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Extractive Separation of Lithium Isotopes Using Benzo-15-Crown-5. Effect of Salt Concentration

Kazushige Nishizawa[a]; Tokuyoshi Takano[a]
[a] Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Osaka, Japan

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NOTE

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KAZUSHIGE NISHIZAWA and TOKUYOSHI TAKANO

DEPARTMENT OF NUCLEAR ENGINEERING
FACULTY OF ENGINEERING
OSAKA UNIVERSITY
2-1, YAMADAOKA, SUITA, OSAKA, JAPAN 565

Abstract

In an extractive separation of lithium isotopes with benzo-15-crown-5, the greater separation factor is obtained from more concentrated LiCl solution. The intrinsic separation factor of benzo-15-crown-5 is determined to be α = 1.045 at 20°C.

INTRODUCTION

An isotopic exchange equilibrium in an extractive separation using crown ether is described by the following equation:

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

where the subscripts (aq) and (org) indicate the corresponding isotopic ions found in aqueous and organic phases, respectively, and L denotes the ligand of the crown ether. A single-stage separation factor α, commonly used in isotope chemistry, is the same as the equilibrium constant K of Eq. (1):

$$\alpha = ([^{6}\mathrm{Li}]/[^{7}\mathrm{Li}])_{\mathrm{org}}/([^{6}\mathrm{Li}]/[^{7}\mathrm{Li}])_{\mathrm{aq}} \qquad (2)$$

where $([^6Li]/[^7Li])_{org}$ and $([^6Li]/[^7Li])_{aq}$ are isotopic abundance ratios in the organic and aqueous phases, respectively. It should be noted that Eq. (1), and as a necessary consequence Eq. (2), do not involve a term for the counteranion.

Previously, the isotopic separation factors of lithium by benzo-15-crown-5 were measured by two groups (*1*, *2*) independently. As has been pointed out by each author, the greater separation factor is given by the softer counteranions. Even with the same anion, however, the measured values have shown a large difference: one has been $\alpha = 1.002$ (*1*) and another has been $\alpha = 1.014$ (*2*) for Cl^-. Such a great difference could come from the extractive conditions; for example, the concentration of the lithium salts, the pH value of the aqueous phases, and the concentration of benzo-15-crown-5 in the organic phase. In the present experiment we examined the effect of LiCl concentration in the initial aqueous solution to the separation factor of the lithium isotopes.

EXPERIMENTAL

Crown ether used in the present experiment was a commercially available benzo-15-crown-5 from Merck. The lithium salt was extracted into the organic phase containing benzo-15-crown-5 from the aqueous LiCl solution. All extractions were carried out at 20 ± 0.5°C. Detailed procedures can be found elsewhere (*1*, *3*).

Analysis of lithium salt was by flame photometry. Isotopic compositions were measured with a mass spectrometer with a thermal ionizing ion source. The standard deviation of the separation factors was less than ±0.002.

RESULTS AND DISCUSSION

The measured isotopic separation factors are illustrated by circles in Fig. 1 as a function of LiCl concentrations in the initial aqueous phase. The fact that the crown ether has an isotope effect means that the stability constant of the ^{6}Li-crown complex has a different value from that of the ^{7}Li-crown complex; i.e., there is a difference of free enerlgy changes between the following two equilibrium equations:

$$^6Li^+_{(OH_2)} + A^- + L = {}^6Li^+LA^- \qquad (3)$$

$$^7Li^+_{(OH_2)} + A^- + L = {}^7Li^+LA^- \qquad (4)$$

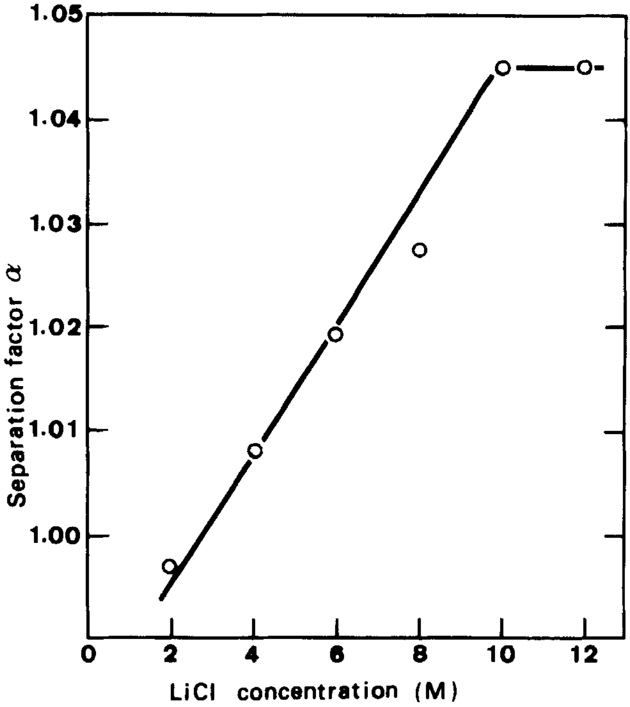

FIG. 1. Relationship between separation factor and LiCl concentration in the initial aqueous phase.

where L shows a ligand of crown ether and A^- the counteranion. Hydrated lithium ion is denoted by $Li^+_{(OH_2)}$. Equations (3) and (4) are reduced to

$$^6Li^+_{(OH_2)} + {}^7Li^+LA^- \overset{K}{=} {}^6Li^+LA^- + {}^7Li^+_{(OH_2)} \tag{5}$$

The equilibrium constant K of Eq. (5) is

$$K = \left(\frac{[^6Li^+LA^-]}{[^7Li^+LA^-]}\right) \Big/ \left(\frac{[^6Li^+_{(OH_2)}]}{[^7Li^+_{(OH_2)}]}\right)$$

$$= \left(\frac{^6Li}{^7Li}\right)_{org} \Big/ \left(\frac{[^6Li^+_{(OH_2)}]}{[^7Li^+_{(OH_2)}]}\right)_{aq} \tag{6}$$

where $(^6Li/^7Li)_{org}$ means the isotopic abundance ratio of lithium distributed into the organic phase, and $([^6Li^+_{(OH_2)}]/[^7Li^+_{(OH_2)}])_{aq}$ is the isotopic abundance ratio of hydrated lithium ion in the aqueous phase. In the aqueous solution, especially in the concentrated solution, lithium ions exist not only as hydrated but also as coordinated with the anion. Since they cannot be separated in a simple way, the isotopic content measurable in the aqueous phase is that of the mixture.

Kakihana (*4*) developed a method to determine the isotopic separation factor accompanying ion-pair formation in his study on isotopic separations with ion exchangers. By using his method, one can estimate separately the isotope effects in formations of the Li^+-crown complex and of the ion pair. The isotopic separation factor α of liquid-liquid extraction is defined as the ratio of isotopic content in the organic phase to that in the aqueous phase:

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

where $([^6Li]/[^7Li])_{org}$ and $([^6Li]/[^7Li])_{aq}$ are the isotopic ratios found in the organic and aqueous phases, respectively. This equation is rewritten to:

$$\alpha = \left(\frac{[^6Li]}{[^7Li]}\right)_{org} \left(\frac{[^7Li^+_{(OH_2)}] + [^7Li^+ \cdots Cl^-]}{[^6Li^+_{(OH_2)}] + [^6Li^+ \cdots Cl^-]}\right)_{aq} \tag{8}$$

where $[^6Li^+ \cdots Cl^-]$ and $[^7Li^+ \cdots Cl^-]$ denote the mole fractions of ^6Li and ^7Li existing as the ion pairs. If the equilibrium constant of the ion pair to the hydrated cation is K_p and that of the Li-crown complex to the ion pair is K_c, they are

$$K_p = \frac{([^6\mathrm{Li}^+\cdots\mathrm{Cl}^-]/[^7\mathrm{Li}^+\cdots\mathrm{Cl}^-])}{([^6\mathrm{Li}^+_{(\mathrm{OH}_2)}]/[^7\mathrm{Li}_{(\mathrm{OH}_2)}])} \tag{9}$$

$$K_c = \frac{[^6\mathrm{Li}^+\mathrm{L}]/[^7\mathrm{Li}^+\mathrm{L}]}{[^6\mathrm{Li}^+\cdots\mathrm{Cl}^-]/[^7\mathrm{Li}^+\cdots\mathrm{Cl}^-]} \tag{10}$$

Equation (8) can be reduced to

$$\ln\alpha = \ln K_c + \ln K_p - \frac{K_p - 1}{1 + ([^7\mathrm{Li}^+_{(\mathrm{OH}_2)}]/[^7\mathrm{Li}^+\cdots\mathrm{Cl}^-])} \tag{11}$$

In a dilute solution, 2.0 *M* in this experiment, the population of the hydrated ions is much larger than that of the ion pairs; $[^7\mathrm{Li}^+_{(\mathrm{OH}_2)}]/[^7\mathrm{Li}^+\cdots\mathrm{Cl}^-] \rightarrow \infty$. In the condensed solutions, 10.0 and 12.0 *M*, the reverse is the case; $[^7\mathrm{Li}^+_{(\mathrm{OH}_2)}]/[^7\mathrm{Li}^+\cdots\mathrm{Cl}^-] \rightarrow 0$. Equation (11) is rewritten to

$$\ln\alpha_{2.0} = \ln K_c + \ln K_p \tag{12}$$

$$\ln\alpha_{10.0} = \ln K_c + \ln K_p - (K_p - 1) \tag{13}$$

where $\alpha_{2.0}$ and $\alpha_{10.0}$ indicate the separation factors observed in the cases of extraction from 2.0 and 10.0 *M* aqueous solutions, respectively. If the measured separation factors $\alpha_{2.0} = 0.997$ and $\alpha_{10.0} = 1.045$ are into Eqs. (12) and (13), $K_p = 0.953$ and $K_c = 1.045$ are obtained. Since it relates to the isotopic effect of Li-crown complex formation, the K_c value represents the intrinsic ability of the crown ether to separate the lithium isotopes. From the definition of the K_c value mentioned above, it does not vary with the kind of counteranions. In the other words, the separation factor for extraction from a concentrated aqueous solution shows a characteristic value for the crown ether itself. An α value smaller than 1.000 in the case of 2.0 *M* means that ^{7}Li is enriched in the ion-pair phase rather tahn in the hydrated-ion phase. The results of the present study are consistent with those induced from the experimental results (*5*) of lithium isotopic separation using a cryptand polymer and a water–methanol solution of the lithium salts.

Distribution coefficients of lithium ions and the mole ratios of the Li-crown complex to total crown ether in the organic phase are illustrated in Table 1 as a function of the concentration of the salt in the initial

TABLE 1
Distribution Coefficient of Lithium and Molal Ratio of Li-Crown-Complexes to Total Crown Ethers in the Organic Phase

	Salt concentration in initial aqueous phase (M)					
	2.0	4.0	6.0	8.0	10.0	12.0
Distribution coefficient	7.7×10^{-5}	1.1×10^{-3}	1.4×10^{-3}	2.9×10^{-3}	1.5×10^{-2}	1.9×10^{-2}
(Li-crown)/(crown ether) (%)	0.083	2.3	4.5	12.3	78.2	100

aqueous phase. The population of the crown ethers occupied by the lithium ion is large in the concentrated solution, which is favorable for isotopic separation on a technical scale.

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