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Chromatographic Lithium Isotope Separation Using Cubic Antimonic Acid as Column-Packing Material

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Abstract: Ion-exchange chromatographic lithium isotope separation was performed by using granular cubic antimonic acid as column packing material at 50°C. While the single-stage separation factor for the lithium isotopes was 1.0020, independent of the flow rate, HETP was a monotonously increasing function of flow rate both in breakthrough and reverse breakthrough experiments. After 442 cm chromatographic development, the ^{6}Li atomic fraction increased to 0.256 in the reverse breakthrough experiment and decreased to 0.026 in the breakthrough experiment both from its original value of 0.074.

Keywords: Lithium, Lithium isotopes, Cubic antimonic acid, Isotope separation

INTRODUCTION

Methods of lithium isotope separation have been studied, and ion-exchange chromatography is among the promising methods. Commercially available organic ion exchangers are traditionally used as column packing materials, with the single-stage separation factor for the lithium isotopes, *S*, of up to about 1.003 being observed at room temperature (1). Here, S is

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defined as

$$S = \frac{(\text{Amount of } ^{6}\text{Li in ion exchanger})}{(\text{Amount of } ^{7}\text{Li in ion exchanger})} \times \frac{(\text{Amount of } ^{7}\text{Li in solution})}{(\text{Amount of } ^{6}\text{Li in solution})}.$$

This isotope separation effect is small, and the development of ion exchangers with large lithium isotope effects is hoped for. It is reported that some inorganic ion exchangers in the hydrogen form show lithium isotope effects from several times to one order of magnitude larger than those of organic ion exchangers. They include manganese oxides-based ion exchangers (2–4), niobic and tantalic acids (5), and titanium/zirconium phosphates-based ion exchangers (6–12).

Measurements of S values with those materials have been carried out batchwise and not chromatographically. A reason for this is that they are synthesized as powders and thus are not suited for chromatographic experiments. These ion exchangers will be used as column packing materials in practical chromatographic lithium isotope separation processes. Therefore, they should not only show large lithium isotope effects but also be excellent column packing materials.

Cubic antimonic acid, hereafter abbreviated as C-SbA, is another ion exchanger in the hydrogen form that shows lithium isotope effects one order of magnitude larger than those of organic ion exchangers (13, 14). Although C-SbA is obtained in the powdery form, C-SbA in the granular from is commercially available, which can be used as column packing material. In the previous paper (14), we found experimental conditions under which displacement-type breakthrough and reverse breakthrough chromatography with C-SbA was realized. These conditions are very limited since the granular C-SbA is mechanically and chemically not very stable; it easily decomposed into fine particles. In this paper, we report the flow rate dependence of the performance of chromatographic lithium isotope separation process using C-SbA as column packing material and a 150-cm-long column under the experimental conditions previously found (14). We also report the results of chromatographic experiments using three 150 cm columns connected in series.

EXPERIMENTAL

Antimonic Acid and Reagents

C-SbA in the granular form was obtained from Toagosei Chemical Industry Co. Properties of C-SbA (13–15) are briefly as follows.

The chemical formula of C-SbA is expressed as $Sb_2O_5 \cdot 4H_2O$ and is considered to consist of three $H_3Sb_3O_5(OH)_8$ units and one $H_5Sb_5O_6(OH)_{18}$ unit per unit cell. (Our elemental analysis, however, shows that about 1.2% hydrogen ions in the granular C-SbA are replaced by sodium ions.) The specific surface area measured by the BET method is $20\,m^2/g$. The theoretical ion-exchange capacity is 5.1 meq/g and selectivity for group 1 metal ions is in the decreasing order of $Na > Cs > Rb > K > Li$. C-SbA works as a cation exchanger at around $pH = 2.2$ or higher and the lithium ion uptake is a monotonously increasing function of pH. Ion-exchange equilibrium with a lithium ion-containing solution is attained in about 2 h at 25°C and 1 h at 50°C. ^6Li is preferentially taken up by C-SbA over ^7Li, and S values obtained batchwise are 1.025 at 25°C and 1.013 at 70°C.

All reagents used were of analytical-reagent grade and were used without further purification.

Chromatographic Experiments

Eight chromatographic experiments were carried out, four in the displacement-type breakthrough manner and four in the displacement-type reverse breakthrough manner under the experimental conditions reported before (14). A Pyrex glass column of 150 cm × 1.0 cm i. d. with a water jacket was used as the separation column in three breakthrough and three reverse breakthrough experiments. In the fourth breakthrough and the fourth reverse breakthrough experiments, three 150 cm × 1.0 cm i. d. columns connected in series with 1/16 in. i. d. Tygon tubes were used for prolonged chromatographic developments. In every experiment, the temperature of columns was kept constant at 50.0 ± 0.4°C by passing thermostatted water through the water jackets.

In a breakthrough experiment, the granular C-SbA was suspended in dilute hydrochloric solution. (Note that the granular C-SbA is easily decomposed into fine powders in pure water to become unusable as column packing material.) The suspended C-SbA was poured into the column to form the C-SbA bed. The lithium feed solution of the natural lithium isotope abundance was then fed to the column at a constant flow rate and the effluent from the bottom of the column was collected and portioned into small fractions with a fraction collector. The pH and lithium concentration of each fraction were measured with a pH meter and with an atomic absorption spectrometer operated in the flame photometric mode, respectively. $^7Li/^6Li$ isotopic ratios of selected fractions of the effluent were measured with the surface ionization technique on a Finnigan Mat 261 mass spectrometer as before (1). The experimental conditions of the three breakthrough experiments are basically the same each other except for the flow rate.

In a reverse breakthrough experiment, lithium ions taken up by the C-SbA packed in the column in the corresponding breakthrough experiment are eluted with an appropriate eluent. The effluent from the column is treated as in the case of the breakthrough experiment.

Experimental conditions are summarized in Table 1.

RESULTS AND DISCUSSION

The chromatograms (—) and the ^{7}Li/^{6}Li isotopic ratios (●) of the breakthrough using a 150 cm column are depicted in Figs. 1 (bt1), 2 (bt2), and 3 (bt3), and those of the reverse breakthrough experiments are in Figs. 4 (rbt1), 5 (rbt2), and 6 (rbt3). It is observed for both the breakthrough and reverse breakthrough chromatograms that the boundary of the lithium adsorption zone becomes broad with increasing flow rate. The ^{7}Li/^{6}Li ratio gradually increases toward the front-most fraction of the lithium adsorption zone in every breakthrough experiment and gradually decreases toward the

Table 1. Experimental conditions[a]

Run	Operating manner[b]	Li feed solution[c,d]	Eluent[c,e]	C-SbA bed height (cm)	Flow rate (cm^3/h)
bt1	bt	0.11 M LiOH; 8.8 M HAc		145	9.6
bt2	bt	0.11 M LiOH; 9.2 M HAc		134	58.8
bt3	bt	0.10 M LiOH; 9.0 M HAc		140	120.5
bt4	bt	0.10 M LiOH; 9.2 M HAc		442	40.6
rbt1	rbt	0.11 M LiOH; 8.8 M HAc	0.10 M KAc; 0.71 M HAc; 0.055 M HCl	138	9.0
rbt2	rbt	0.11 M LiOH; 9.2 M HAc	0.11 M KAc; 0.79 M HAc; 0.058 M HCl	134	56.9
rbt3	rbt	0.10 M LiOH; 9.0 M HAc	0.10 M KAc; 0.67 M HAc; 0.048 M HCl	140	120.5
rbt4	rbt	0.10 M LiOH; 9.2 M HAc	0.10 M KAc; 0.70 M HAc; 0.048 M HCl	442	40.6

[a] Temperature = 50 ± 0.4°C.

[b] bt = Breakthrough; rbt = Reverse breakthrough.

[c] Ac = acetate ion; M = mol/dm^3.

[d] pH = 2.25.

[e] pH = 3.46.

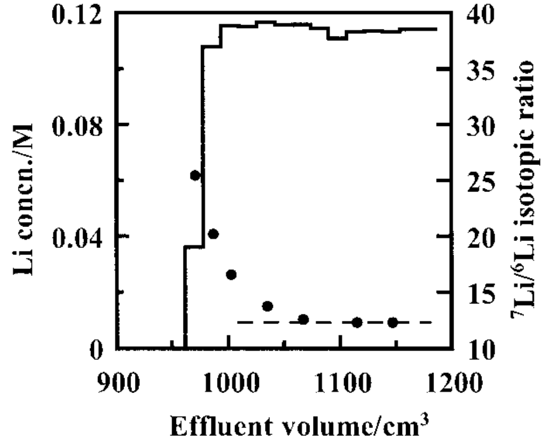

Figure 1. The chromatogram (—) and ^{7}Li/^{6}Li (●) of bt1. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

rear-most fraction in every reverse breakthrough experiment, showing that the lighter isotope ^{6}Li is preferentially taken up by the ion exchanger.

Using the experimental data on the lithium isotopic ratios and the lithium concentrations, the S value, the HETP (height equivalent to a theoretical plate) and the number of theoretical plates, N_{TP}, are calculated for each experiment and summarized in Table 2. The S (=$\varepsilon + 1$) value is calculated by using Eq. (18),

$$\varepsilon = \Sigma f_i |R_i - R_0| / [QR_0(1 - R_0)],$$

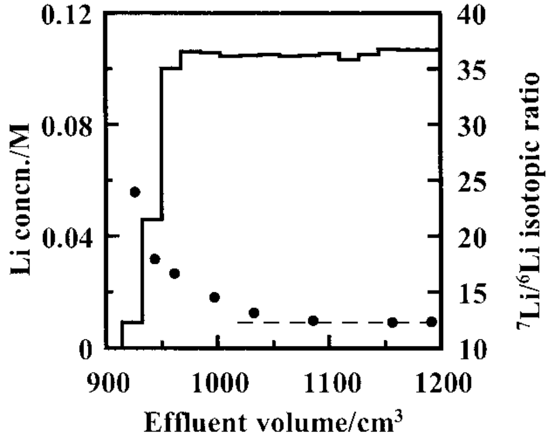

Figure 2. The chromatogram (—) and ^{7}Li/^{6}Li (●) of bt2. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

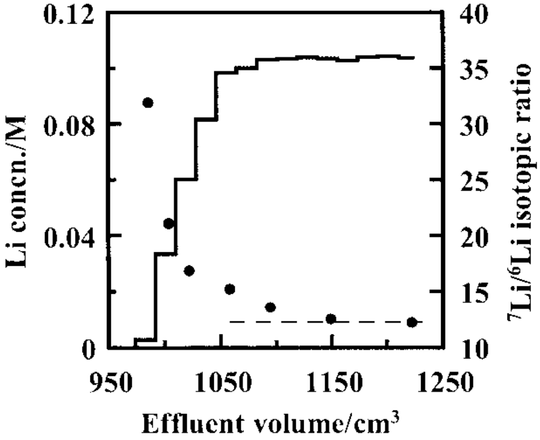

Figure 3. The chromatogram (—) and ^{7}Li/^{6}Li (●) of bt3. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

where f_i is the amount of lithium ion in the i-th fraction of the effluent, R_i the atomic fraction of ^{6}Li in the i-th fraction, R_0 the atomic fraction of ^{6}Li in the feed solution, Q the total ion-exchange capacity of the C-SbA bed, and the summation is taken over all the fractions where R_i differs from R_0. As is seen in Table 2, S is independent of flow rate within experimental errors, indicating that isotope exchange equilibrium has been maintained between the solution phase and the ion-exchanger phase in every experiment.

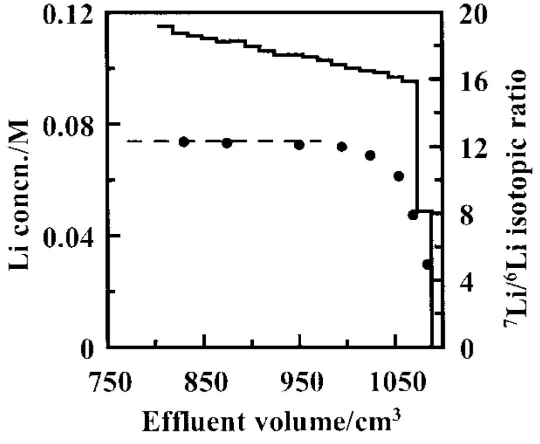

Figure 4. The chromatogram (—) and ^{7}Li/^{6}Li (●) of rbt1. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

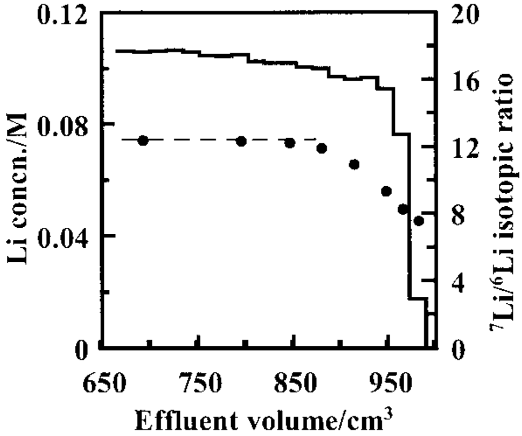

Figure 5. The chromatogram (—) and ^{7}Li/^{6}Li (●) of rbt2. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

The HETP is calculated using Eq. (19),

$$\text{HETP} = \varepsilon/k + 1/(k^2 L),$$

where L is the distance of the chromatographic development (bed height) and k is the slope of the plot of $\ln(r - r_0)$ against $(x - L)$. Here, x is the position in the C-SbA bed with $x = 0$ at the top of the bed, r is the ^{7}Li/^{6}Li (or ^{6}Li/^{7}Li) isotopic ratio at x, and r_0 is that of the feed solution. The quantity N_{TP} is calculated as L/HETP. As a result of the calculations, HETP from 1.4 to 3.8 mm

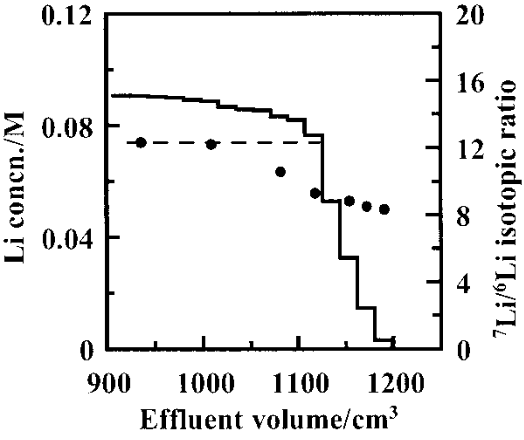

Figure 6. The chromatogram (—) and ^{7}Li/^{6}Li (●) of rbt3. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

Table 2. Experimental results

Run	Figure	ε (=$S-1$)	HETP (mm)	N_{TP}
bt1	Fig. 1	0.022 ± 0.001	1.7	853
bt2	Fig. 2	0.020 ± 0.001	2.9	462
bt3	Fig. 3	0.020 ± 0.002	3.5	400
bt4	Fig. 7	0.018 ± 0.003	3.2	1380
rbt1	Fig. 4	0.022 ± 0.002	1.4	950
rbt2	Fig. 5	0.020 ± 0.002	2.2	515
rbt3	Fig. 6	0.021 ± 0.002	3.8	368
rbt4	Fig. 8	0.020 ± 0.002	3.1	1430

is obtained. As is expected, EHTP is a monotonously increasing function of flow rate both in the breakthrough and in the reverse breakthrough experiments within the present experimental conditions. It is also seen that HETP is nearly independent of the operational manner for a given flow rate.

The chromatograms (—) and the ^{7}Li/^{6}Li isotopic ratios (●) of the breakthrough and the reverse breakthrough experiments using three 150 cm columns in series are depicted in Figs. 7 (bt4) and 8 (rbt4), respectively. The values of S, HETP N_{HP} are summarized in Table 2. Although S values of bt4 and rbt4 are nearly equivalent to those of the experiments of the shorter developments, the HETP values are not as small as expected from the data of the shorter development experiments. This is most probably because three columns are connected with Tygon tubes in bt4 and rbt4. No isotope enrichment occurs inside the tubes; instead, mixing of the isotopes

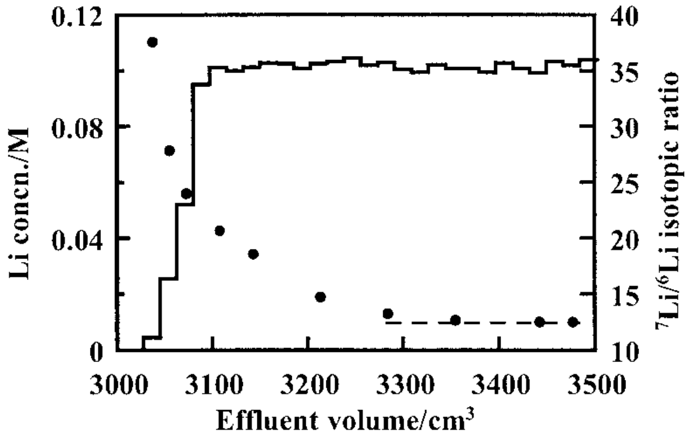

Figure 7. The chromatogram (—) and ^{7}Li/^{6}Li (●) of bt4. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

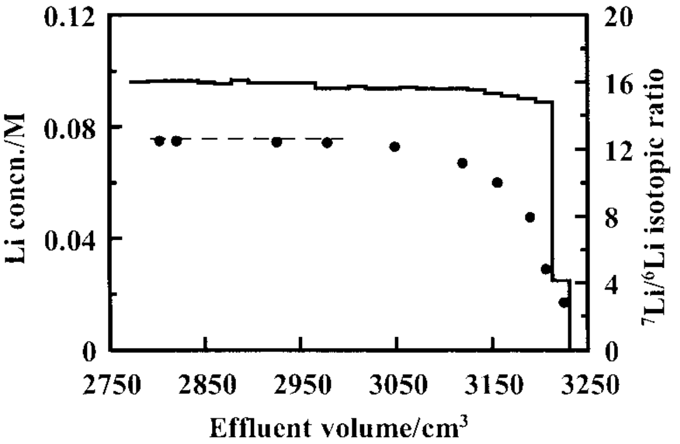

Figure 8. The chromatogram (—) and ^{7}Li/^{6}Li (●) of rbt4. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. Experimental conditions are summarized in Table 1.

occurs, which leads to the increase in HETP. The ^{6}Li atomic fraction in the front-most fraction of the effluent in bt4 decreased to 0.026 from its original value of 0.074 in the feed solution, and in rbt4 it reaches to 0.256 in the rear-most fraction of the effluent.

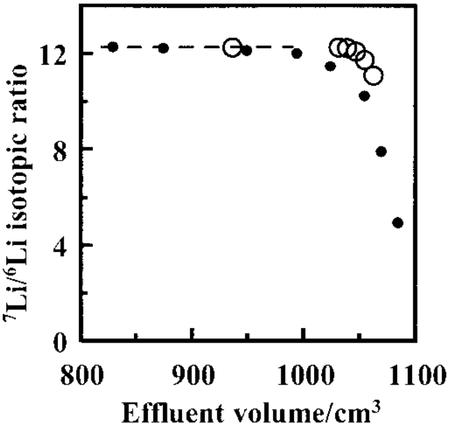

Figure 9. A comparison of ^{7}Li/^{6}Li profiles of an experiment with C-SbA (rbt1) (●) and that with an organic ion exchanger (○) operated at similar scales. The broken line shows the ^{7}Li/^{6}Li ratio in the feed solution. The experimental conditions of the experiment with an organic ion exchanger are temperature, 25°C; ion exchanger, Toray strongly acidic cation exchange fiber; ion exchanger bed, 200 cm × 1.0 cm i. d.; lithium feed solution, 0.104 M lithium lactate solution; eluent, 0.114 M potassium lactate solution; flow rate, 5.30 cm^3/h; ε, 0.0015.

To show the superiority of C-SbA to organic ion exchangers as column packing material for the chromatographic lithium isotope separation, Fig. 9 is provided, where results of two chromatographic experiments of similar scales are compared. The $^7Li/^6Li$ profile of rbt1 (●) is compared with that of previously reported chromatographic experiment (○) (1) using an organic ion-exchange fiber as column packing material. For the similar effluent volume, the degree of ^7Li depletion (or ^6Li enrichment) is much substantial in the experiment with C-SbA, starting from the same natural abundance ratio of $^7Li/^6Li = 12.3$.

CONCLUSION

In this paper, we show that the granular C-SbA can be used as a column packing material for the chromatographic separation of lithium isotopes. The HETP value increases with increasing flow rate within the present experimental conditions, while the S value remains constant both in the breakthrough and the reverse breakthrough experiments.

It is known that lithium uptake by C-SbA is a monotonously increasing function of pH, which means chromatographic operation should be performed at as high pH as possible to make better use of C-SbA. However, at present, pH values of lithium feed solution and an eluent have to be kept low to realize displacement-type chromatograms and to avoid the decomposition of the granular C-SbA. To find experimental conditions in which displacement chromatography can be realized at a higher pH seems thus important.

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