text{ex}}$ and $\log K_{\text{ex}^+}$ for comparison. The both values agreed with each other within experimental errors, except for the NB systems. Also, the values for the $o\text{DCBz}$ system were close to those [17] reported before. Considering the order, the both values even for the NB system agreed with each other. These facts indicate that the procedure proposed here, the approximate one, is effective for the determination of such extraction constants. The approximation procedure can be used for the primary diagnosis of the system at least.

Table 1: Data of the plots for composition determination of extracted species in the CdPic$_2$ extraction with 18C6 at 298 K.

| Diluent | Plot (1B) $^{1)}$ | Plot (2C) | Plot (3C) |
|---------|-----------------|-----------|-----------|
|         | $A^{2)}$ | $b^{3)}$ | $a^{3)}$ | $b^{4)}$ | $a^{5)}$ | $b^{5)}$ |
| oDCBz   | 0.76     | 3.39     | 1.02     | 2.01     | 0.94     | -0.51    |
| DBE     | 1.02     | 4.61     | 0.96     | 0.78     | 0.99     | -1.53    |
| NB      | 0.55     | 4.80     | 0.99     | 4.92     | 1.05     | 3.23     |

$^{1)}$See ref. [17].
$^{2)}a$: slope; $b$: intercept.
$^{3)}$Values corresponding to $\log K_{\text{ex}}$, when $a \leq 1$.
$^{4)}$Values corresponding to $\log K_{\text{ex}^+}$, when $a \approx 1$.
$^{5)}$Values corresponding to $\log K_{\text{Cd}/\text{CdL}}$, when $a \approx 1$.

Table 2: Fundamental data for comparisons between the both procedures.

| Diluent | $\log K_{\text{ex}}$ | $\log K_{\text{ex}^+}$ | $\log K_{\text{Cd}/\text{CdL}}$ |
|---------|-------------------|---------------------|-------------------|
| This Report | Ref. [17] $^{1)}$ | This Report | Calculated $^{2)}$ |
| oDCBz   | 4.4 $\pm$ 0.4 $^5)$ | 4.31, 4.21 | 2.4 $\pm$ 0.2 $^5)$ | -0.2 $\pm$ 0.2 |
| BBz     | 4.2 $\pm$ 0.4 $^5)$ | 4.38 | 1.7 $\pm$ 0.5 $^5)$ | 1.9 $\pm$ 0.4 $^5)$ | -1.1 $\pm$ 0.3 $^5)$ |
| DBE     | 3.8 $\pm$ 0.5 $^5)$ | 4.2 | 1.1 $\pm$ 0.3 $^5)$ | 1.8 $\pm$ 0.5 $^5)$ | -1.3 $\pm$ 0.3 $^5)$ |
| NB      | 6.6 $\pm$ 0.4 $^5)$ | 6.14 | 4.96 $\pm$ 0.04 | 4.6 $\pm$ 0.1 | 2.95 $\pm$ 0.03 |

$^{1)}$Values determined with the formal procedure. $^{2)}$Values calculated from the data in ref. [17] by using $\log K_{\text{ex}^+} = \log \left(\frac{K_{\text{ex}^+} K_{\text{Cd/Pic}}}{{K_{\text{D/Pic}}}}\right)$.

$K_{\text{ex}}$ or $K_{2,\text{org}}$ yielded a straight line of $a = 1.16$ and $b = -0.74$ at $R = 0.995$ and $N = 13$ (Figure 4). Similarly, these facts indicate that the results of the approximate procedure well reflect those of the formal one.

Figure 2: A distribution in $I_{\text{opt}}$ among the plots, (1B), (2C), and (3C) for the BBz extraction system. The symbol $N$ refers to the number of data.

Figure 3: A distribution in $I_{\text{opt}}$ among the plots, (1B), (2C), and (3C) for the NB extraction system; see Figure 2 for $N$. This is the case of the minimum overlap in the report.
From the values in Table 2, the following constants were obtainable: \( K_{\text{org}} = \frac{K_{\text{ex}}}{K_{\text{dil}}} \) and \( K_{\text{dil}} = \left[ L \right]_{\text{org}} \left[ L \right]_{\text{dil}} \left[ CdL^{2+} \right] \left[ Cd^{2+} \right] \), and \( K_{\text{ex}} = \frac{K_{\text{dil}}}{K_{\text{org}}} \) \( \left( K_{\text{org}} \right)^2 \) \[14\]. These constants \( K_{\text{org}} \) and \( K_{\text{dil}} \), and \( K_{\text{ex}} = K_{\text{dil}} \left( *K_{\text{org}} \right) \), respectively. Their logarithmic values are summarized in Table 3. The \( K_{\text{org}} \) values were larger than or equal to the \( K_{\text{dil}} \) ones. These facts suggest that a coordination structure around Cd(II) does not almost change in the two-step reactions with Pic⁻ \[18\]. Also, the \( K_{\text{org}} \) values thus-calculated were the same as those done from the formal procedures within experimental errors. As similar to the results in Table 2, these facts show the validity of the present procedure.

Figure 2 & 3 show the degrees of the overlap of the \( I_{\text{BB}} \) and \( I_{\text{NB}} \) data used for calculation. These degrees, together with those of the other two systems, rationally make comparisons between or among the data, such as \( K_{\text{ex}} \), \( K_{\text{org}} \), and \( K_{\text{dil}} \), possible, although the finding of the NB system may create dissatisfaction.

Discussion

Simplification of the convoluted procedures \[3,4,10,12-17\] for the M(II) extraction systems, compared with the procedures \[1-3,5,6,8,9,11\] for the monovalent-metal extraction ones, must stimulate an estimate of \( L \) functions by many workers. Unfortunately, there are still complicated treatments for the determination of some extraction constants, because the procedure uses directly the experimental \( D \) values. Besides, such constants derive valuable component equilibrium-constants from several thermodynamic cycles, as shown in Case Presentation. Additionally, Figure 2 & 3 suggest an importance of the ionic strength for the phases in the determination of the equilibrium constants by the extraction experiments \[1,6,8-11,13\].

Conclusion

It was shown that Eqs. (1b), (2c), and (3c) with \( D = D_a = D_b = D_2 \) are useful for the primary-diagnostic determination of \( K_{\text{ex}} \), \( K_{\text{org}} \), and \( K_{\text{dil}} \), respectively. In the present extraction systems, the \( K_{\text{org}} \) and \( K_{\text{dil}} \) values were newly obtained from the \( K_{\text{ex}} \) values. These results facilitate applications for next stages with the extraction experiments by other users.

Conflict of Interest

Any financial interest or any conflict of interest does not exist in the report.

References

1. Frensdorff HK (1971) Salt complexes of cyclic polyethers. Distribution equilibria. J Am Chem Soc 93(19): 4684-4688.
2. Danesi PR, Melder-Gorican H, Chiariuzia R, Scibona G (1975) Extraction selectivity of organic solutions of a cyclic polyether with respect to the alkali cations. J Inorg Nucl Chem 37: 1479-1483.
3. Jawaid M, Ingman F (1978) Ion-pair extraction of Na⁺, K⁺, and Ca²⁺ with some organic counter-ions and dicyclohexyl-18-crown-6 as adduct-formation reagent. Talanta 25: 91-95.
4. Takeda Y, Katô H (1979) The solvent extraction of bivalent metal picrates by 15-crown-5, 18-crown-6, and dibenzo-18-crown-6. Bull Chem Soc Jpn 52(4): 1027-1030.
An Approximation Method for Determining Key Extraction Constants in the Equilibrium-Analysis of Cd(II) Extraction with 18-Crown-6 Ether into Some Diluents

5. Iwachido T, Minami M, Naito H, Tobe K (1982) The extractability of potassium as picrates (KPic and K(L)Pic, L: 18-crown-6) and its relationship to the properties of the solvents. Bull Chem Soc Jpn 55(8): 2378-2382.

6. Kolthoff IM, Chantooni MK, Wang WJ (1993) Partitioning of crown ether complexed univalent metal dichloropicates between water and 1,2-dichloroethane at 298 K. Thermodynamic representation. J Chem Eng Data 38(4): 556-559.

7. Mohapatra PK, Manchanda VK (1996) Ion-pair extraction of tetravalent plutonium from hydrochloric acid medium using crown ethers. J Incl Phenom Mol Recognition Chem 25(4): 257-265.

8. Kikutani K, Sakamoto Y, Sawada K (1998) Partition of alkali-metal ions and complex formation with poly(oxyethylene) derivatives in 1,2-dichloroethane. J Chem Soc Faraday Trans 94(4): 105-109.

9. Takeda Y, Kawababayashi A, Endo K, Yahata T, Kudo Y, et al. (1998) Solvent extraction of alkali metal (Li-Cs) picrates with 18-crown-6 into various diluents. Elucidation of fundamental equilibrium which govern the extraction-ability and selectivity. Anal Sci 14(1): 215-223.

10. Kastuta S, Tuchiya F, Takeda Y (2000) Equilibrium studies on complexation in water and solvent extraction of zinc(II) and cadmium(II) with benzo-18-crown-6. Talanta 51: 634-644.

11. Levitskaia TG, Mayr L, Van Berkel GI, Moyer BA (2007) Anion partitioning and ion-pairing behavior of anions in the extraction of cesium salts by 4,5''-bis(tert-octylbenzo)dibenzo-24-crown-8 in 1,2-dichloromethane. Inorg Chem 46(1): 261-272.

12. Touati M, Bensa Zayani M, Kbiri Ariguib N, Trabelsi-Ayadi M, Buch A, et al. (2008) Extraction of cadmium from phosphoric acid media by di(2-ethylhexyl) dithiophosphoric acid. Solvent Extraction & Ion Exchange 26(4): 420-434.

13. Makrilik E, Vaňura P (2010) Solvent extraction of calcium into n-tetraldehyde by using hydrogen dicarbollacylcobaltate in the presence of dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8. J Radioanal Nucl Chem 285: 593-598.

14. Kudo Y, Katsuta S, Takeda Y (2012) Evaluation of the overall extraction constants for the crown ether-complex ions of alkali and alkaline-earth metal with counter picrate ion from water into n-tetraldehyde andbenzene based on their component equilibrium constants. J Mol Liquids 173: 66-70.

15. Kudo Y, Horiuchi N, Katsuta S, Takeda Y (2013) Extraction of cadmium bromide and picrate by 18-crown-6 ether into various less-polar diluents: analysis of overall extraction equilibria based on their component equilibria with formation of their ion pairs in water. J Mol Liquids 177: 257-266.

16. Kudo Y, Takahashi Y, Numako C, Katsuta S (2014) Extraction of lead picrate by 18-crown-6 ether into various diluents: examples of sub-analysis of overall extraction equilibrium based on component equilibria. J Mol Liquids 194: 121-129.

17. Kudo Y, Katsuta S, Ohsawa Y, Nozaki K (2015) Solvent extraction of cadmium picrate by 18-crown-6 ether into several less-polar diluents and n-tetraldehyde: re-evaluation of the corresponding overall extraction systems. J Thermodyn Catal. 6 (2): 6.

18. Shriver DF, Atkins PW (2002) Inorganic Chemistry. (3rd edn), Oxford University Press, Oxford, UK, pp. 241-243.