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Communications

The Separation of Lithium Isotopes with Novel Azacrown Ion Exchangers

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There are two naturally occurring isotopes of the element lithium, ⁶Li at 7.53% and ⁷Li at 92.47% relative abundance.¹ Each isotope plays an important role in the nuclear science and industry due to the great difference in their nuclear characteristics. Highly enriched ⁷Li in lithium hydroxide is used for adjustment of coolant pH in pressurized light water reactors,² whereas ⁶Li, in the form of LiH, is employed as a shield against thermal neutrons.^{3,4} Lithium compounds containing ⁶Li up to 90% may be used for the tritium breeder blanket in DT fueled fusion reactors in the future.^{4,5} Because of the large cross section for thermal neutron in the nuclear reaction, ⁶Li(n, α)T and ⁷Li(n, an)T in fast neutron, a variety of isotopic ratio of the element lithium have been proposed for releasing energy or production of tritium more effectively.⁶

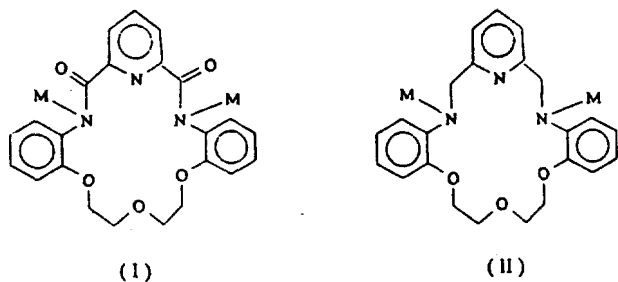
Although many techniques have been developed over the years for the separation of isotopes in general,^{4,7-9} not all of them are applicable to the lithium case. There are several methods applicable to separation of lithium isotopes. One of such methods is ion exchange chromatography. The first use of ion exchangers for the lithium isotope separation by Taylor and Urey¹⁰ was in 1937. And Glueckauf *et al.*¹¹ first attempted synthetic organic ion exchangers to lithium isotope

separation. Band displacement chromatography was applied to lithium isotope separation by Hagiwara and Takakura¹²⁻¹³ for the first time. In these chromatographic operations, they found that the ⁷Li and ⁶Li were enriched to 97.09% and 14.64 %, respectively, in the front and rear edges of the band. Fujine *et al.*¹⁴⁻¹⁵ carried out continuous displacement chromatography in a laboratory. Oi *et al.*¹⁶ also carried out cation exchange chromatography for the lithium isotope separation in aqueous ion exchange systems. From the results, they found that the values of the separation factors were in the range of 1.00089 to 1.00171 at 25 °C. After the discovery of new cation complexing agents such as crown ethers and cryptands, two-phase liquid systems have come under study again, with encouraging results.⁴ Jepson and DeWitt¹⁷ first applied macrocyclic polyether complexes to the calcium isotope separation and obtained the value of the separation factor of 1.0026 ± 0.0002 for the ⁴⁴Ca-⁴⁰Ca isotope pair. Jepson *et al.*¹⁸⁻¹⁹ also have determined the separation factors for the lithium isotopes by cryptand extraction. They reported the large separation factors in the range of 1.026 to 1.041 for some two-phase chemical exchange systems composed of an aqueous solution of a lithium salt and a chloroform solution of lithium cryptand complex. Nishizawa *et al.*²⁰⁻²² determined similar separation factors of 1.042 using benzo-15-crown-5 as an extractant, and of 1.047 by cryptand polymer. Previously, lithium isotope separation was performed in a series of studies to determine the influence of various physicochemical parameters upon the separation factor.²³⁻²⁶ Previous work of our laboratory, with monobenzo-15-crown-5 ion exchanger, separation factor of lithium isotopes was observed to be 1.053 with 5% acetonitrile aqueous solution as the eluent.²⁶ In this work, lithium isotopes have been separated in a similar method.

The azacrown ion exchangers, {(4,5):(13,14)-dibenzo-6,9,12-trioxa-3,15,21-triazabicyclo[15.3.1] heneicosa-1(21),17,19-triene-2,16 dione ion exchanger} (I) and {(4,5):(13,14)-dibenzo-6,9,12-trioxa-3,15,21-triazabicyclo[15.3.1] heneicosa-(1,17,19)(18,20,21) triene ion exchanger} (II) were synthesized in our laboratory.²⁷ The structures of these two ligands are as follows:

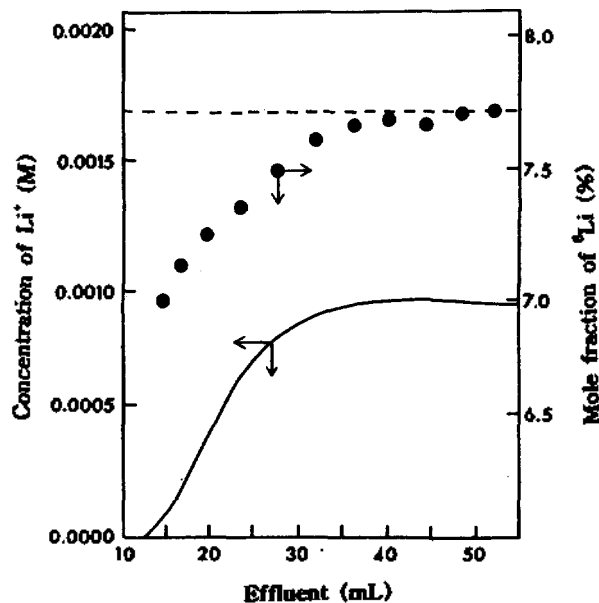
Table 1. Lithium isotope separation factors for the different ion exchangers and solvents

Species	Solvent	Donicity ^a	Separation Factor, α			
			Azacrown Ion Exchange Resin		$\epsilon/\Delta m \times 10^3$	
			(I)	(II)	(I)	(II)
Propylene Carbonate		15.1	1.029	1.031	29	31
Dimethyl Formamide		26.6	1.018	1.019	18	19

^aReference 32.

The water jacketed glass ion exchange columns used in these separation experiments were generally 250 mm long with inner diameter 6 mm. The ion exchange resins were azacrown ion exchangers, (I) and (II), respectively. Reagent grade chemicals were used to prepare the eluents and the feed solutions. Ion exchangers, (I) and (II) were slurried in the solvents. The slurried ion exchangers were then packed in the glass columns. And the temperature was maintained at 20 °C with an water circulator, HAAKE, A-80. The lithium chloride concentration of feed solutions was 1.0×10^{-3} M. The lithium feed solution was then passed through the column under gravity. The flow rate was controlled by fine stopcock to be 1 drop/20 sec. Each effluent containing isotopes was collected as a fraction of 40 drops with an automatic fraction collector. The breakthrough technique of column chromatography was used for the separation of the lithium isotope in these experiments. The lithium amount of each fraction was determined with a polarized Zeeman atomic absorption spectrophotometer, Z-2000, Hitachi, Japan. The measurements of lithium isotope ratio were carried out using thermal ionization mass spectrometer, Finnigan, MAT 262, with a rhenium double filament. Amount of 1.0-2.0 μ g lithium with the MAT 262 was loaded on an evaporation filament. Ionization was then performed by passing a heating electric current through the ionization filament. After the ion beam intensities of ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$ became sufficiently high, the ${}^6\text{Li}$ and ${}^7\text{Li}$ mass peaks were repeatedly recorded. The mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The mole fraction of ${}^6\text{Li}$ of each feed solution was an average of three times in our measurement.

As expected the enrichment factor ($\epsilon = \alpha - 1$) for the isotopes separated by ion exchange chromatography depended upon the mass of the isotope as well as the difference in the masses of the isotope pairs.²⁸⁻²⁹ In comparing the enrichment factors per mass unit ($\epsilon/\Delta m$) for the element lithium

**Figure 1.** The breakthrough chromatographic separation of lithium isotopes for azacrown ion exchange resin (II)-propylene carbonate system. The breakthrough curve is shown by the solid line. The mole fraction of ${}^6\text{Li}$ at the different fractions in the effluent is shown by dark circles.

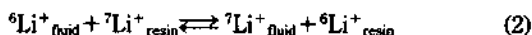
with increasing the donicity of solvents, it was shown in Table 1 that the separation factor increases as the donicity decreases.

The lithium isotope enrichment profile for the azacrown ion exchanger(II)-propylene carbonate system is shown in Figure 1. In the lower half of Figure 1 is drawn the concentration of Li^+ eluted and the effluent volume. In the upper part is shown the mole fraction of ${}^6\text{Li}$ isotope. The separation factor of lithium isotopes was obtained by applying the treatment of Jepsen.³⁰ Enrichment factor, ϵ is calculated by using the Equation³⁰:

$$\epsilon = \left(\frac{1}{Q_i} \right) \sum q_i \left[\left(\frac{R_0}{R_i} \right) - 1 \right] \quad (1)$$

where Q_i is the total amount of Li^+ in the resin phase and q_i is the total amount of Li^+ in the i th sample. The isotope ratio for each sample and feed solution are R_i and R_0 , respectively. The adsorption capabilities of lithium ions on azacrown ion exchangers were increased as the donicity of the solvents decreased.³¹ The donicities of each solvent are, respectively, 15.1 for the propylene carbonate and 26.6 for the dimethyl formamide.³² As shown in Table 1, the separation factors of the lithium isotopes for the azacrown ion exchangers, slightly depended upon the ligand conformation. On the other hand, the solvent species and their donicities were strongly affected to the separation factors. Our separation factors were between 1.018 and 1.031 depending upon the solvent species and ion exchange resins. The value of 1.031 of ours is of the same order of magnitude as Jepsen *et al.*¹⁸⁻¹⁹ Nishizawa *et al.*²⁰⁻²² and Kim *et al.*²³⁻²⁶ However, this value of ours is greater than those of the results obtained by Oi *et al.*¹⁶ In our experiments, ${}^6\text{Li}$ concentrated in the resin phase, while the heavier isotope, ${}^7\text{Li}$ is enriched

in the fluid phase. This chemical ion exchange reaction can be represented by the following Equation:



The subscripted symbols, such as fluid and resin refer to the fluid phase and resin phase in this isotope exchange. Klinskii *et al.*³³ and Oi *et al.*¹⁶ reported that the heavier isotopes were enriched in the resin phase of ion exchange chromatography. These phenomena are a contrast to the results of our experiments. On the other hand, Aaltonen,³⁴ Heumann and Lieser,³⁵ Russell and Papanastassiou,³⁶ Jepson and Shockey,³⁷ and Kobayashi *et al.*³⁸ stated that the heavier isotopes were preferentially concentrated into the solution phase of chromatography using strongly acidic cation exchangers. This discrepancy, still, cannot be explained at this time and further work must be done to resolve the phenomena.

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Introduction of Cyclopentene Annulation and Propargyl Group in Chromones

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Although chromone can be regarded as an α,β -unsaturated ketone, there are few synthetic methods for the introduction of carbon nucleophiles at the C₂ position of the heterocyclic ring.¹ In this connection, Wallace *et al.*² showed that introduction of an alkyl group into the C₂ position of chromone derivatives by using a lithium dialkylcuprates is possible. More recently, Akiba and co-workers³ reported a facile method for the regioselective introduction of an allyl group into chromone *via* silyloxybenzopyrylium cations by means