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Calcium Hydroxide Isotope Effect in Calcium Isotope Enrichment by Ion Exchange

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Abstract

The enrichment of calcium isotopes has been observed in ion-exchange chromatography with an aqueous phase of calcium hydroxide and a solid phase of sulfonic acid resin. The band front was exceedingly sharp as a result of the acid-base reaction occurring at the front of the band. Single-stage separation coefficients were found to be $\varepsilon(^{44}Ca/^{40}Ca) = 11 \times 10^{-4}$ and $\varepsilon(^{48}Ca/^{40}Ca) = 18 \times 10^{-4}$. The maximum column separation factors achieved were 1.05 for calcium-44 and 1.09 for calcium-48 with the heavy isotopes enriching in the fluid phase. The calcium isotope effect between fully hydrated aqueous calcium ions and undissociated aqueous calcium hydroxide was estimated. For the calcium-44/40 isotope pair the separation coefficient was 13×10^{-4}.

INTRODUCTION

The use of ion-exchange chromatography for metal isotope separation was first attempted 45 years ago (*1*); however, it has been only recently that the method has been seriously considered for the production of enriched isotopes. Enrichment of uranium isotopes by redox ion-exchange chromatography is now being done at the bench-scale level of development (*2*). Lithium isotope separation by ion exchange has recently been advocated (*3, 4*). These processes have overcome two of the major shortcomings of chromatography: the batchwise nature of single column operation and band

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spreading which occurs when the elution technique is used to drive the band. A cyclic arrangement of columns permits continuous movement of the band, and the displacement technique is used to drive the band. Fujine has recently investigated theoretical aspects of displacement band chromatography and compared elution and displacement techniques (*4*).

There is a continuing interest in finding a practical chemical method for the separation of calcium isotopes. At the present time calcium isotopes are separated with calutrons (electromagnetic separators) at Oak Ridge National Laboratory. The rare, heavy calcium isotopes separated by this method are expensive, and their use as stable tracers is limited by cost. Calcium isotope enrichment by ion exchange has not been studied extensively due in part to the difficulty of calcium isotope ratio measurements. Further, the isotope effects in calcium ion exchange are usually quite small. Single-stage separation coefficients per unit mass (ε_0) reported in the literature generally fall in the vicinity of 10^{-4} to 10^{-5} (*5–11*). Two exceptions to this are noted here. A separation coefficient of 8.5×10^{-4} for the ^{44}Ca-^{40}Ca isotope pair was reported for calcium ion exchange with sulfonate exchange resin (*12*). On a per unit mass basis, this corresponds to an ε_0 of 2.1×10^{-4}. This isotope effect was obtained by eluting calcium through a column with 12 *N* lithium chloride solution. A considerably large isotope effect was found for calcium ion exchange with an iminodiacetate exchange resin. Here a separation coefficient, $\varepsilon(^{44}Ca/^{40}Ca)$, of 41×10^{-4} was obtained (*13*), corresponding to an ε_0 of 10×10^{-4}. In both of these cases, chloride was the aqueous-phase counterion for calcium ions. In our work that follows we describe a calcium ion-exchange system which differs from prior work in that hydroxide was used as the fluid-phase counterion for calcium. The isotope-exchange reaction is written as

$$^{40}Ca(OH)_{2(aq)} + {}^{44}Ca(SO_3R)_{2(res)} \rightleftharpoons {}^{44}Ca(OH)_{2(aq)} + {}^{40}Ca(SO_3R)_{2(res)} \tag{I}$$

where $^{-}SO_3R$ is the sulfonate anion bonded to the resin. The separation coefficient ε is defined as $\varepsilon = K - 1$, where K is the equilibrium coefficient of the reaction. An acid-base (reflux) reaction takes place at the front of the band,

$$Ca(OH)_{2(aq)} + 2HSO_3R \rightarrow Ca(SO_3R)_2 + 2H_2O$$

resulting in a very sharp band front. This exchange system is thus well suited to a displacement type of operation. The frontal analysis technique was used to obtain the single-stage separation coefficients.

EXPERIMENTAL

Bio-Rad analytical grade sulfonic acid resin-type AG-50W-X4, 200-400 mesh was used. Four normal HCl was passed through the packing until Ca and K impurities could no longer be detected. Excess HCl was removed with water to an eluent pH of 5.5. Since K interferes with Ca isotope ratio measurements, special care was taken to avoid K contamination. Reagent grade $CaCO_3$ was converted to $Ca(NO_3)_2$ and the potassium removed by an ammonium oxalate precipitation. A calcium recovery of greater than 99.9% was obtained by using concentrated solutions and maintaining a pH greater than 6. CaO was obtained by firing the calcium oxalate precipitate to 1000°C, and a feed solution of 0.017 *M* $Ca(OH)_2$ was prepared. This was close to the maximum concentration which could be achieved at room temperature. Potassium concentration in this solution was <0.5 ppm according to atomic absorption analysis. A mass spectrometer standard was prepared from this solution. A 75-cm long, 9 mm i.d. jacketed column was used with the temperature maintained at 25.0°C. Fluid flow rate was 7.95 cc/h. Isotope ratio measurements were done with a Nuclide SU-7 thermal ionization mass spectrometer. The standard deviations of the individual isotope ratio measurements for the $^{44}Ca/^{40}Ca$ ratio ranged from ±0.2 to 0.3% of the ratio. For the $^{48}Ca/^{40}Ca$ ratio this range was ±0.2 to 0.5%. Calcium concentrations at the front of the band were measured with an Orion calcium specific electrode. Calcium concentrations in the remainder of the band were more accurately calculated from an overall calcium material balance. The calcium capacity of the column was 1750 mg.

RESULTS

The calcium breakthrough curve is shown in Fig. 1 along with the corresponding isotope enrichments of calcium-44 and -48 in atom-%. The single-stage separation coefficient, ε, was calculated from the initial transport equation which can be written:

$$\tau_0 = \sum g_i(n_i - n_0) = \varepsilon Q n_0(1 - n_0) \qquad (1)$$

where τ_0 = net transport of the isotope
g_i = mg total of calcium in the ith sample
n_i = atom fraction of isotope in the ith sample
n_0 = atom fraction of isotope in feed
Q = total column capacity

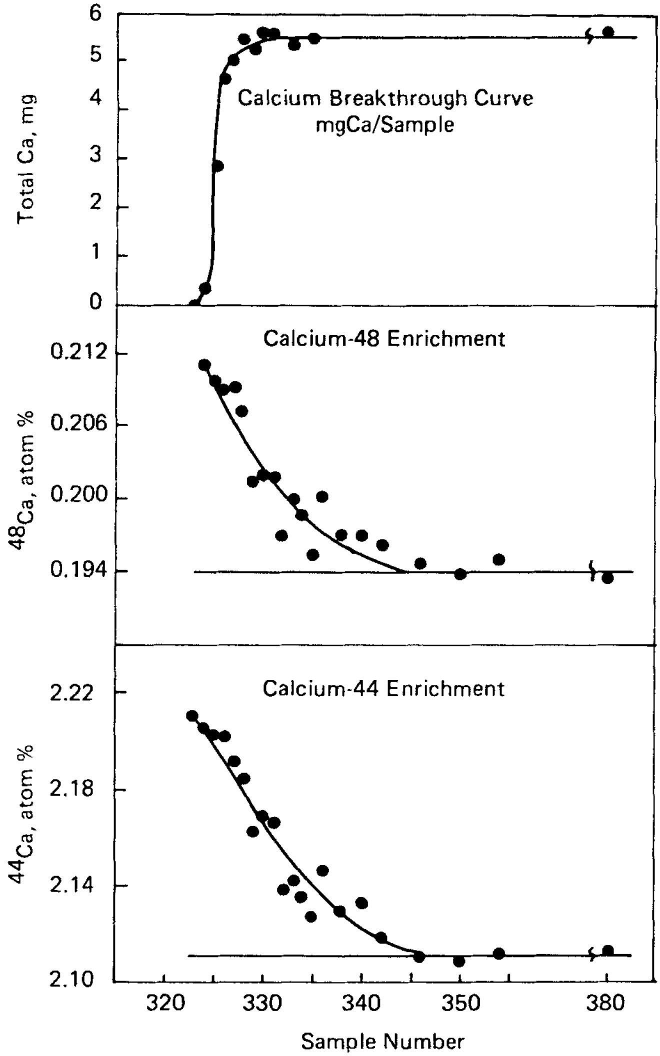

FIG. 1. Calcium breakthrough curve and isotope enrichments.

The results of these calculations were $\varepsilon(^{44}Ca/^{40}Ca) = 10.6 \times 10^{-4}$ and $\varepsilon(^{48}Ca/^{40}Ca) = 18.4 \times 10^{-4}$. Experimental error in the calculated value of ε emerges primarily from the term $(n_i - n_0)$ in Eq. (1) since the quantities g_i, Q, and n_0 are more accurately known. The enrichment profiles, n_i, for calcium-44 and -48 in Fig. 1 were fitted to polynomials to obtain standard deviations. These were found to be ±0.008 atom-% for ^{44}Ca and ±0.002 atom-% for ^{48}Ca. The resulting error in the separation coefficient for ^{44}Ca is $\pm 1.4 \times 10^{-4}$ yielding $\varepsilon(^{44}Ca/^{40}Ca) = (10.6 \pm 1.4) \times 10^{-4}$ or, on a per mass unit basis, $\varepsilon_0 = (2.7 \pm 0.4) \times 10^{-4}$. For ^{48}Ca the error was $\pm 3.3 \times 10^{-4}$, yielding $\varepsilon(^{48}Ca/^{40}Ca) = (18.4 \pm 3.3) \times 10^{-4}$.

Figure 2 shows, for the front portion of the band, local separation factors for calcium-42, -43, -44, and -48. The local separation factor for each isotope is defined as

$$S_i = \frac{n_i/(1 - n_i)}{n_0/(1 - n_0)} \tag{2}$$

where n_i and n_0 are the same as defined in Eq. (1). Figure 2 illustrates the influence of mass on the isotope effect and consequently the local column separation factor. From the standpoint of chemical-exchange theory, the influence of mass on the isotope effect is quite complicated. For many situations, however, it can be shown that the log of the partition function ratio

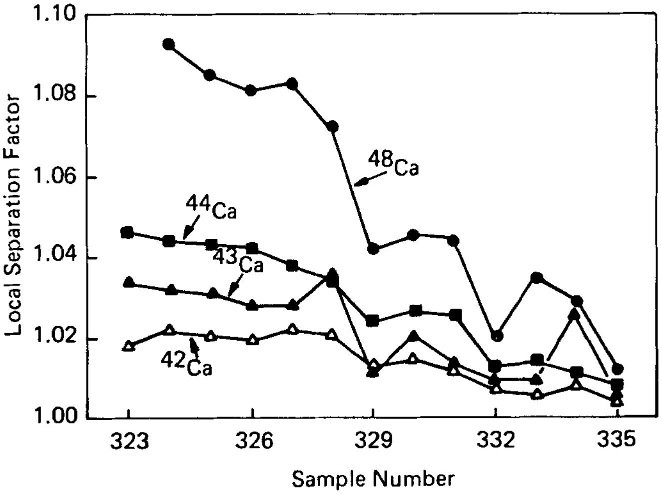

FIG. 2. Local separation factors.

for a pair of isotopes is proportional to the mass difference of a pair of isotopes and inversely proportional to the product of the masses (*14*). This latter relationship of the product of the masses is generally ignored, but calcium with its wide range of isotopic masses presents a special case for comparison with chemical exchange theory. From these proportionalities one can calculate that $\varepsilon(^{48}\mathrm{Ca}/^{40}\mathrm{Ca})$ is expected to be a factor of 1.8 greater than $\varepsilon(^{44}\mathrm{Ca}/^{40}\mathrm{Ca})$. In this work $\varepsilon(^{48}\mathrm{Ca}/^{40}\mathrm{Ca})$ was a factor of 1.7 greater than $\varepsilon(^{44}\mathrm{Ca}/^{40}\mathrm{Ca})$, which is consistent with the theory.

Single-stage separation coefficients for calcium-43 and -42 were not calculated since experimental error became quite large; however, it is evident from Fig. 2 that these also correspond with theory. The local separation factor for ^{42}Ca is approximately one-half that of ^{44}Ca, and the separation factor for ^{43}Ca with allowance for analytical deviations is very roughly three-fourths that of ^{44}Ca.

DISCUSSION

Calcium Hydroxide Isotope Effect

The single-stage separation coefficient (ε_0) of 2.7×10^{-4} per unit mass found in this work for calcium ion exchange with a sulfonate resin is larger than those reported in the literature. For ion-exchange systems in which calcium ions are fully hydrated (i.e., with noncomplexing counterions) in the aqueous phase, the separation coefficients are on the order of 0.5×10^{-4} per unit mass (*5, 7*). In the case of calcium hydroxide the exchange reactions are influenced by the fact that $\mathrm{Ca(OH)_2}$ is only partially dissociated in aqueous solution. Three calcium species exist in the aqueous phase, molecular undissociated $\mathrm{Ca(OH)_2}$; the partially dissociated cation $\mathrm{Ca(OH)^+}$; and fully hydrated $\mathrm{Ca^{2+}}$ ions. The overall exchange process is thus described by Reaction (I), shown above, and the following reactions:

$$^{40}\mathrm{Ca}^{2+}_{(\mathrm{aq})} + {}^{44}\mathrm{Ca(SO_3R)}_{2(\mathrm{res})} \rightleftharpoons {}^{44}\mathrm{Ca}^{2+}_{(\mathrm{aq})} + {}^{40}\mathrm{Ca(SO_3R)}_{2(\mathrm{res})} \qquad \text{(II)}$$

$$^{40}\mathrm{Ca(OH)}^{+}_{(\mathrm{aq})} + {}^{44}\mathrm{Ca(SO_3R)}_{2(\mathrm{res})} \rightleftharpoons {}^{44}\mathrm{Ca(OH)}^{+}_{(\mathrm{aq})} + {}^{40}\mathrm{Ca(SO_3R)}_{2(\mathrm{res})} \qquad \text{(III)}$$

Reactions (I), (II), and (III) are concurrent (parallel) reactions and thus contribute to the overall observed isotope effect according to the expression

$$\varepsilon^{\mathrm{obs}} = \frac{1}{M_T} \sum_{\mathrm{I}}^{\mathrm{III}} m_r \varepsilon^r \qquad (3)$$

where ε^{obs} = observed separation coefficient, 44/40
ε^{r} = separation coefficient for reaction r, 44/40
m_r = molarity of aqueous calcium species in reaction r
M_T = total molarity of calcium, $m_I + m_{II} + m_{III}$

The concentrations, m_r, of each of the species of calcium may be calculated from the first and second dissociation constants (K_b) of $Ca(OH)_2$ which are 3.74×10^{-3} and 4.0×10^{-2}, respectively (*15*). From these, concentrations of 0.0105 *M* $Ca(OH)_2$, 0.0058 *M* Ca^{2+}, and 0.0008 *M* $Ca(OH)^+$ were obtained for the 0.017 *M* solution used in this work. It is now possible to estimate ε^{I} since ε^{obs} and ε^{II} are known. First, an assumption must be made for ε^{III}. Reaction (III) is a minor contributor to the overall observed isotope effect as a result of the low $Ca(OH)^+$ concentration. The mole fraction of calcium in this form is only 0.05. For this calculation ε^{III} was assumed to be $\frac{1}{2}\varepsilon^{I}$ based upon the presence of only one Ca—OH bond rather than two. The estimated value of ε^{I} then becomes 15×10^{-4}.

Another exchange reaction of theoretical interest is the isotope exchange between the aqueous hydrated calcium ion and the aqueous calcium hydroxide species. This reaction is written

$$^{44}Ca^{2+}_{(aq)} + {}^{40}Ca(OH)_{2(aq)} \rightleftharpoons {}^{40}Ca^{2+}_{(aq)} + {}^{44}Ca(OH)_{2(aq)} \qquad \text{(IV)}$$

Reactions (II) and (IV) are consecutive reactions, the sum of which yields Reaction (I). The equilibrium coefficients ($K = 1 + \varepsilon$) are related according to the expression $K^{I} = K^{II}K^{IV}$ or $(1 + \varepsilon^{I}) = (1 + \varepsilon^{II})(1 + \varepsilon^{IV})$. The separation coefficient for Reaction (IV) is less than that of Reaction (I) with $\varepsilon^{IV} = 13 \times 10^{-4}$.

Practical Applicability

The separation coefficient found in this work is larger than most ion-exchange results, but is still considerably smaller than that of other chemical-exchange systems. In calcium chemical exchange with macrocyclic compounds, separation coefficients per mass unit from 10×10^{-4} (*16*) to 20×10^{-4} (*17*) have been reported. Even larger coefficients of 13×10^{-4} (*18*) and 25×10^{-4} (*19*) have been reported for calcium amalgam chemical exchange. This in and of itself does not preclude the practical applicability of ion exchange for calcium isotope enrichment. In the case of lithium isotope separation, for example, ion exchange with an ε of 0.003 has been advocated as an enrichment method (*4*) despite the fact lithium amalgam chemical exchange has an ε greater than 0.05 (*20*). Here, the ion-exchange process is much simpler than the amalgam process.

Calcium hydroxide ion exchange has a second more serious limitation, however; the low solubility of calcium in the fluid phase. This would result in lower than desirable calcium band velocities in column operation. On the basis of these considerations, it is concluded that the calcium hydroxide process has limited applicability compared to other chemical-exchange processes.

CONCLUSIONS

Calcium isotope enrichment was observed in ion-exchange chromatography with aqueous-phase calcium hydroxide and sulfonic acid resin. Single-stage separation coefficients were found to be $\varepsilon(^{48}\mathrm{Ca}/^{40}\mathrm{Ca}) = 18 \times 10^{-4}$ and $\varepsilon(^{44}\mathrm{Ca}/^{40}\mathrm{Ca}) = 11 \times 10^{-4}$. The calcium isotope effect between fully hydrated aqueous calcium ions and undissociated aqueous calcium hydroxide was estimated to be 13×10^{-4} for the calcium 44/40 isotope pair. The low solubility of calcium hydroxide was considered to be a major drawback to the applicability of this process.

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