Separation of Lithium Isotopes by Tetraazamacrocycles Tethered to Merrifield Peptide Resin

Youn Seok Jeon, Nak Han Jang,[†] Byung Moo Kang, Young-Shin Jeon,[‡] Chang Suk Kim,[§] Ki-Young Choi, and Haiil Ryu[*]

Department of Chemistry Education, Kongju National University, Kongju, Chungnam 314-701, Korea
[*]E-mail: hryu@kongju.ac.kr
[†]Department of Science Education, Kongju National University of Education, Kongju, Chungnam 314-711, Korea
[‡]Korea Atomic Energy Research Institute, Yuseong, Daejeon 305-600, Korea
[§]School of Science Education, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea

Tetraazamacrocyclic ion exchangers tethered to Merrifield peptide resin (DTDM, TTTM) were prepared and the ion exchange capacity of these was characterized. The isotope separation of lithium was determined using breakthrough method of column chromatography. The isotope separation coefficient was strongly dependent on the ligand structure by Glueckauf's theory. We found that the isotope separation coefficients were increased as the values of distribution coefficients were increased. In this experiment the lighter isotope, ^{6}Li was enriched in the resin phase, while the heavier isotope, ^{7}Li in the solution phase. The ion radius of lighter isotope, ^{6}Li was shorter than the heavier isotope, ^{7}Li. The hydration number of lithium ion with the same charge became small as mass number was decreased. Because ^{6}Li was more strongly retained in the resin than ^{7}Li, the isotopes of lithium were separated with subsequent enrichment in the resin phase.

Key Words : Separation, Lithium isotopes, Tetraazamacrocyclic ion exchangers, Merrifield peptide resin

Introduction

In old times, natural stones were known generically as zeolite because the stones had an ion exchange ability, but today zeolite generally means inorganic ion exchanger distinguished from ion exchange resin.[1,2] But today's ion exchange resin means organic synthetic ion exchanger.[3]

As one of practical application about polymer, ion exchange resins were used as demineralized agent of water, refining agent of food and medicine, and decolorizing agent of industrial chemicals. These polymers were often used as agents of esterification, hydrolysis, inverter of sugar and catalyzer of condensation. Also, these were used to separate and/or enrich radioactive isotopes in atomic energy industry. Specially, we widely used them to prevent pollution in drain treatment from a point of view. Then collection of organic product from drain, elimination of heavy metal ion, adsorption elimination selectively of nitric acid, phosphoric acid, ammonia. In addition used as analysis chemistry, water purifier at home, mass production for industry, made a study about these fields actively.

In Korea, scientist make a use of ion exchanger as separation of transition element and alkali earth metal element, make a study to absorb, collect heavy metal ion such as Cd, Hg, Pb, to separate arsenic compound, boron isotope. They used preparation of new macrocyclic crown ion exchange to react macrocyclic crown ether Merrifield peptide resin and also made a study of physicochemical quality of this resin. They reported a wide study of various isotope separation condition.[4-7]

Ion exchange effect of lithium ion in an aqueous NH_4Cl solution, measurement of distribution coefficient, separation factor would be performed. We try to find the efficiency of lithium isotope separation. The separation of isotope ^{6}Li and ^{7}Li was performed in lithium chloride aqueous solution. Relative shift difference in resin and eluent of ions contributed in lithium isotope separation. In general, the lighter isotope, ^{6}Li, was enriched in the resin phase, while the heavier isotope, ^{7}Li in the solution phase.

In this experiment after preparation of tetraazamacrocyclic compound with Merrifield peptide resin. We tried to find general tendency, reason. Specially, one of isotope separation methods, ion exchange chromatography used by macrocyclic compound. In study, new prepared resin 3,14-dimethy-2,6, 13,17-tetraaza-ztricyclo[4,10,4,0$^{1.18}$,0$^{7.12}$] docosane tethered to Merrifield peptide resin (DTDM) and 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM) were used and were found the character, difference, reason of lithium isotope separation.

Experimental Section

Materials and Instruments. To prepare Tetraazacycloes ion exchangers tethered to Merrifield peptide resin, Merrifield peptide resins were purchased from Sigma Chemical Co. USA. Lithium chloride for separation of isotope was purchased from Aldrich products. All other chemicals and reagents were of analytical and reagents grade. Also, 0.001, 0.01, 0.1, 1, 2 M NH_4Cl standard solution and 0.1, 1 M HCl standard solution were used.

ICP-OES (OPTIMA 2000 DV, Perkin Elmer Asia, Singapore) was used to determine the lithium ions concentration in the solution. All isotopic analyses were carried out on a Finnigan MAT 262 multicollector thermal ionization mass

spectrometer with a 90° magnet sector and an effective radius of 64 cm. The instrument equipped with a secondary electron multiplier (SEM) which allows detailed monitoring of any early emission of lithium and magnesium ions at low temperatures. Rhenium filaments (0.025 × 0.75 mm) were degassed at 4.5 A for 25 minutes prior to loading sample and the dried on the distance between two filaments was adjusted to 1 mm. The measuring sample was taken up 1-4 μL (depend on the sample concentration) of 1.0 M nitric acid solution and dried on the filament with a current of 0.7 A. The current was then raised slowly to 1.5 A until the fume was completely expelled.

After introduction into the mass spectrometer, the ionization filament was gradually increased to 1.5 A where the K^+ peak at mass 39 was monitored to optimize the beam focus and the ^7Li ion signal was carefully monitored by SEM. Only a very small ^7Li ion signal could be observed at this current stage. The evaporation filament current was then raised slowly from 0.4 to 0.6 A until a stable ion beam more than 1×10^{-11} A was achieved. The $^6Li/^7Li$ ratio was then measured against a base line at mass 6.5 using a single Faraday cup collector in a peaks jumping method. The integration times were 8 and 16 sec. for the lithium peaks and the baseline, respectively, and about 50 ratios in five blocks were collected in a normal run. The absolute isotopic abundance of lithium in the IRM, IRMM-016, containing Li of natural isotopic compositions, was redetermined using a new set of synthetic isotopic mixtures.

Preparation of DTDM and TTTM. To prepare for tetra-azamacrocycloes tethered to Merrifield peptide resin (DTDM, TTTM), macrocyclic tetraazacycloes (DTD, TTT) were first synthesized and characterized as the previous.[8-12]

DTDM was prepared by 1 mmol of synthesized macrocyclic ligand, 3,14-dimethyl-2,6,13,17-tetraazatricyclo[4,10, 4,0$^{1.18}$,0$^{7.12}$]docosane (DTD), 2.5 mmol of Merrifield resin and 1.2 mL of trimethylamine using a lot of DMF as solvent. Trimethylamine promoted to leave H^+ from compound. Temperature was maintained to 80 °C, refluxing for 72 hours. Prepared resins were washed by ether and ethanol, and dried finally.

TTTM was also prepared by 1.5 mmol of synthesised macrocyclic ligand, 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane (TTD) and 200 mL of DMF in 500 mL three necked round flask. This solution with 3 mL of triethylamine (21.4 mmol) was mixed with 2% Merrifield peptide resin 5 g (5 mmol). Temperature was maintained to 80 °C, refluxing for 72 hours. We obtained 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM) by drying product (Figure 1).[5-7]

Determination of Ion Exchange Capacity and Distribution Coefficient. For the determination of the capacities of ion exchangers, DTDM and TTTM, these were transformed into H-formation. DTDM and TTTM 0.2 g were placed in a beaker. After these were stirred with 1 M HCl for 30 minutes, only ion exchanger was restirred with 1 M HCl. This process was repeated by 7-8 times, the residue was washed with distilled water, dried in 65 °C.
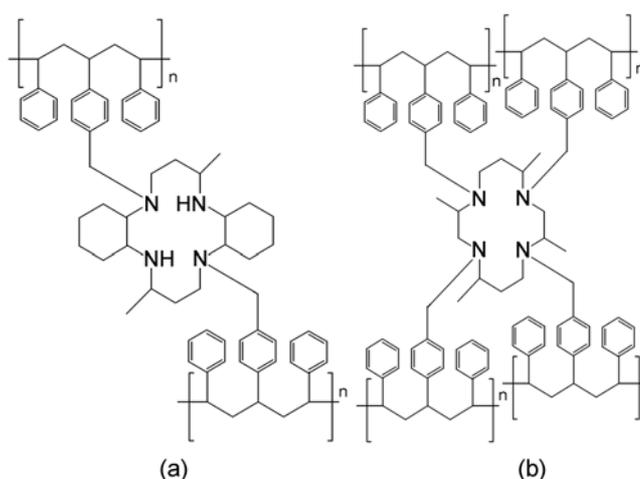
Figure 1. Structures of (a) 3,14-dimethyl-2,6,13,17-tetraazatricyclo [4,10,4,0$^{1.18}$,0$^{7.12}$] docosane tethered to Merrifield peptide resin (DTDM) and (b) 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM).

The determination process of ion exchanger capacity was performed in this way.

DTDM and TTTM, dried resins of H-form was weighed accurately 0.2 g, and transferred into a dry 250 mL Erlenmeyer flask containing exactly 50 mL of 0.1 N NaOH with 5% NaCl, and was allowed to stand overnight. Of the supernatant liquid in the Erlenmeyer flask, 20 mL aliquots were back-titrated with 0.1 N HCl against phenolphthalein. The capacity was calculated by the formula.[13,14]

$$\text{Capacity (meq/g)} = \frac{V_{NaOH}N_{NaOH} - V_{HCl}N_{HCl}}{\text{Sample weight} \times \% \text{ dried matirial}/100}$$

where V_{HCl} was the volume of HCl and N_{NaOH} was normal concentration. It presents total weight of exchanger. The exchanger sample of 0.2 g was weighted into a weighing bottle, dried at 110 °C overnight.

The capacity of ion exchange resin is expressed in milliequivalents per gram of dry resin. The resin must be completely in the H-form before weighing of the sample, since difference in equivalent weights of different ions would lead to errors. The standard sodium hydroxide solution was treated with 5% sodium chloride to obtain a completely exchange equilibrium by the excess of sodium ions.

For the determination of the distribution coefficient, batch method was employed. Each portion of 0.25 g of the each ion exchange resin, DTDM and TTTM which have been dried to constant at 60 °C, was weighed out and transferred into a 100 mL polyethylene vial with a polyethene screw top. Then 1.0 mL of 0.01 M lithium chloride solution was added, followed by 49 mL of ammonium chloride solution of the desired concentration (0.001, 0.01, 0.1, 1, 2 M) to give a final volume of 50 mL. The reaction mixture was subjected to reciprocal shaking for 24 hours. The concentration of lithium ions in the supernatant was determined using ICP. Distribution coefficient, K_d was calculated by the following equation:[15,16]

$$K_d = \frac{(C_{st} - C_{eq})V_{soln}}{C_{eq} \times M_p}$$

where M_p is the mass in g of dry resin indicated, V_{soln} the total volume in mL of the solution, C_{st} is the metal ion concentration of the standard solution.

The slurried resin was packed in a water jacketed glass column (0.2 cm I.D. × 35 cm height). The resin was packed through the column under gravity flow. The volume of column was $\pi \times 0.04$ cm^2 × 34 cm, 4.2704 cm^3. The NH$_4$Cl concentration of the feed solutions was 2 M. After NH$_4$Cl was flowed in first, not to contain air, input 1500 ppm LiCl 0.1 mL continually. 2 M NH$_4$Cl solution was passed in repeat. The flow rate was controlled by a fine stopcock to be 0.6 mL/hr. The effluent composed of a fraction of 0.1 mL was collected with vial numbered from no. 1 to no. 20. These solutions were diluted with distilled water to 40 times, analyzed by ICP-OES. Elution curve and concentration of metal ions were obtained.

Results and Discussion

Determination of the Ion Exchanger Capacity and Measurement of Distribution Coefficient. The ion exchange capacity of DTDM and TTTM was determined and listed in the following Table 1. Comparing between DTDM and TTTM, the ion exchange capacity of DTDM was higher than TTTM. In addition, ions were located in the center of these ion exchangers. Because macrocyclic compound could make complex compound with many ions, the ion exchange capacity of complex compound was related in ion size and cavity of macrocyclic compound.[5,17] As in the result, tetra-azacycloes tethered to Merrifield peptide resin (DTDM and TTTM) were showed to the high ion exchange capacity.

The distribution coefficient (K$_d$) is defined as the ratio of metal transferred into an organic phase from an initial aqueous phase. The distribution coefficients of lithium ions on DTDM and TTTM ion exchangers were measured with changing the concentration of NH$_4$Cl solution from 0.001 to 2.0 M (Figures 2 and 3). The elution time was increased with the increment of distribution coefficient due to the high adsorption of ions on the resin phase in the column. As shown in Figures 2 and 3, the distribution coefficients of lithium ions on DTDM and TTTM were varied in a non-linear manner with increasing concentration over a range of various NH$_4$Cl solution. The curve of DTDM showed in a minimum near 0.1 M concentration of NH$_4$Cl solution, whereas TTTM showed near 0.01 M concentration. Both distribution coefficients were relatively high in 2.0 M NH$_4$Cl aqueous solution. The distribution coefficient of DTDM was relatively higher than TTTM. In addition, as the ion exchange capacity of DTDM was higher than TTTM, the lithium ion should be bonded and be free with DTDM well.

Isotope Separation by DTDM and TTTM Column Chromatography. The column was occupied with stationary phase. The efficiency of column presented isolation rate from stationary phase. In chromatogram, we can see the

Table 1. Ion exchange capacity of 3,14-dimethyl-2,6,13,17-tetra-azatricyclo [4,10,4,0$^{1.18}$,0$^{7.12}$]docosane tethered to Merrifield peptide resin (DTDM) and 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclo-tetradecane tethered to Merrifield peptide resin (TTTM)
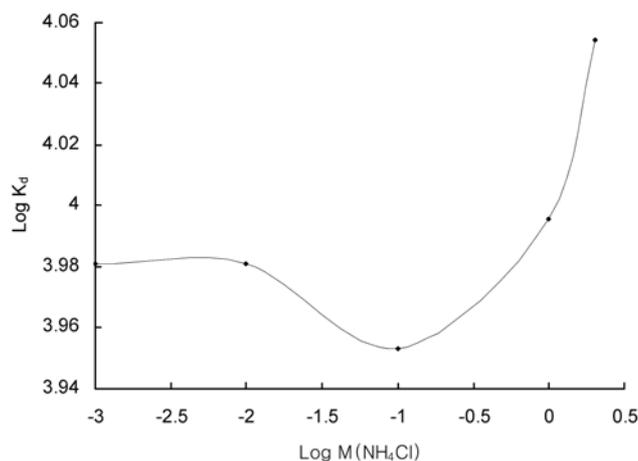
cation exchanger	DTDM	TTTM
capacity(meq/g)	3.50	1.71

resolving power of column from the theoretical plate number. The number of theoretical plates was calculated by following equation.[18]
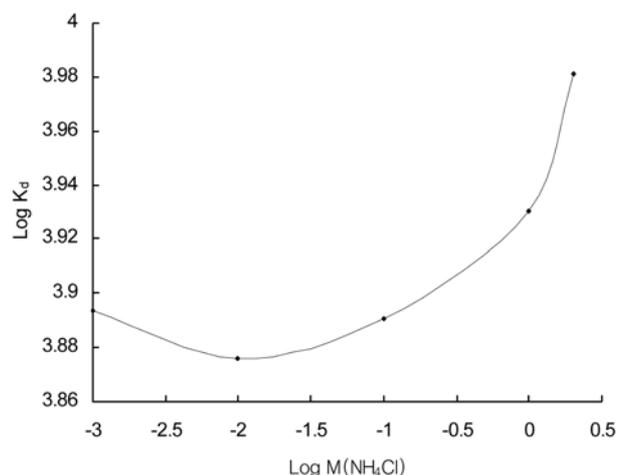
$$N = 16\left(\frac{t_R}{W}\right)^2$$

$$H = \frac{L}{N} \text{ (cm/plate)}$$

H was Height equivalent to a theoretical plate, L was the length (cm) of the column. In this equation, if the theoretical

Figure 2. Plot of log distribution coefficient in various concentrations of NH$_4$Cl for lithium with 3,14-dimethyl-2,6,13,17-tetra-azatricyclo[4,10,4,0$^{1.18}$,0$^{7.12}$]docosane tethered to Merrifield peptide resin (DTDM).

Figure 3. Plot of log distribution coefficient in various concentrations of NH$_4$Cl for lithium with 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM).

plate number increases, the retention volume also increases and the width of peak will be narrow. The more smaller H was, the more higher N was.

N or H was used by scale to estimate the efficiency of column. If column and solvent are same, what N is large means the width of peak is small. That is, it means that the isolation efficiency is good. Also, if the width of peak is small, N increases.

The chromatogram was obtained from the column operation with 1.0 M NH$_4$Cl solution as an eluent at 20 $^{\circ}$C. The number of theoretical plates was calculated from the chromatogram by following equation.[19]

$$N = 8 \times \left(\frac{V_{max}}{\beta}\right)^2$$

where V_{max} is the retention volume and β is the band width at the concentration $C = C_{max}/e = 0.368 C_{max}$.

The separation factor of lithium isotope was calculated by Glueckauf theory.[19] While increasing development speeds causes a reduction in the number of theoretical plates, also it is associated with increasing the processing flow rate. Thus, changes of the development speed provide contradictory effect on separation. The elution curves for lithium isotope separation with DTDM and TTTM ion exchanger tethered to Merrifield peptide resin in 2.0 M NH$_4$Cl were shown in Figures 4 and 5 according to the number of theoretical plates. In comparison with these figures, the pattern of both elution curves were similar. However, DTDM was somewhat more effective than TTTM because the width of elution curve was narrow.

The advantage of these DTDM and TTTM column chromatography is that many equilibrium stages are connected directly in series. Using ion exchange chromatography, N-values of some hundreds up to some thousands are available. In contrast to batch experiments, the isotopic separation factor (α) and the ε-value are not determinable directly by chromatographic methods. However, the ε-value and the number of equilibrium stages N in a column can be calculated with an approximation method measuring the isotopic enrichment dependent on the eluted amount of substance and evaluating the elution curve (Figure 6).

$$N = 2\pi \times \left(\frac{C_{max} \times v}{m}\right) \quad (1)$$

$$N = 8 \times \left(\frac{v}{\beta}\right)^2 \quad (2)$$

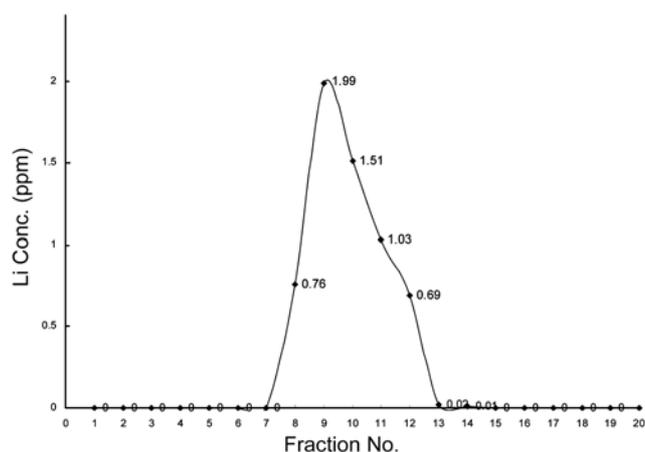C_{max} : concentration at maximum of elution curve
v : effluent volume at C_{max}
m   : sum of eluted element amount
β : width of elution curve at C_{max}/e

On the basis of the chromatographic experiments, Glueckauf's approximation results in the following equation for ε

$$\ln R \approx \varepsilon \sqrt{N} \times t \quad (3)$$

Figure 4. Elution curve for lithium isotope separation with 3,14-dimethyl-2,6,13,17-tetraazatricyclo[4,10,4,0$^{1.18}$,0$^{7.12}$]docosane tethered to Merrifield peptide resin (DTDM) in 2.0 M NH$_4$Cl.
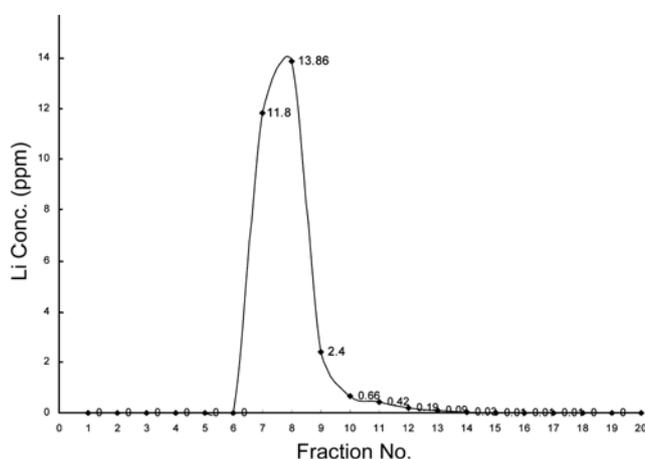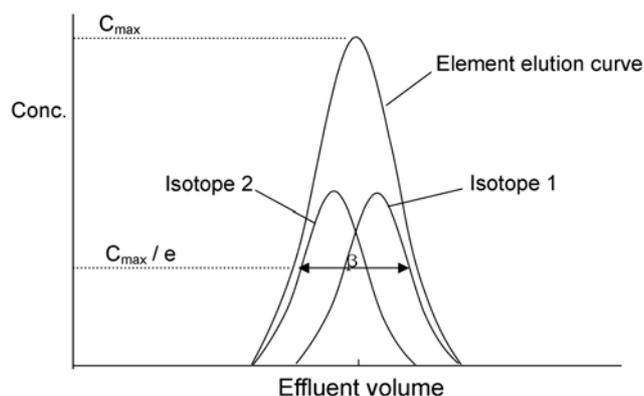
Figure 5. Elution curve for lithium isotope separation with 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM) in 2.0 M NH$_4$Cl.

$$\alpha = \frac{\Delta \ln R}{\Delta t} \approx \varepsilon \times \sqrt{N} \quad (4)$$

From the graphically determined α-value and from the number of equilibrium stages N obtained by Eqs. (1) and (2), ε and α can be calculated for an isotopic exchange reaction. Because the described method is an approximation, the following conditions have to be fulfilled: (a) The elution band should be small compared with the column length; (b) The dynamic volume of the column (volume not occupied by the resin) should be small compared with the effluent volume; (c) The width of the elution curve should not be too wide.

The Separation Factor of Ion Exchangers Resin, DTDM and TTTM. In the present experiment, the separation factor at 20 $^{\circ}$C of ion exchangers resin, DTDM and TTTM, was found and listed in Tables 2 and 3.

Jepson and Carins[20] first reported the large separation factors in the range of 1.026 to 1.041 by using cryptand for two-phase chemical exchange systems composed of an aqueous solution of a lithium salt and a chloroform solution.

Figure 6. Schematic figure of the elution curve of an element with two isotopes.

Table 2. The local enrichment factor for lithium isotopes in each fraction of 3,14-dimethyl-2,6,13,17-tetraazatricyclo[4,10,4,0$^{1.18}$, 0$^{7.12}$]docosane tethered to Merrifield peptide resin (DTDM)

| Fraction	^{6}Li/^{7}Li	R	$\Delta m/m \times 100$	log R
1st	0.067901	0.847208	40.49417	−0.07201
2st	0.068389	0.853297	88.05765	−0.0689
3st	0.068820	0.858677	96.29375	−0.06617
4st	0.069358	0.865387	98.55868	−0.06279
5st	0.070278	0.876859	99.99	−0.05707

Table 3. The local enrichment factor for lithium isotopes in each fraction of 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM)

Fraction	^{6}Li/^{7}Li	R	$\Delta m/m \times 100$	log R
1st	0.069927	0.872489	12.29773	−0.05924
2st	0.070019	0.873636	44.49838	−0.05867
3st	0.070232	0.876294	68.93204	−0.05735
4st	0.070425	0.878699	85.59871	−0.05616
5st	0.070880	0.884382	99.99	−0.05336

Nishizawa *et al.*[21] obtained a separation factor of 1.047 using Merrifield resin with cryptand, which is a kind of macrocyclic compound used to separate lithium isotope. Also, they reported a maximum separation factor of 1.068 using N$_3$O$_3$ trimerrifield ion exchanger. In these experiment, lighter isotope, ^{6}Li, was concentrated in the resin phase, while the heavier isotope, ^{7}Li, was concentrated in the solution phase. The chemical isotope exchange reaction can be represented by

$$6Li_{solution} + 7Li_{resin} \rightleftharpoons 7Li_{solution} + 6Li_{resin}$$

The subscripts refer to the solution and resin phases. Oi *et al.*[23] stated that the heavier isotopes of the lithium were preferentially concentrated into the resin phase. Ooi *et al.*[24] have also mined separation factors for lithium isotope in an aqueous ion exchange system, using titanium phosphate ion exchangers granulated with polyvinyl chloride or an inorganic binder. They reported that the separation factor of lithium isotopes was roughly 1.007, and the lighter isotope ^{6}Li was preferentially fractionated into the ion exchanger
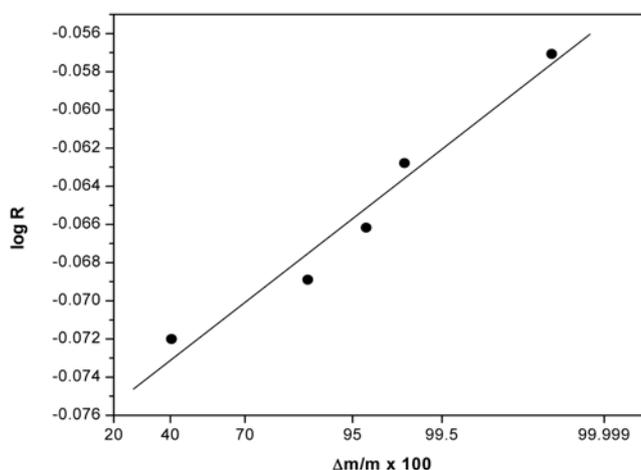
Figure 7. The graphic determination of ε with the results of a chromatographic elution for lithium ion with 3,14-dimethyl-2,6,13, 17-tetraazatricyclo[4,10,4,0$^{1.18}$,0$^{7.12}$]docosane tethered to Merrifield peptide resin (DTDM).

phase. In the present experiment, the lighter isotope, ^{6}Li, was enriched in the resin phase, while the heavier isotope, ^{7}Li in the solution phase. This means that the complexing ability of ^{6}Li with DTDM and TTTM in the resin phase is larger than that of ^{7}Li.

The separation factors of lithium isotopes with DTDM and TTTM were calculated by the Glueckauf's theory.[19]

The natural abundance ratio for lithium metal is given in Eq. (5):

^{6}Li of % = 7.42
^{7}Li of % = 92.58
^{7}Li/^{6}Li rate = 12.477089   (5)

$$R = \left(\frac{^6Li}{^7Li}\right) \times \left(\frac{^7Li}{^6Li}\right)_o$$

where R is the enrichment factor, and $\left(\frac{^7Li}{^6Li}\right)_o$ refers natural abundance ratio of lithium metal.

The data were plotted on probability paper where the
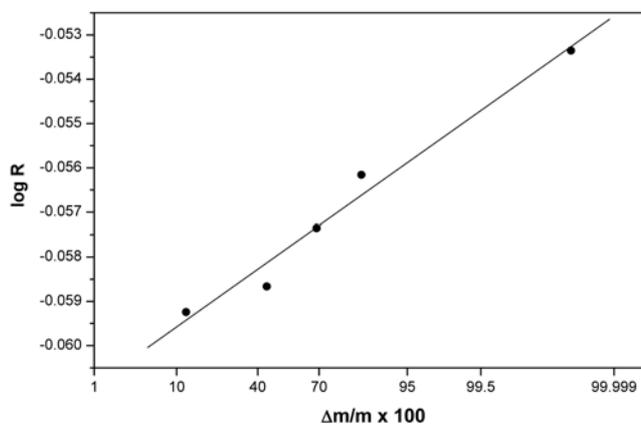
Figure 8. The graphic determination of ε with the results of a chromatographic elution for lithium ion with 1,4,8,11-tetramethyl-2,5,9,12-tetraazacyclotetradecane tethered to Merrifield peptide resin (TTTM).

456 *Bull. Korean Chem. Soc.* **2007**, Vol. 28, No. 3

Youn Seok Jeon et al.

Table 4. Distribution coefficient (K_d) versus separation factor (α) of lithium for ion exchangers in 2.0 M NH_4Cl

Resin	Distribution coefficient (K_d) 2.0 M NH_4Cl Li	Separation factor (α) 2.0 M NH_4Cl Li
DTDM	11339	1.0005204
TTTM	9570	1.0001246

abscissa was a probability scale and the ordinate was a linear scale. The local enrichment factor (log R) was the ordinate and the fraction of the eluted mixture ($\Delta m/m$) was the abscissa. These plot were linear for DTDM and TTTM, respectively (Figures 7 and 8).

The slope of the straight line obtained would be $\varepsilon\sqrt{N}$, and separation factor α, will be $\varepsilon + 1$. The separation factor, α, was determined from the slope of least squares line drawn through the points as shown in Figures 7 and 8. In this experiments, the separation factor with DTDM and TTTM for ^6Li-^7Li were be found to be from 1.0005204 to 1.0001246 at 20 °C for our systems (Table 4).

As the hydration of lithium ion increased, the separate factor, α, of DTDM and TTTM increased. This contributes to separating lithium isotope in experiment. Ions in resin phase were less hydrated than ions in solution phase. This contributes to the enrichment of light isotope. The separate factor, α, for DTDM and TTTM was the large value for lithium ion.

Conclusions

DTDM and TTTM ion exchangers tethered to Merrifield peptide resins were successfully prepared, and ion exchange capacities of these polymers was found to be 3.50 meq/g (DTDM) to 1.71 meq/g (TTTM) dry resin. The distribution coefficients of lithium ion on each ion exchanger decreased with the non-linear manner according to increasing from 0.001 M to 0.1 M NH_4Cl aqueous solution. However, the distribution coefficient showed a turning point at 0.1 M concentration, after that the values progressively increased. The distribution coefficient was relatively high in 2.0 M concentration.

The heavier isotopes were preferentially enriched into the solution phase of chromatography using DTDM and TTTM. This means that the complicated ability of ^6Li with DTDM and TTTM in the resin phase is larger than that of ^7Li. Also the ion species in the resin phase is less hydrated than the ion species in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotope in the resin phase. This phenomenon can be explained by the fact that the isotope effect accompanying complexion of ^6Li with DTDM and TTTM is larger than that of the hydration

due to the properties of DTDM and TTTM ion exchange resin. The ion radius of the heavier isotope was less than the lighter isotope. Hydration number of lithium ion with same charge decrease, as mass number was small, ^6Li was enriched in the resin phase mainly than ^7Li.

The separation factor of DTDM was 1.0005204 and that of TTTM was 1.0001246. DTDM was more effective than TTTM in lithium isotope separation because the ligand content per gram of DTDM was large than TTTM. Also the separation factor of these ion exchangers was of value. Finally, that meaned the separation of lithium isotopes was very effective with tetraazamacrocycles tethered to Merrifield peptide resin .

References

1. Lim, W. T.; Choi, S. Y.; Kim, B. J.; Kim, C. M.; Lee, I. S.; Kim, S. H.; Heo, N. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 1090-1096.
2. Yoon, K. B. *Bull. Korean Chem. Soc.* **2006**, *27*, 17-26.
3. Kartal, S.; Tokalloğlu, S.; Ozkan, B. *Bull. Korean Chem. Soc.* **2006**, *27*, 694-698.
4. Kim, D. W.; Jeon, B. K.; Kang, B. M.; Choi, K. Y.; Ryu, H. *Main Group Metal Chem.* **2001**, *24*, 751-755.
5. Kim, D. W.; Lee, N. S.; Kim, C. S.; Ryu, H.; Kim, J. S.; Kang, B. M.; Jeon, Y. S. *European Poly. J.* **2002**, *38*, 2101-2108.
6. Kim, D. W.; Kang, B. M.; Lee, N. S.; Kim, J. S.; Ryu, H.; Jeon, B. K. *Main Group Metal Chem.* **2002**, *25*, 505-510.
7. Kim, D. W.; Kang, B. M.; Jeon, B. K.; Ryu, H. *J. Coll. Interf. Sci.* **2002**, *254*, 190-194.
8. Kang, S.; Kweon, J. K.; Jung, S. *Bull. Korean Chem. Soc.* **1991**, *12*, 483-487,
9. Choi, K.; Ryu, H.; Kim, Y. *J. Korean Chem. Soc.* **2003**, *47*, 104-108.
10. Choi, J.; Park, Y. C. *Bull. Korean Chem. Soc.* **2003**, *24*, 384-388.
11. Choi, K.; Kim, M.; Kim, D.; Kim, Y.; Kim, J.; Ryu, H.; Lim, Y.; Kang, S.; Lee, K.; Hong, C. *Bull. Korean Chem. Soc.* **2002**, *23*, 1062-1066.
12. Choi, K.; Kim, M.; Ryu, H.; Lim, Y.; Sung, N.; Shin, U.; Suh, M. *Inorg. Chem. Commu.* **2003**, *6*, 414-415.
13. Dorfner, K. *Ionenaustauscher*, 3rd ed; Dritte, A., Ed.; Waler de Gruyter: Berlin, 1970; p 17.
14. *Ion Exchangers*; Dorfner, K., Ed.; Waler de Gruyter: Berlin, 1991; p 323.
15. Kim, D. W.; Hong, C. P.; Kim, C. S.; Jeong, Y. K.; Jeon, Y. S.; Lee, J. K. *J. Radioanal. Nucl. Chem.* **1997**, *220*, 229-231.
16. Kim, D. W.; Jeon, B. K.; Kim, C. S.; Jeon, Y. S. *J. Radioanal. Nucl. Chem.* **2000**, *245*, 509-511.
17. Kim, D. W.; Knag, B. M. *Chem. Lett.* **2001**, *250*, 291-292.
18. Kim, J. K. *Analytical Chemistry*; Free Academy Publishing: Seoul, 1998; p 688.
19. Glueckauf, E. *Trans. Faraday Soc.* **1955**, *51*, 1235-1244.
20. Jepson, B. E.; Carins, G. A. *Mound Activities in Chemical and Physical Research*, *Report MLM-2622*; EG&G Mound Applied Technologies: Maiamisburg, OH, 1979; p 30.
21. Nishizawa, K.; Takano, T.; Ikeda, I.; Okahara, M. *Sep. Sci. Technol.* **1988**, *23*, 233-238.
22. Oi, T.; Shimizu, K.; Hosoe, M. *Sep. Sci. Technol.* **1999**, *34*, 805-813.
23. Ooi, K.; Miyai, Y.; Makita, Y.; Kanoh, H. *Sep. Sci. Technol.* **1999**, *34*, 1133-1139.