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Kazushige Nishizawa[a]; Tokuyoshi Takano[a]; Isao Ikeda[b]; Mitsuo Okahara[b]
[a] DEPARTMENT OF NUCLEAR ENGINEERING FACULTY OF ENGINEERING, OSAKA UNIVERSITY, SUITA, OSAKA, JAPAN [b] DEPARTMENT OF APPLIED CHEMISTRY FACULTY OF ENGINEERING, OSAKA UNIVERSITY, SUITA, OSAKA, JAPAN

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Extractive Separation of Lithium Isotopes by Crown Ethers

KAZUSHIGE NISHIZAWA and TOKUYOSHI TAKANO
DEPARTMENT OF NUCLEAR ENGINEERING

ISAO IKEDA and MITSUO OKAHARA
DEPARTMENT OF APPLIED CHEMISTRY

FACULTY OF ENGINEERING
OSAKA UNIVERSITY
YAMADA-OKA, SUITA, OSAKA, JAPAN

Abstract

Separative abilities of crown ethers to lithium isotopes were investigated for the number of oxygen atoms composing crown rings and for the substituted groups to 15-crown-5. The separation factors at 0°C were 1.057 for 12-crown-4, 1.042 for benzo-15-crown-5, 1.041 for lauryloxymethyl-15-crown-5, 1.043 for tolyloxymethyl-15-crown-5, and 1.024 for dicyclohexano-18-crown-6. The enthalpy change of the isotopic equilibrium in the absolute value was the greatest for 12-crown-4; $\Delta H^\circ = -0.78$ kJ/mol. In the substituted 15-crown-5s the separation factor was greatest for tolyloxymethyl-15-crown-5, and ΔH° values decreased in the order: benzo- > tolyloxymethyl- > lauryloxymethyl-15-crown-5. For enthalpy changes, benzo-15-crown-5 has the possibility of giving a larger separation factor than the present one, $\alpha = 1.042$, by choosing more suitable conditions. In spite of its large distribution coefficient, dicyclohexano-18-crown-6 is not superior for isotopic separation of lithium in regard to the small enthalpy change of isotopic equilibrium; $\Delta H^\circ = -0.15$ kJ/mol. The addition of DMSO to the initial solution of LiI caused a remarkable increase in the distribution coefficient without changing the isotopic separation factors.

INTRODUCTION

Recent work on isotopic separation by cyclic polyethers has made it clear that lithium isotopes have been separated with high separation factors (*1–6*). Jepson and Cairns (*3*) reported in their pioneer work that ^{6}Li and ^{7}Li were separated with the single-stage isotopic separation factor $\alpha = 1.041$ by using cryptand[2,2,1]. A polymer resin with cryptand[2_B,2,1] as an anchor group, cryptand[2_B,2,1] polymer, was reported to have $\alpha = 1.047$ (*1*). Although the separation factors of lithium isotopes by a crown ether show a variety of values depending on the experimental conditions, the maximum attained was $\alpha = 1.042$ for benzo-15-crown-5 (*2*). All the separation factors of cyclic polyethers for lithium isotopes published to date are large for chemical exchange reactions, giving a ten times larger enrichment factor ε ($= \alpha - 1$) than by an ion exchanger. Heumann (*7*) published a detailed review on isotopic separation by cyclic polyethers, containing separation factors of lithium isotopes published up to 1984.

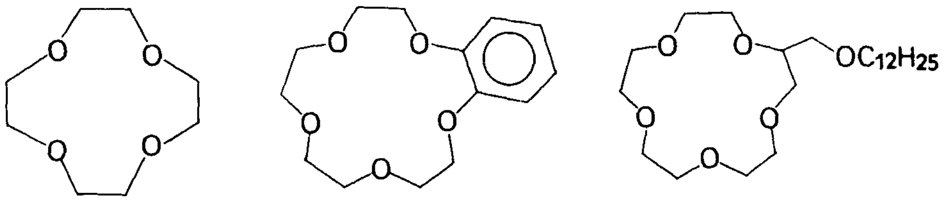
Because of the different nuclear properties of ^{6}Li and ^{7}Li, isotopically pure lithium is required for nuclear research and industries. Since ^{6}Li has a large cross section for the thermal neutron ^{6}Li(n,α)T, it is useful as a source of tritium, one of the fuels or blanket materials of a fusion reactor. Isotopically pure ^{7}LiOH is used as a pH-value adjuster for the primary coolant of a pressurized water reactor.

In every separation experiment using polyethers, ^{6}Li is known to be enriched in Li-crown complexes. Although the separation factors, the ratios of stability constants of ^{6}Li-crown complexes to ^{7}Li-crown complexes, present different values depending on the experimental conditions, it is commonly recognized that the lighter isotope is held more stably in the hole of a polyether than the heavier one.

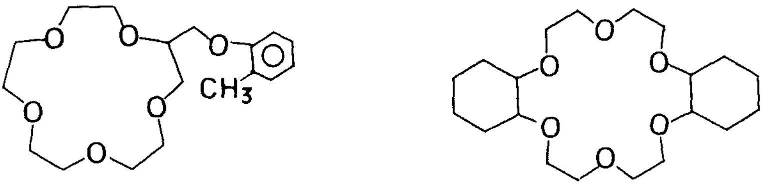
Previously reported separation factors of the cyclic polyethers to lithium isotopes suggest that the smaller the inner diameter of the ether, the greater the separation factor (*3*): cryptand[2,2,1] > cryptand[2,2,2] and 15-crown-5 > 18-crown-6. The most effective crown ether for lithium isotope separation will be selected by comparing three crown ethers with different hole diameters: 12-crown-4, 15-crown-5, and 18-crown-6 (Fig. 1).

Crown ethers having the same number of oxygen atoms are known to give different stability constants to the lithium ions depending on their side chains (*8*). The isotope effects induced by the substituted groups will be investigated by comparing the separation factors of (II), (III), and (IV).

A counteranion added to the lithium ion in the aqueous phase of extraction causes changes in the isotopic separation factor. Lithium iodide gives the greatest separation factor in lithium halides (*2*). Throughout the present experiment, a 2.0 *M* lithium iodide solution was used as an aqueous phase.



I. 12-crown-4 II. benzo-15-crown-5 III. lauryloxymethyl-15-crown-5



IV. tolyloxymethyl-15-crown-5 V. dicyclohexano-18-crown-6

FIG. 1. Crown ethers used in the present experiment.

In the extractive separation of lithium isotopes, especially for industrial separation, a large distribution coefficient is desirable. The correlation of the separation factor and the distribution coefficient will be discussed along with enlargement of the distribution coefficient by adding dimethylsulfoxide (DMSO).

Separation Factor

The isotopic exchange equilibrium between the aqueous lithium ion and the crown-ether-Li$^+$ complex in the organic phase is represented in the following equation for a liquid-liquid extraction system:

$$^{6}\mathrm{Li}^{+}_{(aq)} + {}^{7}\mathrm{Li}^{+}\mathrm{L}_{(org)} \overset{K}{=} {}^{6}\mathrm{Li}^{+}\mathrm{L}_{(org)} + {}^{7}\mathrm{Li}^{+}_{(aq)} \qquad (1)$$

where L denotes the ligand of crown ether, and the subscripts (aq) and (org) are the corresponding ionic species found in the aqueous phase and in the organic phase of the extraction system. The separation factor α is a value defined as the ratio of isotopic abundances in one phase and another:

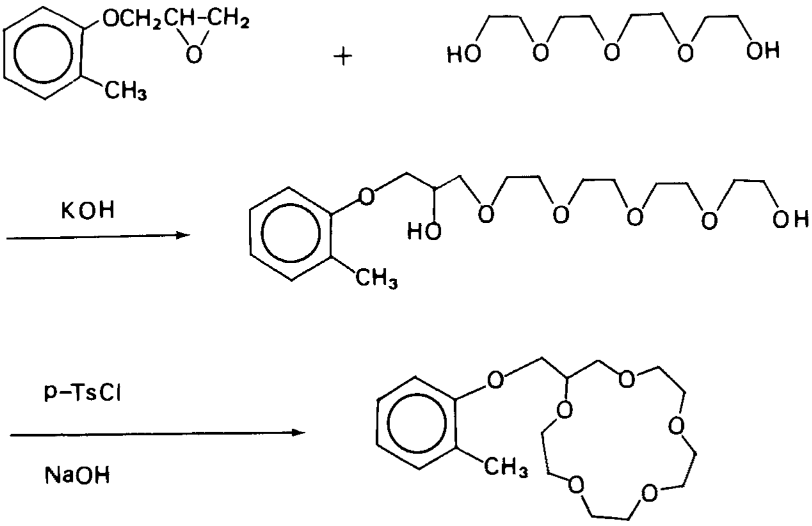
$$\alpha = \left(\frac{[^6\mathrm{Li}]}{[^7\mathrm{Li}]}\right)_{(\mathrm{org})} \Bigg/ \left(\frac{[^6\mathrm{Li}]}{[^7\mathrm{Li}]}\right)_{(\mathrm{aq})} \tag{2}$$

The equilibrium constant K of Eq. (1) has the same meaning as the separation factor; $\alpha = K$.

EXPERIMENTAL

Chemicals

Commercially available crown ethers, 12-crown-4 and dicyclohexano-18-crown-6 (Nisso products) and benzo-15-crown-5 (Merck) were used. The other two, lauryloxymethyl- and tolyloxymethyl-15-crown-5 were synthesized by using a method of intramoleculer cyclization which was developed by the present authors (9). The way of producing tolyloxymethyl-15-crown-5 is illustrated in Scheme 1 as an example, where p-TsCl indicates *p*-toluenesulfonyl chloride. The yield of the crown ether was ~40%. The crown ethers were identified for their chemical construction with a ^{1}H-NMR and a mass spectrometer.



SCHEME 1.

Lithium iodide (Reagent Grade) was used without further purification. Commercial lithium salts do not always have the same isotopic content: ^{6}Li-depleted salts, however, do not affect determination of the isotopic separation factors because they are defined as the ratio of isotopic abundances distributed in the two phases of the extraction system.

Crown ethers dissolved in chloroform were washed several times with a large amount of water. Chloroform used in the organic solvent was of Reagent Grade.

Procedure

Each 20 mL of a 2.0 *M* aqueous solution of LiI and 0.186 *M* crown ether in chloroform was stirred in a flat-bottomed flask by a magnetic stirrer for 30 min. This process was carried out at a regulated temperature by means of a water bath. The liquid mixture was kept undisturbed in a separating funnel for 30 min for complete disengagement of aqueous/organic phases at the same temperature as the extraction process. After separation of the two phases, the organic phase was scrubbed with 20 mL distilled water for 30 min to put the lithium salt back into the water. Almost all the salt was put into the water by three back-extractions.

The distribution coefficient was determined by comparing salt concentrations in the aqueous phases extracted and back-extracted. The salt concentrations in both solutions were analyzed by flame photometry.

The aqueous solution of lithium iodide extracted or back-extracted was diluted with distilled water or evaporated to be 70 ng Li/μL. Exactly 3.0 μL of this solution was put on a sample filament (one of the triple filaments) of a thermal ionizing mass spectrometer. This amount of lithium (210 ng) was determined empirically to give the most precise isotopic abundance ratio for the mass spectrometer (Hitachi, MHU-301) in our laboratory. The filament charged with lithium iodide was dried under a heat lamp before being mounting in the mass spectrometer.

An ionizing filament made of rhenium ribbon was heated gradually with a charging electric current, keeping a pressure of 10^{-6} torr in an ion source. The ion currents of ^{6}Li and ^{7}Li increased with increasing filament current. Even after keeping the filament current constant (1.8 A), the ion current increased for about 1 h before reaching a maximum. About 20 pairs of lithium isotopic peaks just before and after the maximum ion current were sampled for averaging. The relative standard deviation of the lithium isotopic ratio measurement was 0.02%.

RESULTS AND DISCUSSION

Lithium Isotope Effects of 12-Crown-4, 15-Crown-5, and 18-Crown-6

The temperature dependencies of the isotopic separation factors of crown ethers (I), (II), and (V) are illustrated in Fig. 2 as van't Hoff plots of Eq. (1). The measured values at 0°C are $\alpha = 1.057$, 1.041, and 1.028 for (I), (II), and (V), respectively. At almost all the measured points, the smaller the cavity sizes of the crown ethers give the greater separation factors. The separation factor of 12-crown-4 at 0°C is the greatest reported to date for cyclic polyethers. For the various kinds of chemical exchange methods of lithium isotopic enrichment, only a few exceed $\alpha = 1.057$. For most mercury amalgam and lithium salt exchanges (which are the only methods used for lithium isotopic enrichment on an industrial scale), the separation factors are barely above 1.05 (*10*). Strong basic ion exchangers, which were investigated as isotopic separators of lithium isotopes, gave almost a tenth smaller enrichment factors (*11*) than the present crown ethers. The crown ethers used in the present experiment, except for dicyclohexano-18-crown-6, show promise for the industrial separation of lithium isotopes.

The ability of crown ethers to distinguish alkali metals depends strongly on the fit between the cavity diameter of the crown ether and the cationic radius of the metal. Stability constants of lithium (*12*) and sodium complexes (*13*) with 15-crown-5 can be found in the literature. The logarithms of the stability constants of lithium and sodium complexes of 15-crown-5 versus Pauling's ionic radius are plotted in Fig. 3. With a given ionic radius difference in ^{6}Li and ^{7}Li [$r_6 - r_7 = 4 \times 10^{-2}$ pm (*14*)], log K values should be different, and an isotopic fractionation should be observed in such a system. The isotopic shift of log K for lithium is shown on the right side of Fig. 3. It is obvious that the slope for lithium and sodium ions is flatter than for ^{7}Li and ^{6}Li. This fact indicates that the separative ability of benzo-15-crown-5 to lithium isotopes cannot always be attributed to the size fitness of the crown cavity to the cation. The slope difference of the stability constants of lithium isotopes and alkali metals is amplified for dicyclohexano-18-crown-6. Heumann (*7*) showed that the separative abilities of cryptand[2,2,1] and [2,2,2] for calcium isotopes are caused by size effects: the slopes of the stability constants for ^{40}Ca, ^{44}Ca, and ^{48}Ca are the same as those for alkaline earth cations. As a consequence, the use of the crown ethers for lithium isotopic separation is more effective than for calcium isotopes.

Since the separation factors of crown ethers for isotopes are largely

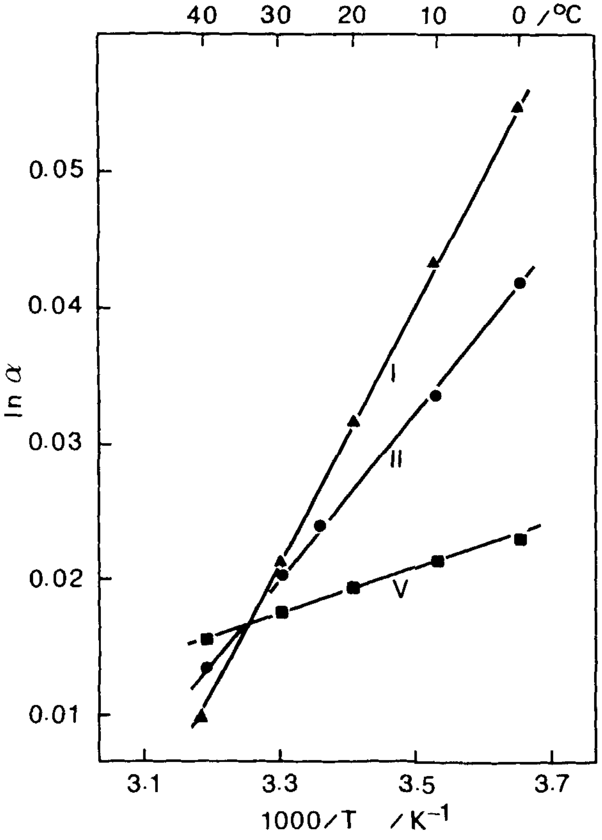


FIG. 2. Van't Hoff plots of isotopic equilibria: $^6Li^+ + {}^7Li^+L = {}^6Li^+L + {}^7Li^+$, where L represents the ligand of a crown ether. (I) 12-Crown-4, (II) benzo-15-crown-5, (V) dicyclohexano-18-crown-6.

influenced by such system conditions as the temperature, the kind of counteranion, and concentration of the salt in the aqueous phase, the published values of the separation abilities for even the same crown ether may differ for different authors. The enthalpy and entropy changes of isotopic equilibrium shown in Eq. (1) can be obtained by applying the well-known thermochemical equation, $-RT \ln K = \Delta H° - T\Delta S°$, to the van't Hoff plot of Fig. 2, where K represents the separation factor of the isotopes. These figures are shown in Table 1 along with the separation factors at 0°C. An enthalpy change means the difference of bond energies between ^6Li and ^7Li to oxygen atoms in the crown ether. Enthalpy

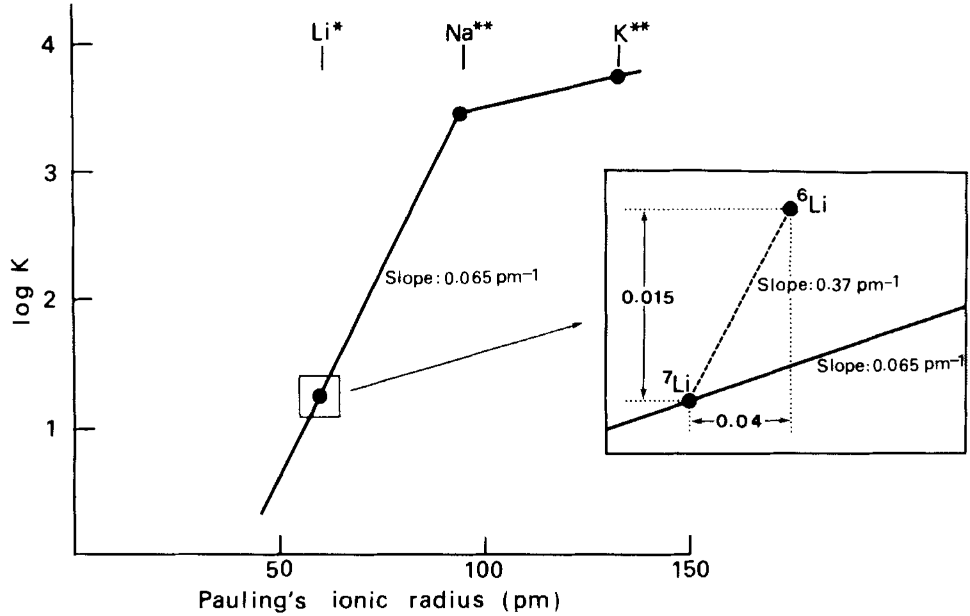


FIG. 3. Stability constants of alkali-crown complexes on metal ionic radius with lithium isotopic shift. *Values of log K reproduced from Smetana and Yano (*12*). **Values of log K reproduced from Lamb et al. (*13*).

changes between the isotopes are substantially invariable for a given crown ether, as can be presumed from Eq. (1), although they fluctuate a little with variation of the system, e.g., cation–anion or anion–ligand interaction.

The absolute values of enthalpy changes decrease in the order 12-

TABLE 1
Lithium Isotopic Separation Factors (α) at 0°C and Enthalpy Changes ($\Delta H°$) and Entropy Changes ($\Delta S°$) of Isotopic Equilibrium: $^6Li^+ + {}^7Li^+L = {}^6Li^+L + {}^7Li^+$

	α at 0°C	$\Delta H°$ (kJ/mol)	$\Delta S°$ ($J \cdot mol^{-1} \cdot K^{-1}$)
12-Crown-4	1.057	−0.78	−2.4
Benzo-15-crown-5	1.042	−0.47	−1.4
Lauryloxymethyl-15-crown-5	1.041	−0.22	−0.50
Tolyloxymethyl-15-crown-5	1.043	−0.26	−0.63
Dicyclohexano-18-crown-6	1.024	−0.15	−0.34

crown-4 > benzo-15-crown-5 > dicyclohexano-18-crown-6 (Table 1). This result agrees with the assumption that lithium isotopes can be distinguished effectively by a crown ether having a small cavity.

Isotope Effects Given by Side Chain

It is well known that the side chain of a crown ether changes the stability constant of a metal-crown complex. From this it can be postulated that the ratio of the stability constants of ^{6}Li-crown and ^{7}Li-crown, the separation factor, is also affected by the side chain. Van't Hoff plots of isotopic exchange equilibria are illustrated in Fig. 4 for 15-crowns-5 substituted with the lauryloxymethyl group (III) and tolyloxymethyl group (IV), along with the benzo-15-crown-5 as a reference. The slopes of (III) and (IV) are remarkably small in comparison to that of (II). A practical separating process should be stable against fluctuating temperatures. In this sense, (III) and (IV) are more advantageous than (II) if they are applied under conditions similar to the ones used here (aqueous 2.0 *M* LiI, 0.186 *M* crown ethers in $CHCl_3$ and 0–40°C). Since it is difficult to separate the phases with lauryloxymethyl-15-crown-5 because it activates the surface, it is unfavorable for the extractive separation of lithium isotopes on a technical scale which requires repeated use of the crown ether.

The absolute value of enthalpy change for (II) is greater than for (III) and (IV), as can be seen from the slope of the van't Hoff plots in Fig. 4. The enthalpy changes of these three crown ethers are different, while the separation factors at 0°C are roughly equal, indicating that the contributions of entropy changes are negative and the absolute values are large for (II) and small for (III) and (IV). The entropy change includes all the parameters of isotope effects in both phases of the extraction system, except for the difference of bonding energies between ^{6}Li-crown and ^{7}Li-crown. The entropy change therefore varies depending on the conditions of both phases, for example, the kind of counteranion, the concentration of the lithium salt, and the pH value of the aqueous phase, and also on the kind and concentration of solvent used for the crown ether. Fluctuations of the entropy change cause parallel shifts to the van't Hoff plots for isotopic equilibria. Because of this, it is possible to move the van't Hoff plots of (I) in Fig. 2 and of (II) in Fig. 4 upward, leading to greater separation factors for 12-crown-4 and benzo-15-crown-5. The different separation factors of benzo-15-crown-5 to lithium isotopes, as measured independently by two groups (*2*, *5*), can be attributed to the different entropy changes caused by different extractive systems.

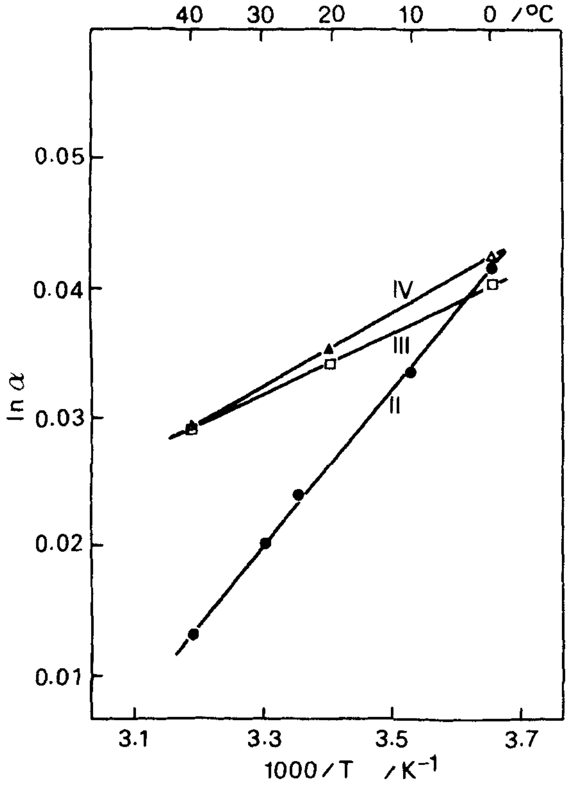


FIG. 4. Van't Hoff plots of isotopic equilibria: $^6Li^+ + {}^7Li^+L = {}^6Li^+L + {}^7Li^+$, where L represents the ligand of a crown ether. (II) Benzo-15-crown-5, (III) lauryloxymethyl-15-crown-5, (IV) tolyloxymethyl-15-crown-5.

Distribution Coefficient

In order to remove an enriched lithium isotope by extraction, multistage separation method is necessary. Precise distribution coefficients are required to design a cascade. The distribution coefficients of lithium in the extractive experiment from aqueous 2.0 *M* LiI at 0°C are shown in Table 2. Since a part of the complexes with 12-crown-4 and 12-crown-4 dissolve in the aqueous phase because of their hydrophilic properties, the amount of lithium ions distributed in the organic phase is very small. The distribution coefficient by 18-crown-6 is larger than by 15-crown-5, which agrees with previous result (*15*).

TABLE 2

Distribution Coefficients (D) at 0°C and Enthalpy Changes ($\Delta H°$) and Entropy Changes ($\Delta S°$) of Extraction Equilibrium: $Li^+_{(aq)} + I^-_{(aq)} + L_{(org)} = Li^+LI^-_{(org)}$

	D at 0°C	$\Delta H°$ (kJ/mol)	$\Delta S°$ ($J \cdot mol^{-1} \cdot K^{-1}$)
12-Crown-4	2.0×10^{-5}	—	—
Benzo-15-crown-5	7.1×10^{-3}	−53	−205
Lauryloxymethyl-15-crown-5	8.1×10^{-3}	−24	−118
Tolyloxymethyl-15-crown-5	5.0×10^{-3}	−26	−129
Dicyclohexano-18-crown-6	2.8×10^{-2}	−31	−122

Enthalpy and entropy changes in the extractive equilibria indicated in the following equation were calculated from the van't Hoff plots:

$$Li^+_{(aq)} + I^-_{(aq)} + L_{(org)} \xrightarrow{K_e} Li^+LI^-_{(org)} \tag{3}$$

where L denotes the ligand of crown ether and K_e is the extraction equilibrium constant. These values are tabulated with the distribution coefficients at 0°C. Since $\Delta H°$ and $\Delta S°$ in extraction are the values induced from ln K_e vs $1/T$ curves and are dependent on the lipophilicities of the counteranions, as can be seen from Eq. (3), they cannot be directly compared with the stability constants of complexes accumulated so far. Because every enthalpy and entropy change in the extractions has a negative value, further comparisons will be carried out in absolute values. In the present system (aqueous phase, 2.0 *M* solution; organic phase, 0.186 *M* crown ether in $CHCl_3$), lauryloxymethyl- and tolyloxymethyl-15-crown-5 have smaller $\Delta H°$'s in extractive reactions than has 18-crown-6, while the enthalpy changes in isotopic equilibria are large for the 15-crowns-5 and small for the 18-crown-6 (see Table 1). This result is strange from the point of energetics on host–guest coordination, and it remains to be resolved by further investigations.

The equilibrium constant K_e in Eq. (3) is a value defined for a solution of unconcentrated solute whose activity is proportional to the salt concentration. In a concentrated solution, as in the present experiment, the population of ion pairs, $Li^+ \ldots I^-$, is greater than that of the aqua-complex of lithium, leading to the easy formation of a Li-crown complex (*2*). If the activity of the aqua-complex is decreased in the aqueous phase, K_e is increased, and as a result a large distribution coefficient can be obtained.

Effects of DMSO

In order to decrease the activity of the aqua-complex in the aqueous phase, dimethylsulfoxide (DMSO) was added to the initial solution of lithium salt. The distribution coefficients of lithium at 10°C from a water–DMSO mixture to a 0.186 *M* solution of benzo-15-crown-5 in $CHCl_3$ are shown in Table 3 as a function of weight percentage of DMSO. Almost ten times more lithium is extracted from a solution of 60% DMSO compared with that of pure water. The separation factors of the lithium isotopes are the same at all DMSO concentrations. From these results it can be understood that a part of the hydrating water molecules in the lithium-crown complex are replaced by DMSO molecules, and the complex coordinated by DMSO can exist more stably in the organic phase than in water. It is effective in practical separating processes to use a water–DMSO mixture as the initial solution of LiI in order to transfer a large amount of enriched ^{6}Li into the organic phase.

CONCLUSIONS

(1) Lithium isotopic separation factors are observed to be 1.057, 1.041, and 1.028 at 0°C for 12-crown-4, benzo-15-crown-5, and dicyclohexano-18-crown-6, respectively. The smaller the crown ring, the larger the separation factor obtained for the crown ethers investigated in the present experiment.

(2) The separation factor of 12-crown-4 surpasses that of the mercury amalgum method.

(3) Enthalpy changes of the isotopic equilibria are in the order 12-crown-4 > 15-crown-5 > 18-crown-6 in their absolute values.

TABLE 3

Distribution Coefficients (*D*) and Lithium Isotopic Separation Factors (α) at 10°C from Water–DMSO Solution[a] to Benzo-15-Crown-5[b] in $CHCl_3$

DMSO (wt%)	*D*	α
0	9.1×10^{-4}	1.034
20	1.9×10^{-3}	
40	4.0×10^{-3}	
60	9.2×10^{-3}	

[a] Concentration of LiI: 2.0 *M*.

[b] Concentration of crown ether: 0.186 *M*.

(4) Greater separation factors are observed than expected from the selectivities of crown ethers to alkali metals.

(5) The separation factors at 0°C do not show large differences in the substituted 15-crowns-5, but the enthalpy changes for isotopic equilibria vary remarkably, depending on their side chains. Benzo-15-crown-5 is expected to have a greater separation factor under suitable separating conditions.

(6) Although the distribution coefficient of lithium is larger for dicyclohexano-18-crown-6 than for benzo-15-crown-5 in the present system, the larger enthalpy change of benzo-15-crown-5 in extraction suggests that greater distribution of lithium into the organic phase can be attained.

(7) The addition of DMSO to the initial aqueous solution can increase the lithium distribution into the organic phase without changing the isotopic separation factors.

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