Case Report

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 were defined as $\left[CdLA_2\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]^2$, $\left[CdLA^+\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]$ and $\left[CdL^{2+}\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}$, 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:
$K_{ex} \approx D / \left[L\right]_{org}\left[A^-\right]^2$, and $K_{ex} \approx D / \left[L\right]_{org}\left[A^-\right]$, where $K_{Cd/CdL} \approx D / \left[L\right]_{org}$ efers 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

Yoshihiro Kudo
Graduate School of Science, Chiba University, Japan

Correspondence: Yoshihiro Kudo, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan, Tel +81 43-290-2786, Fax -3126, Email iakudo@faculty.chiba-u.jp
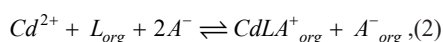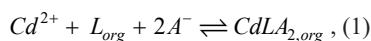
Abbreviations: ORG, organic; oDCBz, o-dichlorobenzene; BBz, bromobenzene; DBE, dibutylether; NB, nitrobenzene; Cd, cadmium; 18C6, 18-crown-6 ether; Pic−, picrate ion
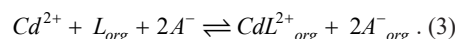
Introduction

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:

$$Cd^{2+} + L_{org} + 2A^- \rightleftharpoons CdLA_{2,org} \text{, (1)}$$

$$Cd^{2+} + L_{org} + 2A^- \rightleftharpoons CdLA^+{}_{org} + A^-{}_{org} \text{,(2)}$$

And

$$Cd^{2+} + L_{org} + 2A^- \rightleftharpoons CdL^{2+}{}_{org} + 2A^-{}_{org} \text{. (3)}$$

The expressions of these equilibria as equilibrium constants are

$$K_{ex} = \left[CdLA_2\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]^2 \text{, (1a)}$$

$$K_{ex\pm} = \left[CdLA^+\right]_{org}\left[A^-\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]^2 \text{, (2a)}$$

And

$$K_{ex2\pm} = \left[CdL^{2+}\right]_{org}\left(\left[A^-\right]_{org}\right)^2 / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]^2 \text{. [3,15] (3a)}$$

When one defines conditional distribution ratios, D_0, $D_\pm$, and $D_{2\pm}$ as $\left[CdLA_2\right]_{org} / \left[Cd^{2+}\right]$, $\left[CdLA^+\right]_{org} / \left[Cd^{2+}\right]$, and $\left[CdL^{2+}\right]_{org} / \left[Cd^{2+}\right]$ respectively, Eqs. (1a), (2a), and (3a) become

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

$$K_{ex\pm} = D_\pm\left[A^-\right]_{org} / \left[L\right]_{org}\left[A^-\right]^2 = D_\pm K_{D,A} / \left[L\right]_{org}\left[A^-\right] \text{, (2b)}$$

And

$$K_{ex2\pm} = D_{2\pm}\left(\left[A^-\right]_{org}\right)^2 / \left[L\right]_{org}\left[A^-\right]^2 = D_{2\pm}\left(K_{D,A}\right)^2 / \left[L\right]_{org} \text{.(3b)}$$

Moreover, expressing as $K_{ex\pm} / K_{D,A} = K_{ex+}\left(= \left[CdLA^+\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\left[A^-\right]\right) K_{ex2\pm} / \left(K_{D,A}\right)^2 = K_{Cd/CdL}\left(= \left[CdL^{2+}\right]_{org} / \left[Cd^{2+}\right]\left[L\right]_{org}\right)$, Eqs. (2b) and (3b) become

$$K_{ex+} = D_\pm / \left[L\right]_{org}\left[A^-\right] \text{ (2C)} \qquad K_{Cd/CdL} = D_{2\pm} / \left[L\right]_{org} \text{, (3c)}$$

An approximation method for determining key extraction constants in the equilibrium-analysis of Cd(II) extraction with 18-crown-6 ether into some diluents

Copyright:
©2017 Kudo. **274**

respectively. Here, although it was a rough handling, we assumed that the D0,

$D_\pm$, $D_{2\pm}$ values equal the experimental distribution ratio (D).

So, these assumptions were examined experimentally by comparison in K_{ex}, K_{ex+}, and $K_{2,org}$ between the procedures. The K_{ex} values can be directly compared with each other. The K_{ex+} values can be also compared with those calculated from the relation $K_{ex+} = *K_{ex\pm} / (*K_{D,A})$.[15,17] Furthermore, the $K_{2,org} \left(= [CdLA_2]_{org} / [CdLA^+]_{org}[A^-]_{org}\right)$ values calculated from $K_{ex} / K_{ex+} (*K_{D,A})$ can be compared with those done from $*K_{ex} / (*K_{ex+})$.[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, $[A^-]_{org} / [A^-]$ 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 $\left(D / [Pic^-]^2\right) versus \log[L]_{BBz}$ for $L = 18C6$ and $A^- = Pic^-$ has given the straight line with the slope (a) of 0.81 and an intercept (b) of 3.90, the value corresponding to $\log\log D versus \log[L]_{BBz}$ (circle in Figure 1). Here $[L]_{BBz}$, $[Pic^-]$ and [Cd2+]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 $CdLPic_2$ in the BBz phase.[17]
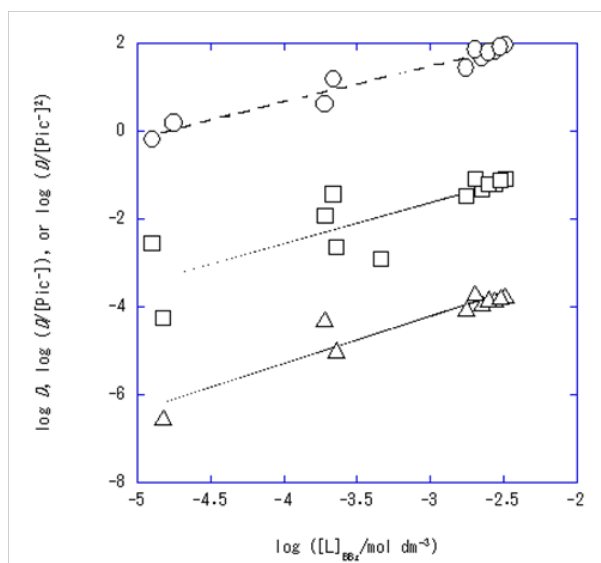
Figure 1 The plots (1B) (circle), (2C) (square), and (3C) (triangle) for the BBz system with L = 18C6.

The plot of $\log\log\left(D / [Pic^-]\right) versus \log[L]_{BBz}$ 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 $CdLPic^+$ into the BBz phase. The plot of $\log\log\log D versus \log[L]_{BBz}$ gave a straight line with $a = 1.08$ and $b = -0.97$, the value to $\log K_{Cd/CdL}$ (Figure 1). This a value shows the extraction of CdL^{2+} into the BBz phase. From these

results, one can easily see the co-extraction of $CdLPic_2$, $CdLPic^+$ and CdL^{2+} into the BBz phase. Here, we call the $\log[L]_{BBz}$ (x-axis) plots of $\log\left(D / [Pic^-]^2\right)$, $\log\left(D / [Pic^-]\right)$ and logD 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 $CdLPic_2$ in the oDCBz and NB phases.

In discussing the data obtained from the above plots, it is important to examine the overlap of the [L]org or ionic strength (I) values used for the data analyses; especially, the (Iorg) values 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 IBBz among the plots for the extraction system with $org = BBz$. On the other hand, Figure 3 shows an example of a minimum I_{NB} 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 Iorg overlap increased with the order, $org = NB < oDCBz < BBz < DBE$.

Table 2 lists the data of mainly logKex and logKex+ for comparison. The both values agreed with each other within experimental errors, except for the NB systems. Also, the values for the oDCBz 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.

The orders in Kex, Kex+, and KCd/CdL were $DBE \leq BBz \leq oDCBz < NB$, except for the Kex order in the reference.[17] Such orders were also observed in the plots, (2C) and (3C), with the a values of about unity (Table 1). A plot of log (approximate Kex, Kex+, or K2,org) versus log (formal *Kex, *Kex or *K2,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.

From the values in Table 2, the following constants were obtainable:

$K_{1,org}\left\{= K_{ex+} / K_{Cd/CdL}\left(*K_{D,Pic}\right)\right\}$,

$K_{2,org}\left\{= K_{ex} / K_{ex+}\left(*K_{D,Pic}\right)\right\}$ [15-17],

$K_{D,CdL}\left(= K_{Cd/CdL}K_{D,L} / K_{CdL}; K_{D,L} = [L]_{org} / [L], K_{CdL}[CdL^{2+}] / [Cd^{2+}][L]\right)$,

and $K_{ex2\pm}\left\{= K_{Cd/CdL}\left(*K_{D,Pic}\right)^2\right\}$.[14] These constants K1,org, K2,org, and $K_{D,CdL}$, are defined as $[CdLPic^+]_{org} / [CdL^{2+}]_{org}[Pic^-]_{org}$, $[CdLPic_2]_{org} / [CdLPic^+]_{org}[Pic^-]_{org}$, and $[CdL^{2+}]_{org} / [CdL^{2+}]$, respectively. Their logarithmic values are summarized in Table 3. The K1,org values were larger than or equal to the K2,org 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 K2,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 IBBz and INB data used for calculation. These degrees, together with those of the other two systems, rationally make comparisons between or among

An approximation method for determining key extraction constants in the equilibrium-analysis of Cd(II) extraction with 18-crown-6 ether into some diluents

Copyright:
©2017 Kudo.

275

the data, such as Kex , Kex+ , and K1,org , 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 evaluation of equilibrium concentrations, such as $\left[Cd^{2+}\right]$, $\left[L\right]_{org}$ and $\left[A^-\right]$, by the successive approximation,[17] before

the use of the present procedure. However, the procedure proposed here can be useful for the workers who expect a primary diagnostic 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]

Table 1 Data of the plots for composition determination of extracted species in the CdPic2 extraction with 18C6 at 298 K

Diluent	Plot (1B)[1]		Plot (2C)		Plot (3C)	
	$A^{2)}$	$b^{2,3)}$	$a^{2)}$	$b^{2,4)}$	$a^{2)}$	$b^{2,5)}$
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

Table 2 Fundamental data for comparisons between the both procedures

Diluent	log K_{ex}		log K_{ex+}		log $K_{Cd/CdL}$
	This Report	Ref. [17][1]	This Report	Calculated[1,2]	This Report
oDCBz	$4.4_4 \pm 0.4_6$	4.31, 4.21	$1.9_8 \pm 0.2_2$	$2.4_6 \pm 0.2_8$	$-0.2_5 \pm 0.2_0$
BBz	$4.2_6 \pm 0.4_5$	4.38	$1.7_0 \pm 0.5_7$	$1.9_7 \pm 0.4_2$	$-1.1_1 \pm 0.3_9$
DBE	$3.8_1 \pm 0.5_3$	4.2	$1.1_3 \pm 0.3_4$	$1.8_1 \pm 0.5_3$	$-1.3_3 \pm 0.3_2$
NB	$6.6_3 \pm 0.4_0$	6.14	$4.9_6 \pm 0.0_4$	$4.6_1 \pm 0.1_4$	$2.9_5 \pm 0.0_3$

[1]Values determined with the formal procedure. 2) Values calculated from the data in ref. [17] by using log K_{ex+} = log {*K_{ex+}/(*$K_{D,Pic}$)}

Table 3 Some equilibrium constants estimated from K_{ex}, K_{ex+}, and $K_{Cd/CdL}$ for the CdPic2 extraction with 18C6 at 298K[1]

Diluent (log *$K_{D,Pic}$)[2]	log $K_{1,org}$	log $K_{2,org}$)[2]	log $K_{D,CdL}$	log $K_{ex2}\pm$
oDCBz (−5.5, −4.2)	$8.2_0 \pm 0.3_7$	$7.9_5 \pm 0.5_3$ (7.3, 7.5)	−1.33	$-11.2_3 \pm 0.2_8$
BBz (−4.6)	$7.7_2 \pm 0.6_1$	$7.2_0 \pm 0.7_5$ (7.0)	−2.18	$-10.3_9 \pm 0.4_9$
DBE (−5.1)	$8.2_1 \pm 0.7_5$	$7.7_5 \pm 0.7_6$ (7.5)	−4.05	$-11.4_8 \pm 0.6_8$
NB (−2.35)	$4.0_2 \pm 0.1_5$	$4.0_2 \pm 0.4_0$ (3.9)	2.00	$-1.7_6 \pm 0.07$

[1]See the text. [2] Values reported in ref.[17]
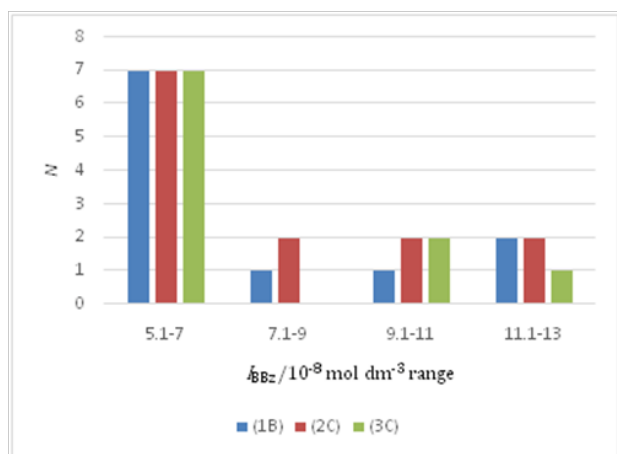
Figure 2 A distribution in I_{BBz} among the plots, (1B), (2C), and (3C) for the BBz extraction system. The symbol N refers to the number of data.
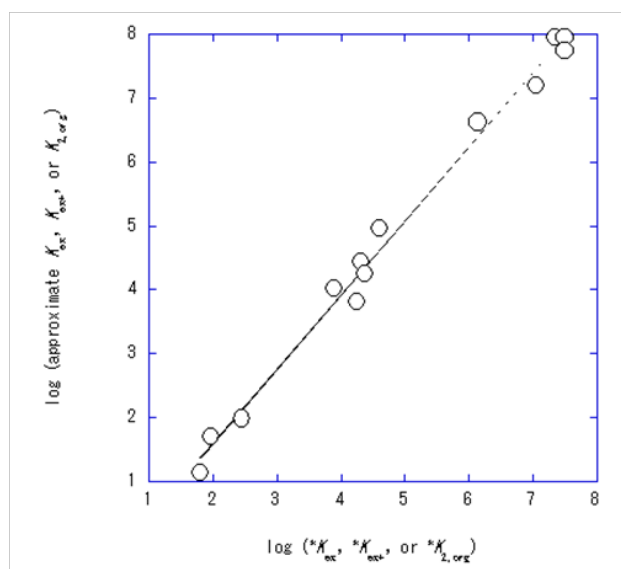
Conclusion

It was shown that Eqs. (1b), (2c), and (3c) with $D\left(= D_0 = D_\pm = D_{2\pm}\right)$ are useful for the primary-diagnostic determination of K_{ex}, K_{ex+}, and $K_{Cd/CdL}$ respectively. In the present extraction systems, the $K_{1,org}$ and

$K_{ex2\pm}$ values were newly obtained from the K_{ex+} and $K_{Cd/CdL}$ alues. These results facilitate applications for next stages with the extraction experiments by other users.
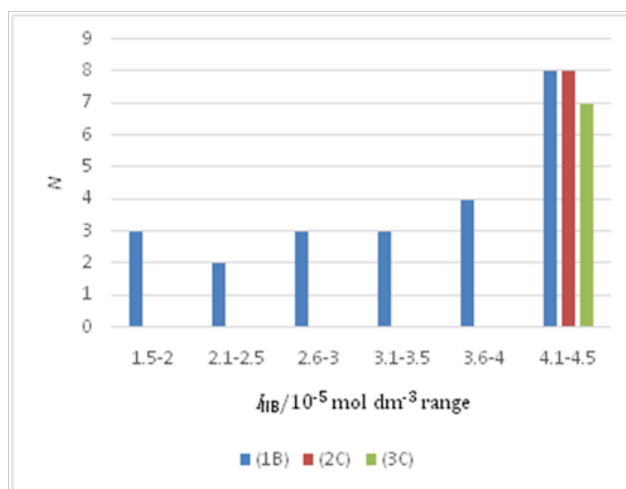
Figure 3 A distribution in INB among the plots, (1B), (2C), and (3C) for the NB extraction system; see Figure 2 for N. This is the case of the minimum overlap in the report.

Citation: Kudo Y. An approximation method for determining key extraction constants in the equilibrium-analysis of Cd(II) extraction with 18-crown-6 ether into some diluents. *J Anal Pharm Res*. 2017;5(3):273–276. DOI: 10.15406/japlr.2017.05.00144

An approximation method for determining key extraction constants in the equilibrium-analysis of Cd(II) extraction with 18-crown-6 ether into some diluents

Copyright:
©2017 Kudo. **276**

Figure 4 A plot of log (approximate K_{ex}, K_{ex+}, or $K_{2,org}$) vs. log (formal $*K_{ex}$, $*K_{ex+}$, or $*K_{2,org}$)[17] for the CdPic2 extraction with 18C6.

Conflicts of interest

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

References

1. Frensdorff HK. Salt complexes of cyclic polyethers. Distribution equilibria. *J Am Chem Soc.* 1971;93(19):4684–4688.

2. Danesi PR, Meider-Gorican H, Chiarizia R. Extraction selectivity of organic solutions of a cyclic polyether with respect to the alkali cations. *J Inorg Nucl Chem.* 1975;37:1479–1483.

3. Jawaid M, Ingman F. Ion-pair extraction of Na⁺, K⁺, and Ca²⁺ with some organic counter-ions and dicyclohexyl-18-crown-6 as adduct-formation reagent. *Talanta.* 1978;25:91–95.

4. Takeda Y, Katō H. The solvent extraction of bivalent metal picrates by 15-crown-5, 18-crown-6, and dibenzo-18-crown-6. *Bull Chem Soc Jpn.* 1979;52(4):1027–1030.

5. Iwachido T, Minami M, Naito H, et al. 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.* 1982;55(8):2378–2382.

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

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

8. Kikuchi Y, Sakamoto Y, Sawada K. Partition of alkali-metal ions and complex formation with poly(oxyethylene) derivatives in 1,2-dichloroethane. *J Chem Soc Faraday Trans.* 1998;91(4):105–109.

9. Takeda Y, Kawarabayashi A, Endō K, et al. Solvent extraction of alkali metal (Li-Cs) picrates with 18-crown-6 into various diluents. Elucidation of fundamental equilibria which govern the extraction-ability and -selectivity. *Anal Sci.* 1998;14(1):215–223.

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

11. Levitskaia TG, Maya L, Van Berkel GJ, et al. 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-dichloroethane. *Inorg Chem.* 2007;46(1):261–272.

12. Touati M, Benna Zayani M, Kbir Ariguib N, et al. Extraction of cadmium from phosphoric acid media by di(2-ethylhexyl) dithiophosphoric acid. *Solvent Extraction & Ion Exchange.* 2008;26(4):420–434.

13. Makrlík E, Vaňura P. Solvent extraction of calcium into nitrobenzene by using hydrogen dicarbollylcobaltate in the presence of dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8. *J Radioanal Nucl Chem.* 2010;285:593–598.

14. Kudo Y, Katsuta S, Takeda Y. 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 nitrobenzene based on their component equilibrium constants. *J Mol Liquids.* 2012;173:66–70.

15. Kudo Y, Horiuchi N, Katsuta S. 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.* 2013;177:257–266.

16. Kudo Y, Takahashi Y, Numako C. 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.* 2014;194:121–129.

17. Kudo Y, Katsuta S, Ohsawa Y, et al. 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. *J Thermodyn Catal.* 2015;6(2): 6.

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