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FRACTIONATION OF LITHIUM ISOTOPES IN ION EXCHANGE CHROMATOGRAPHY WITH TITANIUM PHOSPHATE EXCHANGER

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ABSTRACT

Ion exchange chromatography of lithium was carried out to study the lithium isotope effect in an aqueous ion-exchange system, using titanium phosphate exchangers granulated with polyvinyl chloride or an inorganic binder. The sample granulated with PVC showed significant isotope fractionations when a 0.05 M $(NH_4)_2CO_3$ solution was used as an eluent. The lighter isotope ^6Li was preferentially fractionated into the exchanger phase. The isotope separation factor was roughly evaluated as 1.007, which is smaller than that (1.017) obtained by batch experiment in a preceding paper. The smaller separation factor could be explained by the fact that the number of sites effective for Li^+ exchange is less than the number evaluated from the ion exchange capacity. The exchanger granulated with an inorganic binder did not show lithium isotope fractionation in spite of its large capacity for retention of lithium.

INTRODUCTION

The element lithium consists of two stable isotopes with masses of 6 and 7. The study of lithium isotope effects is important not only for industrial nuclear science, but also for fundamental material and geological sciences. Lithium isotope fractionations by two-phase chemical exchanges have been studied extensively in various systems (1). Ion exchange chromatography is one of the promising methods for separating lithium isotopes. Commercially available ion-exchange resins, however, are not suitable for chromatographic

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separation, because their separation factors for lithium isotopes are too low to separate the isotopes effectively by the column method.

Inorganic ion exchangers have attracted attention because of their high selectivity for certain ions or groups of ions, and because of their chemical stability. They have an ion-sieve effect for various ions, depending on the hydrated or dehydrated size of the adsorbing ions. We have investigated the lithium isotope fractionation properties of inorganic ion exchangers by batch method and found that spinel type manganese oxide (2), cubic antimonic acid (3), α-titanium phosphate (4), and heat-treated α-tin phosphate (4) show lithium isotope fractionation properties with separation factors of 1.014, 1.024, 1.017, and 1.015, respectively. The isotope fractionation properties could be well explained by considering two factors: the difference in hydration circumstances of Li^+ between the exchanger and the solution phase and the influence of Li^+ stabilization in the exchanger phase (3). Other inorganic ion exchangers have also shown high separation factors for lithium isotopes (5 – 7).

Elution or displacement chromatography is a potentially practical method for lithium isotope separation with an exchanger. There have been several studies on ion-exchange chromatographic separation of lithium isotopes using organic resins (8,9) and inorganic ion exchangers (7). The present paper describes a fundamental study of lithium isotope fractionation in ion exchange chromatography with α-titanium phosphate exchanger. The α-titanium phosphate has a layered structure with exchangeable protons among the layers (10). It is characterized by having a large ion exchange capacity (7.76 mmol/g) and a relatively high separation factor for lithium isotopes. The large ion exchange capacity is advantageous in column operation, but there have been no chromatographic studies using titanium phosphate as an exchanger. It must be granulated before chromatographic study, since α-titanium phosphate is obtained in powdered form.

EXPERIMENTAL

Materials

Two kinds of granulated titanium-phosphate exchangers, TiP(PVC) and TiP(TOA), were used for the column separation studies. Sample TiP(PVC) was prepared with polyvinyl chloride (molecular weight, 40,000) as a binder. A powdered sample of α -titanium phosphate (Toagosei Co. Ltd.) was added to a DMF solution which dissolved the PVC, and then the mixture was thoroughly stirred. The weight of added PVC was set as 35% that of powdered titanium phosphate. The suspension was dropped into a water-methanol solution (1 : 1 by volume) using the equipment shown in Fig. 1 (11). The granules obtained were washed with water and sieved through a mesh between 1.4 and 2.0 mm in size. TiP(TOA) was supplied from TOA Co. Ltd.; it has a cylindrical shape with an inorganic material as a binder. Since sample TiP(TOA) was obtained in Na^+ form, it was changed to NH_4^+ form before column operation by conditioning with a 0.3 M $(NH_4)_2CO_3$ solution. The SEM observations of the granulated exchangers were carried out on a Hitachi type S-2460N scanning microscope.

Lithium hydroxide (Wako Pure Chem. Ind., Ltd., ^7Li / ^6Li = 12.40) was used as the lithium source for the isotope fractionation study.

Ion Exchange Properties

Studies of the ion exchange properties of the granulated exchangers were carried out by a batch method. The lithium ion exchange capacities was determined using a 0.1 M LiOH solution. The desorption of Li^+ from the Li^+-loaded exchangers were studied using several kinds of solutions containing ammonium salts or acetic acid. These solutions were adopted for the convenience of isotopic analysis of lithium in the eluate by thermal ionization mass spectrometry.

Chromatographic Process

The granulated exchanger was packed in a Pyrex column (150 cm x 1 cm I.D.) with a bed height of 130 cm. A lithium feed solution (0.1 M LiOH) was fed into the column at a constant flow rate to form a lithium band. The elution of the Li^+ was carried out using a CH_3COOH or a $(NH_4)_2CO_3$ solution as an eluent at the same flow rate. The effluent from the bottom was collected and divided into small fractions (10 cm^3) by a fraction collector. The temperature of the column was kept constant (20 ± 1℃) throughout the experiment in a temperature controlled room. The experimental conditions are summarized in Table 1.

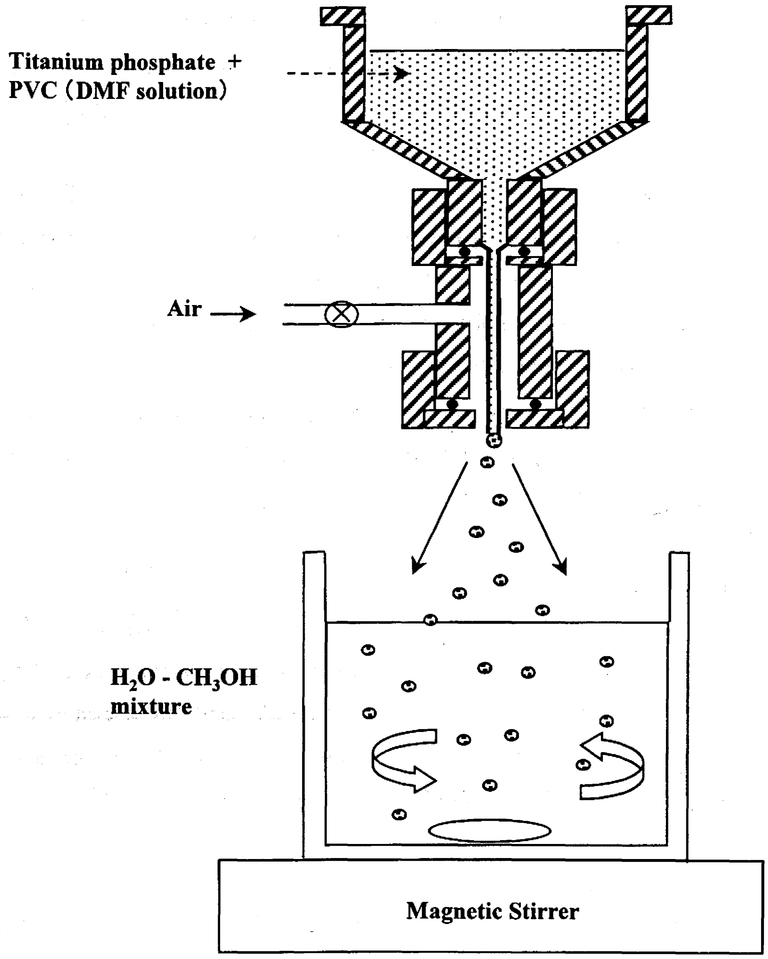

FIGURE 1. Equipment for granulation.

Analysis

The lithium concentration in the solutions was determined by atomic absorption spectrometry. The $^7Li/^6Li$ isotopic ratios were measured by the thermal ionization technique with a VG-336 mass spectrometer (3).

TABLE 1. EXPERIMENTAL CONDITIONS AND SEPARATION FACTORS

	Experiment		
Parameter	Run 1	Run 2	Run 3
Temperature/ ℃	20 ± 1	20 ± 1	20 ± 1
Adsorbent	TiP(PVC)	TiP(PVC)	TiP(TOA)
Bed height/ cm	130	130	130
Adsorbent weight/ g	16.8 (dry)	16.8 (dry)	73 (dry)
Operating manner	Band	Band	Band
Li^+ feed solution	0.1 M LiOH (150 cm^3)	0.1 M LiOH (150 cm^3)	0.1 M LiOH (100 cm^3)
Eluent	0.1 M CH_3COOH	0.2 M $(NH_4)_2CO_3$	0.05 M $(NH_4)_2CO_3$
Flow-rate/ cm^3h^{-1}	4.0	3.1	3.6
Separation factor	1.0002	1.007	——

RESULTS AND DISCUSSION

Ion-exchange Properties of Granulated Exchangers

SEM photographs of the granulated exchangers are shown in Fig. 2. Sample TiP(PVC) consists of nearly spherical particles with a smooth surface. The cross section of the particle shows that it is in the form of a PVC microcapsule. The surface consists of a thin layer of PVC. The titanium phosphate powders aggregate inside the layer. Sample TiP(TOA) consists of cylindrical particles 0.9 mm in diameter. The particles of TiP(TOA) are more compact than those of TiP(PVC).

The particle densities of TiP(PVC) in dry and wet states were 0.20 and 1.07 g/cm^3 , respectively. The porosity, calculated as 0.81 from the densities, is larger than that of the conventional granulated inorganic exchangers. The larger porosity is an advantage in column operation from the point of view of increasing the Li^+ diffusion rate, but is a disadvantage in that it decreases the ion exchange capacity per unit volume of exchanger and increases void volume. The particle densities of TiP(TOA) were 0.69 and 1.17 g/cm^3 in dry and wet states, respectively. The porosity was evaluated as 0.48 from these values.

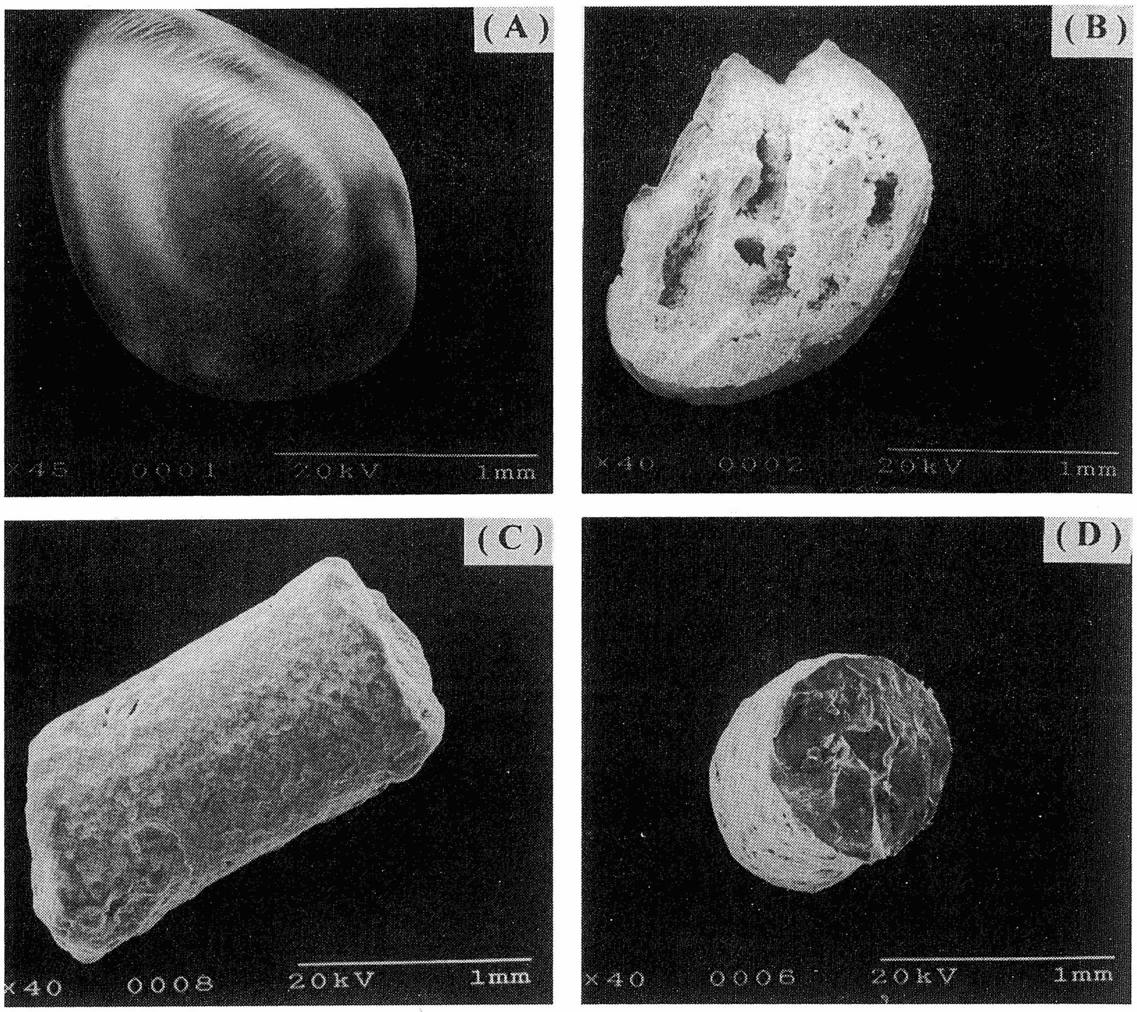

FIGURE 2. SEM photographs of TiP(PVC) and TiP(TOA).
(A): TiP(PVC), (B): TiP(PVC) cross section,
(C): TiP(TOA), (D): TiP(TOA) cross section.

The lithium ion-exchange properties were investigated in a 0.1 M LiOH solution. The rates of lithium uptake were fast for both granulated exchangers; the reactions reached equilibrium in 1 day. The ion exchange capacities of TiP(PVC) and TiP(TOA) were evaluated as 2 and 1.4 mmol per gram of dry adsorbent, respectively. Powdered α-titanium phosphate has been known to have an ion exchange capacity of 7.76 mmol/g (10); while the ion exchange capacities of the granulated exchangers are smaller than the values expected from the ion-exchange capacity of the original powdered exchanger. This suggests that some of the ion exchange sites are blocked by the added binders in the granules.

The desorption of Li^+ from the exchangers was studied by a batch method using several kinds of solutions (Table 2). TiP(PVC) with ammonium salt solutions, except for $(NH_4)_2CO_3$ show desorption of about 80% Li^+, independent of salt concentration. The $(NH_4)_2CO_3$ solutions with concentrations above 0.1 M show desorption of more than 94% of Li^+. A 0.1 M CH_3COOH solution shows desorption of 97% Li^+, while a 0.01 M CH_3COOH solution only 67% Li^+. A solution having a high Li^+ desorption ability is suitable for obtaining a good elution curve in the column experiment. Therefore, we used a 0.1 M CH_3COOH or a 0.05 M $(NH_4)_2CO_3$ solution as an eluent for column elution.

Li^+ desorption was only studied in $(NH_4)_2CO_3$ solutions for TiP(TOA). The fraction of Li^+ desorption increases slightly from 93 to 98% with an increase in the $(NH_4)_2CO_3$ concentration from 0.1 to 0.5 M (Table 2).

Column Elution Curves

Elution curves and $^7Li/^6Li$ isotopic ratios for the three column experiments are given in Figs. 3 – 5. The original lines in the figures show the isotopic ratio in the feed solution ($^7Li/^6Li$ = 12.40). The lithium concentration profiles show the deviation from that of ideal displacement chromatography. This may be because the particle size of the exchanger is too large to have a good elution or displacement band. The isotope-fractionation profiles are largely dependent, not only on the kinds of exchanger, but also on the kinds of eluent. The elution of Li^+ progresses easily when the CH_3COOH solution is used with the TiP(PVC) column (Fig. 3). Since titanium phosphate is a weak acid exchanger, the adsorbed Li^+ can easily be exchanged with protons, even in a weak acid solution.

The elution curve shows two peaks at the effluent volume of 80 and 160 cm^3. This suggests the presence of two kinds of ion-exchange site in TiP(PVC) with different affinities for Li^+. The H^+/Li^+ exchange properties of α-titanium phosphate have been studied by several authors (10, 12, 13). The pH titration curve with LiOH has exhibited a single plateau in the region of Li^+ loading below 6 mequiv./g, while a pH increase in the region above 6 mequiv./g (12). This also suggests the presence of two kinds of ion-exchange site in α-titanium phosphate.

The isotopic fractionation is not observed in the front part of the elution. This suggests that the ion exchange site with low affinity for lithium are ineffective for the isotope

TABLE 2. DESORPTION PROPERTIES OF Li$^+$ FROM GRANULATED TITANIUM PHOSPHATES

Sample	Solution	pH	Amount of Li$^+$ desorbed / %
TiP(PVC) (Li$^+$ uptake = 2 mmol/g)	0.1 M NH_4Cl	4.7	80
	0.1 M NH_4NO_3	4.9	73
	1 M CH_3COONH_4	7.3	76
	0.1M CH_3COONH_4	7.0	76
	0.01M CH_3COONH_4	7.0	76
	1 M $(NH_4)_2CO_3$	9.4	97
	0.1 M $(NH_4)_2CO_3$	9.4	86
	0.01M $(NH_4)_2CO_3$	9.3	65
	0.1 M CH_3COOH	3.1	97
	0.01M CH_3COOH	3.4	67
TiP(TOA) (Li$^+$ uptake = 1.4 mmol/g)	0.5 M $(NH_4)_2CO_3$	9.4	98
	0.2 M $(NH_4)_2CO_3$	9.4	94
	0.1 M $(NH_4)_2CO_3$	9.4	93

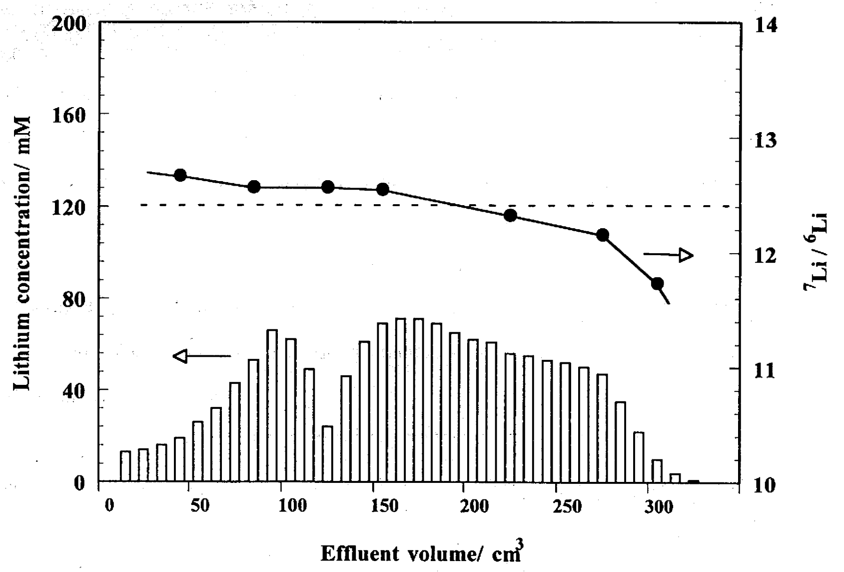

FIGURE 3. Lithium concentration profile and the $^7Li/^6Li$ isotopic ratios of the chromatographic experiment. Column: TiP(PVC), eluent: CH_3COOH.

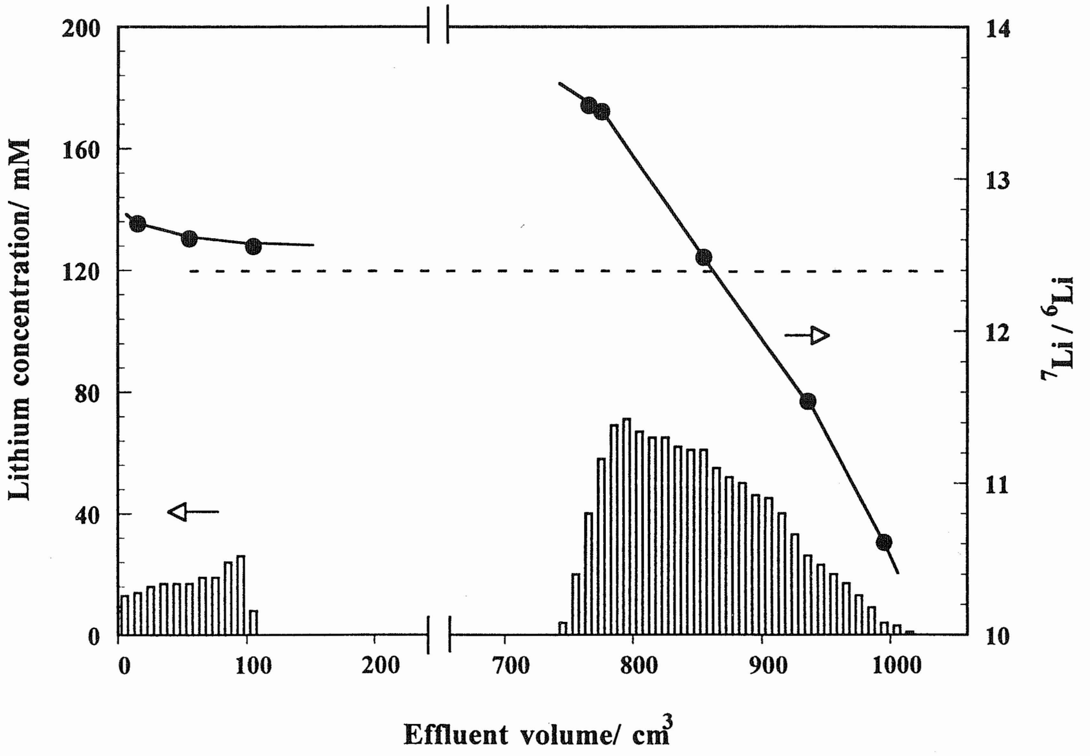

FIGURE 4. Lithium concentration profile and the ^{7}Li/^{6}Li isotopic ratios of the chromatographic experiment. Column: TiP(PVC), eluent: $(NH_4)_2CO_3$.

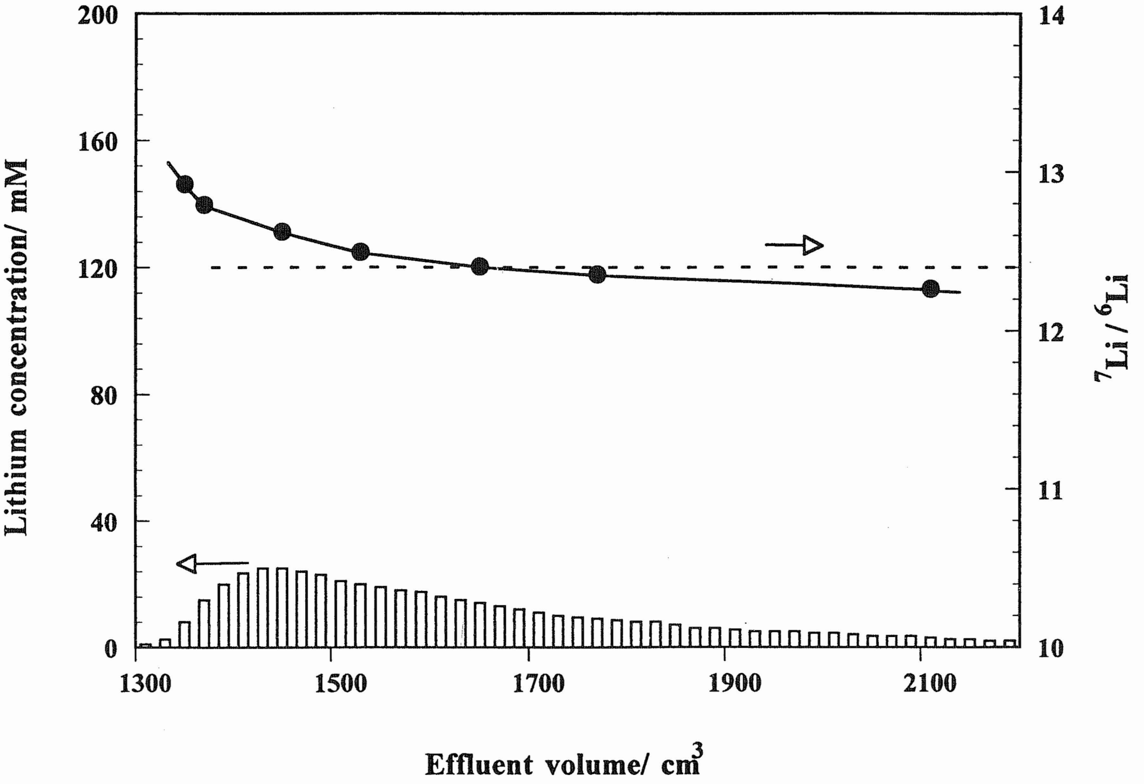

FIGURE 5. Lithium concentration profile and the ^{7}Li/^{6}Li isotopic ratios of the chromatographic experiment. Column: TiP(TOA), eluent: $(NH_4)_2CO_3$.

fractionation. Usually H^+/Li+ exchange reactions proceed without dehydration of Li^+ for exchangers with low affinity for Li^+. Therefore, the isotopic fractionation due to the dehydration of Li^+ may be ineffective in the front part of the elution, owing to the insufficient dehydration of Li^+ in the solid phase. The ^{7}Li/^{6}Li ratio decreases in the rear parts of the lithium band, that is, ^{6}Li is preferentially fractionated in the exchanger phase. This tendency agrees with the preceding batch result, but the degree of isotopic fractionation is markedly smaller than that expected from the separation factor (1.017) of α-titanium phosphate. Since the retention volume is very small in this system, the repetition of Li^+ - H^+ exchange effective for isotope fractionation may be insufficient during the migration of Li^+ through the exchange bed.

When a 0.05 M $(NH_4)_2CO_3$ solution is used with the TiP(PVC) column, the elution curve is separated into two bands with peaks at effluent volumes of 90 and 800 cm^3. This also suggests the presence of two kinds of exchange sites in TiP(PVC). The eluates in the first band do not show isotopic fractionation, while those in the second band give significant fractionations. The ^{7}Li/^{6}Li ratio in the second band changes from 13.48 in the front part to 10.60 in the rear part of the elution curve. This result shows that the exchange sites with higher affinity for Li^+ are effective for lithium isotope fractionation.

The TiP(TOA) sample does not show isotope fractionation properties in spite of the fact that the retention volume is the largest among the three systems. Since the ion exchange capacity of TiP(TOA) is markedly smaller than that expected from the original powdered exchanger, we think that the ion exchange sites effective for lithium isotope fractionation are blocked by the inorganic binder added.

Evaluation of Isotope Separation Factors

Rough estimations of the single separation factors, S (= ε + 1), were carried out for TiP(PVC) exchanger using the following equation (14)

$$\varepsilon = \Sigma | R_i - R_o | f_i / [Q\, R_o\, (1 - R_o)] \qquad (1)$$

where, R_o is the isotopic mole fraction (0.0746) of ^{6}Li in the feed solution, R_i is that of in the ith fraction, f_i is the amount of lithium in the ith fraction, Q is the total exchange capacity of the exchanger, and summation is taken over all the fractions that are enriched or depleted in ^{6}Li. The total exchange capacity was evaluated as 33.6 mmol from the experimental values of the ion exchange capacity (2.0 mmol/g) of TiP(PVC) and the weight (16.8 g) of the exchanger in the column. The ε values were calculated from the rear parts of the elution curves, assuming that the ^{7}Li/^{6}Li ratio varies linearly between the observed values. The ε value is 0.007 for the system TiP(PVC) – $(NH_4)_2CO_3$; this is about a half that (0.017) of the batch experiment. The reason for the smaller ε value may be that the number of the effective exchange sites for lithium isotope fractionation is smaller than that derived from the ion exchange capacity. The ε value is very small (0.0002) for the system TiP(PVC) – CH_3COOH. Since titanium phosphate is a weak acid ion exchanger, the protonated sites are almost unexchangeable with other metal ions in an acidic solution. Therefore, the actual Q value may be very small compared to that calculated from the exchange capacity. These results suggests that an acidic eluent is not appropriate for column separation of lithium isotope with a weakly acidic ion exchanger. It is important to control the pH of the eluate to obtain an elution curve with high fractionation behavior for lithium isotopes.

CONCLUSIONS

α-titanium phosphate granulated with polyvinyl chloride is promising as an exchanger for lithium isotope separation by elution chromatography with a $(NH_4)_2CO_3$ eluent.

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