

Spectrophotometric Studies on the Solvent Extraction of Lithium Picrate with Dibenzo-14-crown-4 and its Analogs*

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Abstract

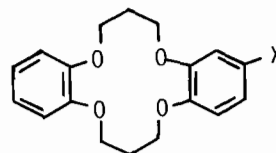
The distributions of lithium cation, picrate anion and dibenzo-14-crown-4 (DB14C4) and its analogs between water and various solvents, as well as the formation of ion pairs of lithium picrate and crown in these solvents, were studied spectrophotometrically at $24 \pm 1^\circ\text{C}$. The solvents used included benzene, chloroform, dichloromethane, 1,2-dichloroethane, nitromethane, and nitrobenzene. A 1:1 complexation was formed between Li^+ and crown among these solvents. Three different kinds of ion pairs of Li^+ -crown complex cation and picrate anion could be determined from a series of absorption maximum shifts. The effects of substituent groups on DB14C4 and solvents upon the extraction constant are presented. A plausible extraction mechanism is also suggested.

Introduction

Although there are several reports on the solvent extraction of lithium ion from aqueous solution either with chelating extractants such as β -diketone [2] and tributyl phosphate [3] or water-immiscible alcohols [4] such as n-hexanol, 2-ethylhexanol etc., the extractabilities of these extractants are not still high enough for practical use. Macrocyclic polyethers, known as crown ethers, with four oxygen atoms can form very stable stoichiometric complexes with lithium ion. This is because these crown ethers have a better cavity size (1.2–1.5 Å) [5] that matches well with that of the lithium ion (1.3–1.5 Å) [6]. For example, Pedersen [7] used dicyclohexyl-14-crown-4 to extract alkali metals in dichloromethane/water system in his earlier research. He found that the crown-4 compound has specific selectivity for the Li^+ ion. Takeda [8] and Pacey and Wu [9] used 12-crown-4 to extract alkali metals in the benzene/water system; the extent of extraction

is in the sequence: $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. Here the strong hydration of Li^+ ion results in less extraction of Li^+ into the organic phase than the Na^+ ion. Strzelbicki and Bartsch [10] introduced neutral crown ethers with pendant ionizable groups which were utilized to extract alkali metals from aqueous solutions of chlorides or sulfates into chloroform. They demonstrated that metal ion extraction did not involve the transfer of the aqueous phase anion into the organic medium. However, the extraction efficiency for Li^+ ion observed with *sym*-dibenzo-14-crown-4-oxyacetic acid is low [11]. Recently, Kitazawa *et al.* [12] demonstrated that the crown-4 compounds with 14 and 15 member rings are much more selective, reacting with lithium ion rather than other macrocyclics.

In our previous studies [1, 13], we have shown that the complex formation constants of DB14C4 and its analogs with Li^+ ion are larger than those of 12C4 and 15C5 in several nonaqueous solvents. Moreover, the substituent group on the benzene ring of DB14C4 has a substantial effect on the complexation reaction with the lithium ion. This indicates that DB14C4 and its analogs will be promising reagents for extracting Li^+ ion. The purpose of this work was to study the distribution of lithium ion between water and solvents covering a broad range of dielectric constants and dipole moments in the presence of DB14C4 with two different substituents (X), X = t-butyl and chloro (Fig. 1). The picrate anion was chosen as the counter ion so that the ion-pair formed could be determined colorimetrically.



X = H (1), Cl (2), t-Bu (3).

Fig. 1 Macrocylic ligands used in this investigation: DB14C4 (1), Cl-DB14C4 (2) and t-Bu-DB14C4 (3).

*Based in part on *Ph.D. Thesis* of Chi-Sung Chen [1].

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Experimental

Materials

Macrocylic polyethers of 1, 2 and 3 (Fig. 1) were synthesized from catechol and 1-chloro-3-propanol as described in previous work [14–16] using a high dilution apparatus. The final products were recrystallized from n-heptane, methanol and n-heptane, respectively.

Lithium picrate was synthesized by reaction of lithium carbonate with picric acid in aqueous ethanol according to the method of Fuoss [17]. Pure salt was obtained by recrystallization twice from mixtures of benzene and small amounts of acetone.

All chemicals were obtained from E. Merck. Chloroform contains about 1% of alcohol as a stabilizer, which can be removed by shaking several times with deionized water. Benzene was agitated with concentrated sulfuric acid, and was then washed with deionized water. 1,2-dichloroethane was washed with diluted potassium hydroxide solution and then with deionized water. The other solvents were used without further purification. The solvents were saturated with each other before use to prevent volume changes in the phases during extraction equilibrium.

Measurement of Partition Coefficient

Partition coefficients of crown ethers (P_L) between aqueous phase and organic solvents were determined by (i) shaking two equal volumes of each phase solution for 30 min to reach equilibrium, (ii) pouring out the aqueous phase solution and then (iii) analyzing the content of crown ethers in the aqueous phase after CCl_4 extraction. For this purpose, a series of calibration curves (concentration of crown ethers versus absorbance) for different crown ethers in CCl_4 were recorded on a Shimadzu UV-240 spectrophotometer (Japan) beforehand ($\epsilon(278 \text{ nm})$: $4.44 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for t-Bu-DB14C4, $5.56 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for DB14C4 and $4.76 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for Cl-DB14C4).

Measurement of Distribution Ratio

Two equal volumes (10 cm^3 each) of aqueous solution containing lithium picrate ($8.0 \times 10^{-4} \text{ mol dm}^{-3}$) and various organic solutions containing crown ethers ($1.0 \times 10^{-3} \sim 4.0 \times 10^{-2} \text{ mol dm}^{-3}$) were put together in a 50 cm^3 separatory funnel and thoroughly agitated on a mechanical shaker for 30 min, which was found to be sufficient for equilibration. Generally the phase boundaries were clean enough to effect separation after standing, though centrifugation was necessary in the case of nitromethane. After separation, 5 cm^3 of the organic phase solution was taken to determine the lithium picrate concentration by measuring the absorbance spectrophotometrically. In the case of

nitrobenzene, the aqueous phase solution was taken instead. The concentration of picrate ions in the aqueous phase solution after equilibration was shaken with small portions of benzene (to remove traces of the interfering nitrobenzene) and finally measured spectrophotometrically. The distribution ratio was calculated according to the following equation:

$$D = \frac{\text{total concentration of Li}^+ \text{ ion in organic phase}}{\text{total concentration of Li}^+ \text{ ion in aqueous phase}}$$

All the experiments were carried out at $24 \pm 1^\circ \text{C}$.

Results and Discussion

Based on extraction, an equilibrium between the aqueous phase solution containing both a lithium ion (Li^+) and a picrate anion (A^-), and the organic phase solution containing a crown ether (L) can be expressed by eqn. (1).



Since the extent of partition of LiA into the organic phase solution is far less than that of crown ether into the aqueous solution, the extraction equilibrium is considered as follows:



where the upper bar denotes species in the organic phase, K_{ex} is the overall extraction constant, P_L is the partition coefficient of crown ether between two phases, K_{LiL} is the complex formation constant and K'_{ex} is the ion-pair extraction constant. Equilibrium constants corresponding to the reactions of eqns. (1) to (4) are defined as:

$$K_{\text{ex}} = \frac{[\overline{\text{LiLA}}]}{[\text{Li}^+][\text{A}^-][\bar{\text{L}}]} \quad (5)$$

$$P_L = \frac{[\text{L}]}{[\bar{\text{L}}]} \quad (6)$$

$$K_{\text{LiL}} = \frac{[\text{LiL}^+]}{[\text{Li}^+][\text{L}]} \quad (7)$$

$$K'_{\text{ex}} = \frac{[\overline{\text{LiLA}}]}{[\text{LiL}^+][\text{A}^-]} \quad (8)$$

where the brackets denote the molar concentration. The values of $[\bar{\text{L}}]$ and $[\text{A}^-]$ in eqn. (5) were calculated from eqns. (9) and (10), respectively.

$$[\bar{\text{L}}] = ([\bar{\text{L}}]_0 - [\overline{\text{LiLA}}]) / (1 + P_L) \quad (9)$$

$$[\text{A}^-] = [\text{LiA}]_0 - [\overline{\text{LiLA}}] \quad (10)$$

TABLE I. Partition Coefficients of Crown Ethers (P_L) between Various Solvents and Water

Solvent	Cl-DB14C4	DB14C4	t-Bu-DB14C4
C ₆ H ₆	2.04×10^{-3}	3.09×10^{-2}	3.64×10^{-2}
CHCl ₃	4.08×10^{-3}	2.61×10^{-2}	9.89×10^{-2}
CH ₂ Cl ₂	9.01×10^{-4}	4.25×10^{-2}	7.84×10^{-2}
1,2-C ₂ H ₄ Cl ₂	9.87×10^{-3}	5.05×10^{-2}	7.04×10^{-2}
CH ₃ NO ₂	8.72×10^{-2}	4.27×10^{-2}	1.89×10^{-2}
C ₆ H ₅ NO ₂	2.62×10^{-2}	2.17×10^{-2}	3.43×10^{-3}

where $[\bar{L}]_0$ and $[\text{LiA}]_0$ denote the initial concentrations of ligand in the organic phase and lithium picrate in the aqueous phase respectively. The distribution ratio (D) of the metal ion can be defined as:

$$D = \frac{[\text{Li}\bar{L}]}{([\text{Li}^+] + [\text{LiL}^+])} \quad (11)$$

However, since the dissociation of the ion pair in the nonpolar solvent may be negligible, and since $[\text{LiL}^+]$ was found to be much smaller than $[\text{Li}^+]$ under the conditions of the present work, as will be seen, eqn. (11) can be written as:

$$D = K_{\text{ex}}[\text{A}^-][\bar{L}] \quad (12)$$

$$\log D/[\text{A}^-] = \log K_{\text{ex}} + \log[\bar{L}] \quad (13)$$

According to eqn. (13), the linear plot of $\log D/[\text{A}^-]$ versus $\log[\bar{L}]$ would give a slope of 1.0 and an intercept of K_{ex} .

The P_L values of the crown ethers listed in Table I are in the range of 10^{-2} . This means that the concentration of the ligand in the aqueous phase is smaller than that in the organic solvent. The P_L value of DB14C4 in water/benzene is 3.09×10^{-2} , which is small in comparison with 0.2 of DB18C6 [18]. The reason may be that DB14C4 has two oxygen atoms less than DB18C6, making it more hydrophobic than DB18C6. From Table I, the P_L values of crown ethers with different substituent groups in the nonpolar or less polar solvents such as benzene, chloroform, dichloromethane and 1,2-dichloroethane appear in the order Cl-DB14C4 < DB14C4 < t-Bu-DB14C4, while in the polar solvents the order is reversed: Cl-DB14C4 > DB14C4 > t-Bu-DB14C4. The trend in nonpolar or less polar solvents shows that the effect of the electronic character is larger than that of the bulky factor. It indicates that the charge density of the etherate oxygen on the crown ether is augmented by the releasing group such as t-butyl which increases the solubility of the ligand in water more than that of the withdrawing group such as chloro. While the trend in the case of polar solvents shows that the effect of the bulky factor is larger than that of the electronic character. This means that the bulky ligand will increase the solubility of the crown ether in polar solvents and com-

pensate the unfavorable effect caused by the releasing factor. A similar trend was also found by Hiraoka [18] in the order of DCH18C6 < DB18C6 < 18C6 in the water/benzene system. Table I also reveals that the P_L values of DB14C4 in either less polar or nonpolar solvents are about in the same range ($\sim 4 \times 10^{-2}$). But the P_L values of t-Bu-DB14C4 in the nonpolar solvents are greater than those in the less polar solvents; in the case of crown with withdrawing group on it such as Cl-DB14C4, their P_L values in various solvents have the reverse trend, representing the effectiveness of the interaction between etherate oxygen on the crown and the solvent molecules.

The linear plots of $\log D/[\text{A}^-]$ versus $\log[\bar{L}]$ in Figs. 2 to 4 give a slope approximately to 1.0 in every case, indicating that DB14C4 and its derivatives form the 1:1 complex with the lithium ion. The stoichiometry of the crown ether–lithium complex also means that the lithium ion fits well into the 14-crown-4 cavity. Figure 5 is a typical absorption spectra of the DB14C4/lithium picrate system. It shows that only an isobestic point appears at 331 nm, but the absorption maximum (λ_{max}) does not shift to a higher wavelength when it reaches 357 even with further addition of a large excess of crown ether. This phenomenon was also observed by other workers [19,20], suggesting that only a 1:1 species exists. These arguments are consistent with the results of NMR measurements [13, 21].

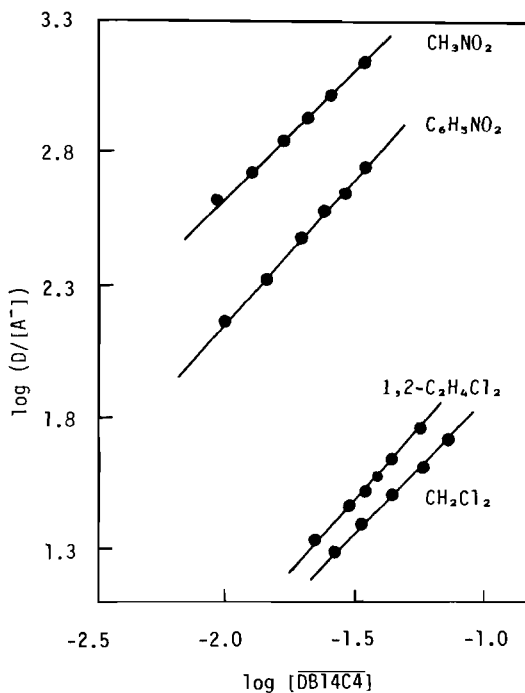


Fig. 2. Plots of $\log(D/[\text{A}^-])$ vs. $\log[\bar{L}]$ for the DB14C4 system.

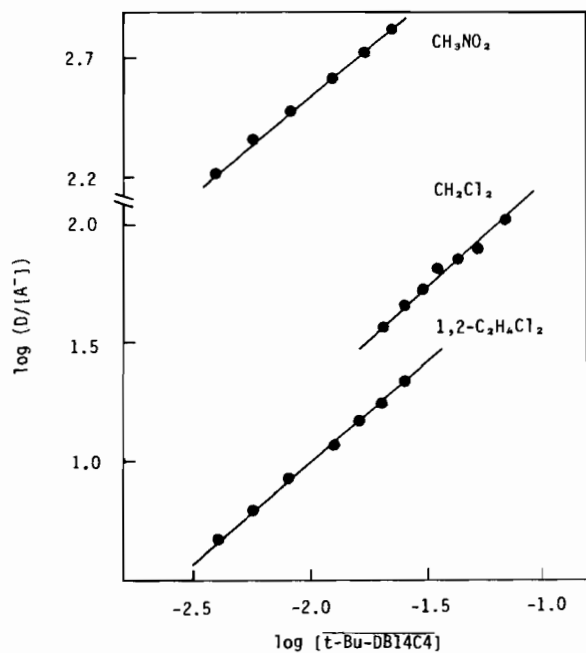


Fig. 3. Plots of $\log(D/[A^-])$ vs. $\log [\bar{L}]$ for the *t*-Bu-DB14C4 system.

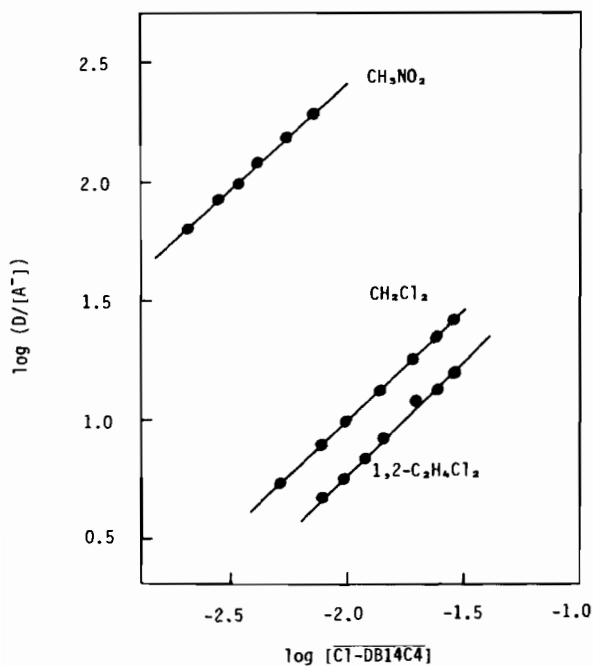


Fig. 4. Plots of $\log(D/[A^-])$ vs. $\log [\bar{L}]$ for the Cl-DB14C4 system.

The absorption maxima of the complexes between lithium picrate and crown ethers in various solvents are listed in Table II. The λ_{\max} values of the complexes in Table II clearly reveal the dependence of the absorption maxima of the crown complexes

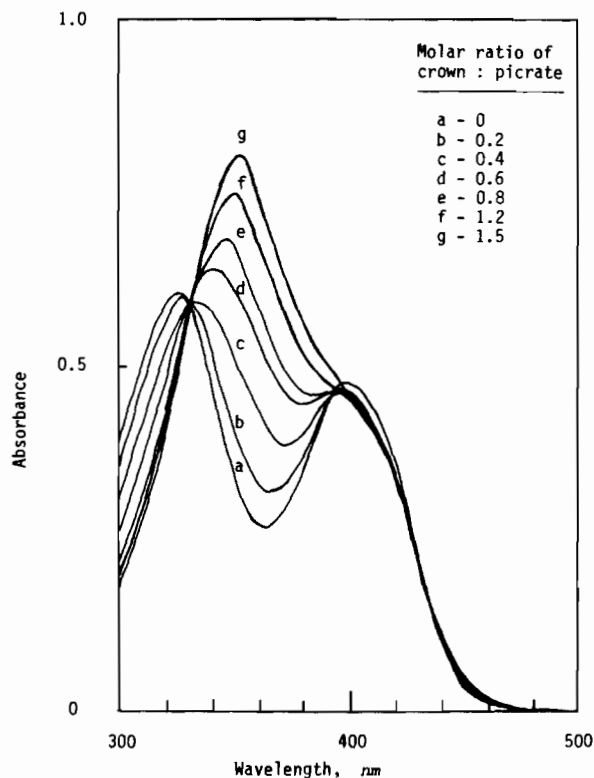


Fig. 5. Optical spectra of 10^{-4} mol dm^{-1} 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ solution of lithium picrate in the presence of varying amounts of DB14C4.

on the nature of the solvent and structure of the crown ether. It is assumed that there are at least three types of crown ether–lithium picrate complexes existing in these media with different polarities. One is the tight ion pairs with an absorption maximum at 331 nm in benzene and chloroform. The second is the less tight ion pairs with an absorption maximum lying between 346 and 370 nm in dichloromethane and 1,2-dichloroethane. The third is the solvent separated ion pairs with an absorption maximum at 377 nm in nitromethane. These different types of absorption maxima seem to arise distinctly from the different solvent polarities. After addition of the crown ether to a solution of benzene or chloroform containing lithium picrate, the absorption band shifts from 324 [22] to 331 nm. This shift reflects the more delocalization of electrons on the picrate anion due to the complex ion formation of Li^+ –crown. The relatively small red shift shows this complex cation may form a tight counter ion pair with the picrate anion in nonpolar solvents. The same phenomenon was also found by Takaki *et al.* [23], in the study of the interaction of 4-methyl-benzo-15-crown-5 with fluorenyl sodium in tetrahydropyran.

TABLE II. Spectral Data^a for Lithium Picrate–Crown Ether Complexes in Various Solvents

Solvent	Cl-DB14C4		DB14C4		t-Bu-DB14C4	
	λ_{\max}	$\epsilon \times 10^{-3}$	λ_{\max}	$\epsilon \times 10^{-3}$	λ_{\max}	$\epsilon \times 10^{-3}$
C ₆ H ₆	331	8.15	331	8.05	331	3.05
CHCl ₃	331	8.21	331	9.08	331	7.21
CH ₂ Cl ₂	346	10.0	353	11.8	364	10.3
1,2-C ₂ H ₄ Cl ₂	358	10.6	357	13.1	370	17.0
CH ₃ NO ₂	377	25.2	377	20.6	377	25.0

^a λ_{\max} : absorption maximum (nm); ϵ : molar absorptivity ($\text{mol}^{-1} \text{cm}^{-1}$).

TABLE III. Logarithmic Extraction Constants ($\log K_{\text{ex}}$) of Lithium Picrate with Crown Ethers between Various Solvents and Water

Solvent	Dielectric constant	Dipole moment	Cl-DB14C4	DB14C4	t-Bu-DB14C4	Other systems [9]
C ₆ H ₆	2.28	0	<1	<1	<1	-1.62 ^a
CHCl ₃	4.8	1.15	<1	<1	<1	NE ^b
CH ₂ Cl ₂	9.08	1.55	2.95	2.89	3.34	1.49 ^a
1,2-C ₂ H ₄ Cl ₂	10.36	2.06	2.84	2.96	2.97	
CH ₃ NO ₂	35.87	3.17	4.48	4.57	4.70	
C ₆ H ₅ NO ₂	34.82	3.99		4.27		

^aFor 12C4. ^bFor B12C4, NE = no extraction.

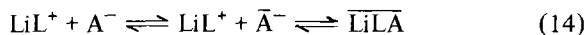
In the case of less polar solvents dichloromethane and dichloroethane, the less tight counter ion pairs are formed between crown, Li⁺ and A⁻. Unlike in the nonpolar solvents the somewhat solvation between lithium–crown complex and less polar solvent molecules occurs and somehow reduces interaction between the lithium crown complex and the picrate anion. This may further delocalize electrons on the picrate anion and result in the further red shift from 331 to 370 nm. In dichloromethane solvent the absorption maxima are 346, 353 and 364 nm for lithium picrate with Cl-DB14C4, DB14C4 and t-Bu-DB14C4 system, respectively, whereas in 1,2-dichloroethane solvent the absorption maxima are 358, 357 and 370 nm, respectively. Here the rational dependence of the absorption maxima on the nature of either the polarity of the solvent or the electronic character of the substituent group on the crown molecule is further evidenced as the formation of less tight counter ion pairs. Finally in the polar solvents such as nitromethane, the lithium crown complex is completely insulated by the polar solvent molecules. Hence, the absorption maximum of the picrate anion in the presence of three different kinds of crown ether is 377 nm. This is similar to the situation in the system only involving lithium picrate and nitromethane solvent as evidenced by its absorption maximum at 374 nm [22].

The molar absorptivities (ϵ) of the crown ether complexes in various solvents are all different (Table

II). For example DB14C4: the molar absorptivity for the tight ion pair complex in benzene and chloroform is 8.05×10^3 and 9.08×10^3 , respectively; for the less tight ion pair complex in dichloromethane and 1,2-dichloroethane it is 1.18×10^4 and 1.31×10^4 , respectively; and for the solvent separated ion pair complex in nitromethane it is 2.06×10^4 , indicating the molar absorptivities of the complex increase with the change of the complex form from tight ion pair to separated ion pair in various solvents. As mentioned in this context, the lithium picrate ion forms a separated ion pair with crown ether in nitromethane and has the largest bathochromic shift of 377 nm. This absorption band overlaps with a solvent environment-independent 400 nm absorption band which corresponds to the $\pi \rightarrow \pi^*$ transition of the picrate ion (see Fig. 5), resulting in the largest molar absorptivity. This phenomenon agrees with the observation of Bourgoin *et al.* [19] who found that molar absorptivities for the separated B15C5 \cdot K⁺·A⁻ ion pair complex are higher than those of the tight ion pair B15C5·NH₄⁺·A⁻.

The extraction constants, $\log K_{\text{ex}}$, obtained from the intercepts of the linears shown in Figs. 2 to 4, are summarized in Table III. The dielectric constants, dipole moments of the solvents and $\log K_{\text{ex}}$ values of other crown-4 systems [9] are also listed in Table III for comparison. They indicate that the magnitudes $\log K_{\text{ex}}$ of our system are greater than those of the other crown-4 systems [8, 9]. From

the orderness of $\log K_{\text{ex}}$ in Table III, it was found that the extraction of lithium is favorable in the presence of the crown ether with an electron releasing group on it and in more polar solvents. In comparison with two other crown ethers, t-Bu-DB14C4 forms a more stable complex with lithium ion in water; it may be plausible that eqn. (3) in the extraction mechanism (see above) is the dominant step. Meanwhile eqn. (4) may be further illustrated as:



which is favorable to occur in polar solvents.

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