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

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ABSTRACT

The applicability of granular cubic antimonic acid (C-SbA) as column packing material in chromatographic lithium isotope separation was investigated. The feed solution should have the buffer capacity to promote lithium uptake, and its pH has to be kept as low as 2.25 to prevent the decomposition of the granular C-SbA in order to obtain a sharp front boundary of the lithium sorption zone. The pH and the chemical composition of the eluent should be finely controlled to obtain a displacement-type chromatogram. The lithium isotope separation effect was about ten times larger than that achieved on an organic ion exchanger.

INTRODUCTION

Ion-exchange column chromatography is a promising method for separating the lithium isotopes ^{6}Li and ^{7}Li (1). Commercially available organic ion exchangers are usually used as column-packing materials, and a single-stage

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separation factor, S, of up to about 1.003 is observed at room temperature. Here, S is defined as

$$S = \frac{\text{(the amount of } {}^{6}\text{Li in the exchanger phase)}}{\text{(the amount of } {}^{7}\text{Li in the exchanger phase)}} \times \frac{\text{(the amount of } {}^{7}\text{Li in the solution phase)}}{\text{(the amount of } {}^{6}\text{Li in the solution phase)}}$$

This isotope separation effect is rather small compared to those in amalgam and macrocyclic polyether systems (2, 3), and the development of ion exchangers with large lithium isotope effects is hoped for.

We and other researchers have reported that some inorganic sorbents and ion exchangers showed lithium isotope effects from several times to one order of magnitude larger than those of organic ion exchangers. They include manganese oxide-based sorbents/ion exchangers (4–6), zirconium phosphate-based ion exchangers (7), antimonic acids (4, 8), and niobic and tantalic acids (9). Measurements of lithium isotope effects with these materials have been carried out batchwise and not chromatographically. This is partly because most of them are commercially unavailable and homemade, and it is not easy to produce them in amounts large enough to be used for chromatographic experiments. These sorbents/ion exchangers will be used as column-packing materials in practical lithium isotope separation processes. Thus, they should not only show large lithium isotope effects but also be excellent column-packing materials.

Cubic antimonic acid shows lithium isotope effects one order of magnitude larger than those of organic ion exchangers (4, 8). This effect is the largest among the effects we have so far observed with the inorganic sorbents/ion exchangers under similar experimental conditions (4–8). In addition, cubic antimonic acid is commercially available. In this paper we report on its feasibility as a column packing material for chromatographic lithium isotope separation.

EXPERIMENTAL

Antimonic Acid

Cubic antimonic acid (abbreviated C-SbA) in the granular form was purchased from Toagosei Chemical Industry Co. Its chemical formula is expressed as $Sb_2O_5 \cdot 4H_2O$ (10) and it 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 (11). According to our elemental analysis, about 1.2% hydrogen ions in the purchased C-SbA are replaced by sodium ions. A SEM photograph of granular C-SbA taken with a Hitachi S-4500 electron microscope is shown in Fig. 1(a). Its

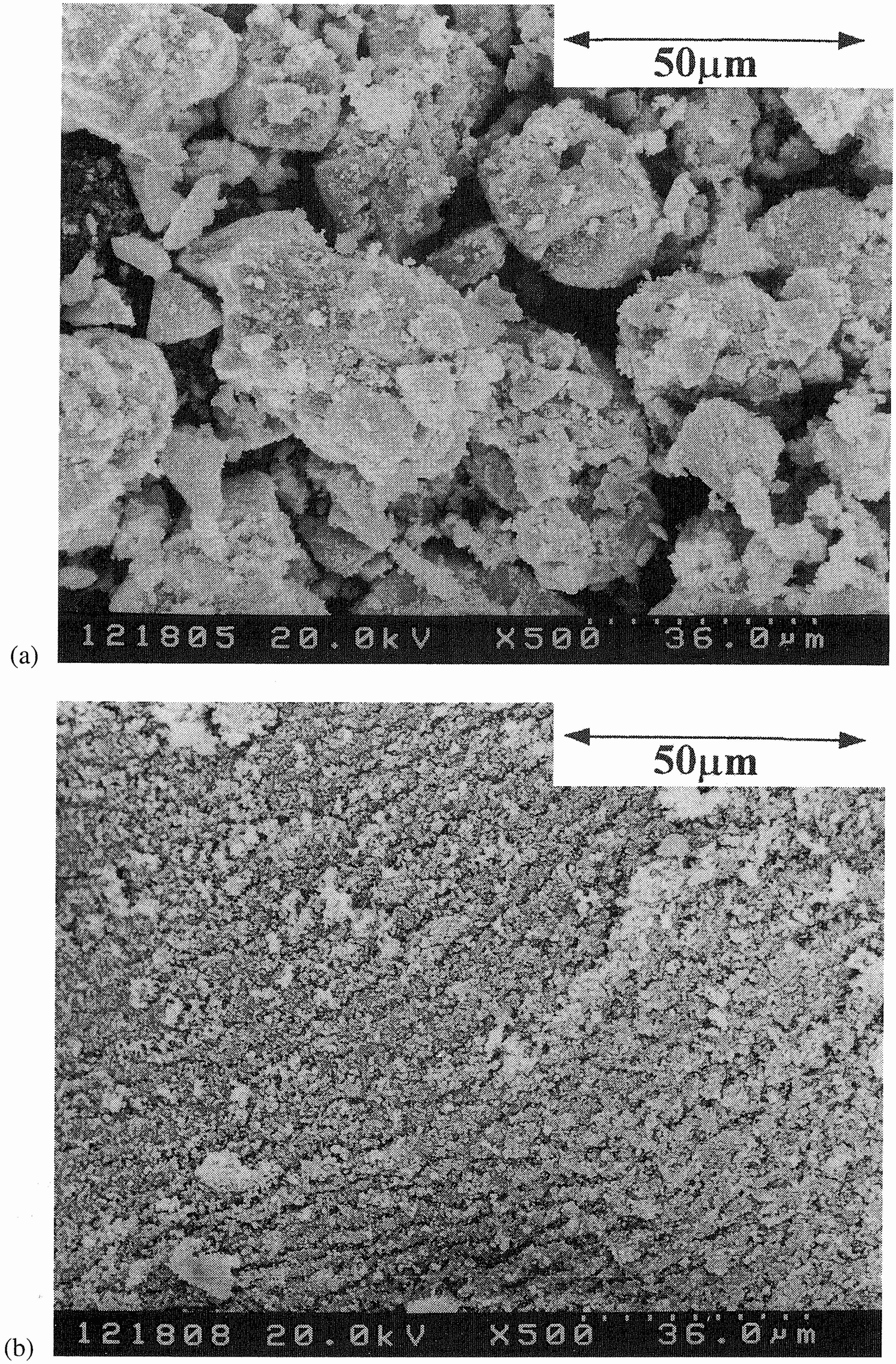

FIG. 1 SEM photographs of C-SbA. (a) Granular C-SbA as purchased; (b) C-SbA being decomposed into fine particles.

TABLE 1
Some Properties of Cubic Antimonic Acid as an Ion Exchanger

	Cf.	Ref.
Selectivity for alkali metal ion $Na \gg Cs > Rb > K \gg Li$		12
Ion exchange capacity, 5.1 meq/g	Theoretical value	12
Lithium isotope selectivity, $^6Li > {}^7Li$		4, 8
Separation factor for Li isotope, 1.025 (25°C), 1.013 (70°C)	Solution phase: 0.1 M LiOH	8

shape is roughly spherical with an average diameter of about 70 μm, and its specific surface area measured by the BET method is 20 m^2/g. The chemical properties of C-SbA as an ion exchanger so far reported are briefly summarized in Table 1.

Characterization

In addition to the properties listed in Table 1, we examined the rate of lithium sorption and pH dependence of the lithium uptake.

Rate of Lithium Sorption

A 1-g sample of granular C-SbA was placed in 50 cm^3 of 0.1 M LiOH solution at a prefixed temperature (25 or 50°C). Transfer of lithium ions from the solution to C-SbA commenced immediately. A small volume of the solution was sampled periodically with a micropipet, and the lithium concentration of the sampled solution was determined flame photometrically after appropriate dilution. The amount of lithium ions sorbed was calculated from the concentration difference between the original solution and the sampled solution.

pH Dependence of Li Uptake

A 0.1-g sample of C-SbA was placed in 10 cm^3 of a mixture of 0.1 M LiOH and 0.1 M LiCl solutions at 50°C. After equilibrium was attained between the solution and C-SbA phases, the two phases were separated by filtration. The pH of the solution was measured and the amount of lithium uptake was calculated from the concentration difference of the solution phase before and after sorption.

Chromatographic Experiments

Experiments with a 30-cm Column

Breakthrough and reverse breakthrough experiments were carried out to search for the conditions under which displacement-type chromatograms were formed. Displacement chromatography is considered superior as an isotope separation technique to elution chromatography. The chromatographic column used was a Pyrex glass column of 1 cmϕ × 30 cm with a water jacket for temperature control. The temperature, the flow rate, and the lithium ion concentration of the feed solution were fixed at 25°C, 20 cm^3/h, and about 0.1 M, respectively, in every experiment.

In a breakthrough experiment, a lithium feed solution was fed to a column packed with granular C-SbA. The effluent from the column was portioned into small fractions (5–10 cm^3), and the pH and lithium concentration in each fraction were measured. We tried various chemical compositions of feed solutions in our search for the composition of the feed solution which produced the best displacement-type boundary at the front of the lithium sorption zone.

In a reverse breakthrough experiment, lithium ions sorbed on the C-SbA using the "best" feed solution determined in the breakthrough experiments described above were eluted with an eluent. We attempted various eluents and sought the chemical composition of the eluent that "best" produced the displacement-type boundary at the rear of the lithium sorption zone.

Experiments with a 150-cm Column

Using the most appropriate lithium feed solution and the most appropriate eluent determined above and a Pyrex glass column of 1 cmϕ × 150 cm with a water jacket, we carried out breakthrough and reverse breakthrough experiments. The aim of these experiments was twofold. One was to confirm that displacement-type chromatograms would be maintained even after a long (ca. 150 cm) chromatographic development, and the other was to observe lithium isotope fractionation. The C-SbA bed heights were 146.8 cm and 142.3 cm for the breakthrough and reverse breakthrough experiments, respectively. The flow rate was 18.1 cm^3/h in both the cases. Lithium isotopic ratios of some selected fractions of the effluents were measured with the surface ionization technique on a Finnigan Mat 261 or a MAT CH-5 mass spectrometer as before (5, 13).

RESULTS AND DISCUSSION

Characterization of Granular C-SbA

Rate of Lithium Sorption

The amount of lithium ions taken up by C-SbA is plotted against time in Fig. 2. As is shown, equilibrium was reached in about 1 hour at 50°C and 2 hours at 25°C. These times are equivalent to those observed with commercially available organic ion exchangers and short compared with that of the in-

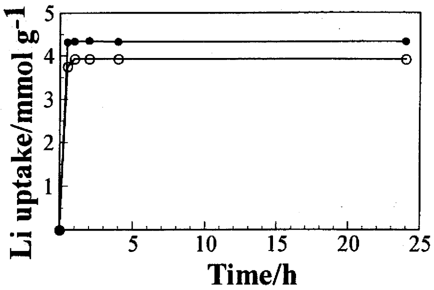

FIG. 2 Plot of lithium uptake against reaction time. Temperature: 25°C (○); 50°C (●).

organic manganese oxide-based sorbent (5). Thus, granular C-SbA is compatible in rate of sorption/ion exchange reaction with organic ion exchangers.

pH Dependence of Li Uptake

The amount of lithium taken up by C-SbA is plotted against pH in Fig. 3. Below a pH of around 2, C-SbA shows no ion-exchange capability; it does not work as an ion exchanger. Above pH 2, the lithium uptake increases with increasing pH, and at pH 12 it becomes equivalent to the theoretical ion-exchange capacity (cf. Table 1). A higher pH is thus preferable to make better use of the capability of C-SbA as an ion exchanger.

Chromatographic Experiments

Breakthrough Experiments with a 30-cm Column

Chromatograms of the selected breakthrough experiments using a 30-cm column are depicted in Fig. 4(a)–4(d). Chemical compositions of lithium

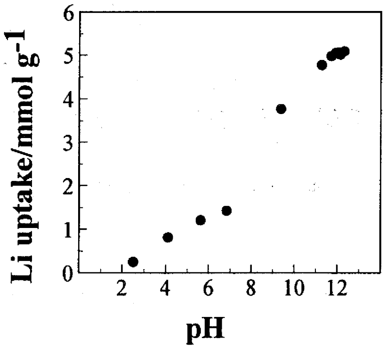

FIG. 3 Lithium uptake from 0.10 M (LiOH + LiCl) solution at 50°C.

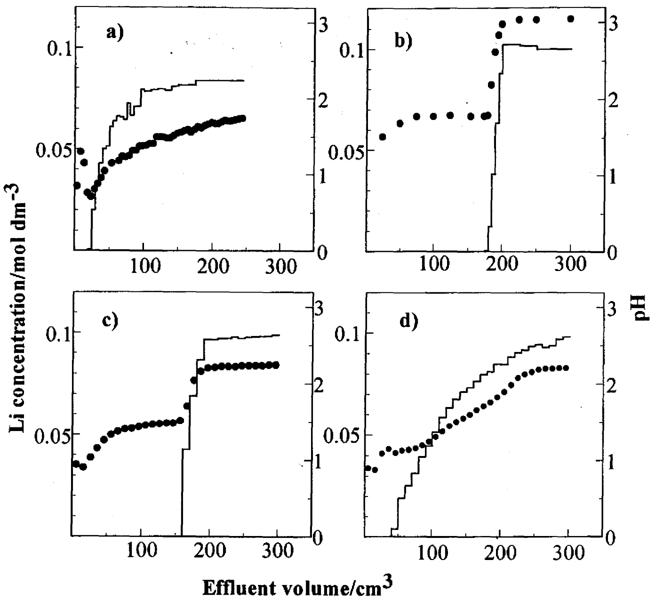

FIG. 4 The chromatograms of the selected breakthrough experiments using a 30-cm column. Li concentration (——); pH (●). The experimental conditions are summarized in Table 2.

feed solutions corresponding to these chromatograms are summarized in Table 2.

The chromatogram in Fig. 4(a) (Run bt1) is an example of the chromatograms obtained with lithium feed solutions as strong electrolyte solutions. In this case the feed solution was a 0.1-M LiCl solution with pH 9.62

TABLE 2
Experimental Conditions of Selected 30-cm Column Experiments[a]

Run	Fig.	Operating manner[b]	Li feed solution[c]	Eluent[c]	C-SbA bed height (cm)
bt1	4(a)	bt	0.1 M LiCl + LiOH; pH 9.62	—	25
bt2	4(b)	bt	0.1 M LiAc + HAc; pH 3.08	—	25
bt3	4(c)	bt	0.1 M LiAc + HAc; pH 2.25	—	26
bt4	4(d)	bt	0.1 M LiAc + HAc + HCl; pH 2.25	—	25
rbt1	5(a)	rbt	0.1 M LiAc + HAc; pH 2.25	0.1 M NaAc + HAc; pH 2.25	25
rbt2	5(b)	rbt	0.1 M LiAc + HAc; pH 2.25	0.1 M NaAc + HAc; pH 2.69	25
rbt3	5(c)	rbt	0.1 M LiAc + HAc; pH 2.25	0.1 M NaAc + HAc + HCl; pH 2.25	25
rbt4	5(d)	rbt	0.1 M LiAc + HAc; pH 2.25	0.1 M NaAc + HAc + HCl; pH 3.46	24

[a] Temperature = 25 °C; flow rate = 20 cm^3/h.
[b] bt = breakthrough; rbt = reverse breakthrough.
[c] Ac = acetate ion.,

adjusted by LiOH. As shown, lithium ions flowing out of the column are little sorbed on C-SbA. At the very beginning of column operation, hydrogen ions in C-SbA are exchanged with lithium ions in the feed solution. The pH of the feed solution in contact with C-SbA immediately decreases since the feed solution has no buffer capacity. C-SbA does not take up lithium ions at very low pH values as shown in Fig. 3. The chromatogram in Fig. 4(a) thus shows that the feed solution should have a buffer capacity. In addition, Fig. 3 indicates the pH of the feed solution should be higher than about 2. In the following experiments we chose to use lithium acetate as the lithium source so that the feed solution would have buffer capacity.

The chromatogram in Fig. 4(b) (Run bt2), obtained by using 0.1 M lithium acetate solution with pH 3.08 adjusted with acetic acid as the feed solution, is seemingly of the displacement-type shape. In this experiment, however, a part of the packed C-SbA comes out of the column through a 0.1-μm filter placed at the bottom of the column and is suspended in the effluent. A part of the granular C-SbA is decomposed into fine particles with a diameter of less then 0.1 μm at this feed solution condition. A SEM photograph of the decomposed C-SbA after being dried is shown in Fig. 1(b). A similar phenomenon is more or less observed when the pH of the feed solution adjusted with acetic acid is above about 2.3. In addition, a pH value in this range often results in the filter at the bottom of the column becoming stuffed with decomposed C-SbA, and the flow of the feed solution is stopped. These observations indicate the following. Fine particles of C-SbA forming granular C-SbA are not firmly combined to each other; the bonding between two neighboring fine particles is not chemically and mechanically strong. Hence, fine particles of C-SbA are easily separated upon H^+/Li^+ ion exchange, which may be accompanied by a slight change in the unit cell dimension of C-SbA.

Figure 4(c) (Run bt3) depicts a nearly ideal displacement-type chromatogram obtained using a feed solution adjusted with acetic acid to pH 2.25. Decomposition of granular C-SbA is not observed in this case. As Fig. 3 shows, however, the exchange capacity of C-SbA is very low at this pH, only a small fraction of its potential capability as an ion exchanger is utilized.

The chromatogram in Fig. 4(d) (Run bt4) was obtained using a feed solution adjusted by acetic and hydrochloric acids to pH 2.25. The shape of the chromatogram is far from ideality. This is probably ascribable to the insufficient buffer capacity of the feed solution caused by the addition of HCl.

To summarize, a nearly ideal displacement-type chromatogram is realized by using as the lithium feed solution a 0.1-M lithium acetate solution with pH 2.25 adjusted only with acetic acid. At this pH, however, only a small fraction of the ion-exchange capability of C-SbA is utilized. At a higher pH, a part of the packed granular C-SbA is decomposed into fine particles.

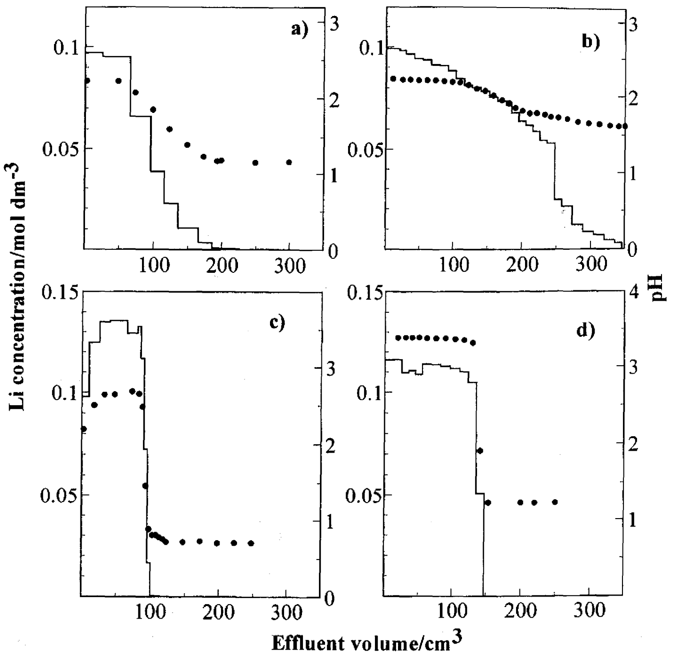

FIG. 5 The chromatograms of the selected reverse breakthrough experiments using a 30-cm column. Li concentration (——); pH (●). The experimental conditions are summarized in Table 2.

Reverse Breakthrough Experiments with a 30-cm Column

Chromatograms of selected reverse breakthrough experiments using a 30-cm column are depicted in Figs. 5(a)–5(d). The conditions of eluents corresponding to these chromatograms are summarized in Table 2. Sodium ions were chosen as replacing cations in those eluents. Lithium sorption to the column was carried out using the lithium feed solution of Run bt3.

Figure 5(a) (Run rbt1) shows the chromatogram obtained using the eluent of a 0.1-M sodium acetate solution with pH 2.25, the same as that of the lithium feed solution, adjusted only with acetic acid. A tailing phenomenon is observed. When the pH of the eluent is increased to 2.69 and the chromatogram of Fig. 5(b) (Run rbt2) is obtained, a similar tailing of the chromatogram is observed. As these two examples indicate, a solution consisting of a weak acid and its salt is not appropriate as an eluent; its buffer capacity seems too high.

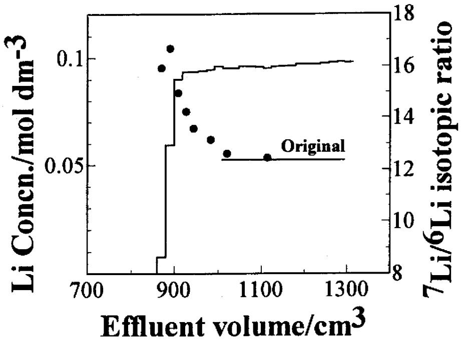

FIG. 6 The chromatogram (——) and ^{7}Li/^{6}Li isotopic ratios (●) of the breakthrough experiment using a 150-cm column. The "Original" line shows the lithium isotopic ratio in the feed solution. The experimental conditions are the same as those of Run bt3 in Table 2 except that the C-SbA bed height is 146.8 cm and the flow rate is 18.1 cm^3/h.

When the pH of the eluent was adjusted to 2.25, the same as that of Run rbt1, with acetic and hydrochloric acids to reduce its buffer capacity, we obtained the chromatogram in Fig. 5(c) (Run rbt3). A sharp boundary is realized at the rear end of the lithium sorption zone. The lithium concentration in the effluent, however, is much higher than 0.1 M, which means lithium ions sorbed on C-SbA are eluted too abruptly. A pH of 2.25 is therefore too low for the eluent.

The pH of the eluent, adjusted with acetic and hydrochloric acids, was raised to 3.46. As a result, we finally obtained a nearly ideal displacement-

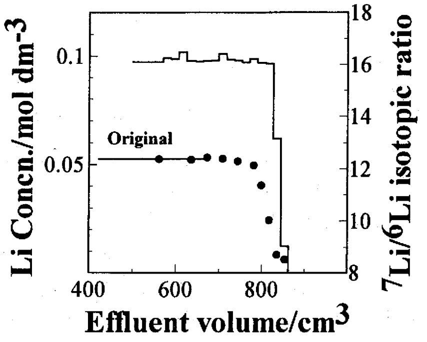

FIG. 7 The chromatogram (——) and ^{7}Li/^{6}Li isotopic ratios (●) of the reverse breakthrough experiment using a 150-cm column. The "Original" line shows the lithium isotopic ratio in the feed solution. The experimental conditions are the same as those of Run rbt4 in Table 2 except that the C-SbA bed height is 142.3 cm and the flow rate is 18.1 cm^3/h.

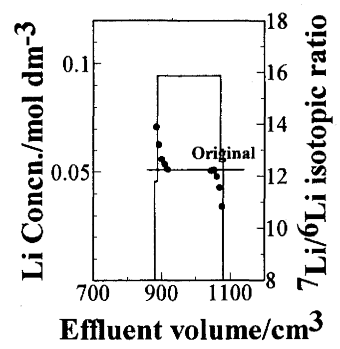

FIG. 8 The chromatogram (——) and ^{7}Li/^{6}Li isotopic ratios (●) of a band experiment using an organic ion exchanger as the column packing material (13). The "Original" line shows the lithium isotopic ratio in the feed solution. Experimental conditions: ion exchanger, Toray TIN-100 ion-exchange fiber (H^+ form) with the sulfo group; temperature, 25°C; ion exchanger bed height, 191 cm (the size of the chromatographic column used was 1 cmϕ × 200 cm), flow rate, 7 cm^3/h; lithium feed solution, 0.10 M lithium acetate; eluent, 0.094 M potassium acetate.

type chromatogram at this eluent condition as shown in Fig. 5(d) (Run rbt4). The displacement-type chromatogram can thus be realized when the pH of the eluent is higher and its buffer capacity is lower than those of the lithium feed.

Experiments with a 150-cm Column

The chromatograms and the ^{7}Li/^{6}Li isotopic ratios of the breakthrough and reverse breakthrough experiments using a 150-cm column are depicted in Figs. 6 and 7, respectively. The chemical compositions of the lithium feed solution and the eluent are the same as those of Runs bt3 and rbt4, respectively. Sharp boundaries are formed at the front and rear ends of the lithium sorption zones, and displacement-type chromatograms are maintained after chromatographic developments of ca. 145 cm. The maximum and minimum ^{7}Li/^{6}Li isotopic ratios achieved are 16.69 and 8.52, respectively, starting from the natural abundance ratio of 12.4. The separation factor for the lithium isotopic pair calculated from the present chromatographic data using the equation given in Ref. 14 is 1.016. These results should be compared with the results of a similar chromatographic experiment on a similar scale using an organic ion exchanger as the column-packing material. The chromatogram and the ^{7}Li/^{6}Li isotopic ratios of one such experiment are reproduced in Fig. 8 (13). The maximum and minimum isotopic ratios and the separation factor obtained in that experiment were 13.91, 10.86, and 1.0016, respectively. The lithium isotope separation effect in this work is thus about 10 times larger that of the experiment with an organic ion exchanger (13).

CONCLUDING REMARKS

In this paper we demonstrate that commercially available granular C-SbA can be used as a column-packing material for the chromatographic separation of lithium isotopes. It shows a lithium isotope separation effect one order of magnitude larger than that of organic ion exchangers. However, granular C-SbA has a couple of drawbacks.

Displacement-type chromatograms in the breakthrough and reverse breakthrough operations without decomposition of the granular C-SbA into small particles are realized for limited chemical compositions of the lithium feed solution and the eluent. The pH of a lithium feed solution with buffer capacity has to be held as low as 2.25. At that pH, however, only a small fraction of its ion-exchange capacity is utilized. To make better use of C-SbA, the pH of the lithium feed solution should be higher. For that purpose, the method of granulating C-SbA has to be reinvestigated, and the chemical and mechanical stability of granular C-SbA should be improved. Such an improvement of C-SbA may make band displacement chromatography possible, which could not be achieved in the present work.

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