

# Magnesium Isotope Effects by Ion Exchange Using Monoazacrown Bonded Merrifield Peptide Resin

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Magnesium Isotope Effects, Ion Exchange, Elution Chromatography

Magnesium isotope effects by ion exchange using monoazacrown (1-aza-18-crown-6) bonded Merrifield peptide resin were investigated. The capacity and distribution coefficient were determined. The separation factors,  $(^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+})_{\text{Resin}}/(^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+})_{\text{Solution}}$ ,  $(^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Resin}}/(^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Solution}}$ , and  $(^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Resin}}/(^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Solution}}$  were 1.0071, 1.0132, and 1.0068, respectively. The heavier magnesium isotopes were enriched in the solution phase, while the lighter isotopes were enriched in the resin phase. It was found that the hydration and isotope mass effects are more significant than that of the complexation.

## Introduction

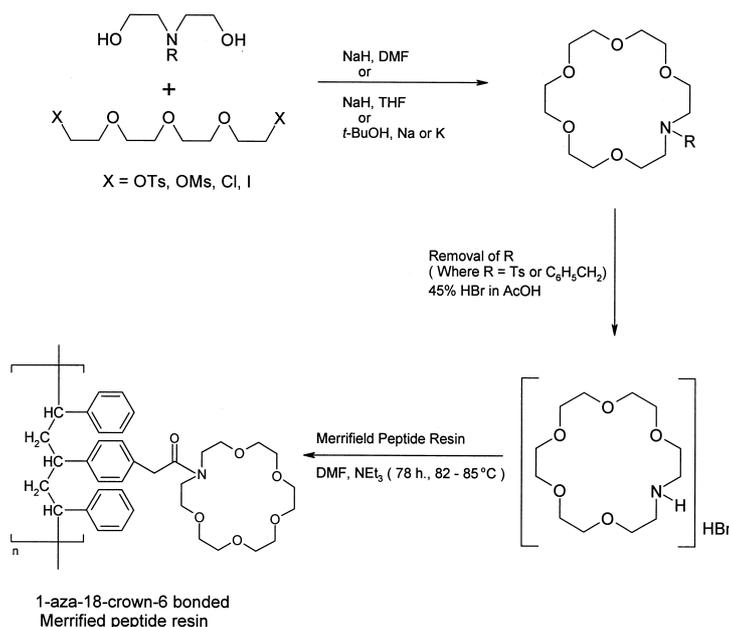
The separation of the pairs of the isotope ions  $^{63}\text{Cu}^{2+}$ – $^{65}\text{Cu}^{2+}$  and  $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$  was first attempted by Roberts *et al.* [1] and Martin *et al.* [2]. Konstantinov *et al.* [3] investigated the separation of  $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$  and  $^{63}\text{Cu}^{2+}$ – $^{65}\text{Cu}^{2+}$  isotope pairs in aqueous solutions of magnesium chloride and copper chloride using the method of counter-current electromigration. Aaltonen [4] reported the separations of magnesium and calcium isotopes using a recycle ion exchange technique. He found that the separation factors of magnesium,  $^{25}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$  and calcium,  $^{40}\text{Ca}^{2+}$ – $^{48}\text{Ca}^{2+}$  were 1.00016 and 1.00087, respectively. Nishizawa *et al.* [5] 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 DC18C6. The production of isotopically pure  $^{24}\text{Mg}$  is important because this magnesium isotope is a precursor of  $^{22}\text{Na}$  through the nuclear reaction of  $^{24}\text{Mg}(\text{d},\alpha)^{22}\text{Na}$ . 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 [5]. Ion exchange with macrocyclic compounds is a promising method for the separation of isotopes due to the larger separation factor and the ability of complexation with cations, especially, alkali and alkaline earth metal ions [6, 7]. In this work, mag-

nesium isotope effects were investigated using a novel 1-aza-18-crown-6 bonded Merrifield peptide resin by the ion exchange chromatography.

## Results and Discussion

The 1-aza-18-crown-6 bonded Merrifield peptide resin was prepared according to literature procedures [8–11] as shown in Scheme 1. In a TGA thermogram, the degradation of the triaza-crown polymer began at 285 °C and ended at 480 °C, and  $T_{\text{max}}$  was 375 °C.

The ion exchange capacity of the 1-aza-18-crown-6 bonded Merrifield peptide resin was found to be 2.3 meq/g dry resin. This value is in the same order of magnitude as AV-21 (anion exchanger, 2.3 meq/g), KF-3 (cation exchanger, 3.5 meq/g), and AN-20 (anion exchanger, 3.0 meq/g) [12]. The distribution coefficient ( $K_d$ ) of magnesium ion on the resin was measured by changing the concentration of an  $\text{NH}_4\text{Cl}$  solution from  $1.0 \times 10^{-3}$  M to 2.0 M using a batch method. As shown in Fig. 1, the distribution coefficient of magnesium ions on 1-aza-18-crown-6 bonded Merrifield peptide resin increases in a non-linear manner with increasing concentration. The elution time increased with the distribution coefficients due to the high adsorption of ion on the resin phase in the column. For this reason, as expected, the



Scheme 1. Synthetic routes in preparation of the 1-aza-18-crown-6 bonded Merrifield peptide resin.

eluent have the values of the  $K_d$  range from 30 to 300. The chromatogram was obtained from a column operation with 2.0 M NH<sub>4</sub>Cl solution ( $K_d = 156$ ) at 20 °C. From the elution curve, the number of theoretical plates,  $N$ , in the column was calculated by the equation [13]:

$$N = 8 \cdot \left( \frac{V_{\max}}{\beta} \right)^2 \quad (1)$$

where  $V_{\max}$  is the peak elution volume, and  $\beta$  the band width at the concentration  $C = C_{\max}/e$ , and

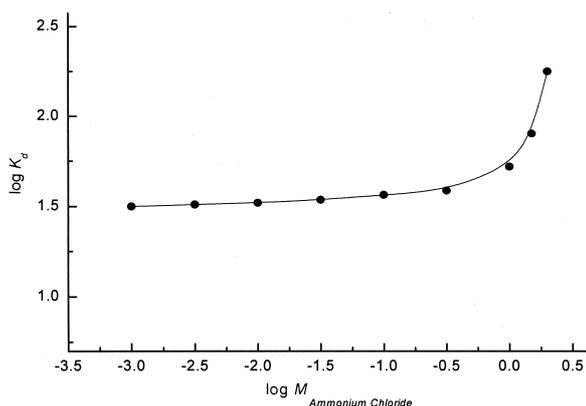


Fig. 1. Plot of  $\log K_d$  for magnesium ions on 1-aza-18-crown-6 bonded Merrifield peptide resin as a function of NH<sub>4</sub>Cl solution concentration.

$C_{\max}$  the concentration of solute at the maximum peak height of the elution curve.

From the elution curve and isotopic assay data, the separation factors,  $(^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+})_{\text{Resin}}/(^{24}\text{Mg}^{2+}/^{25}\text{Mg}^{2+})_{\text{Solution}}$ ,  $(^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Resin}}/(^{24}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Solution}}$ , and  $(^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Resin}}/(^{25}\text{Mg}^{2+}/^{26}\text{Mg}^{2+})_{\text{Solution}}$ , were calculated by the Glueckauf theory [14]. The data were plotted on probability paper where the abscissa was a probability scale and the ordinate was a linear scale. The isotopic 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 isotope ratio of the standard is denoted by  $C_1^0/C_2^0$  and the local enrichment factor,  $R$ , for a fraction by  $(C_1/C_2)/(C_1^0/C_2^0)$ . In addition,  $\Delta m/m$  is the proportion of total magnesium eluted in all fractions up to and including the particular fraction. 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  $\varepsilon\sqrt{N}$ , and the separation factor,  $\alpha$ , is  $\varepsilon + 1$ .  $\alpha$  was determined from the slope of a least squares line drawn through the points as shown in Fig. 2. In this experiment, the magnesium isotope separation factors for  $^{24}\text{Mg}^{2+}$ - $^{25}\text{Mg}^{2+}$ ,  $^{24}\text{Mg}^{2+}$ - $^{26}\text{Mg}^{2+}$ , and  $^{25}\text{Mg}^{2+}$ - $^{26}\text{Mg}^{2+}$  were obtained as 1.0071, 1.0132, and 1.0068, respectively. These values are larger than

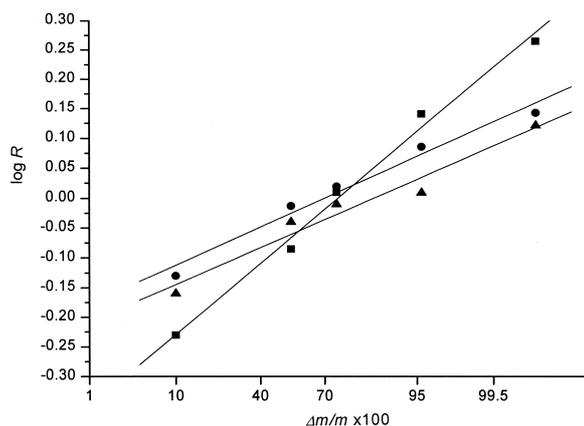
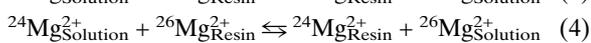
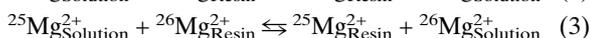
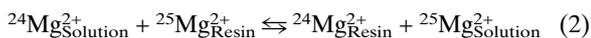


Fig. 2. Enrichment of magnesium isotopes by cation exchange chromatography. ●:  $^{24}\text{Mg}^{2+}$ – $^{25}\text{Mg}^{2+}$ , ■:  $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ , ▲:  $^{25}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ .

1.00016 given for the  $^{25}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$  pair [4] and 1.0112 for the  $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$  pair [5]. From the experimental data, it appears that the isotope exchange reaction can be represented by the following equations:



The subscripted symbols refer to the  $\text{NH}_4\text{Cl}$  solution and 1-aza-18-crown-6 bonded resin phase in this chemical isotope exchange. The data suggest that the complexing ability of the lighter isotope ions is larger than that of the heavier. It was 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 [4]. The investigators also reported that the heavier isotopes were preferentially enriched into the solution phase in chromatography using strongly acidic cation, anion, titanium phosphate and polymer-bound crown ether exchangers [15–20]. These results agree with our work. On the other hand, it was reported that the heavier isotopes were preferentially enriched in the resin phase in cation and anion exchange chromatography [21–27]. Halide ions are considered to be structure breakers, except for fluoride ion which is a structure maker [28–30]. It was

pointed out that the structure breaking property of the anions enhances the solvation of the cations [29]. Consequently, the solvation number of lithium ions increases in aqueous solutions. As the partial dehydration of the lithium ions in the exchange resin phase remains the same, this overall increase in the solvation of the lithium ions in solution in the presence of the structure breaker anions increases the difference of the hydration numbers of the ions in solution and resin phase, and hence the isotope effect [31]. This means that the structure breaking anions, such as chloride ions, produce a larger isotope effect. The heavier isotope ion has the larger hydration number than the lighter isotope ion [32, 33]. Therefore, the heavier isotope ion is enriched in the solution phase, and confirmed by our work. 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 [25]. These phenomena are also consistent with our system. The enrichment factor ( $\epsilon = \alpha - 1$ ) 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 [25]. In comparing the enrichment factor per mass unit ( $\epsilon/\Delta m$ ) for some divalent elements with increasing atomic mass, it was shown in Table 1 that the separation factor decreases as the mass number increases. Isotopes within approximately the same mass range may have an increase or decrease in the 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 [25]. From the experimental data, the separation factor increases as the mass difference of the isotope pairs increases, and the values of the enrichment factor per mass unit ( $\epsilon/\Delta m$ ) are approximately the same under the same experimental conditions. The magnesium isotope separation system in this work can, therefore, be explained by the fact that the hydration and isotope mass effects are more significant than those of complexation.

Table 1. The separation of isotopes of some divalent elements by ion exchange.

Atomic number	Isotope pair	Separation factor	$\epsilon \times 10^3$	$\frac{\epsilon}{\Delta m} \times 10^3$	Reference
12	$^{25}\text{Mg}^{2+} - ^{26}\text{Mg}^{2+}$	1.00016	0.16	0.16	4
	$^{24}\text{Mg}^{2+} - ^{26}\text{Mg}^{2+}$	1.0112	11.2	5.6	5
	$^{24}\text{Mg}^{2+} - ^{25}\text{Mg}^{2+}$	1.0071	7.1	7.1	this work
	$^{24}\text{Mg}^{2+} - ^{26}\text{Mg}^{2+}$	1.0132	13.2	6.6	this work
	$^{25}\text{Mg}^{2+} - ^{26}\text{Mg}^{2+}$	1.0068	6.8	6.8	this work
20	$^{40}\text{Ca}^{2+} - ^{44}\text{Ca}^{2+}$	1.00047	0.47	0.12	4
	$^{40}\text{Ca}^{2+} - ^{48}\text{Ca}^{2+}$	1.00087	0.87	0.11	4
	$^{40}\text{Ca}^{2+} - ^{47}\text{Ca}^{2+}$	1.00026	0.26	0.04	25
	$^{40}\text{Ca}^{2+} - ^{44}\text{Ca}^{2+}$	1.028	28	7	15
	$^{40}\text{Ca}^{2+} - ^{48}\text{Ca}^{2+}$	1.048	48	6	15
38	$^{84}\text{Sr}^{2+} - ^{88}\text{Sr}^{2+}$	1.0000036	0.0036	0.0009	17
	$^{86}\text{Sr}^{2+} - ^{88}\text{Sr}^{2+}$	1.0000023	0.0023	0.0012	17
	$^{87}\text{Sr}^{2+} - ^{88}\text{Sr}^{2+}$	1.00000097	0.00097	0.00097	17
56	$^{130}\text{Ba}^{2+} - ^{138}\text{Ba}^{2+}$	1.000032	0.032	0.004	16
	$^{135}\text{Ba}^{2+} - ^{138}\text{Ba}^{2+}$	1.000017	0.017	0.0057	16
	$^{137}\text{Ba}^{2+} - ^{138}\text{Ba}^{2+}$	1.0000071	0.0071	0.0071	16

## Experimental Section

### *Synthesis of 1-aza-18-crown-6 bonded Merrifield peptide resin*

Synthetic procedure of the resin is as follows [8–11]. In to 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  $\text{NEt}_3$ . The oily 1-aza-18-crown-6 in 50 ml of dry DMF was added slowly from an additional funnel. After the mixture was stirred for 72 h at 88–90 °C, the residue was washed with water and methanol to leave a yellow powder with a particle size of 200–400 mesh. The C–Cl stretching vibration of the Merrifield peptide resin was found at 690  $\text{cm}^{-1}$  in the IR spectrum. In the IR spectrum of the yellow product, the C–Cl absorption (KBr, 690  $\text{cm}^{-1}$ ) peak has a lower intensity. This indicates a N–C bond formation between a nitrogen atom of the crown and the Merrifield peptide resin.  $^1\text{H}$  NMR  $\delta$  2.53 (s, 1 H), 2.72 (t, 4 H), 3.57 (m, 16 H).

### *Reagents and apparatus*

$\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$  were purchased from Sigma Chemical Co., USA. An atomic absorption spectrophotometer (AAS, Hitachi Z-8000) was used to determine the magnesium ion concentration in the solution. Measurement of the magnesium isotope ratio was carried out using a thermal ionization mass spectrometer (Finnigan MAT 262) with a

rhenium double filament. An amount of 1.0–2.0  $\mu\text{g}$  of 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  $^{24}\text{Mg}^{2+}$ ,  $^{25}\text{Mg}^{2+}$ , and  $^{26}\text{Mg}^{2+}$  became sufficiently high, the  $^{24}\text{Mg}^{2+}$ ,  $^{25}\text{Mg}^{2+}$ , and  $^{26}\text{Mg}^{2+}$ , 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 fraction of  $^{24}\text{Mg}^{2+}$ ,  $^{25}\text{Mg}^{2+}$ , and  $^{26}\text{Mg}^{2+}$  of each feed solution was an average of three measurements.

### *Ion exchange capacity [34]*

The cation exchanger was transformed into the H-form by treatment with about one liter of 1.0 N HCl in the funnel. Subsequently, it was washed to neutrality with distilled water, and dried in air. Of this quantity, 1.000  $\pm$  0.005 g was weighed into a dry 250 ml Erlenmeyer flask containing 200 ml of 0.1 N NaOH with 5% sodium chloride, and was allowed to stand overnight. 1.0 g ion exchanger samples of the same material were 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 backtitrated with 0.1 N HCl against phenolphthalein. The capacity was then calculated by the equation:

$$\text{Capacity(meq/g)} = \frac{\{(200 \cdot \text{Normality}_{\text{NaOH}}) - 4(\text{mL}_{\text{acid}} \cdot \text{Normality}_{\text{acid}})\}}{\text{Sample Weight} \cdot (\% \text{Solid}/100)} \quad (5)$$

It represents the total weight of the exchanger in the dry H-form. The resin must be completely in the H-form before weighing of the sample, since a 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 complete exchange equilibrium by the excess of sodium ions. A reproducibility of  $\pm 1\%$  was obtained.

#### *Measurement of distribution coefficients [26–27]*

Each portion of 0.2 g of the 1-aza-18-crown-6 bonded Merrifield peptide resin, 200 ~ 400 mesh, which has been dried to constant weight at 60 °C, was weighed out 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 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, and the distribution coefficient,  $K_d$  calculated by the following equation:

$$K_d = \frac{(C_{st} - C_{eq})}{C_{eq}} \cdot \frac{V}{m} \quad (6)$$

where  $C_{st}$  is the metal ion concentration of the standard solution,  $C_{eq}$  the value after equilibration,  $V$  the total volume in ml of the solution, and  $m$  the mass in g of dry resin indicated.

#### *Separation of magnesium isotope [26–27]*

The 1-aza-18-crown-6 bonded Merrifield peptide resin 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.  $\times$  50 cm height). The temperature was maintained at 20 °C with a water circulator (HAAKE A-80). The amount of 500 ppm of magnesium ion in distilled water was loaded on the top of the resin bed. A 2.0 M  $\text{NH}_4\text{Cl}$  solution ( $K_d = 156$ ) 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).

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