Enrichment of Magnesium Isotopes by Monoazacrown Bonded Merrifield Peptide Resin

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Magnesium isotope separation was investigated by chemical ion exchange with the 1-aza-12-crown-4 bonded Merrifield peptide resin using an elution chromatographic technique. The capacity of the novel azacrown ion exchanger was 1.0 meq/g dry resin. The heavier isotopes of magnesium were enriched 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 $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ were 1.008, 1.019, and 1.006, respectively.

Keywords : Magnesium isotope separation, Monoazacrown resin, Capacity, Isotope effect, Elution chromatography.

Introduction

Macrocyclic polyethers and their analogues have the remarkable property of complexation with cations, especially, alkali and alkaline earth metal ions. Therefore, their unique ability to form stable complexes with various cations has been used to separate isotopes of alkali and alkaline earth metal ions. The separation of isotopes, $^{63}Cu^{2+}$-$^{65}Cu^{2+}$ and $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ was first attempted by Roberts *et al.*[1] and Martin *et al.*.[2] Konstantinov *et al.*[3] investigated the separation of $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ 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 et al. showed that, as the concentration of the magnesium chloride and copper chloride solutions increased, the relative difference in the mobilities of the isotope $^{24}Mg^{2+}$ and $^{26}Mg^{2+}$ ions and the mobilities of the $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ ions also increased, and concluded that, at the high concentrations employed, magnesium chloride and copper chloride might not be completely dissociated. Neubert *et al.*[4] also reported the isotope enrichment of magnesium, calcium, strontium, and barium through the migration of ions in molten halides. Aaltonen[5] reported the separation of magnesium and calcium isotopes using a recycle ion exchange technique. He found that the separation factors of magnesium isotopes, $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ and calcium isotopes, $^{40}Ca^{2+}$-$^{48}Ca^{2+}$ were 1.00016 and 1.00087, respectively. Jepson *et al.*[6] first reported the separation of calcium isotopes with macrocyclic polyethers. Nishizawa *et al.*[7] obtained a separation factor of 1.0112 as a maximum value for the $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ isotope pair by a liquid-liquid extraction system using the DC18C6.

The production of isotopically pure ^{24}Mg is important because the magnesium-24 is a precursor of ^{22}Na through the nuclear reaction of $^{24}Mg(d,\alpha)^{22}Na$. 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.[7] Kim *et al.*[8] carried out an elution chromatographic separation of magnesium isotopes with a N_3O_2 azacrown ion exchanger. They also found that the heavier isotope, $^{26}Mg^{2+}$, was enriched in the resin phase, while the lighter isotopes, $^{24}Mg^{2+}$ and $^{25}Mg^{2+}$, were enriched in the solution phase.

Ion exchange elution chromatography with macrocyclic compounds is a promising method for the separation of isotopes due to the ability of complexation with cations, especially, alkali and alkalaine earth metal ions. In this work, magnesium isotope separation was examined magnesium isotope separation using a novel 1-aza-12-crown-4 bonded Merrifield peptide resin by ion exchange elution chromatography.

Experimental Section

Materials and Methods. The novel 1-aza-12-crown-4 bonded Merrifield peptide resin was prepared by the method given in the literatures.[9-11] Synthetic route of the resin is shown in Scheme 1. The capacity of the resin was determined novel by the method given in the literature.[12] Magnesium chloride and ammonium chloride were purchased from Sigma Chemical Co., USA. An Atomic Absorption Spectrophotometer (Hitachi Z-8000) was used to determine the magnesium ion concentrations in the solutions. Measurement of the magnesium isotope ratio was carried out using Thermal Ionization Mass Spectrometer (Finnigan MAT 262) with a rhenium double filament. Amount of 1.0-2.0 μg magnesium 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, the $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ 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 fractions of $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ of

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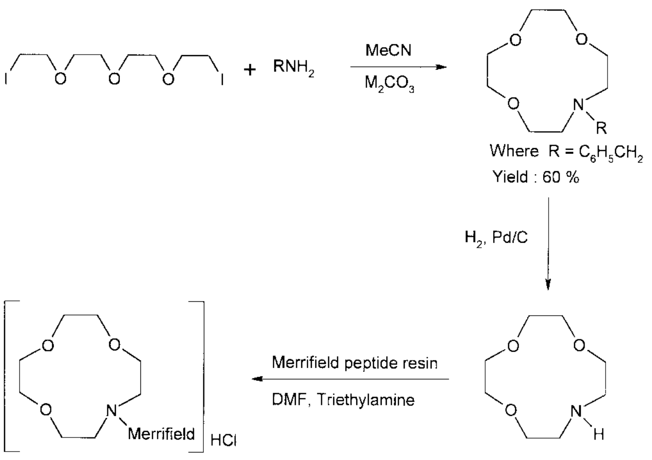

Scheme 1. Synthetic route of the 1-aza-12-crown-4 bonded Merrifield peptide resin.

each feed solution were measured in triplicate(in this manner).

Measurement of Distribution Coefficient. The batch method was employed for the determination of the distribution coefficients.[13] Each portion of 1.0 g of the 1-aza-12-crown-4 bonded Merrifield peptide resin, 200-400 mesh, which had been dried to a constant weight at 60 °C, was weighed out 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 appropriate concentration to give a final volume of 50 mL. The reaction mixture was subjected to reciprocal shaking at 100 strokes/min for 24 h, and then centrifuged for 5 min at 5,000 rev/min. The concentration of magnesium ions in the supernatant was determined using the AA-Spectrophotometer. The distribution coefficient, K_d, was calculated by the following equation:

$$K_d = \frac{(C_{st} - C_{eq})}{C_{eq}} \cdot \frac{V}{m} \qquad (1)$$

where C_{st} is the metal ion concentration of the standard solution, C_{eq} the metal ion concentration after equilibrium of the solution, V the total volume in mL of the solution, and m the mass in g of dry resin.

Ion Exchange Capacity. Ion exchange capacity was determined by the method given in the literature.[12] The 1-aza-12-crown-4 ion exchanger was transformed into the H-form by slow treatment with about 1.0 N HCl in the funnel. Subsequently, it was washed to neutrality with distilled water, and dried in air. Then, 1.000 ± 0.005 g of the dry resin was weighed into a 250 mL Erlenmeyer flask containing exactly 200 mL of 0.1 N NaOH with 5% sodium chloride. The mixture was allowed to stand overnight. An exchanger sample of 1.0 g was separately weighed into a weighing bottle, dried at 110 °C overnight, and weighed again to determine the percentage of solids. Of the supernatant liquid in the Erlenmeyer flask, 50 mL aliquots were titrated with 0.1 N HCl using phenolphthalein indicator. The capacity was calculated by the formula:

$$\text{Capacity (meq/g)} = \frac{(200 \cdot \text{Normality}_{\text{NaOH}}) - 4(\text{mL}_{\text{acid}} \cdot \text{Normality}_{\text{acid}})}{\text{Sample Weight} - (\%\ \text{Solid}/100)} \qquad (2)$$

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 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.

Separation of Magnesium Isotopes. The 1-aza-12-crown-4 bonded Merrifield peptide resin was slurried in ammonium chloride solution. The slurried resin was packed in a water-jacketed glass column of 35 cm long with inner diameter of 0.2 cm. The temperature was maintained at 20 °C with an Water Circulator (HAAKE A-80). Five hundred ppm of magnesium ion in distilled water was loaded on the top of the resin bed. One molar NH_4Cl solution (K_d=128) 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/h. 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-12-crown-4 bonded Merrifield peptide resin was 1.0 meq/g dry resin. This value is comparable to those of the DIAION SK 102 (cation exchanger, 0.60 meq/g) and DIAION SK 103 (cation exchanger, 0.9 meq/g).[14] The distribution coefficients of magnesium ion on the resin were measured by changing the concentration of NH_4Cl solution from 1.0×10^{-3} M to 2.0 M using a batch method. The distribution coefficients were calculated using Eq. (1). As shown in Figure 1, the distribution coefficient of magnesium ion on the resin increased in a non-linear manner with increasing concentration over a range from 1.0×10^{-3} M to 2.0 M NH_4Cl solution. Five times of

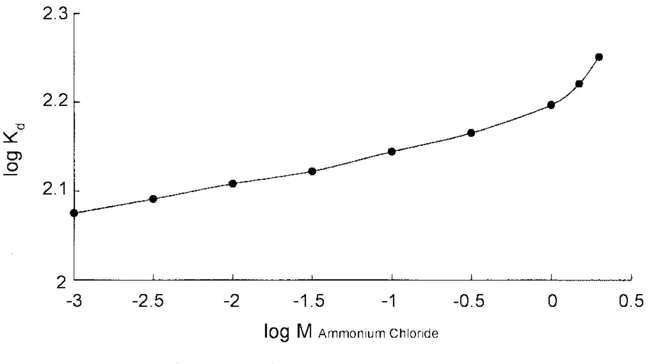

Figure 1. Plot of log K_d for magnesium ions on the 1-aza-12-crown-4 bonded Merrifield peptide resin as a function of NH_4Cl solution concentration.

experimental trials were done to obtain accurate values of the ion exchange capacity and the distribution coefficient. A 35 cm long ion exchange column was used to obtain a substantial total separation from which the single stage separation factor was calculated.

The chromatogram was obtained from column operation with 1.0 M NH_4Cl solution (K_d=128) at 20 °C. The elution time increased with increasing the distribution coefficient due to the high adsorption of ions on the resin phase in the column. For this reason, the eluents with the distribution coefficient range of 30 to 300 were used to separate isotopes in my laboratory.

From the elution curve, the number of theoretical plates in the column was calculated by the equation:[15]

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

where $V_{\max}$ is 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.

From the elution curve and isotopic assay data, the single stage separation factors, $({}^{24}Mg^{2+}/{}^{25}Mg^{2+})_{Resin}/({}^{24}Mg^{2+}/{}^{25}Mg^{2+})_{Solution}$, $({}^{24}Mg^{2+}/{}^{26}Mg^{2+})_{Resin}/({}^{24}Mg^{2+}/{}^{26}Mg^{2+})_{Solution}$ and $({}^{25}Mg^{2+}/{}^{26}Mg^{2+})_{Resin}/({}^{25}Mg^{2+}/{}^{26}Mg^{2+})_{Solution}$, were determined by the Glueckauf theory.[16] The data were plotted on probability paper where the abscissa was a probability scale and the ordinate was a linear scale. The local enrichment percentage was the ordinate and the fraction of the eluted mixture was the abscissa. This gave a linear plot. The slope is $\varepsilon\sqrt{N}$, and separation factor is $1+\varepsilon$. The separation factor, α, was determined from the slope of a least square line drawn through the points as shown in Figure 2. This is a typical plot of the isotopic assays in this experiment. In this experiment, the magnesium isotope separation factors for ${}^{24}Mg^{2+}$-${}^{25}Mg^{2+}$, ${}^{24}Mg^{2+}$-${}^{26}Mg^{2+}$, and ${}^{25}Mg^{2+}$-${}^{26}Mg^{2+}$ were obtained as values of 1.008, 1.019, and 1.006, respectively. These values are considerably larger, perhaps tenfold more, than 1.00016 for the ${}^{25}Mg^{2+}$-${}^{26}Mg^{2+}$ pair obtained by Aaltonen.[5] Aaltonen[5] 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 the ${}^{25}Mg^{2+}$-${}^{26}Mg^{2+}$ pair was 1.00016. Nishizawa *et al.*[7] reported the separation factor for the ${}^{24}Mg^{2+}$-${}^{26}Mg^{2+}$ pair of 1.0112 as a maximum value in a liquid-liquid extraction system including the dicyclohexano-18-crown-6(DC18C6). From the experimental data, it appears that the isotope exchange reaction can be represented by the following equations:

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

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

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

The subscripted symbols, such as solution and resin refer to the solution and resin phases in this chemical isotope exchange. Eqs. (4), (5), and (6) state that the heavier isotopes of magnesium are enriched in the resin phase, while the lighter isotopes are enriched in the solution phase. Aaltonen[5] reported that the heavier isotopes of magnesium were enriched in the front parts of magnesium adsorption bands formed in chromatographic separation columns, packed with a strongly acidic cation exchanger, Dowex 50 × 8, 400 mesh. He used ammonium lactate solution as an eluent for the separation of magnesium isotopes. Kondoh *et al.*,[17] Heumann *et al.*,[18] Oi *et al.*,[19] Ooi *et al.*,[20] Jepson *et al.*,[21] and Fujine *et al.*[22] also reported that the heavier isotopes were preferentially concentrated into the solution phase of chromatography using strongly acidic cation exchangers, anion exchanger, titanium phosphate exchangers and polymer-bound crown ethers. These results were in contrast with that of my work. On the other hand, Kim *et al.*,[8] Oi *et al.*,[23] Klinskii *et al.*,[24] Heumann *et al.*,[25] Aaltonen *et al.*,[26] and Lee[27] reported that the heavier isotopes were enriched in the resin phase of cation and anion exchange chromatography.

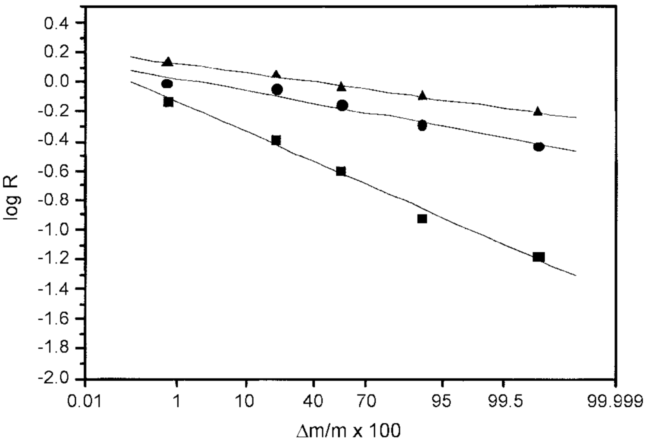

Figure 2. Enrichment of magnesium isotopes by cation exchange chromatography; ● :${}^{24}Mg^{2+}$-${}^{25}Mg^{2+}$, ■ :${}^{24}Mg^{2+}$-${}^{26}Mg^{2+}$; ▲ :${}^{25}Mg^{2+}$-${}^{26}Mg^{2+}$.

Lee[27] has shown that the metal ion species is less hydrated in the resin phase than in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotopes in the exchanger phase. These phenomena are in contrast with my system. The enrichment factor ($\varepsilon=\alpha-1$) for isotopes separated by ion exchange or extraction chromatography depends upon the mass of the isotope as well as the difference in the masses of the isotope pairs.[27] As can be seen in Table 1, the separation factor decreased as the mass of the isotopes increased, and increased as the difference in the masses (Δm) of the isotope pairs increased.[17,27] Isotopes within approximately the same mass range may have an increase or decrease in separation factor due to ion complexing, but the mass effect is more significant[27] as shown in Table 1. Of the magnesium isotope separations, the crown ion exchanger is more effective to separate isotopes than Dowex exchanger. The magnesium isotope separation system in this work, can, therefore, be explained by the fact that the hydration and complexation effects are lesser than the isotope mass effect.

Table 1. Separation of isotopes of some divalent elements by cation exchange

Atomic Number	Isotope Pair	Separation Factor (α=1+ε)	Enrichment Factor$\times10^3$ (ε=α–1)	$\frac{\varepsilon}{\Delta m}\times10^3$	Method	Reference
12	$^{25}Mg^{2+}$-$^{26}Mg^{2+}$	1.00016	0.16	0.16	Elution Dowex50 × 8	5
	$^{24}Mg^{2+}$-$^{26}Mg^{2+}$	1.0112	11.22	5.6	Extraction DC18C6	7
	$^{24}Mg^{2+}$-$^{25}Mg^{2+}$	1.008	8	8	Elution Azacrown	This Work
	$^{24}Mg^{2+}$-$^{26}Mg^{2+}$	1.019	19	8	Elution Azacrown	This Work
	$^{25}Mg^{2+}$-$^{26}Mg^{2+}$	1.006	6	6	Elution Azacrown	This Work
20	$^{40}Ca^{2+}$-$^{44}Ca^{2+}$	1.00047	0.47	0.12	Elution Dowex50 × 8	5
	$^{40}Ca^{2+}$-$^{48}Ca^{2+}$	1.00087	0.87	0.11	Elution Dowex50 × 8	5
	$^{40}Ca^{2+}$-$^{47}Ca^{2+}$	1.00026	0.26	0.04	Elution Dowex50 × 12	27
	$^{40}Ca^{2+}$-$^{44}Ca^{2+}$	1.028	28	7	Elution Dowex50 × 12	18
	$^{40}Ca^{2+}$-$^{48}Ca^{2+}$	1.048	48	6	Elution Dowex50 × 12	18
38	$^{84}Sr^{2+}$-$^{88}Sr^{2+}$	1.0000036	0.0036	0.00090	Breakthrough Asahi LS-6	19
	$^{86}Sr^{2+}$-$^{88}Sr^{2+}$	1.0000023	0.0023	0.00115	Breakthrough Asahi LS-6	19
	$^{87}Sr^{2+}$-$^{88}Sr^{2+}$	1.00000097	0.00097	0.00097	Breakthrough Asahi LS-6	19
56	$^{130}Ba^{2+}$-$^{138}Ba^{2+}$	1.000041	0.041	0.0052	Breakthrough Asahi LS-6	17
	$^{135}Ba^{2+}$-$^{138}Ba^{2+}$	1.000016	0.016	0.0055	Breakthrough Asahi LS-6	17
	$^{137}Ba^{2+}$-$^{138}Ba^{2+}$	1.0000053	0.0053	0.0053	Breakthrough Asahi LS-6	17

Conclusions

Separation of magnesium isotopes was investigated by chemical ion exchange with the 1-aza-12-crown-4 bonded Merrifield peptide resin using an elution chromatographic technique. The capacity of the novel monoazacrown ion exchanger was 1.0 meq/g dry resin. The heavier isotopes of magnesium were enriched 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 $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ were 1.008, 1.019, and 1.006, respectively.

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References

1. Roberts, H.; Curtis, H. *J. Res. Nat. Bur. Stand.* **1948**, *41*, 41.
2. Martin, H.; Harmsen, E. *Z. Elecktrochem.* **1958**, *2*, 153.
3. Konstantinov, B.; Bakulin, P. E. A. *Russ. J. Phys.Chem.* **1965**, *39*, 1.
4. Neubert, A.; Klemm, A. *Z. Naturforsch.* **1961**, *16a*, 685.
5. Aaltonen, J. *Suom. Kemi.* **1971**, *B44*, 1.
6. Jepson, B. E.; De Witt, R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1175.
7. Nishizawa, K.; Nishida, T.; Miki, T.; Yamamoto, T.; Hosoe, M. *Separ. Sci. Technol.* **1996**, *31*, 643.
8. Kim, D. W.; Kim, B. G.; Kim, C. S.; Jeong, Y. K.; Kim, J. S.; Jeon, Y. S. *J. Radioanal. Nucl. Chem.* **1997**, *222*, 253
9. Arnold, K. A.; Viscariello, A. M.; Kim, M.; Gandour, R. D.; Fronczek, F. R.; Gokel, G. W. *Tetrahedron Lett.* **1988**, *29*, 3025.
10. Arnold, K. A.; Mallen, J.; Trafton, J. E.; White, B. D.; Fronczek, F. R.; Gehrig, L.M.; Gandour, R. D.; Gokel, G. W. *J. Org. Chem.* **1988**, *53*, 5652.
11. Sakamoto, H.; Kimura, K.; Koseki, Y.; Matsudo, M.; Shono, T. *J. Org. Chem.* **1986**, *51*, 4974.
12. Dorfner, K. *Ionenaustauscher*; Dritte Aufl. Walter de Gruyter: Berlin, 1970; p 47.

13. Kim, D. W.; Kim, C. S.; Choi, K. Y.; Lee, Y. I.; Hong, C. P.; Kwon, H. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 716.
14. Dorfner, K. *Ionenaustauscher*; Dritte Aufl. Walter de Gruyter: Berlin, 1970; pp 292-299.
15. Glueckauf, E. *Trans. Faraday Soc.* **1955**, *51*, 34.
16. Glueckauf, E. *Trans. Faraday Soc.* **1958**, *54*, 1203.
17. Kondoh, A.; Oi, T.; Hosoe, M. *Separ. Sci. Technol.* **1996**, *31*, 39.
18. Heumann, K. G.; Lieser, K. H. *Z. Naturforsch*. **1972**, *27b*, 126.
19. Oi, T.; Ogino, H.; Hosoe, M.; Kakihana, H. *Separ. Sci. Technol.* **1992**, *27*, 631.
20. Ooi, K.; Miyai, Y.; Makita, Y.; Kanoh, H. *Separ. Sci. Technol.* **1999**, *34*, 1133.
21. Jepson, B. E.; Novotny, M. A.; Evans, W. F. *Mound Activities in Chemical and Physical Reseach* : January-December 1990, MLM-3695; EG&G Mound Applied Technologies: 1991; p 30.
22. Fujine, S.; Saito, K.; Shiba, K. *J. Nucl. Sci. Technol.* **1983**, *20*, 439.
23. Oi, T.; Kawada, K.; Hosoe, M.; Kakihana, H. *Separ. Sci. Technol.* **1991**, *26*, 1353.
24. Klinskii, G. D.; Knyazev, D. A.; Vlasova, G. I. *Zh. Fiz. Khim.* **1974**, *48*, 659.
25. Heumann, K. G.; Schiefer, H. P. *Angew. Chem.* **1980**, *92*, 406.
26. Aaltonen, J.; Heumann, K. G.; Pietila, P. *Z. Narturforsch.* **1974**, *29b*, 190.
27. Lee, D. A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 161.