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Fractionation of Calcium Isotopes in Cation-Exchange Chromatography

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ABSTRACT

Ion-exchange displacement chromatography of calcium has been carried out successfully for the purpose of observing calcium isotope fractionation effects. Small but definite accumulation of the heavier isotopes has been observed at the front parts of the calcium adsorption bands, which means they are preferentially fractionated into the solution phase. The average values of the single-stage separation factor minus one per unit mass difference between isotopes ($\epsilon/\Delta M$) have been 2.0×10^{-5} for the calcium chloride system, 5.2×10^{-5} for the calcium lactate system, and 2.3×10^{-5} for the calcium acetate system at 25°C. The reduced partition function ratios of the calcium species involved in the present study have been estimated by using separation factor data and available data on calcium hydration under appropriate assumptions. The reduced partition function ratios of the complex species have been found to be larger than that of the simple hydrated calcium ion, which is a cause of the experimental results that the separation factor values of the calcium lactate and acetate systems are larger than that of the calcium chloride system. It has also been found that, for the alkali and alkaline earth metals, the magnitude of isotope effect per unit mass difference between isotopes accompanying pure ion exchange is nearly inversely proportional to the square of the atomic mass.

INTRODUCTION

The separation of stable isotopes of calcium is presently being accomplished with electromagnetic separators (calutrons) at Oak Ridge National

Laboratory (1, 2). The calcium isotopes produced by this electromagnetic method are expensive, and their use is very limited mainly due to high cost.

Chemical processes for separating the calcium isotopes have been studied as alternatives to the above-mentioned method. Ion-exchange chromatography is certainly one of them, and it has been investigated by various authors (3–10). Kobayashi et al. (11) reported the ion-exchange chromatographic calcium isotope separation system with an electromigration counterflow.

In general, the enrichment of calcium isotopes by ion-exchange chromatography seems at present impractical mostly due to small isotope separation effects. Apart from the practical aspect, however, there is a continuing interest in investigating calcium isotope effects in ion-exchange systems. Their directions and magnitudes observed in such systems are important in and will contribute to fertilizing the basic isotope effect theory, together with those of the other alkaline earth metals, magnesium (8, 13) and strontium (14, 15). Calcium isotopes may also provide another example of odd-even anomaly in isotope effects which could be attributable to the odd-even difference in the mass number of isotopes and has been found for uranium isotopes by Fujii et al. (16, 17).

This paper reports the results of a fundamental study on cation-exchange chromatographic separation of calcium isotopes. Single-stage separation factor values obtained for the calcium isotopes are compared with those of the other alkaline earth metals and the alkali metals. The isotopic reduced partition function ratios (RPFRs) of the calcium species involved in the present experiments are estimated by analyzing the experimental results under a few reasonable assumptions.

EXPERIMENTAL

Reagents

The ion-exchange resin used was a highly porous, strongly acidic cation exchange resin, Asahi LS-6, in the H^+ form, 100–200 mesh, having sulfo groups ($—SO_3^- H^+$) as the exchange group. The exchange capacity of the resin in the H^+ form (dried at 80°C and at 5 torr for 24 hours) was 2.75 meq/g. Reagents, used without further purification, were all Wako's special-grade chemicals, and the pure water used was distilled water.

Chromatographic Process

Three experiments were carried out, one in the breakthrough operation and two in the band displacement operation. Experimental conditions are

summarized in Table 1. For each experiment, two chromatographic columns (210 cm in length × 10 mm in inner diameter, made of Pyrex glass, with a water jacket) were connected in series with a Teflon tube (1 mm in inner diameter), so that the total resin bed height was ~400 cm. In the breakthrough experiment (Ca8801), a calcium feed solution was fed to the first column packed with the resin in the H^+ form at a constant rate by a peristaltic pump, and the effluent from the second column was collected and portioned into fractions of 5 cm^3. In the band displacement experiments (Ca8803, Ca8804), calcium adsorption bands formed on the H^+-form resin bed were eluted by appropriate eluents containing barium ions as the replacement ion for Ca^{2+}. Effluents from the second columns were collected and portioned into fractions of 5 cm^3.

The temperature of the columns was kept at 25.0 ± 0.2°C throughout the experiment by passing temperature-controlled water through water jackets attached to the columns.

Analysis

For each of the fractions of the effluents, the pH was measured and the calcium concentration was determined by atomic absorption spectroscopy after appropriate dilution with pure water. For the feed solutions and several fractions in the front and rear parts of the calcium adsorption

TABLE 1
Experimental Conditions[a]

	Run		
	Ca8801	Ca8803	Ca8804
Operating manner	Breakthrough	Band	Band
Ca feed solution	0.106 *M* $CaCl_2$ (pH 7.10)	0.105 *M* $Ca[CH_3CH(OH)COO]_2$ + 0.30 *M* $CH_3CH(OH)COOH$ (pH 3.40)	0.104 *M* $Ca(CH_3COO)_2$ + 0.30 *M* CH_3COOH (pH 4.38)
Eluent	—	0.106 *M* $Ba[CH_3CH(OH)COO]_2$ + 0.30 *M* $CH_3CH(OH)COOH$ (pH 3.77)	0.0977 *M* $Ba(CH_3COO)_2$ + 0.30 *M* CH_3COOH (pH 4.42)
Resin bed height (cm)	400.3	403.5	393.3
Ca band length (cm)	—	30.2	27.0
Flow rate ($cm^3 \cdot cm^{-2} \cdot h^{-1}$)	6.33	6.48	8.13
Band velocity (cm/h)	1.23	1.16	1.43

[a] 1 *M* = 1 mol/dm^3; temperature = 25.0 ± 0.2°C; resin = strongly acidic cation-exchange resin, Asahi LS-6, H^+ form, 100–200 mesh.

bands (there was no rear part in Ca8801), the isotopic ratios, $^{40}Ca/^{44}Ca$, $^{42}Ca/^{44}Ca$, $^{43}Ca/^{44}Ca$, and $^{44}Ca/^{48}Ca$, were measured. The procedure was briefly as follows.

In Ca8801, an aliquot of a fraction containing about 0.1 mmol calcium was treated to prepare the sample for mass spectrometry (mass sample). The aliquot was passed through a chromatographic column packed with an anion-exchange resin (Muromac 1-x8, 200–400 mesh, ~1 g) in the OH^- form. To the effluent from the column, which was, in fact, an aqueous calcium hydroxide solution, was added nitric acid, yielding a calcium nitrate solution. This solution was evaporated to dryness, and then pure water was added so that the final calcium concentration became 0.1 M (1 M = 1 mol/dm^3).

In Ca8803 and Ca8804, an aliquot of a fraction containing 0.1 mmol calcium was also treated. The aliquot was first evaporated to dryness in a platinum crucible and was then incinerated at about 1000°C for at least 1 hour in an electric furnace, yielding calcium oxide. The calcium oxide thus obtained was then dissolved in a nitric acid solution and was evaporated to dryness again. The resultant calcium nitrate was dissolved in pure water, and its concentration was adjusted to 0.1 M.

The calcium isotopic ratios of a mass sample were measured with the double-filament thermal ionization technique using a Finnigan MAT 261 mass spectrometer at the National Defense Academy. The filament unit for the calcium isotopic ratio measurements consisted of two filaments, one a vaporizing filament and the other an ionization filament, both made of rhenium ribbon. An aliquot of the mass sample (calcium nitrate) containing 2 μg calcium was loaded on the surface of the vaporizing filament. Ionization was performed by passing an electric current through the ionization filament and a much smaller current through the vaporizing filament (about one-tenth of the current through the ionization filament). When the ion beam intensities of ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, and ^{48}Ca became sufficiently high about 1 hour after initiation of heating, the ^{40}Ca–^{48}Ca mass peaks were repeatedly recorded. The mass scanning was repeated eight times in a block, and in most cases 10 blocks were recorded as one measurement. The measuring time was about 2 hours, and hence the total time spent for one measurement was about 3 hours. The calcium isotopic ratios of a block were calculated by averaging all the peak-height ratios in the block except for the ratios whose deviations from the averages were large, and those of the mass sample were calculated as the averages of the isotopic ratios of the 10 blocks. The relative standard deviation of a measurement was typically 0.02% for the $^{40}Ca/^{44}Ca$ isotopic pair, 0.06% for the $^{42}Ca/^{44}Ca$ pair, 0.2% for the $^{43}Ca/^{44}Ca$ pair, and 0.1% for the $^{44}Ca/^{48}Ca$ pair. No attempt was made to measure the ^{46}Ca peak heights.

RESULTS AND DISCUSSION

Chromatograms and isotopic ratios of the three experiments are shown in Figs. 1, 2, and 3. In the lower half of each figure is drawn the calcium concentration profile. In the upper part are shown the isotopic ratios, $^{42}Ca/^{40}Ca$, $^{43}Ca/^{40}Ca$, $^{44}Ca/^{40}Ca$, and $^{48}Ca/^{40}Ca$, in the fractions divided by the corresponding ratios in the feed solution, i.e., local separation factors. A local separation factor value larger than unity means that the heavier isotope is enriched in that fraction.

It is seen that in every experiment the heavier isotopes are enriched in the front part of the calcium adsorption band. Correspondingly, they are depleted in the rear parts of the two band experiments. That is, they are preferentially fractionated into the solution phase. The direction of the calcium isotope fractionation observed in the present study is the same as that reported by other researchers except for a few. It is also the same as those observed for magnesium (8, 13), strontium (14, 15) and lithium (18) isotope fractionations but is opposite to the direction of the potassium (19) and rubidium isotope fractionations (20, 21). It is also seen in the figures that the deviation of the local separation factor value from unity is larger for the isotopic pair with a larger mass difference in a given fraction.

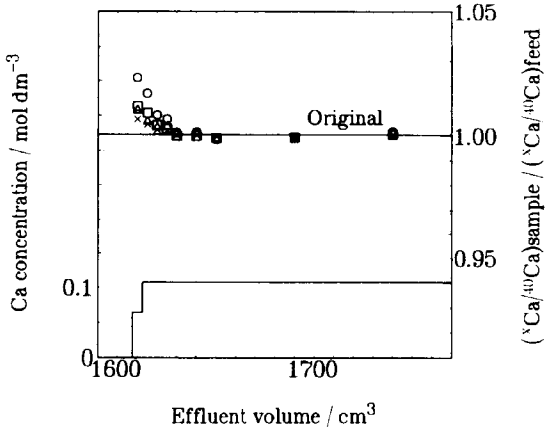

FIG. 1 Chromatogram and the calcium isotopic ratios in the effluent relative to the corresponding isotopic ratios in the feed solution for the calcium chloride system (Ca8801). The circles (○) represent the $^{48}Ca/^{40}Ca$ isotopic ratios, the squares (□) the $^{44}Ca/^{40}Ca$ isotopic ratios, the triangles (△) the $^{43}Ca/^{40}Ca$ isotopic ratios, and the crosses (×) the $^{42}Ca/^{40}Ca$ isotopic ratios. Experimental conditions are given in Table 1.

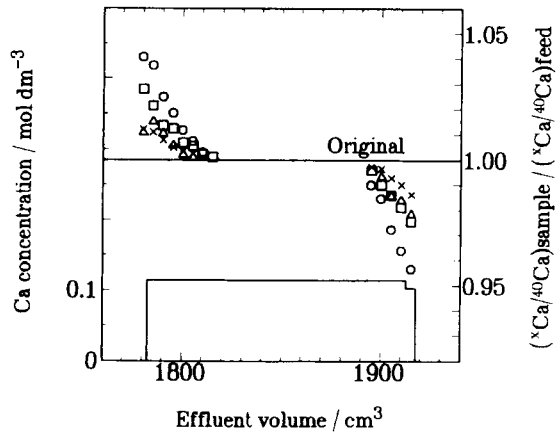

FIG. 2 Chromatogram and the calcium isotopic ratios in the effluent relative to the corresponding isotopic ratios in the feed solution for the calcium lactate system (Ca8803). The circles (○) represent the $^{48}Ca/^{40}Ca$ isotopic ratios, the squares (□) the $^{44}Ca/^{40}Ca$ isotopic ratios, the triangles (△) the $^{43}Ca/^{40}Ca$ isotopic ratios, and the crosses (×) the $^{42}Ca/^{40}Ca$ isotopic ratios. Experimental conditions are given in Table 1.

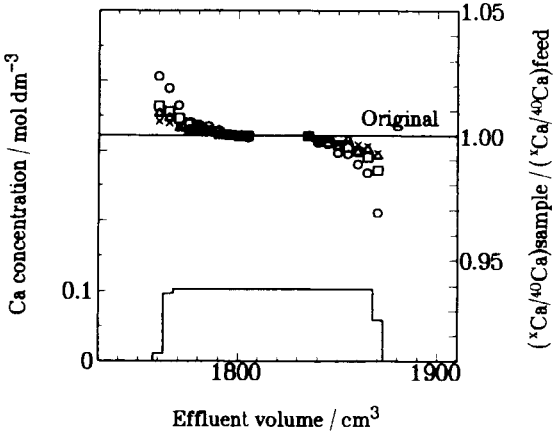

FIG. 3 Chromatogram and the calcium isotopic ratios in the effluent relative to the corresponding isotopic ratios in the feed solution for the calcium acetate system (Ca8804). The circles (○) represent the $^{48}Ca/^{40}Ca$ isotopic ratios, the squares (□) the $^{44}Ca/^{40}Ca$ isotopic ratios, the triangles (△) the $^{43}Ca/^{40}Ca$ isotopic ratios, and the crosses (×) the $^{42}Ca/^{40}Ca$ isotopic ratios. Experimental conditions are given in Table 1.

The single-stage separation factors, $S(42/40)$ for the $^{42}Ca/^{40}Ca$ isotopic pair, $S(43/40)$ for the $^{43}Ca/^{40}Ca$ pair, $S(44/40)$ for the $^{44}Ca/^{40}Ca$ pair, and $S(48/40)$ for the $^{48}Ca/^{40}Ca$, were calculated by using the equation (22)

$$S = 1 + \sum | R_i - R_o | f_i/[QR_o(1 - R_o)] \quad (1)$$

where, assuming a two-isotope system (^{40}Ca and ^{x}Ca with $x = 42$, 43, 44, or 48), R_o is the isotopic molar fraction of the heavier isotope in the feed solution, R_i is that in the ith fraction of the effluent, f_i is the amount of calcium in the ith fraction, Q is the total exchange capacity of the resin bed, and the summation is taken over all fractions that were depleted or enriched in the heavier isotope. The calculated results are summarized in Table 2. Data are given in two forms, ϵ ($= S - 1$) and $\epsilon/\Delta M$, ϵ per unit mass difference between the two isotopes. For Ca8803 and Ca8804, ϵ and $\epsilon/\Delta M$ are the arithmetic means of those calculated from the experimental data at the front and rear parts of the calcium adsorption bands, while they are obtained from the data only at the front part of the band in Ca8801. The $\epsilon/\Delta M$ values obtained are on the order of 10^{-5} as a whole. Compared with the previous values reported by other researchers, the present results are comparable except for a few cases. An ion-exchange chromatographic system with an aqueous phase of calcium hydroxide solution (10) showed $\epsilon/\Delta M$ values one order of magnitude larger than those of this work. Systems with a strongly acidic cation exchanger and a solution containing

TABLE 2
Separation Factors Obtained[a]

Run	System	Isotopic pair	ϵ[b]	$\epsilon/\Delta M$	Av $\epsilon/\Delta M$
Ca8801	Calcium chloride	$^{42}Ca/^{40}Ca$	4.1×10^{-5}	2.1×10^{-5}	2.0×10^{-5}
		$^{43}Ca/^{40}Ca$	4.7×10^{-5}	1.6×10^{-5}	
		$^{44}Ca/^{40}Ca$	8.0×10^{-5}	2.0×10^{-5}	
		$^{48}Ca/^{40}Ca$	1.8×10^{-4}	2.2×10^{-5}	
Ca8803	Calcium lactate	$^{42}Ca/^{40}Ca$	1.1×10^{-4}	5.3×10^{-5}	5.2×10^{-5}
		$^{43}Ca/^{40}Ca$	1.6×10^{-4}	5.4×10^{-5}	
		$^{44}Ca/^{40}Ca$	2.1×10^{-4}	5.4×10^{-5}	
		$^{48}Ca/^{40}Ca$	3.7×10^{-4}	4.6×10^{-5}	
Ca8804	Calcium acetate	$^{42}Ca/^{40}Ca$	5.0×10^{-5}	2.5×10^{-5}	2.3×10^{-5}
		$^{43}Ca/^{40}Ca$	6.7×10^{-5}	2.2×10^{-5}	
		$^{44}Ca/^{40}Ca$	9.6×10^{-5}	2.4×10^{-5}	
		$^{48}Ca/^{40}Ca$	1.6×10^{-4}	2.0×10^{-5}	

[a] Temperature = 25.0 ± 0.2°C.
[b] $\epsilon = S - 1$.

polyether or with condensation resins with polyether or cryptand (12, 23) also had $\epsilon/\Delta M$ values much larger than those of this work.

It is seen in Table 2 that, for a given system, a larger ϵ value is obtained for the isotopic pair with a larger mass difference. However, $\epsilon/\Delta M$ is the same for all the isotopic pairs examined within experimental errors (the experimental errors of ϵ's were typically about 10%, mostly due to errors in the isotopic ratio measurements.) That is, the calcium isotope effect is proportional to the mass difference between isotopes for a given system. This is consistent with what is predicted by the classical Bigeleisen–Mayer theory on isotope effects (24), and no evidence of the odd-even anomaly in isotope effects (16, 17) was found. However, one should not regard the present results as evidence that totally rules out the existence of anomalous calcium isotope effects in ion-exchange systems. Errors of 10% or so on ϵ values are too large to detect expectedly small anomalous isotope effects, if any. Much longer chromatographic developments to magnify small differences in calcium isotope effects will be necessary to give a decisive conclusion on this subject.

It is also observed in Table 2 that, for a given isotopic pair, the calcium–lactate ion (Ca–La) system (Ca8803) yielded a larger ϵ value than the calcium–acetate ion (Ca–Ac) system (Ca8804), which gives a slightly larger ϵ value than the calcium–chloride ion (Ca–Cl) system (Ca8801). (Although the $^{48}Ca/^{40}Ca$ isotopic pair gave a slightly larger ϵ value in the chloride system than in the acetate system, the two values are equal within experimental errors.) Thus, $\epsilon(\text{Ca–La}) > \epsilon(\text{Ca–Ac}) \geqq \epsilon(\text{Ca–Cl})$. This sequence is the same as that found for the strontium isotope effect (15). The result that the Ca–La and Ca–Ac systems have larger ϵ values than the Ca–Cl system corresponds to the fact that the complex formations of the calcium ion with the lactate and acetate ions in the external solution phase make positive contributions to the overall isotope effects in ion-exchange systems. This point will be discussed in a more detailed fashion in terms of the heavier-isotope-to-lighter-isotope isotopic reduced partition function ratios (RPFRs) of calcium species in the next section.

Estimation of the Reduced Partition Function Ratios of the Calcium Species Involved in the Present Work

It is possible to estimate the RPFRs of the calcium species involved in the present systems by using the separation factor data obtained, Bigeleisen and Mayer's simplifying formula of RPFR calculations (24), data on the hydration number of the calcium ion and of the Ca^{2+}–H_2O symmetric stretching frequency in aqueous solutions, and the theory of isotope distribution between two phases (25) under a few appropriate assumptions. For

the Ca–La and Ca–Ac systems, S can be expressed in terms of the RPFRs and molar fractions of the calcium species involved in the systems as

$$\ln S = \ln(x_{Ca}f_{Ca} + x_{CaL}f_{CaL}) - \ln(y_{Ca}g_{Ca} + y_{CaL}g_{CaL}) \quad (2)$$

where x_{Ca} and f_{Ca} are the molar fraction and the RPFR of the simple hydrated calcium ion in the solution phase, x_{CaL} and f_{CaL} are those of CaL^+ [L = lactate ion (La^-) or acetate ion (Ac^-)] in the solution phase, and y and g are, respectively, the quantities in the resin phase corresponding to x and f. Under the present experimental conditions, there is no need to consider higher-order complexes between Ca^{2+} and La^- or Ac^- (26). That is, $x_{Ca} + x_{CaL} = 1$ and $y_{Ca} + y_{CaL} = 1$. Although the degree of hydration occurring is not indicated in Eq. (2) and in equations hereafter for simplicity, it should be noted that all the calcium 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 (27).

In the Ca–Cl system, no appreciable complex formation between the calcium ions and the chloride ions is expected under the present experimental conditions. Thus, $x_{CaL} = y_{CaL} = 0$ (L = Cl^-) and Eq. (2) is simplified to

$$\ln S = \ln(f_{Ca}/g_{Ca}) \quad (3)$$

Equation (3) shows that the separation factors of the Ca–Cl system are nothing but the equilibrium constants of the following calcium isotope exchange reaction between the solution and the resin phases,

$$Ca'^{2+}_{(s)} + Ca^{2+}_{(r)} = Ca^{2+}_{(s)} + Ca'^{2+}_{(r)} \quad (4)$$

where the primed quantities are those of the lighter isotope and the nonprimed quantities are those of the heavier isotope, and the subscripts (s) and (r) refer to the solution phase and the resin phase, respectively.

The RPFR of the simple hydrated calcium ion in the solution phase, f_{Ca}, is calculable by using the Bigeleisen–Mayer formula (24),

$$\ln f = [nm\Delta M/(24MM')](hc\omega/kT)^2 \quad (5)$$

where n is the hydration number, m is the mass of a hydrating water molecule, M and M' are the masses of the heavier and lighter calcium isotopes, $\Delta M = M - M'$, h is the Planck constant, c is the velocity of light, ω is the Ca^{2+}–H_2O totally symmetric stretching frequency in cm^{-1} in aqueous solutions, k is the Boltzman constant, and T is the temperature. The symmetry numbers are omitted. Neutron diffraction and molecular dynamics calculation studies (28–31) reported that the hydration number in the primary hydration sphere around a calcium ion is 9–10. In this paper we adopted $n = 10$. ω was observed at 290 cm^{-1} in an aqueous calcium

perchlorate solution (32). With these data and taking only the hydration in the primary hydration sphere into consideration, f_{Ca} can be estimated from Eq. (5). The RPFRs of Ca^{2+} in the resin phase, g_{Ca}, are obtainable from the f_{Ca} values and the separation factor data in the Ca–Cl system.

In order to estimate the RPFRs of the complex species of calcium, f_{CaL} and g_{CaL}, in and outside the resin phase of the Ca–La and Ca–Ac systems, the molar fractions of these species are required. Their molar fractions in the solution phase can be estimated by using the data of stability constants of $CaLa^+$ (33) and $CaAc^+$ (34) and of the dissociation constants of lactic acid (35) and acetic acid (36). Molar fractions of the complex species in the resin phase may be estimated from knowledge of the calcium band velocities in the Ca–La and Ca–Ac systems relative to the velocity in the Ca–Cl system, as had been applied to the magnesium (13) and strontium (15) isotope separations. Values of x_{CaL} and y_{CaL} thus obtained are listed in Table 3, together with those of x_{Ca} and y_{Ca}. By using these values and a reasonably assumed simplifying relation,

$$f_{CaL}/f_{Ca} = g_{CaL}/g_{Ca} \tag{6}$$

the RPFRs of all the calcium species viable in the present systems were calculated and the results are summarized in Table 4. Although the accuracy of the RPFR values in this table is questionable due to approximations employed and uncertainties in parameter values used in our RPFR calculations, the relative order of the magnitudes of the RPFR values in Table 4 will be unchanged even if some other approximations are adopted and/or different values of the stability constants, dissociation constants, hydration numbers, etc. are used.

It is seen in Table 4 that the RPFR of the complex species is larger than that of the corresponding simple hydrated calcium ion ($f_{CaL} > f_{Ca}$ and $g_{CaL} > g_{Ca}$) for any isotopic pair except for the $f(CaAc^+)$ and $g(CaAc^+)$ of the $^{48}Ca/^{40}Ca$ isotopic pair. (If one considers experimental errors of separation factors, however, this exception is of no significance.) It is then understood in Eq. (2) that the complex formations in the solution

TABLE 3
Calculated Molar Fractions of the Calcium Species In and Outside the Resin Phase

Run	System	x_{Ca}	y_{Ca}	x_{CaL}	y_{CaL}
Ca8801	Ca–Cl	1.000	1.000	0.000	0.000
Ca8803	Ca–La	0.433	0.763	0.567	0.237
Ca8804	Ca–Ac	0.692	0.892	0.308	0.108

TABLE 4
Values of the Reduced Partition Function Ratios of the Calcium Species at 25°C

Species[a]	Phase	Isotopic pair			
		$^{42}Ca/^{40}Ca$	$^{43}Ca/^{40}Ca$	$^{44}Ca/^{40}Ca$	$^{48}Ca/^{40}Ca$
Ca^{2+}	Solution (f)	1.017681	1.026028	1.034033	1.063309
	Resin (g)	1.017638	1.025980	1.033951	1.063122
$CaLa^{+}$	Solution (f)	1.017879	1.026386	1.034455	1.063935
	Resin (g)	1.017837	1.026337	1.034372	1.063748
$CaAc^{+}$	Solution (f)	1.017727	1.026131	1.034116	1.063203
	Resin (g)	1.017684	1.026083	1.034034	1.063016

[a] Hydration is ignored in the expressions.

and the resin phases increase and decrease the overall separation factor values, respectively. The experimental result that the separation factors in the Ca–La and Ca–Ac systems are larger than those of the Ca–Cl system is attributable in most part to the fact that $f_{CaL} > f_{Ca}$ and the degree of complex formation is larger in the solution phase than in the resin phase ($x_{CaL} > y_{CaL}$).

It is also seen in Table 4 that $f > g$ for any isotopic pair of any calcium species examined. $f_{Ca} > g_{Ca}$ is equivalent to $S(Ca–Cl) > 1$. $f_{CaL} > g_{CaL}$ is a logical consequence of this fact and an assumed Relation (6).

Comparison of Isotope Effects of the Alkali and Alkaline Earth Metals Observed in Metal Chloride Systems at 25°C (13, 15, 18, 19, 21)

In Fig. 4 the logarithm of the absolute value of ϵ per unit isotopic mass difference is plotted against the logarithm of the square of the atomic mass for the metal chloride systems of the elements of Groups IA (18, 19, 21) and IIA (13, 15) of the periodic table. The experimental temperature and the resin were common to all the systems and were 25°C and Asahi LS-6, respectively. Since no appreciable complex formation or ion association is expected in those systems, the isotope effects observed are isotope effects accompanying nearly pure ion exchanges. As seen in Fig. 4, a nearly linear relationship between $\log(|\epsilon|/\Delta M)$ and $\log M^2$ with a negative slope is obtained. Thus, it is indicated that the magnitude of isotope effect in pure ion exchange is inversely proportional to the square of the mass of the element.

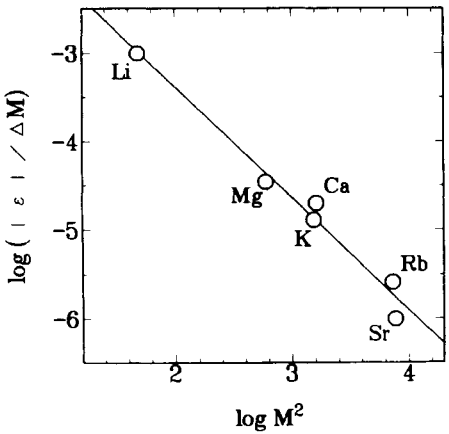

FIG. 4 Relationship between the magnitude of ε per unit mass difference of isotopes and the square of the atomic mass in the ion-exchange systems of chlorides of the alkali and alkaline earth metals at 25°C.

CONCLUSION

To summarize, we make the following statements:

1. Heavier calcium isotopes were preferentially fractionated into the solution phase in all the chromatographic experiments conducted.
2. The values of ε per unit mass difference were 1.6–2.2 $\times$ 10^{-5} for the calcium chloride system, 2.2–2.5 $\times$ 10^{-5} for the calcium acetate system, and 4.6–5.4 $\times$ 10^{-5} for the calcium lactate system at 25°C. Complex formations in the solution phase increase the overall separation factors.
3. Using the presently available data and assumptions, the RPFRs of the calcium species involved in the present systems were estimated. The RPFRs of the complex species ($CaLa^+$ and $CaAc^+$) were larger than that of the simple hydrated calcium ion in both the solution and the resin phases.
4. The magnitude of isotope effect per unit mass difference accompanying pure ion exchange is inversely proportional to the square of the atomic mass for the alkali and alkaline earth metals.

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