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Calcium Isotope Effect in Calcium Ion Exchange with a Fluid Phase Containing a Macrocyclic Compound

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ABSTRACT

The separation coefficient for calcium isotope exchange with a macrocyclic polyether was measured by ion exchange chromatography. The isotopic enrichment proceeds according to the chemical exchange reaction:

$$^{44}\mathrm{CaL}^{2+}_{\ \mathrm{Fluid}} + {}^{40}\mathrm{Ca}^{2+}_{\ \mathrm{Resin}} \rightleftarrows {}^{40}\mathrm{CaL}^{2+}_{\ \mathrm{Fluid}} + {}^{44}\mathrm{Ca}^{2+}$$

where L represents the macrocyclic polyether 18-crown-6. The observed separation coefficient for the calcium 40/44 isotope pair, $\varepsilon(40/44)$, was $4.9\mathrm{X}10^{-4}$ ($\pm 1.3\mathrm{X}10^{-4}$, 95% C.L.) with calcium-40 enriched in the fluid phase. A sulfonic acid resin was used with a fluid phase consisting of a 70/30 volume percent mixture of ethanol and water. The isotope effect was smaller than metal-crown isotope effects reported in the literature, and possible reasons for this are discussed.

INTRODUCTION

The use of ion-exchange chromatography for isotope separation was first reported in 1938 (1). Remarkably high enrichments of nitrogen isotopes were accomplished in the early fifties using ammonium hydroxide solutions with the displacement band technique of ion

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exchange (2). More recently, successful enrichments of uranium and lithium have been reported (3,4). There is a continuing interest in finding a practical chemical method for the separation of calcium isotopes. The separation of stable calcium isotopes is presently being accomplished with calutrons (electromagnetic separators) at Oak Ridge National Laboratory. The rare calcium isotopes separated by this method are expensive, and their use is often limited by cost.

In general, the enrichment of calcium isotopes by ion exchange chromatography has been impractical primarily as a consequence of very small separation coefficients.

Several exceptions to this are noted here. Heumann (5) and Gutsykov (6) have reported considerably larger isotope effects. Calcium hydroxide ion exchange has also exhibited an increased separation coefficient (7). Liquid-liquid chromatography (extraction chromatography) was employed by Horwitz to enrich calcium isotopes (8). This method is analogous to ion exchange in the sense that the extractant retained on the reversed phase solid support functions as an ion exchanger. This also yielded a larger than typical separation coefficient.

Liquid-liquid calcium chemical exchange with dicyclohexano 18-crown-6 also exhibits a large isotope effect (9), and it was of some interest to find whether this would also occur in an ion exchange system. The work below describes the results of calcium isotope exchange using ion exchange chromatography with a fluid phase containing the calcium complex of the macrocyclic compound 18-crown-6. Isotopic enrichment occurs according to the chemical exchange reaction:

$$^{44}\mathrm{CaL}^{2+} + {}^{40}\mathrm{Ca(SO_3R)_2} \rightleftarrows {}^{40}\mathrm{CaL}^{2+} + {}^{44}\mathrm{Ca(SO_3R)_2} \qquad \mathrm{I.}$$

where L represents 18-crown-6 and R the resin. Investigators have reported similar sodium (10) and potassium (11) isotope effects using a macrocyclic compound in conjunction with ion exchange chromatography. In the work which follows, the frontal analysis analytical technique was used to obtain the separation coefficient.

EXPERIMENTAL

Bio-Rad analytical grade sulfonic acid resin type AG-50W-X4, 200-400 mesh was used. Potassium and calcium impurities were removed by passing 4N HCl through the column until K and Ca could not be detected. This was followed by a water wash to remove excess HCl (pH = 5.5) and a final wash with a 70/30 vol % solution of ethanol/water. Potassium-free calcium was prepared according to the following steps: (1) Reagent grade $CaCO_3$ (Fisher) to $Ca(NO_3)_2$; (2) precipitation of calcium with ammonium oxalate followed by washing; (3) firing to CaO at 1000°C; and (4) preparation of an aqueous solution of $CaCl_2$. The 18-crown-6 obtained from PCR, Inc., was used as received in the form of clear crystals. The feed solution consisted of 70 vol % absolute ethanol and 30 vol % water with concentrations of 0.115M $CaCl_2$ and 0.121M 18-crown-6. A 6-mm i.d. column packed to a length of 94 cm with an adjustable plunger was used. The column jacket was maintained at 25.0°C. The fluid flow rate was 9.9 mL/hr, and the column capacity was 1442 mg of calcium.

Samples collected from the ion exchange column contained approximately 5 mg total calcium (after the calcium breakthrough) in a matrix of 70:30 ethanol:water containing approximately 30 mg 18-crown-6. The calcium present in the samples was isolated by evaporation of the ethanol and water with controlled heating via infrared lamps and pyrolysis of the 18-crown-6 at 750 to 800°C in air. Conversion of the $CaCl_2$ to $Ca(NO_3)_2$ was effected by addition of concentrated HNO_3 (5.0 mL) and evaporation to dryness. Spot tests with $AgNO_3$ indicated complete conversion with a single addition/evaporation cycle. Following conversion to CaO at 1000°C in air, the calcium contents of the samples were determined gravimetrically. The total calcium present in the sample as obtained directly from the column was derived by applying a correction factor for any material removed. Measurement of calcium concentrations by atomic absorption for selected samples indicated <2% relative variance between atomic absorption and gravimetric methods.

Samples were diluted to a calcium concentration of 1 mg/mL with 2N HNO_3 for isotopic analysis. Special care was exercised during all sample processing steps to prevent contamination with potassium, which interferes with calcium isotope ratio measurements. Isotopic ratios were obtained with a 15-in., 90° gas mass spectrometer modified with a source designed by Los Alamos National Laboratory for solids analyses by thermal ionization. The instrumental variance over time, as estimated by repetitive analyses of a natural abundance standard, was better than ±0.05% (standard deviation) for the $^{40}Ca/^{44}Ca$ ratio. The standard deviations for the sample $^{40}Ca/^{44}Ca$ ratio measurements ranged from 0.03 to 0.37% of the ratio.

RESULTS AND DISCUSSION

The calcium breakthrough curve is shown in Figure 1 along with the corresponding calcium 40/44 isotope ratios. The single-stage separation coefficient, ε, was calculated from the initial transport equation which can be written:

$$\tau_o = \Sigma g_i(N_i - N_o) = \varepsilon Q N_o(1-N_o)$$

where τ_o = net transport of the isotope
g_i = mg total calcium in the ith sample
N_i = atom fraction of isotope in the ith sample
N_o = atom fraction of isotope in feed
Q = mg total calcium on resin

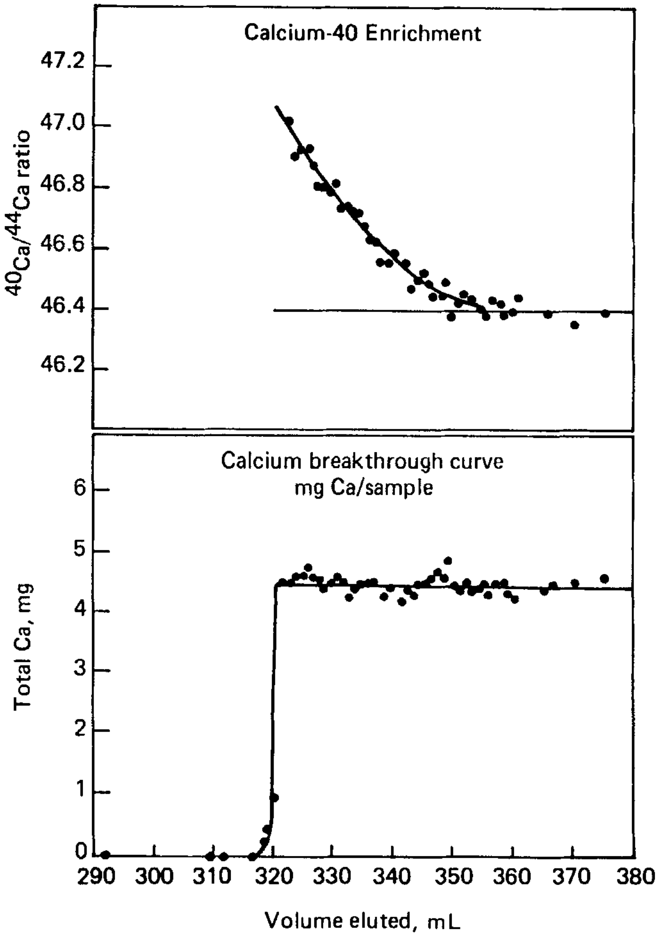

Fig. 1. Calcium isotope enrichment and calcium breakthrough curve.

The results of this calculation yielded an $\varepsilon(44/40)$ of $(4.9 \pm 1.3) \times 10^{-4}$ (95% C.L.). The standard deviation was obtained from a least squares analysis.

Compared with the work cited in the introduction, this isotope effect is relatively small. Heumann reported a separation coefficient, $\varepsilon(44/40)$, of 8.5×10^{-4} using concentrated lithium chloride as an eluant (5). A very large separation coefficient of 41×10^{-4} for the 44/40 pair of isotopes was found for calcium ion exchange with an iminodiacetate resin (6). Our own work with calcium hydroxide ion exchange yielded a separation coefficient of 11×10^{-4} for the same isotope pair (7). In the liquid-liquid chromatography work of Horwitz, a separation coefficient of 29×10^{-4} was found for the 48/40 calcium isotope pair (8). According to chemical exchange theory, the separation coefficient is proportional to the mass difference of the pair of isotopes and inversely proportional to the product of the masses. On this basis the isotope effect found by Horwitz is equivalent to 16×10^{-4} for the 44/40 pair of calcium isotopes. All of the above isotope effects represent significant increases over those obtained in the simple exchange of uncomplexed calcium ions with calcium bound to a sulfonate functional group on a resin.

Measurements of the 18-crown-6 concentrations in the eluant were also made, and a breakthrough curve for this ligand is shown in Figure 2. It is evident from the crown breakthrough curve that a significant quantity of crown was retained in the solid phase, even though the neutral crown molecule would not be expected to adhere to the cation resin. The crown concentration in the ethanolic fluid phase feed displacing the calcium was 31.8 mg/mL. As can be seen in Figure 2, this value of crown concentration was reached only after the calcium breakthrough. The difference between this concentration and those shown in Figure 2 preceding the calcium breakthrough represents the quantity of crown retained on the packing. The total capacity of the column (excluding the fluid phase) was 4010 mg 18-crown-6 and 1442 mg calcium. In terms of mole fractions the crown capacity of the column was approximately 40% that of the calcium. The crown was assumed to be present on the packing as the calcium complex. This explains in part the small calcium separation coefficient ($\varepsilon = 4.9 \times 10^{-4}$) obtained for this system. It is probable that a second exchange reaction occurs as follows:

$$\mathrm{CaL^{2+}}_{\mathrm{fluid}} + {}^{*}\mathrm{CaL^{2+}}_{\mathrm{resin}} \rightleftarrows {}^{*}\mathrm{CaL^{2+}}_{\mathrm{fluid}} + \mathrm{CaL^{2+}}_{\mathrm{resin}} \qquad \mathrm{II.}$$

This exchange occurs in parallel with the exchange reaction (1) shown above.

The separation factor ($\alpha = 1 + \varepsilon$) of 1.00049 was smaller than anticipated. As a general rule in chemical exchange, larger isotope effects are present when the coordination of the metal ion differs by the greatest amount in each of the two phases. In Reaction (I) the fluid phase calcium-crown complex species differs considerably in

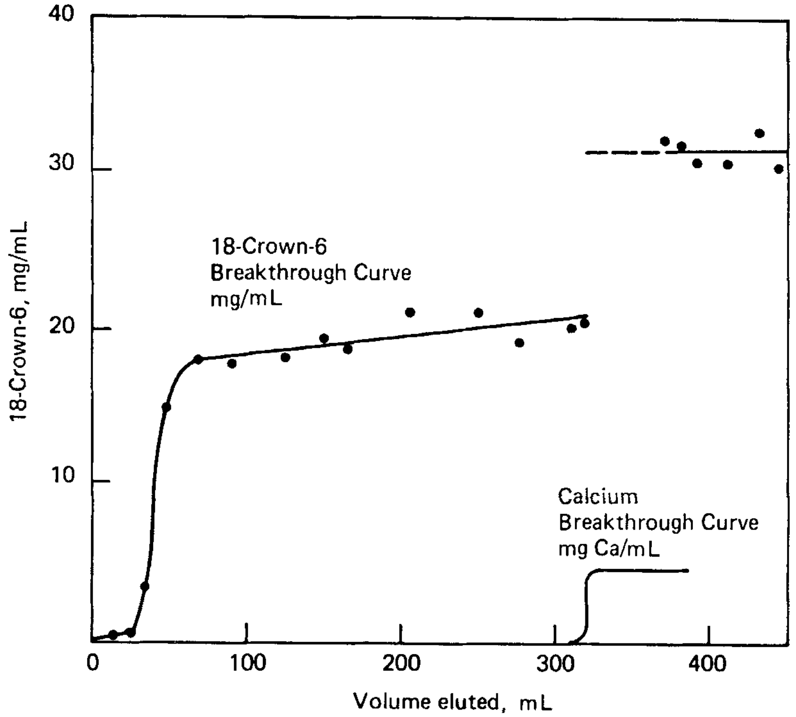

Fig. 2. Crown concentrations and calcium breakthrough curve.

coordination sphere from the solvated calcium species bonded to the resin. In Reaction (II) the crown complexed species exists in both phases with little difference in coordination spheres. Any isotope effect involving Reaction (II) is thus expected to be small, and this, in part, would explain the small size of the experimentally observed isotope effect. The stability constant of the calcium-crown complex in alcohol solutions is large, and the fraction of uncomplexed calcium in the fluid was not significant.

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