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# Magnesium Isotope Fractionation in Cation-Exchange Chromatography

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## Abstract

Band displacement chromatography of magnesium has been carried out successfully for the purpose of magnesium isotope separation by using a strongly acidic cation-exchange resin and the strontium ion as the replacement ion. A small but definite accumulation of the heavier isotopes ($^{25}Mg$, $^{26}Mg$) has been observed at the front parts of the magnesium chromatograms. The heavier isotopes have been fractionated preferentially into the solution phase. The single-stage separation factors have been calculated for the $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ isotopic pairs at 25°C. The reduced partition function ratios of magnesium species involved in the present study have been estimated.

## INTRODUCTION

Magnesium, an important element of living bodies as well as of the earth's crust, has three stable isotopes: $^{24}Mg$ (atomic percent = 78.992%), $^{25}Mg$ (10.003%), and $^{26}Mg$ (11.005%) (*1*), but it has no appropriate radioactive isotope that can be used as a tracer. Thus, the demand for and the use of enriched stable Mg isotopes are expected to increase if they are available at reasonable costs.

Ion-exchange chromatography has been studied as a possible practical method for isotope separation. In 1955, Spedding et al. (*2*) enriched $^{15}N$ to 74% from its original value of 0.365%. Based on a fundamental study by Kakihana et al. (*3*), Aida et al. (*4*) enriched $^{10}B$ from ~20% to over 98% using a weakly basic anion-exchange resin. Under the initial guidance of Kakihana, Seko et al. (*5*) at Asahi Chemical Industry Co. are investigating a $^{235}U$ enrichment process using the U(IV)–U(VI) redox reaction with the goal of commercial production of fuel-grade uranium. Other elements whose isotope separation by ion-exchange chromatography was studied include such important elements as lithium (*6*), carbon (*7*), and sulfur (*8*).

To the best of our knowledge, the only previous work on ion-exchange chromatographic separation of Mg isotopes was by Aaltonen (*9*). By using the elution chromatography technique, he obtained a single-stage separation factor $S(26/25)$ for the $^{26}Mg/^{25}Mg$ isotopic pair. Unfortunately, the accuracy of the $S$ value obtained is unknown.

In this paper we report on the results of a fundamental study on cation-exchange chromatographic separation of Mg isotopes. The aim of the study was twofold: to realize band displacement chromatography, which is regarded as the most appropriate technique for isotope separation among various chromatographic techniques, and to obtain the values of separation factors with a certain accuracy. We also report on the estimation of the isotopic reduced partition function ratios (RPFRs) of the Mg species involved in the present chromatographic systems and on the estimation of equilibrium constants of some Mg isotope exchange reactions.

## EXPERIMENTAL

### Reagents

The ion-exchange resin used was a highly porous, strongly acidic cation-exchange resin, Asahi LS-6, 100–200 mesh. All reagents were of analytical-reagent grade and were used without further purification.

### Chromatographic Process

The cation-exchange resin was packed in chromatographic columns (1 cm inner diameter × 110 cm length, made of Pyrex glass, with water jackets) and was conditioned to the $H^+$ form by ~0.15 $M$ (1 $M$ = 1 mol/dm$^3$) HCl solution. For each run, two columns were connected in series with a Teflon tube (1 mm inner diameter), so that the total resin bed height was ~200 cm.

A Mg feed solution was fed to the first column at a constant rate by a peristaltic pump to form an Mg adsorption band. When the Mg band had grown to be of an appropriate length (20–30 cm), the supply of the feed solution was stopped, and immediately after that an eluent (strontium ion $Sr^{2+}$ was used as the replacement ion for $Mg^{2+}$) was fed to the column at the same speed at which the feed solution had been fed. The Mg band moved downward as elution proceeded, and finally came out of the second column. The effluent from the bottom of the second column was collected and portioned into small fractions (2 $cm^3$) by a fraction collector.

The temperature of the columns was kept constant throughout an experiment by passing temperature-controlled water through water jackets surrounding the columns.

Three experiments were carried out. In the first experiment (Run MgL8602), an $MgCl_2$ solution was used as the feed solution, so that we could determine the direction and the magnitude of Mg isotope effect in ion exchange since in this system no appreciable complex formation between $Mg^{2+}$ and chloride ion ($Cl^-$) was expected. In the second experiment (Run MgL8603), the system contained acetate ion ($Ac^-$), and $Mg^{2+}$ formed complexes with $Ac^-$ in and outside the ion-exchange resin. Thus, it was expected in the second experiment that we could determine the direction and the magnitude of the Mg isotope effect in $Mg^{2+}$–$Ac^-$ complex formation in addition to those in ion exchange. Similar results were expected in the third experiment (Run MgL8606) between $Mg^{2+}$ and lactate ion ($La^-$). The experimental conditions are summarized in Table 1.

### Analysis

The Mg concentration in each fraction of the effluent was determined by a Model SAS-727 Atomic Absorption Spectrometer (Daini Seikosha Co.). For several fractions from the front parts of the Mg bands, the isotopic ratios $^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$ were determined by the thermal ionization technique by using a MAT 261 mass spectrometer with a secondary electron multiplier as the detector. All the isotopic data measured were calibrated against the NBS standard (*1*).

## RESULTS AND DISCUSSION

Elution curves and isotopic ratios of the three experiments are shown in Figs. 1, 2, and 3. In the lower half of each figure are shown the Mg concentration profile and the pH of the effluent. It is seen that in every

TABLE 1
Experimental Conditions and Separation Factors

| | Run | | |
|---|---|---|---|
| | MgL8602 | MgL8603 | MgL8606 |
| Temperature (°C) | $24.5 \pm 1.0$ | $25.0 \pm 1.0$ | $24.5 \pm 1.0$ |
| Mg feed solution | 0.1 *M* $MgCl_2$<br>(pH 7.52) | 0.1 *M* $Mg(CH_3COO)_2$<br>+ 0.3 *M* $CH_3COOH$<br>(pH 4.27) | 0.1 *M* MgO<br>+ 0.2 *M* $CH_3CHOHCOOH$<br>(pH 4.58) |
| Eluent | 0.1 *M* $SrCl_2$<br>(pH 5.65) | 0.1 *M* $Sr(CH_3COO)_2$<br>+ 0.3 *M* $CH_3COOH$<br>(pH 4.32) | 0.2 *M* $Sr(CH_3CHOHCOO)_2$<br>(pH 4.33) |
| Resin bed height (cm) | 203.8 | 199.3 | 197.7 |
| Mg band length (cm) | 29.8 | 28.7 | 18.4 |
| Flow rate ($cm^3cm^{-2}h^{-1}$) | 6.93 | 6.61 | 6.46 |
| Band velocity (cm/h) | 1.17 | 1.06 | 1.00 |
| *S* for $^{25}Mg/^{24}Mg$ | 1.000035<br>$\pm$ 0.000007 | 1.000019<br>$\pm$ 0.000008 | 1.000066<br>$\pm$ 0.000009 |
| *S* for $^{26}Mg/^{24}Mg$ | 1.000069<br>$\pm$ 0.000013 | 1.000020<br>$\pm$ 0.000014 | 1.000221<br>$\pm$ 0.000016 |

experiment the Mg band has sharp boundaries at both ends, and thus band displacement chromatography was realized almost ideally.

In the upper parts of the figures are shown the isotopic ratios $^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$. Error bars indicate the 95% confidence limits calculated from the repeated measurements. It is seen in every experiment that the heavier isotopes ($^{25}Mg$, $^{26}Mg$) are enriched at the front part of the Mg band, i.e., they are preferentially fractionated into the solution phase. Although isotopic measurements were not made for the rear parts of the Mg bands, mainly due to economic reasons, we can expect that the rear parts are enriched in the lighter isotope, $^{24}Mg$.

For each of the experiments the single-stage separation factors, *S*(25/24) for the $^{25}Mg/^{24}Mg$ isotopic pair and *S*(26/24) for the $^{26}Mg/^{24}Mg$ pair, were calculated using the equation (*10*)

$$S = 1 + \Sigma(R_i - R_o)f_i/[QR_o(1 - R_o)] \tag{1}$$

where, assuming a two-isotope system, $R_o$ is the isotopic mole fraction of

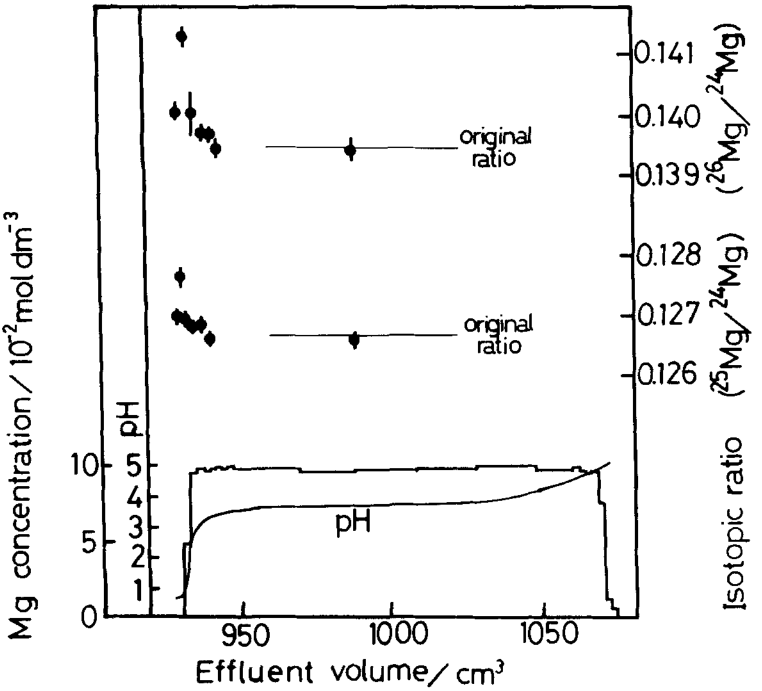

FIG. 1. Chromatogram and Mg isotopic ratios of Run MgL8602. Experimental conditions are summarized in Table 1. Error bars on isotopic ratios show 95% confidence limits calculated from repeated measurements.

the heavier isotope in the feed solution, $R_i$ is that in the $i$th fraction, $f_i$ is the amount of Mg in the $i$th fraction, $Q$ is the total exchange capacity of the column, and the summation is taken over all fractions enriched in the heavier isotope. The $S$ values obtained are listed in the last two rows of Table 1. It is seen in the table that all $S$'s are larger than unity and that $S(26/24)$ is larger than $S(25/24)$ in every experiment. The former result corresponds to the fact that the heavier isotopes are enriched at the front parts of the Mg bands. The latter result indicates that the larger the isotopic mass difference, the larger is the isotope effect. Errors in the $S$ values result mostly from errors in the isotopic ratio measurements because the errors from other sources are minimal. Accidentally or not, our $S(26/25) \simeq S(26/24)/S(25/24) = 1.00016$ of the $Mg^{2+}$-$La^-$ system (Run MgL8606) is in good agreement with that of Aaltonen ($S(26/25) = 1.00016$)) (9). His experiment was also carried out in the $Mg^{2+}$-$La^-$ system but the temperature of his experiment was not specified.

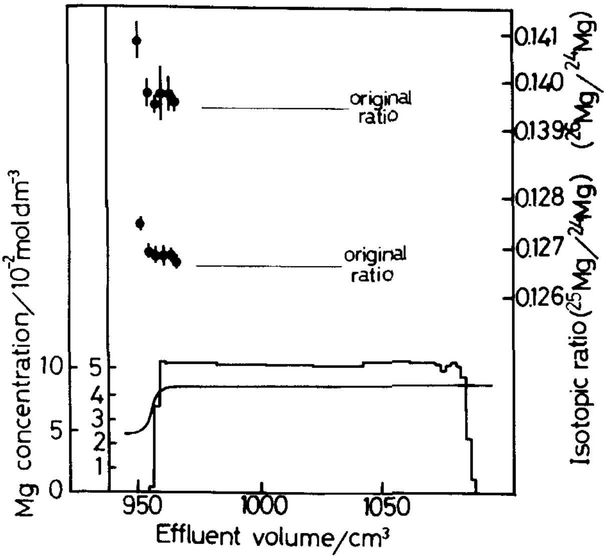

FIG. 2. Chromatogram and Mg isotopic ratios of Run MgL8603. Experimental conditions are summarized in Table 1. Error bars on isotopic ratios show 95% confidence limits calculated from repeated measurements.

## Band Displacement Chromatography

As stated before, band displacement chromatography was used for each of the three experiments. The sharp front edge of the Mg band is due to the fact that the equilibrium constant of the ion-exchange reaction

$$Mg^{2+} + 2\overline{H^+} = \overline{Mg^{2+}} + 2H^+ \qquad (2)$$

is much larger than unity. Similarly, the sharp rear edge is due to the fact that the equilibrium constant of the ion-exchange reaction

$$\overline{Mg^{2+}} + Sr^{2+} = Mg^{2+} + \overline{Sr^{2+}} \qquad (3)$$

is much larger than unity. In Eqs. (2) and (3), the species with overbars mean they exist in the resin phase and the species without overbars mean they are in the solution phase, and the existence of ligands and hydrating water molecules is ignored.

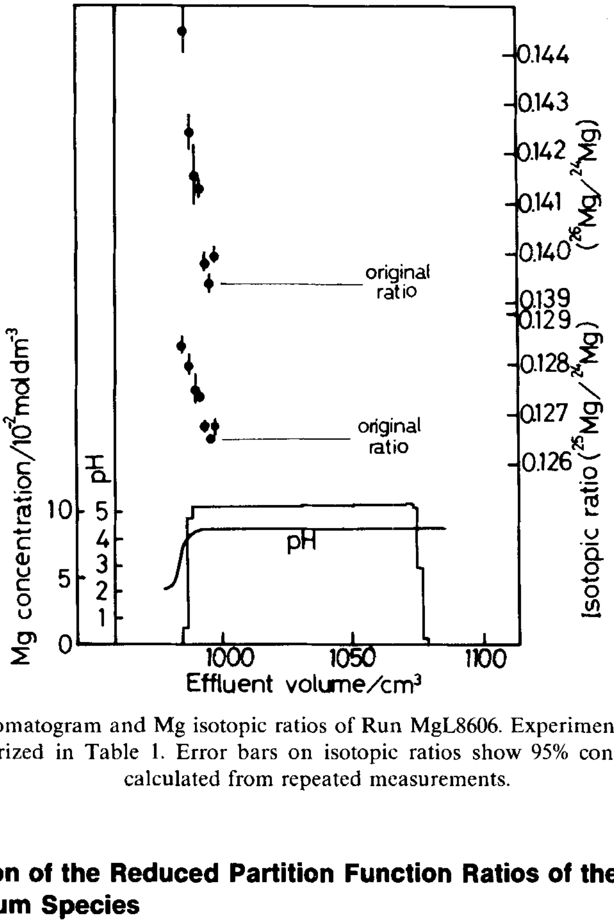

FIG. 3. Chromatogram and Mg isotopic ratios of Run MgL8606. Experimental conditions are summarized in Table 1. Error bars on isotopic ratios show 95% confidence limits calculated from repeated measurements.

## Estimation of the Reduced Partition Function Ratios of the Magnesium Species

It is possible to estimate the isotopic reduced partition function ratios (RPFRs) of the Mg species involved in the present study by using the separation factor data, Bigeleisen and Mayer's simplifying formula of the RPFR (*11*), and the theory of isotope distribution between two phases (*12*). For $Mg^{2+}$-$Ac^-$ and $Mg^{2+}$-$La^-$ systems, $S$ can be expressed as (*12*)

$$\ln S = \ln (x_{Mg^{2+}} f_{Mg^{2+}} + x_{MgL^+} f_{MgL^+}) - \ln (\bar{x}_{Mg^{2+}} \bar{f}_{Mg^{2+}} + \bar{x}_{MgL^+} \bar{f}_{MgL^+}) \tag{4}$$

where $x_A$ and $\bar{x}_A$ are the mole fractions of Species A in the solution phase and in the resin phase ($x_{Mg^{2+}} + x_{MgL^+} = 1$ and $\bar{x}_{Mg^{2+}} + \bar{x}_{MgL^+} = 1$), respectively; $f_A$ and $\bar{f}_A$ are the RPFRs of Species A in the solution phase and in the resin phase, respectively; and L = $Ac^-$ or $La^-$. Under the present experimental conditions there are no higher order complexes between $Mg^{2+}$ and $Ac^-$ or $La^-$ (*13*). Hydration of the Mg species such as $Mg(H_2O)_6^{2+}$ is not shown for simplicity in Eq. (4) or in the following equations, but it should be kept in mind that all the Mg species are hydrated both in the solution phase and in the resin phase and that hydration plays an important role in isotope effects in aqueous systems. For the $Mg^{2+}$-$Cl^-$ system, $x_{MgL^+} = \bar{x}_{MgL^+} = 0$ (L = $Cl^-$) and thus Eq. (4) is simplified to

$$\ln S = \ln (f_{Mg^{2+}}/\bar{f}_{Mg^{2+}}) \tag{5}$$

that is, the separation factors of the $Mg^{2+}$-$Cl^-$ system (Run MgL8602) are nothing but the equilibrium constants of the following isotope exchange reaction between the solution and the resin phases:

$$Mg'^{2+} + \overline{Mg}^{2+} = Mg^{2+} + \overline{Mg}'^{2+} \tag{6}$$

where the primed quantity refers to the lighter isotope and the nonprimed quantity refers to the heavier isotope.

If an atom is symmetrically surrounded by $n$ identical atoms of mass $m$, the RPFR of the central atom can be approximated (*11*), omitting symmetry numbers,

$$\ln f = \frac{nm\Delta M}{24MM'}\left(\frac{hc\omega}{kT}\right)^2 \tag{7}$$

where $M$ and $M'$ are the masses of the heavier and lighter isotopes of the central atom, respectively, $\Delta M = M - M'$; $h$ is the Planck constant; $c$ is the velocity of light; $\omega$ is the totally symmetric stretching frequency in $cm^{-1}$; $k$ is the Boltzman constant; and $T$ is the temperature. The RPFR of the noncoordinated $Mg^{2+}$ in the solution phase, $f_{Mg^{2+}}$, can be estimated by using Eq. (7) and regarding a hydrating water molecule as an atom. The $Mg^{2+}$-$H_2O$ symmetric stretching frequency was observed at 360 $cm^{-1}$ (*14*) and the hydration number $n$ is considered to be 6 (*15*). Once the value of $f_{Mg^{2+}}$ is known, $\bar{f}_{Mg^{2+}}$ can be calculated by using Eq. (5).

To estimate the RPFRs of ligand-coordinated Mg species in and outside the resin phase, one needs to know the mole fractions of these species, $x_{MgL^+}$ and $\bar{x}_{MgL^+}$. Mole fractions in the solution phase can be calculated using the known stability constants of $MgAc^+$ (*16*) and $MgLa^+$ (*17*) and the dissociation constants of acetic acid (*18*) and lactic acid (*19*). Those in the resin phase can be calculated from knowledge of the Mg band velocities in the $Mg^{2+}$-$Ac^-$ and $Mg^{2+}$-$La^-$ systems relative to the velocity in the $Mg^{2+}$-$Cl^-$ system. The mole fractions thus obtained are listed in Table 2. By using these values and a reasonably assumed simplifying relation,

$$f_{MgL^+}/f_{Mg^{2+}} = \bar{f}_{MgL^+}/\bar{f}_{Mg^{2+}} \tag{8}$$

the RPFRs of all the Mg species involved in the present study were estimated and the results are summarized in Table 3. The following points may be extracted from the table:

(1) For a given Mg species, the RPFR value for the $^{26}Mg/^{24}Mg$ isotopic pair is larger than that for the $^{25}Mg/^{24}Mg$ pair. This can easily be understood with the help of Eq. (7).

(2) For a given isotopic pair, any Mg species studied has a slightly larger RPFR value in the solution phase than in the resin phase. This indicates that each Mg species is more stable in the solution phase than in the resin phase. At the same time, however, the very slight difference in RPFR values between the solution and resin phases means that the conditions a species undergoes are very similar in the two phases.

(3) For a given isotopic pair, the RPFR of $MgLa^+$ is largest, that of $MgAc^+$ is smallest, and that of $Mg^{2+}$ is in between the other phases. That is, the lactate complex is more stable than the simple hydrated $Mg^{2+}$ while the acetate complex is less stable than $Mg^{2+}$. The opposite coordination effect of acetic acid and lactic acid to the RPFR may be due to the difference in the nature of coordination (*20*) between the two carboxylic acids, for which we presently have no evidence. Spectroscopic and structural investigation on various Mg carboxylates in aqueous systems as well as the accumulation of separation factor data are certainly needed to give a satisfactory explanation to the Mg isotope effect observed in aqueous systems.

TABLE 2

Mole Fractions of the Mg Species In and Outside the Resin Phase

| Run | System | $x_{Mg^{2+}}$ | $\bar{x}_{Mg^{2+}}$ | $x_{MgL^+}$ | $\bar{x}_{MgL^+}$ |
|---|---|---|---|---|---|
| MgL8602 | $Mg^{2+}$-$Cl^-$ | 1.000 | 1.000 | 0.000 | 0.000 |
| MgL8603 | $Mg^{2+}$-$Ac^-$ | 0.349 | 0.741 | 0.651 | 0.259 |
| MgL8606 | $Mg^{2+}$-$La^-$ | 0.259 | 0.665 | 0.741 | 0.335 |

TABLE 3
Values of the Reduced Partition Function Ratios of the Mg Species at 25°C

| Species[a] | Phase | Isotopic pair | |
|---|---|---|---|
| | | $^{25}Mg/^{24}Mg$ | $^{26}Mg/^{24}Mg$ |
| $Mg^{2+}$ | Solution | 1.022965 | 1.044545 |
| | Resin | 1.022929 | 1.044473 |
| $MgAc^{+}$ | Solution | 1.022923 | 1.044414 |
| | Resin | 1.022887 | 1.044342 |
| $MgLa^{+}$ | Solution | 1.023043 | 1.044936 |
| | Resin | 1.023007 | 1.044864 |

[a] The existence of hydrating water molecules is ignored in the expression.

The hydration number of $Mg^{2+}$, $n = 6$, is highly probable but not definite. For example, Glueckauf (*21*) estimated $n = 5.1$. Also, different authors report different values (*13*) for the stability constants of the Mg complexes and dissociation constants of acetic and lactic acids. Since these quantities have profound effects on the absolute value of a RPFR, and also because of some approximations employed in our RPFR calculations (cf. Eqs. 7 and 8) and experimental errors, the values in Table 3 are probably not very accurate. However, the basic results of RPFR calculations for the Mg species remain unaffected, and the relative order of the magnitudes of the RPFR values in Table 3 is unchanged even if we adopt different values for the stability constants, dissociation constants, and/or hydration numbers.

## Equilibrium Constants of Some Magnesium Isotope Exchange Reactions

Combinations of the RPFRs in Table 3 give equilibrium constants, *K*, of Mg isotope exchange reactions among the Mg species involved in the present study. Some of them are listed in Table 4.

The first reaction corresponds to the isotope effect in pure ion exchange, and the second and the third correspond to isotope effects in complex formations. The ln *K*'s of the second reaction are negative and those of the third reaction are positive. This explains why the separation factors of the $Mg^{2+}$-$La^{-}$ system are larger than those of the $Mg^{2+}$-$Cl^{-}$ system, whereas the separation factors of the $Mg^{2+}$-$Ac^{-}$ system are smaller than those of the $Mg^{2+}$-$Cl^{-}$ system. That is, in the $Mg^{2+}$-$Ac^{-}$ system (Run MgL8603), the directions of the Mg isotope effects in ion

TABLE 4
Values of Equilibrium Constants, *K*, of Some Mg Isotope Exchange Reactions at 25°C[a]

| | ln *K* | |
|---|---|---|
| Reaction | $^{25}Mg/^{24}Mg$ | $^{26}Mg/^{24}Mg$ |
| $\overline{Mg^{2+}} + Mg'^{2+} = \overline{Mg'^{2+}} + Mg^{2+}$ | 0.000035 | 0.000069 |
| $Mg^{2+} + Mg'Ac^{+} = Mg'^{2+} + MgAc^{+}$ | −0.000041 | −0.000125 |
| $Mg^{2+} + Mg'La^{+} = Mg'^{2+} + MgLa^{+}$ | 0.000076 | 0.000374 |
| $\overline{MgAc^{+}} + Mg'La^{+} = \overline{Mg'Ac^{+}} + MgLa^{+}$ | 0.000152 | 0.000569 |

[a] Species with an overbar indicate they exist in the resin phase and those without an overbar indicate they are in the solution phase. Mg′ refers to the lighter isotope and Mg refers to the heavier isotope. Ac is acetate ion and La is lactate ion.

exchange and in complex formation are opposite to each other, whereas both effects are in the same direction in the $Mg^{2+}$-$La^{-}$ system (Run MgL8606).

The opposite trends of the Mg isotope effect in complex formations between $Mg^{2+}$ and $Ac^{-}$ and between $Mg^{2+}$ and $La^{-}$ are due to the order of the RPFR values of $Mg^{2+}$-$La^{-}$ > $Mg^{2+}$ > $Mg^{2+}$-$Ac^{-}$.

The last reaction of Table 4 gives the largest Mg isotope effect among all the possible isotope exchange reactions involved in the present study. This situation might be realized when the ion-exchange resin has the $CH_3COO^{-}$ exchange group and the Mg feed solution contains magnesium lactate.

## Hydration of $Mg^{2+}$ in the Resin Phase

If we assume that the hydration number of $Mg^{2+}$ in the resin phase, $\bar{n}$, is 5, and the symmetric $Mg^{2+}$-$H_2O$ stretching frequency is 360 $cm^{-1}$ (the same as the one observed in aqueous solution), then we obtain for the first reaction of Table 4 ln *K*(25/24) = 0.00363 and ln *K*(26/24) = 0.00726, two orders of magnitude larger than those of Table 4. This suggests that $\bar{n}$ cannot be very different from that in the solution phase, *n*; hydration circumstances around $Mg^{2+}$ in the resin phase and the solution phases are very similar. In fact, assuming $\bar{n} = 6$, the symmetric $Mg^{2+}$-$H_2O$ stretching frequency, with which the experimental separation factors can be reproduced, is calculated to be 359.71 $cm^{-1}$. Thus, the small Mg isotope effect in ion exchange is due to the similarity in the hydration circumstances around $Mg^{2+}$ between the two phases.

## CONCLUSION

Band displacement chromatography of magnesium was successfully carried out using a strongly acidic cation-exchange resin and the strontium ion as the replacement ion for $Mg^{2+}$ for the purpose of Mg isotope separation. The heavier isotopes ($^{25}Mg$, $^{26}Mg$) are enriched in the front parts of the Mg bands. The separation factors obtained at 25°C are 1.000035 and 1.000069 for the $^{25}Mg/^{24}Mg$ isotopic pair and for the $^{26}Mg/^{24}Mg$ pair in the $Mg^{2+}$-$Cl^-$ system, respectively, 1.000019 and 1.000020 for $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ in the $Mg^{2+}$-$Ac^-$ system, respectively, and 1.000066 and 1.000221 for $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ in the $Mg^{2+}$-$La^-$ system, respectively.

The reduced partition function ratios of the Mg species involved in the present study have been estimated, and some equilibrium constants of Mg isotope exchange reactions have also been calculated.

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