

## 앵커 그룹으로서 아자크라운 에테르를 포함한 새로운 이온교환체에 의한 리튬 동위원소의 농축

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(1997. 11. 20 접수)

## Enrichment of Lithium Isotope by Novel Ion Exchanger Containing Azacrown Ether as Anchor Group

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(Received November 20, 1997)

**요 약:** N<sub>3</sub>O<sub>3</sub>가 앵커 그룹으로 포함된 이온교환체를 사용하여 <sup>6</sup>Li와 <sup>7</sup>Li의 분리인자를 측정하였다. 이온교환체의 이온교환 용량은 2.0 meq/g 이었다. 3 M 염화암모늄 수용액을 용리액으로 하였으며, 내경 0.3 cm, 높이 30 cm의 칼럼을 이온교환크로마토그래피에 사용하였다. 가벼운 동위원소 <sup>6</sup>Li는 유체상에, 무거운 동위원소 <sup>7</sup>Li는 수지상에 농축되었다. 용리곡선과 동위원소 비를 가지고 Glueckauf의 이론에 따라 분리인자를 구하였으며, 그 값은 1.018이었다.

**Abstract:** Separation factor for <sup>6</sup>Li and <sup>7</sup>Li has been determined using ion exchange resin having 1,7,13-trioxa-4,10,16-triazacyclooctadecane (N<sub>3</sub>O<sub>3</sub>) as an anchor group. The ion exchange capacity of the N<sub>3</sub>O<sub>3</sub> ion exchanger was 2.0 meq/g dry resin. The lighter isotope, <sup>6</sup>Li, is concentrated in the fluid phase, while the heavier isotope, <sup>7</sup>Li, is enriched in the resin phase. By column chromatography [0.3 cm(I.D)×30 cm (height)] using 3.0 M ammonium chloride solution as an eluent, single separation factor,  $\alpha$ , 1.018, i.e. (<sup>7</sup>Li/<sup>6</sup>Li)<sub>resin</sub>/<sup>7</sup>(Li/<sup>6</sup>Li)<sub>fluid</sub> was obtained by the Glueckauf theory from the elution curve and isotope ratios.

**Key words:** lithium isotope, separation, azacrown ion exchanger, capacity, chromatography

### 1. INTRODUCTION

Ion exchange resins were widely used for the separation of isotopes. One of the specific characteristics of crown compounds is the ability to selec-

tively form complexes by capturing cations, especially alkali and alkaline earth metal cations with an ionic diameter fitted to the cavity of the crown compound, and this leads to a natural application for the separation of isotopes.<sup>1</sup> The first reported use of cyclic polyethers for isotope separation involved work

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by Jepson with calcium salts.<sup>2</sup>

The separations of lithium isotopes by ion exchange chromatography were carried out by Fujine *et al.* and Kim *et al.* using by cryptand and azacrown ether resin.<sup>3-4</sup> The ion exchange method, however, has a disadvantage of small isotope separation factors. Recently, large separation factors for lithium isotopes were found out in several systems containing macrocyclic compounds. Jepson and Cairns, first 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-[2<sub>B</sub>.2.1] cryptand complex.<sup>5</sup> Nishizawa *et al.* have determined similar separation factor of 1.042 for lithium isotope separation using benzo 15-crown-5 as an extractant, and of 1.047 by cryptand [2<sub>B</sub>.2.1] polymer.<sup>6</sup> Recently, Kim *et al.* reported a maximum separation factor of 1.053 using styrene-divinyl benzene copolymer with monobenzo-15-crown-5.<sup>7</sup> They also carried out the lithium isotope separation by chemical exchange with polymer-bound dibenzo pyridino diamide azacrown and reduced dibenzo pyridino diamide azacrown, and obtained the separation factors in the range of 1.017 to 1.035.<sup>8</sup>

In this work, the lithium isotope separation by the ion exchange resin containing the azacrown ether as anchor group was investigated.

## 2. EXPERIMENTAL

### 2.1. Synthesis of ion exchange resin

1,7,13-trioxa-4,10,16-triazacyclooctadecane trihydrobromide was prepared by reported procedures.<sup>9-11</sup> The cyclic triazatrimerrifield was prepared by reaction of the corresponding cyclic amine (N<sub>3</sub>O<sub>3</sub>) with Merrifield peptide resin in benzene. The synthetic procedure was described in the literatures<sup>12-16</sup> and shown in Fig. 1.

### 2.2. Reagents and apparatus

Lithium chloride and ammonium chloride were purchased from Sigma Chemical Co., USA. Atomic absorption spectrophotometer (Hitachi Z-8000) was used to determine the lithium ion concentration in the solution. The measurement of lithium isotope ra-

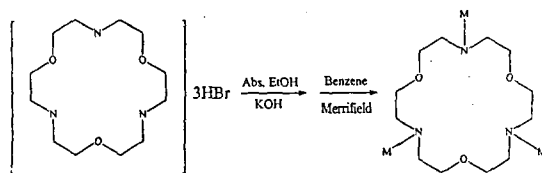


Fig. 1. Synthesis of ion exchange resin with 1,7,13-trioxa-4,10,16-triazacyclooctadecane group.

tio was carried out using thermal ionization mass spectrometry (Finnigan MAT 262) with a rhenium double filament.

### 2.3. Ion exchange capacity

For the determination of the capacity of N<sub>3</sub>O<sub>3</sub> ion exchanger, titration method was employed.<sup>17</sup> Each portion of 0.2 g of cyclic triazatrimerrifield, 200~400 mesh resin of H-form was weighed out accurately, and transferred into a 100 mL polyethylene vial with a polyethylene screw top. Then 50 mL of 0.1 N sodium hydroxide containing 5% sodium chloride was added and incubated at 25°C for 24 hrs. The reaction mixture was centrifuged for 5 min at 5,000 rev/min and then 20 mL of the supernatant was titrated with 0.1 N hydrochloric acid. The capacity of ion exchanger was calculated as

$$\text{Capacity (meq/g)} = \frac{(V_{\text{NaOH}} \times N_{\text{NaOH}}) - (V_{\text{HCl}} \times N_{\text{HCl}})}{\text{mass of resin} \times \% \text{ mass of dry resin} / 100} \quad (1)$$

where  $V_{\text{NaOH}}$  and  $V_{\text{HCl}}$  are the total volume in mL of NaOH and HCl, respectively.  $N_{\text{NaOH}}$  and  $N_{\text{HCl}}$  are the normal concentrations of NaOH and HCl, respectively.

### 2.4. Separation of lithium isotope

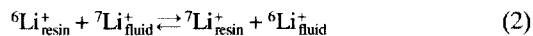
Cyclic triazatrimerrifield resin was slurried in ammonium chloride solution. The slurried resin was packed in a water jacketed glass column (0.3 cm I.D. × 30 cm height). The temperature was maintained at 20°C with a water circulator (HAAKE A-80). 500 μg of lithium ion in distilled water was loaded on the top of the resin bed. 3.0 M NH<sub>4</sub>Cl solution was used as an eluent for the separation. The lithium feed solution was then passed through the column under gravity flow. The flow rate was controlled by

a fine stopcock to be 3 drops/min. The effluent was collected as a fraction of 30 drops each with an automatic fraction collector.

### 3. RESULTS AND DISCUSSION

The resin having N<sub>3</sub>O<sub>3</sub> as an anchor group have a capacity of 2.0 meq/g. This value is less than those of the Dowex 50W-X8, 200~400 mesh, a styrene based sulfonic strongly acidic cation exchanger (4.8 meq/g of dry resin). The value of 2.0 meq/g is of the same order of magnitude as DIAION SK 110 (2.0 meq/g), DIAION SK 112 (2.1 meq/g), and Wofatit CN (2.0 meq/g) cation exchanger.<sup>18</sup>

Fig. 2 shows the plot of Δm/m versus local enrichment percentage (R-1)·100% based on Glueckauf theory.<sup>19</sup> The relationship between the local enrichment percentage and the proportion of eluted lithium is linear, and the local enrichment percentage increases with increasing the proportion of eluted lithium. The separation factor was calculated by Glueckauf theory.<sup>19</sup> In this experiment, the heavier isotope, <sup>7</sup>Li, concentrated in the resin phase, while the lighter isotope, <sup>6</sup>Li, is enriched in the fluid phase. The chemical ion exchange reaction can be represented by the following equation



The subscripted symbols, such as fluid and resin refer to the fluid and resin phase in this isotope exchange reaction. The generalized theory for the direction of isotope enrichment is not established yet. Lee,<sup>20</sup> Klinskij *et al.*<sup>21</sup> and Heumann and Schiefer<sup>22</sup> reported that the heavier isotopes were enriched in the resin phase of ion exchange chromatography. On the other hand, Aaltonen,<sup>23</sup> Heumann and Lieser,<sup>24</sup> Russell and Papanastassiou,<sup>25</sup> and Jepson and Shockley<sup>26</sup> stated that the heavier isotopes were preferentially concentrated into the fluid phase of chromatography using strongly acidic cation exchangers. Previously, we also obtained similar results with the direction of isotope enrichment using an ion exchange resin having crown and azacrown as anchor groups.<sup>8</sup>

The separation factor calculated from the experiment data was 1.018. This value is higher than those of obtained from sulfonic acid ion exchangers. But, the separation factor in this study is inferior to those obtained from the cation exchange resin by other groups, for example, 1.047, obtained by Nishizawa *et al.*, who used Merrifield resin with cryptand [2<sub>B</sub>.2.1] which was a kind of macrocyclic compound, to separate lithium isotopes.<sup>6</sup> In a comparable experimental system, we also obtained the maximum separation factors of 1.053 and 1.035 using mono benzo-15-crown-5 and reduced dibenzo pyridino diamide azacrown as anchor groups, respectively.<sup>8</sup> So it could be thought that the magnitude of the separation factor is slightly depended on the ligand and solvent.<sup>8</sup>

### ACKNOWLEDGMENT

This Work was Supported by the Basic Science Research Institute Program, Ministry of Education, Korea, 1996, Project No. BSRI-96-3435.

### REFERENCES

1. Y. Inoue and G. W. Gokel, *Cation Binding by Macrocycles*, Marcel Dekker: New York, U.S.A (1990).
2. B. E. Jepson and R. De Witt, *J. Inorg. Nucl. Chem.*, **38**, 1175 (1976).
3. S. Fujine, K. Saito, and K. Shiba, *J. Nucl. Sci. Tech.*

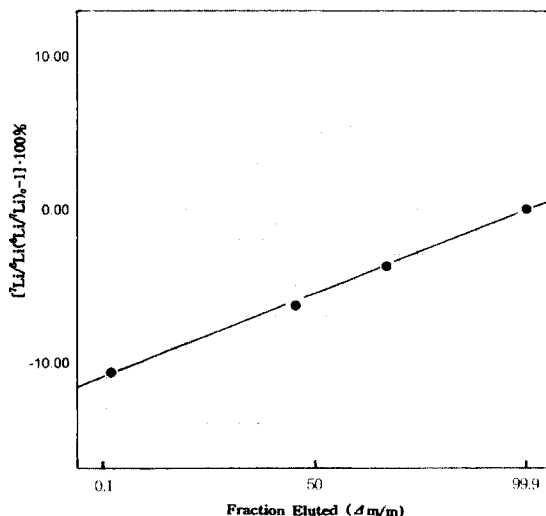


Fig. 2. Result of the <sup>6</sup>Li-<sup>7</sup>Li separation on N<sub>3</sub>O<sub>3</sub> ion exchange resin eluted with 3.0 M NH<sub>4</sub>Cl solution plotted on probability graph paper.

- mol.*, **20**, 439 (1983).
4. D. W. Kim, Ch. P. Hong, Ch. S. Kim, Y. K. Jeong, Y. Sh. Jeon and J. K. Lee, *J. Radioanal. Nucl. Chem.*, **220**, 229 (1997).
  5. B. E. Jepson and G. A. Carins, *Report MLM-2622* (1979).
  6. K. Nishizawa, H. Watanabe, S. Ishino, and M. Shinagawa, *J. Nucl. Sci. Technol.*, **21**, 133 (1984).
  7. D. W. Kim, Y. S. Jeon, T. Y. Eom, M. Y. Suh and C. H. Lee, *J. Radioanal. Nucl. Chem. Letters*, **150**, 417 (1991).
  8. D. W. Kim, Y. S. Jeon, Y. K. Jeong, M. Y. Suh and K. S. Joe, *J. Radioanal. Nucl. Chem. Articles*, **189**, 219 (1995).
  9. C. G. Krespan, *J. Org. Chem.*, **40**, 1205 (1975).
  10. M. T. S. Amorim, J. R. Ascenso, R. Delgado and J. J. Frausto Da Silva, *J. Chem. Soc., Dalton Trans.*, 3449 (1990).
  11. Y. Sun and A. E. M. Welch, *Tetrahedron*, **47**, 8863 (1991).
  12. R. Delgado, Y. Sun, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, **32**, 3320 (1993).
  13. D. W. Kim, C. P. Hong, C. S. Kim, Y. K. Jeong, Y. K. Jeon and J. K. Lee, *J. Radioanal. Nucl. Chem.* **220**, 229 (1997).
  14. D. Chen, P. J. Squattrito, A. E. Martell and A. Clearfield, *Inorg. Chem.*, **29**, 4366 (1990).
  15. H. Tsukube, H. Adachi and S. J. Morosawa, *J. Chem. Soc. Perkin Trans., I*, 89 (1989).
  16. T. Kusama and H. Hayatsu, *Chem. Pharm. Bull.*, **18**, 319 (1970).
  17. K. Dorfner, *Ionenaustauscher*, Dritte Aufl. Walter de Gruyter, Berlin, 1970, p. 47.
  18. *Ibid*, pp. 292-295.
  19. E. Glueckauf, *Trans. Faraday Soc.*, **54**, 1203 (1958).
  20. D. A. Lee, *J. Amer. Chem. Soc.*, **83**, 180 (1961).
  21. K. G. Klinskii, D. A. Knyazev and G. I. Vlasova, *Zh. Fiz. Khim.*, **48**, 659 (1974).
  22. K. G. Heumann and H. P. Schiefer, *Angew. Chem.*, **52**, 406 (1980).
  23. J. Aaltonen, *Suom. Kem.*, **844**, 1 (1972).
  24. K. G. Heumann and K. H. Lieser, *Z. Naturforsch.*, **276**, 126 (1972).
  25. W. A. Russell and D. A. Papanastassiou, *Anal. Chem.*, **50**, 1151 (1978).
  26. B. E. Jepson and G. C. Shockey, *Separ. Sci. Technol.*, **19**, 173 (1984).