Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Magnesium isotope effect in the aqueous-monoazacrown bonded merrifield peptide resin

Dong Won Kim[a]; Byeong Kwang Jeon[a]; Nam-Soo Lee[a]; Young Hun Jang[a]; Hai Il Ryu[b]; Chang Suk Kim[b]
[a] Department of Chemistry, Physical Chemistry Laboratory, College of Natural Science, Chungbuk National University, Cheongju, Korea [b] Department of Chemistry Education, College of Education, Chungbuk National University, Kongju, Korea

To cite this Article Kim, Dong Won , Jeon, Byeong Kwang , Lee, Nam-Soo , Jang, Young Hun , Ryu, Hai Il and Kim, Chang Suk(2002) 'Magnesium isotope effect in the aqueous-monoazacrown bonded merrifield peptide resin', Separation Science and Technology, 37: 8, 1959 — 1971

To link to this Article: DOI: 10.1081/SS-120003054

URL: http://dx.doi.org/10.1081/SS-120003054

SEPARATION SCIENCE AND TECHNOLOGY, 37(8), 1959–1971 (2002)

MAGNESIUM ISOTOPE EFFECT IN THE AQUEOUS-MONOAZACROWN BONDED MERRIFIELD PEPTIDE RESIN

Dong Won Kim,[1,*] Byeong Kwang Jeon,[1]
Nam-Soo Lee,[1] Young Hun Jang,[1]
Hai Il Ryu,[3] and Chang Suk Kim[2]

[1]Department of Chemistry, Physical Chemistry Laboratory,
College of Natural Science and
[2]Department of Chemistry Education, College of Education,
Chungbuk National University, Cheongju 361-763, Korea
[3]Department of Chemistry Education, College of Education,
Chungbuk National University, Kongju 314-701, Korea

ABSTRACT

Separation of magnesium isotopes was investigated by chemical ion exchange with synthesized 1-aza-15-crown-5 bonded Merrifield peptide resin using elution chromatography. The capacity of novel monoazacrown ion exchanger was 2.3 meq g^{-1} dry resin. The heavier isotopes of magnesium are concentrated in the resin phase, while the lighter isotopes are enriched in the solution phase. The glass ion-exchange column used in our experiment was 35-cm long with an inner diameter of 0.2 cm, and 2.0 M NH_4Cl solution was used as an eluent. The single-stage separation factor

---

*Corresponding author. Fax: 82-0431-267-4232; E-mail: chem131@trut.chungbuk.ac.kr

was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factors of $^{24}Mg^{2+}-^{25}Mg^{2+}$, $^{24}Mg^{2+}-^{26}Mg^{2+}$, and $^{25}Mg^{2+}-^{26}Mg^{2+}$ were 1.014, 1.026, and 1.012, respectively.

INTRODUCTION

Ion-exchange chromatography with macrocyclic polyethers is a promising method for the isotope separations, because the polyethers such as crown ethers and cryptands are good complex-forming compounds for most of the metal ions, especially, alkali and alkaline earth metal ions. Konstantinov and Bakulin (1) investigated the separation of $^{24}Mg-^{26}Mg$ and $^{63}Cu^{2+}-^{65}Cu^{2+}$ isotope pairs in aqueous solutions of magnesium chloride and copper chloride using the method of countercurrent electromigration. Konstantinov and Bakulin (1) showed that, as the concentration of the magnesium chloride and copper chloride solutions increased, the relative difference in the mobilities of the $^{24}Mg^{2+}$ and $^{26}Mg^{2+}$ ions, and the mobilities of the $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ ions also increased, and at the high concentrations employed, magnesium chloride and copper chloride may not be completely dissociated. Neubert and Klemm (2) also reported the isotope enrichment of magnesium, calcium, strontium, and barium through the migration of ions in molten halides. Aaltonen (3) reported the separation of magnesium and calcium isotopes by using a recycle ion-exchange technique. He found that the separation factors of magnesium, $^{25}Mg^{2+}-^{26}Mg^{2+}$ and calcium, $^{40}Ca^{2+}-^{48}Ca^{2+}$ were 1.00016 and 1.00087, respectively. Nishizawa et al. (4) obtained a separation factor of 1.0112 as the maximum value for the $^{24}Mg^{2+}-^{26}Mg^{2+}$ isotope pair by a liquid–liquid extraction system using DC18C6.

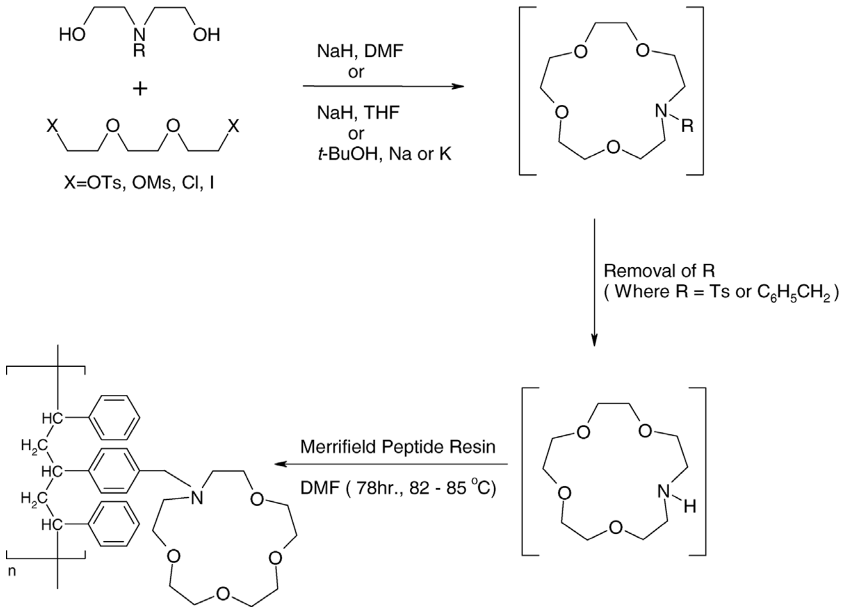
The production of isotopically pure ^{24}Mg is important because magnesium isotope, ^{24}Mg is a precursor of ^{22}Na through the nuclear reaction of $^{24}Mg(d,\alpha)$ and ^{22}Na. The reaction product, ^{22}Na is one of the rare β^{+} emitters and this isotope is used in various scientific fields as a source of annihilation radiation. Recently, Kim et al. (5) carried out an elution chromatographic separation of magnesium isotopes with triazacrown ion exchanger, and obtained large separation factors. They also found that the heavier isotopes, were enriched into the resin phase, while the lighter isotopes were enriched into the solution phase.

In this work, the authors have examined magnesium isotope separation using novel 1-aza-15-crown-5 bonded Merrifield peptide resin by the ion-exchange elution chromatography.

EXPERIMENTAL

Materials and Methods

Magnesium chloride and ammonium chloride were purchased from Sigma Chemical Co., USA. Atomic Absorption Spectrophotometer (Hitachi Z-8000) was used to determine the magnesium ion concentration in the solution. The measurement of magnesium isotope ratio was carried out using thermal ionization mass spectrometer (Finnigan MAT 262) with a rhenium double filament. A measured amount of 1.0–2.0 μg of magnesium 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 $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ became sufficiently high, these 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 $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ of each feed solution was an average of three times in our measurement. The novel 1-aza-18-crown-6 bonded Merrifield peptide resin was prepared by the method given in the literature (6,7), and shown in Sch. 1.



Scheme 1. Synthetic routes of 1-aza-15-crown-5 bonded Merrifield peptide resin.

Synthesis of *N*-Benzylmonoaza-15-crown-5

A 1-L three-necked, N_2-flushed flask was purged with N_2; NaH (50% in oil, 5 g, 0.21 mol) was added to the reaction vessel and washed with hexanes (4 × 100 mL). Tetrahydrofuran (THF) (250 mL) was then added to the flask. This suspension was heated to reflux with vigorous stirring. A solution of the *N*-benzyldiethanolamine (0.1 mol) and triethylene glycol dimesylate (TrEGMs) (0.1 mol) in THF (100 mL) was added dropwise. Reflux was continued for 20 hr. The reaction mixture was cooled and quenched with H_2O, and the solvent was evaporated in vacuum. The residue was dissolved in H_2O (400 mL), which was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were reduced to a minimum volume. The pure product was obtained as colorless oil. Proton nuclear magnetic resonance (^1H NMR): δ 2.77 (t,4SH), 3.67 (m, 18H), 7.30 (S, 5H): IR 3060, 3030, 2860, 1600, 1500, 1455, 1350, 1300, 1250, 1125, 740, 700 cm^{-1}.

Synthesis of 1-Aza-15-crown-5

The 1-aza-15-crown-5 was prepared by hydrogenolysis of *N*-benzylmonoaza-15-crown-5. A solution of *N*-benzylmonoaza-15-crown-5 (9.5 g, 0.03 mol) in absolute EtOH (90 mL) was added to 10% Pd–C (0.9 g) in a Parr hydrogenation apparatus under H_2 (60 psi) and the mixture was shaken for 24 hr at 25°C. The reaction mixture was filtered through a bed of celite and the solvent evaporated. Distillation of the residue in a Kugelrohr apparatus (bp 76°C) gave pure 1-aza-15-crown-5 (6.5 g, 98%) as a colorless oil, which solidified to a soft, white hygroscopic solid: ^1H NMR: δ 2.53 (s, 1H), 2.72 (t, 4H), 3.57 (m, 16H).

Synthesis of 1-Aza-15-crown-5 Bonded Merrifield Peptide Resin

In a 500-mL three-necked flask, equipped with a condenser, two additional funnels, and moisture protector, were placed 20 mL of dry DMF and 2 mL of triethlamine. Oily 1-aza-15-crown-5 in 50 mL of dry DMF from one additional funnel was then added slowly. After the mixture was stirred for 72 hr at 88–90°C, the residue was washed with water and methanol. It gave a yellow powder and its particle size was 200–400 mesh. In an IR (KBR) spectrum, the $—CH_2—Cl$ (690 cm^{-1}) peak gave a lower intensity. In TGA thermogram, the degradation of the polymer began at 285°C and ended at 488°C, and T_{max} was 384°C.

Determination of the Total Weight Capacity

The capacity of the novel 1-aza-15-crown-5 bonded Merrifield peptide resin was determined by the method given in the literature (8). The 1-aza-15-crown-5 cation exchanger was transformed into the H-form by slow treatment with about 1 L of 1.0 *N* HCl in the funnel. Subsequently, it was neutralized by washing with distilled water, and dried in air. Of this quantity, 1.000 ± 0.005 g was weighed into a dry 250 mL Erlenmeyer flask containing exactly 200 mL of 0.1 *N* NaOH with 5% sodium chloride, and was allowed to stand overnight. An exchanger sample of the same material was separately weighed into a weighing bottle, dried at 110°C overnight, and weighed again to determine the percentage of solids. Fifty-milliliter aliquots of the supernatant liquid in the Erlenmeyer flask were back-titrated with 0.1 *N* HCl against phenolphthalein. The capacity was then calculated by the formula:

$$\text{Capacity (meq g}^{-1}\text{)} = \frac{(200 \times \text{Normality}_{\text{NaOH}}) - 4(\text{mL}_{\text{Acid}} \times \text{Normality}_{\text{Acid}})}{\text{Sample Weight}\left(\frac{\%\text{Solid}}{100}\right)} \quad (1)$$

It represents the total weight capacity of the exchanger in the dry H-form. The resin must be completely in the H-form before weighing of the sample, since differences in equivalent weights of different ions would lead to errors. The standard sodium hydroxide solution was treated with 5% sodium chloride to obtain a complete exchange equilibrium by the excess of sodium ions. A reproducibility of ±1% can consequently be obtained.

Measurement of Distribution Coefficient

For the determination of the distribution coefficient (K_d), batch method was used (5). Each portion of 1.0 g of resin, which was dried to constant weight at 60°C, was weighed accurately and transferred into a 100-mL polyethylene vial with a polyethylene screw top. Then 1.0 mL of 0.01 *M* magnesium chloride solution was added, followed by 49 mL of ammonium chloride solution of the desired concentration to give a final volume of 50 mL. The reaction mixture was then subjected to reciprocal shaking at 100 strokes min^{-1} for 24 hr, and then centrifuged for 5 min at 5000 rpm. The concentration of magnesium ions in the supernatant was determined by an atomic absorption spectrophotometer. The distribution coefficient K_d value was calculated by

$$K_d = \frac{(C_i - C_f)}{C_f}\frac{V}{m} \quad (2)$$

where C_i and C_f are the initial and final concentrations of electrolyte solution, m, the mass of dry resins in g, and V, the total volume of the solution in mL. The value of K_d is equal to the concentration of a cation on the ion-exchange resin phase divided by its concentration in the liquid phase.

Separation of Magnesium Isotopes

The 1-aza-15-crown-5 bonded Merrifield peptide resin, 200 mesh, was slurried in 2.0 *M* ammonium chloride solution. The slurried resin was packed in a water-jacketed glass column (0.2 cm I.D. × 35 cm height). The temperature was maintained at 20°C with a Water Circulator (HAAKE A-80). Five-hundred ppm of magnesium ion in distilled water was loaded on the top of the resin bed. Two-molar NH_4Cl solution ($K_d = 165$) was used as an eluent. The magnesium feed solution was then passed through the column under gravity flow. The flow rate was controlled by a fine stopcock to be 0.6 mL hr^{-1}. The effluent was collected as a fraction of 0.1 mL each with an Automatic Fraction Collector (Pharmacia LKB FRAC-100).

RESULTS AND DISCUSSION

The ion-exchange capacity of the 1-aza-15-crown-5 bonded Merrifield peptide resin was 2.3 meq g^{-1} dry resin. As shown in Fig. 1, distribution coefficients of magnesium ions on the 1-aza-15-crown-5 bonded Merrifield peptide resin increased in a nonlinear manner with increasing concentration over

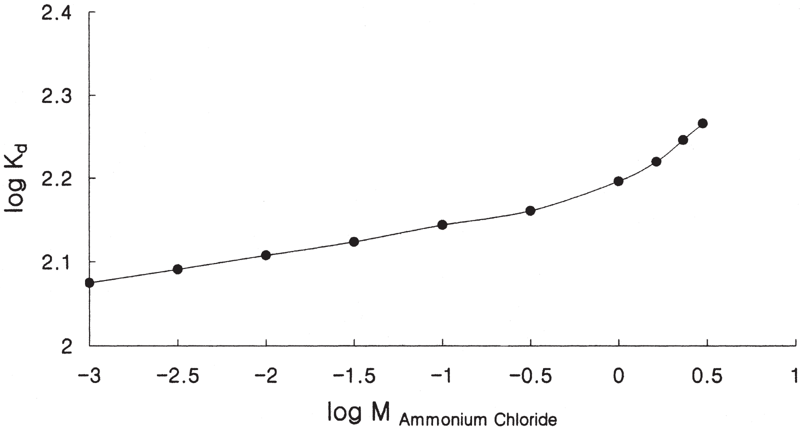


Figure 1. Plot of log K_d for magnesium ions on 1-aza-15-crown-5 bonded Merrifield peptide resin as a function of NH_4Cl solution concentration.

a range from 1.0×10^{-3} to $3.0\,M$ NH_4Cl solutions. The authors obtained the chromatogram from column operation with $2.0\,M$ NH_4Cl solution ($K_d = 165$) at 20°C. From the elution curve, the number of theoretical plates, N, in the column was calculated using equation (9):

$$N = 8\left(\frac{V_{max}}{\beta}\right)^2 \tag{3}$$

where V_{max} is the peak elution volume, and β, the band width at the concentration $C = C_{max}/e$, and C_{max}, concentration of solute at the maximum peak height of the elution curve. The elution time increased with increasing K_d due to the high adsorption of ion on the resin phase in the column. For this reason, as expected, the eluents have the values of the K_d ranging from 30 to 300 and were used to separate isotopes in our laboratory. From the elution curve and isotopic assay data, the separation factors of magnesium isotopes were calculated by Glueckauf theory (10). The isotope ratio of a fraction can be expressed by c_1/c_2, where c_1 and c_2 are the relative abundances of the light and heavy magnesium isotopes. The c_1^0/c_2^0 is the isotope ratio of the standard, and local enrichment factor, R, is denoted by $(c_1/c_2)\ (c_2^0/c_1^0)$. In addition, the total amount of magnesium is denoted by m, and Δm the cumulative amount of magnesium eluted in all fractions upto and including a particular fraction. The data were plotted on a probability paper where the 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. This gave a linear plot. The slope of the straight line obtained will be $\epsilon\sqrt{N}$, and separation factor, α, was defined as $1 + \epsilon$. The separation factor was determined from the slope of a least-squares line drawn through the points as shown in Fig. 2. This, too, is a typical plot of the isotopic assays in this experiment. In our experiment, the separation factors of magnesium isotopes were, 1.014 for ${}^{24}Mg^{2+}$–${}^{25}Mg^{2+}$, 1.026 for ${}^{24}Mg^{2+}$–${}^{26}Mg^{2+}$, and 1.012 for ${}^{25}Mg^{2+}$–${}^{26}Mg^{2+}$ isotope pairs, respectively. These values are larger than those of the factors determined by Aaltonen (3) and Nishizawa et al. (4). Separation factors of our system were considerably larger, perhaps, 100-fold more than 1.00016 for ${}^{25}Mg^{2+}$–${}^{26}Mg^{2+}$ or of the same order of magnitude as 1.0112 for ${}^{24}Mg^{2+}$–${}^{26}Mg^{2+}$, as obtained by Aaltonen (3) or Nishizawa et al. (4). Aaltonen (3) carried out an elution chromatographic separation of magnesium isotopes with a strongly acidic cation exchanger, Dowex 50×8, and reported that the value of the separation factor for ${}^{25}Mg^{2+}$–${}^{26}Mg^{2+}$ pair was 1.00016. Nishizawa et al. (4) reported the separation factor for ${}^{24}Mg^{2+}$–${}^{26}Mg^{2+}$ of 1.0112 as the maximum value in a liquid–liquid extraction system including dicyclohexano-18-crown-6 (DC18C6). From the experimental data, the isotope-exchange reaction can

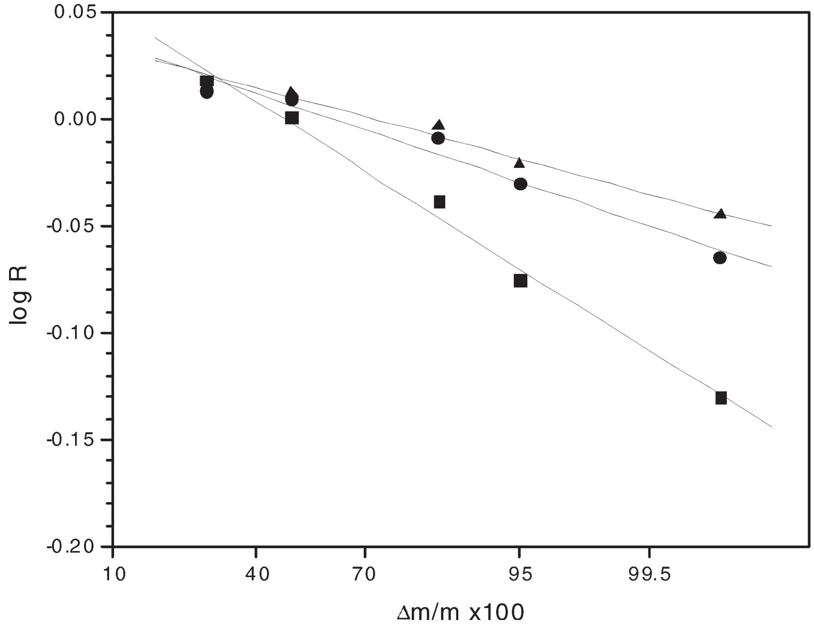


Figure 2. Enrichment of magnesium isotopes by cation exchange chromatography. ●: $^{24}Mg^{2+}-^{25}Mg^{2+}$, ■: $^{24}Mg^{2+}-^{26}Mg^{2+}$, ▲: $^{25}Mg^{2+}-^{26}Mg^{2+}$.

be represented by the following equations:

$$^{24}Mg^{2+}_{Resin} +^{25} Mg^{2+}_{Solution} \leftrightarrows {}^{24}Mg^{2+}_{Solution} +^{25} Mg^{2+}_{Resin} \tag{4}$$

$$^{24}Mg^{2+}_{Resin} +^{26} Mg^{2+}_{Solution} \leftrightarrows {}^{24}Mg^{2+}_{Solution} +^{26} Mg^{2+}_{Resin} \tag{5}$$

$$^{25}Mg^{2+}_{Resin} +^{26} Mg^{2+}_{Solution} \leftrightarrows {}^{25}Mg^{2+}_{Solution} +^{26} Mg^{2+}_{Resin} \tag{6}$$

The subscripted symbols, such as solution and resin refer to the NH_4Cl solution and 1-aza-15-crown-5 bonded resin phase in this chemical isotope exchange. This means that the complexing ability of the heavier magnesium isotopes on the resin phase is significant than that of the lighter isotopes. Aaltonen (3) reported that the heavier isotopes of magnesium are enriched in the front parts of magnesium adsorption bands formed in chromatographic separation columns, packed with strongly acidic cation exchanger, Dowex 50 × 8, 400 mesh and ammonium lactate solution was used as an eluent for the separation of magnesium isotopes. Heumann and Lieser (11), Oi et al. (12), Ooi et al. (13), Jepson et al. (14), Kondoh et al. (15), and Fujine et al. (16) also reported that the heavier isotopes were preferentially concentrated into the solution phase of chromatography using strongly acidic cation exchangers, anion exchangers, titanium phosphate exchangers, and polymer-bound crown ether. These phenomena are in contrast to the results of the authors' work. On the other hand, Oi et al. (17), Klinskii et al. (18), Heumann and Schiefer (19), Aaltonen et al. (20), Kim et al. (5), and Lee (21) reported that the heavier isotopes were preferentially enriched in the resin phase of cation- and anion-exchange chromatography.

A more stable 1:1 complex is formed when the cation has an ionic diameter fitted to the cavity size of the crown ether. The cavity size of 15-crown-5 ether is 1.7–2.2 Å (22), and the ionic diameter of Mg^{2+} is 1.30–1.45 Å (23), respectively. These may produce a stable complex formation and isotope effect. Lee (24) proposed that the hydrating tendency of co-sorbed ions directly affected the separation factor of lithium isotopes. He showed that the separation factor of lithium isotopes increased as the heat of hydration of the co-sorbed ion increased. Gupta (25) has discussed the effect of anions for the isotope effects and showed that halide ions are considered to be structure breakers, except for fluoride ion, and as the partial dehydration of the lithium ions in the resin phase remains the same, this overall increase in the solvation of the lithium ions in the solution, in the presence of the structure-breaker anions increases the difference in the hydration numbers for the ions in solution and the resin phase and hence the isotope effect. Lee (24) showed that the lithium isotope separation factor increased as the degree of hydration of the eluting cation increased. The heat of hydration of eluting NH_4^+ ion is relatively small (24). On the other hand, the counter Cl^- ion is the significant structure breaker (25), and this may also be able to contribute to the effect for the magnesium isotope separation in this experiment.

Lee (21) has shown that the metal ion species in the resin phase is less hydrated than the metal ion species in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotopes in the resin phase. These phenomena are a contrast with the author' system. The enrichment factor ($\epsilon = \alpha - 1$) for isotopes separated by ion-exchange or extraction chromatography depended upon the mass of the isotope as well as the difference in the masses of the isotope pairs (21). In comparing the enrichment factors per mass unit ($\epsilon/\Delta m$) for some divalent elements with increasing atomic mass, it is shown in Table 1 that the separation factor decreases as the mass increases. Isotopes within approximately the same mass range may have an increase or decrease in factor due to ion complexing, but the mass effect is more significant. Therefore, the separation factors for the separation of heavy isotopes by ion exchange are extremely small, and it follows that the accuracy of the separation factors diminishes markedly as these factors become smaller (21). From the experimental data, the separation factor increases as the mass difference of the isotope pairs increases, and the values of the enrichment factors per mass

Table 1. The Separation of Isotopes of Some Divalent Elements by Ion Exchange

Atomic Number	Isotope Pair	Separation Factor	$\epsilon \times 10^3$	$(\epsilon/\Delta m) \times 10^3$	References
12	$^{25}Mg^{2+}$–$^{26}Mg^{2+}$	1.00016	0.16	0.16	(3)
	$^{24}Mg^{2+}$–$^{26}Mg^{2+}$	1.0112	11.2	5.6	(4)
	$^{24}Mg^{2+}$–$^{25}Mg^{2+}$	1.014	14	14	This work
	$^{24}Mg^{2+}$–$^{26}Mg^{2+}$	1.026	26	13	This work
	$^{25}Mg^{2+}$–$^{26}Mg^{2+}$	1.012	12	12	This work
20	$^{40}Ca^{2+}$–$^{44}Ca^{2+}$	1.00047	0.47	0.12	(3)
	$^{40}Ca^{2+}$–$^{48}Ca^{2+}$	1.00087	0.87	0.11	(3)
	$^{40}Ca^{2+}$–$^{47}Ca^{2+}$	1.00026	0.26	0.04	(21)
	$^{40}Ca^{2+}$–$^{44}Ca^{2+}$	1.028	28	7	(11)
	$^{40}Ca^{2+}$–$^{48}Ca^{2+}$	1.048	48	6	(11)
38	$^{84}Sr^{2+}$–$^{88}Sr^{2+}$	1.0000036	0.0036	0.0009	(12)
	$^{86}Sr^{2+}$–$^{88}Sr^{2+}$	1.0000023	0.0023	0.0012	(12)
	$^{87}Sr^{2+}$–$^{88}Sr^{2+}$	1.00000097	0.00097	0.00097	(12)
56	$^{130}Ba^{2+}$–$^{138}Ba^{2+}$	1.000032	0.032	0.004	(15)
	$^{135}Ba^{2+}$–$^{138}Ba^{2+}$	1.000017	0.017	0.0057	(15)
	$^{137}Ba^{2+}$–$^{138}Ba^{2+}$	1.0000071	0.0071	0.0071	(15)

unit ($\epsilon/\Delta m$) are approximately the same for the same experimental conditions. The magnesium isotope separation system in this work, can, therefore, be explained by the fact that the complexation and isotope mass effects are more significant than that of the hydration.

CONCLUSIONS

Separation of magnesium isotopes was investigated by chemical ion exchange with synthesized 1-aza-15-crown-5 bonded Merrifield peptide resin using elution chromatography. The capacity of novel monoazacrown ion exchanger was 2.3 meq g^{-1} dry resin. The heavier isotopes of magnesium were concentrated in the resin phase, while the lighter isotopes were enriched in the solution phase. The single-stage separation factor was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factors of $^{24}Mg^{2+}$–$^{25}Mg^{2+}$, $^{24}Mg^{2+}$–$^{26}Mg^{2+}$, and $^{25}Mg^{2+}$–$^{26}Mg^{2+}$ isotope pairs were 1.014, 1.026, and 1.012, respectively.

ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Institute Program, Ministry of Education, Korea, 1998, Project No. BSRI-98-3435.

REFERENCES

1. Constantinov, B.P.; Bakulin, E.A. Separation $^{24}Mg^{2+}$–$^{26}Mg^{2+}$ and $^{63}Cu^{2+}$–$^{65}Cu^{2+}$ Isotope Pairs in Aqueous Solutions of Magnesium Chloride and Copper Chloride. Russ. J. Phys. Chem. **1965**, *39* (1), 1–4.
2. Neubert, A.; Klemm, A. Isotopenanreicherung bei Mg, Ca, Sr und Ba durch Ionenwanderung in Geschmolzenen Halogeniden. Z. Naturforsch. **1961**, *16a*, 685–692.
3. Aaltonen, J. Separation of Alkaline Earth Metal Isotopes by Ion Exchange. Part I. Studies on Magnesium and Calcium. Suom. Kemistil. B **1971**, *44* (1), 1–4.
4. Nishizawa, K.; Nishida, T.; Miki, T.; Yamamoto, T.; Hosoe, M. Extractive Behavior of Magnesium Chloride and Isotopic Enrichment of Magnesium by Crown Ether. Sep. Sci. Technol. **1996**, *31* (5), 643–654.
5. Kim, D.W.; Jeon, B.K.; Kim, C.S.; Jeon, Y.S. Enrichment of Magnesium Isotopes by N_3O_2 Azacrown Ion Exchange Resin. J. Radioanal. Nucl. Chem. **2000**, *245* (3), 509–511.

6. Amorim, M.T.S.; Delgado, R.; Frausto Da Silva, J.J.R.; Candiada, M.; Vaz, T.A.; Vilhena, F. Metal Complexes of 1-Oxa-4,7,10-Triazacyclododecane-*N*,*N*′,*N*″-Triacetic Acid. Talanta **1988**, *35*, 741–745.
7. Kusama, T.; Hayatsu, H. Use of a Derivatized Merrifield Resin for the Polymer-Supported Synthesis of Oligodeoxyribonucleotides. Chem. Pharm. Bull. **1970**, *18* (2), 319–327.
8. Dorfner, K. Ionenaustauschertypen. *Ionenaustauscher*; 3. Aufl.; Walter de Gruyter & Co.: Berlin, 1970, 45–50.
9. Glueckauf, E. Theory of Chromatography. Part 9. The Theoretical Plate Concept in Column Separations. Trans. Faraday Soc. **1955**, *51*, 34–44.
10. Glueckauf, E. Theory of Chromatography. Part 11. Enrichment of Isotopes by Chromatography. Trans. Faraday Soc. **1958**, *34*, 1203–1205.
11. Heumann, K.G.; Lieser, K.H. Untersuching von Calciumisotopie—Effekten bei Heterogenen Austauschgleichgewichten. Z. Naturforsch. **1972**, *27b*, 126–133.
12. Oi, T.; Ogino, H.; Hosoe, M.; Kakihana, H. Fractionation of Strontium Isotopes in Cation-Exchange Chromatography. Sep. Sci. Technol. **1992**, *27* (5), 631–643.
13. Ooi, K.; Miyai, Y.; Makita, Y.; Kanoh, H. Fractionation of Lithium Isotopes in Ion Exchange Chromatography with Titanium Phosphate Exchanger. Sep. Sci. Technol. **1999**, *34* (6&7), 1133–1144.
14. Jepson, B.E.; Novotny, M.A.; Evans, W.F.; *Separation Research. Calcium Chemical Exchange*. MLM-3695; Mound Activities in Chemical and Physical Research: January–December 1990: EG & G Mound Applied Technologies P.O. Box 3000, Miamisburg, OH 45343-3000, U.S. Department of Energy, Contact No. DE-AC04-88DP43495, 1991; 30–50.
15. Kondoh, A.; Oi, T.; Hosoe, M. Fractionation of Barium Isotopes in Cation-Exchange Chromatography. Sep. Sci. Technol. **1996**, *31* (1), 39–48.
16. Fujine, S.; Saito, K.; Shiba, K. Lithium Isotope Separation by Displacement Chromatography Using Cryptand Resin. J. Nucl. Sci. Technol. **1983**, *20* (5), 439–440.
17. Oi, T.; Kawada, K.; Hosoe, M.; Kakihana, H. Fractionation of Lithium Isotopes in Cation-Exchange Chromatography. Sep. Sci. Technol. **1991**, *26* (10&11), 1353–1375.
18. Klinskii, G.D.; Knyazev, D.A.; Vlasova, G.I. Chromatographic Separation of Calcium Isotopes. Russ. J. Phys. Chem. **1974**, *48* (3), 380–382.
19. Heumann, K.G.; Schiefer, H.P. Calcium Isotope Separation on an Exchange Resin Having Cryptand Anchor Groups. Angew. Chem. **1980**, *92* (5), 406–407.
20. Aaltonen, J.; Heumann, K.G.; Pietila, P. Isotope Effects of Uranium by Ion Exchange in the System Dowex 50/α-Hydroxyisobutyrate. Z. Narturforsch. **1974**, *29b*, 190–194.

21. Lee, D.A. Separation of Isotope of Selected Divalent Elements by Ion Exchange. J. Inorg. Nucl. Chem. **1976**, *38*, 161–163.
22. Hiraoka, M. Characteristics of Crown Compounds. *Crown Compounds. Their Characteristics and Applications*; Studies in Organic Chemistry 12, Elsevier Scientific Publishing Company: Amsterdam, 1982; Vol. 12, 73–74.
23. Conway, B.E. Scales for Ionic Radic in Gases, Crystals and Solutions. *Ionic Hydration in Chemistry and Biophysics*; Studies in Physical and Theoretical Chemistry 12, Elsevier Scientific Publishing Company: Amsterdam, 1982; Vol. 12, 61–64.
24. Lee, D.A. Enrichment of Lithium Isotopes by Ion Exchange Chromatography. III. The Influence of the Nature of the Solution Phase on the Separation Factor. J. Am. Chem. Soc. **1961**, *83*, 1801–1803.
25. Gupta, A.R. Isotope Effects in Ion-Exchange Equilibria in Aqueous and Mixed Solvent Systems. Sep. Sci. Technol. **1979**, *14* (9), 843–857.

Received March 2001
Revised July 2001