Chromatographic separation of magnesium isotopes by monoazacrown bonded Merrifield peptide resins

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Magnesium isotope separation was investigated by chemical ion exchange with the 1-aza-12-crown-4 (I) and the 1-aza-18-crown-6 (II) bonded Merrifield peptide resin using an elution chromatographic technique. The capacities of each novel monoazacrown ion exchanger were 1.0 meq/g for (I) and 2.3 meq/g for (II) bonded Merrifield peptide resins, respectively. The single stage separation factor was determined according to the method of GLUECKAUF from the elution curves and isotopic assays. The separation factors of magnesium isotope pairs, $^{24}\text{Mg}^{2+}$–$^{25}\text{Mg}^{2+}$, $^{24}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ and $^{25}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ were 1.015, 1.029, and 1.014 for (I) and 1.012, 1.024, and 1.009 for (II) bonded Merrifield peptide resin, respectively.

Introduction

Since PERDERSON reported the first results on the macrocyclic polyethers and their complexes with metal ions, many investigations in this new field have been performed. Macro cyclic 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, $^{63}\text{Cu}^{2+}$–$^{65}\text{Cu}^{2+}$ and $^{24}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ was first attempted by ROBERTS et al. and MARTIN et al. JEPSON et al. reported first that calcium isotope separation was investigated with calcium salt and macrocyclic polyethers. KONSTANTINOV et al. investigated the separation of $^{24}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ and $^{63}\text{Cu}^{2+}$–$^{65}\text{Cu}^{2+}$ isotope pairs in aqueous solutions of magnesium chloride and copper chloride using countercurrent electromigration. KONSTANTINOV et al. showed that, as the concentration of the magnesium chloride and copper chloride in the solutions increased, the relative difference in the mobilities of the isotopes $^{24}\text{Mg}^{2+}$ and $^{26}\text{Mg}^{2+}$ ions and the mobilities of the $^{63}\text{Cu}^{2+}$ and $^{65}\text{Cu}^{2+}$ ions also increased. He concluded that at high concentrations, magnesium and copper chloride may not be completely dissociated. NEUBERT et al. also reported the isotope enrichment of magnesium, calcium, strontium, and barium in the migration of ions in molten halides.

AALTONEN reported the separation of magnesium and calcium isotopes using recycling ion exchange technique. He found that the separation factors of magnesium isotopes, $^{25}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ and calcium isotopes, $^{40}\text{Ca}^{2+}$–$^{48}\text{Ca}^{2+}$ were 1.00016 and 1.00087, respectively. NISHIZAWA et al. obtained a separation factor of 1.0112 as a maximum value for the $^{24}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ isotope pair by a liquid-liquid extraction system using the DC18C6.

The production of isotopically enriched $^{24}\text{Mg}$ is important because the $^{24}\text{Mg}$ is a precursor of $^{22}\text{Na}$ through the nuclear reaction of $^{24}\text{Mg}(d,\alpha)^{22}\text{Na}$. The reaction product, $^{22}\text{Na}$, is one of the rare $\beta^+$/emitters and this isotope is used in various scientific fields as a source of annihilation radiation. Recently, KIM et al. carried out an elution chromatographic separation of magnesium isotopes with $\text{N}_3\text{O}_2$ azacrown ion exchanger, and obtained the separation factors for $^{24}\text{Mg}^{2+}$–$^{25}\text{Mg}^{2+}$, $^{24}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ and $^{25}\text{Mg}^{2+}$–$^{26}\text{Mg}^{2+}$ isotope pairs of 1.030, 1.027, and 1.009, respectively. They found that the heavier magnesium isotopes were enriched in the resin phase, while the lighter isotopes 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 alkaline earth metal ions.

In this work, magnesium isotope separation was examined using a novel 1-aza-12-crown-4 (I) and 1-aza-18-crown-6 (II) bonded Merrifield peptide resin by ion exchange elution chromatography.

Experimental

Materials and methods

The novel 1-aza-12-crown-4 (I) and the 1-aza-18-crown-6 (II) bonded Merrifield peptide resins were prepared by the method given in the literature. Magnesium chloride and sodium acetate were purchased from Sigma Chemical Co., USA. An atomic absorption spectrophotometer (Hitachi Z-8000) was used to determine the magnesium ion concentration in the solution. Measurement of magnesium isotope ratio was carried out using thermal ionization mass spectrometer (Finnigan MAT 262) with a rhenium double filament.
Magnesium of 1.0–2.0 µg with MAT 262 was loaded on the evaporation filament. Ionization was performed by passing a heating electric current through the ionization filament. After the ion beam intensities of $^{24}\text{Mg}^{2+}$, $^{25}\text{Mg}^{2+}$, and $^{26}\text{Mg}^{2+}$ became sufficiently high, the mass peaks of the magnesium isotope ions 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 $^{24}\text{Mg}^{2+}$ and $^{25}\text{Mg}^{2+}$ of each feed solution was an average of three measurements.

**Ion exchange capacity**

For the determination of the capacities of each monoazacrown ion exchanger (I) and (II) the titration method was used. Each portion of 1.0 g of ion exchange resins (200–400 mesh, H-form) was weighed accurately, and transferred into a 100 ml polyethylene vial equipped with a polyethylene screw top. Fifty milliliters of 0.1N NaOH solution containing 5% NaCl was added, and the polyethylene vials were stoppered and shaken in a mechanical shaking device at 20 °C for 24 hours. The reaction mixture was centrifuged for 5 minutes at 5,000 rpm, and then 20 ml of supernatant was titrated with 0.1N HCl solution. The capacity of ion exchanger was calculated as:

$$\text{Capacity} = \frac{[V_{\text{NaOH}} \times N_{\text{NaOH}}] - [V_{\text{HCl}} \times N_{\text{HCl}}] \times 2.5 \times 10^2}{m(100 - \% \text{H}_2\text{O})} \text{ meq/g} \quad (1)$$

where $V_{\text{NaOH}}$ is the volume of the aliquot taken for titration, $V_{\text{HCl}}$ is the equivalent volume of HCl in ml for the titration, $N_{\text{NaOH}}$ and $N_{\text{HCl}}$ are the normal concentration of NaOH and HCl, respectively, $m$ is the mass of air dried resins in g and, $\% \text{H}_2\text{O}$ is the weight percent of water in the resin. The capacity of monoazacrown ion exchange resin is expressed in milliequivalents per g of dry (water-free) resin. The factor of 2.5 in Eq. (1) indicated that the titrated volume of reaction solution is 2.5 times smaller than that of total volume.

**Separation of magnesium isotopes**

Two series of isotope separation experiments were carried out, one for (I), and one for (II) bonded Merrifield peptide resins. Other experimental conditions were the same in all cases. The monoazacrown bonded Merrifield peptide resins were slurried in sodium acetate 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 a water circulator (HAAKE A-80). Amount of 0.1 ml of 0.01M MgCl$_2$ solution was loaded on the top of the resin bed in each column. Two molar CH$_3$COONa solutions were 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. 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 (I) 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). On the other hand, the ion exchange capacity of 1-aza-18-crown-6 (II) was 2.3 meq/g dry resin. This value is also comparable to those of the strong acidic cation exchangers, NC-10 (1.9 meq/g) and NC-11 (2.0 meq/g). To obtain an accurate value of the separation factor, 10 samples have been analyzed, and the elution curve was found Gaussian so the theory of GLUECKAUF can be applied. A 35 cm long with 0.2 cm inner diameter ion exchange column has been used to obtain a substantial total separation from which the single stage separation factor was calculated.

The a chromatograms were obtained from column operations with 2.0M CH$_3$COONa solution at 20 °C. From the elution curves, the number of theoretical plates in each column was calculated by:

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

where $V_{\text{max}}$ is the peak elution volume, $\beta$ is the band width at the concentration $C = C_{\text{max}}$, and $C_{\text{max}}$ is the concentration of solute at the maximum peak height of the elution curve.

From the elution curves and isotopic assay data the single stage separation factors, $^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+}$, $^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+}$, $^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+}$, and $^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+}$ were determined by the GLUECKAUF theory. 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. As shown in Table 1, the magnesium isotope separation factors of the isotope pairs, $^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+}$, $^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+}$, and $^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+}$ were 1.015, 1.029, and 1.014 for (I), and 1.012, 1.024, and 1.009 for (II) bonded Merrifield peptide resins, respectively. These values are larger than that of the factor determined by AALTONEN. AALTONEN carried out an elution chromatographic separation of magnesium isotopes with a strongly acidic cation exchanger, Dowex 50X8, and reported that the value of the separation