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Purification of Lithium Chloride Solution and Fractionation Property for Lithium Isotopes of Niobate Crystal

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Abstract

The selectivity of crystalline $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ for alkali metal ions was, based on a batch method, in the order of $\text{Li}^+ \gg \text{K}^+ > \text{Na}^+$, $\text{Rb}^+ \gg \text{Cs}^+$ in alkaline solutions and $\text{K}^+ \gg \text{Na}^+$, $\text{Rb}^+ \gg \text{Li}^+$, Cs^+ in acidic solutions at $\text{pH} < 3.5$. The column elution of a lithium chloride solution containing 236 and 72 mg dm^{-3} of Na^+ and K^+ , respectively, through the niobate bed, caused extreme decreases of Na^+ and K^+ concentrations to less than 0.1 mg dm^{-3} up to 200 and above 400 bed volumes, respectively, with rarely change of the Li^+ concentration. Fractionation of lithium isotopes with the niobate was also investigated by both the batch and column methods. It had a relatively high separation factor of 1.026. The column fractionation study showed that ^7Li was enriched in the front part of the elution band and ^6Li in the rear part, with the maximum and minimum $^7\text{Li}/^6\text{Li}$ ratios of 15.0 and 11.2, respectively.

Key words: ion exchange, niobate, purification, lithium chloride, lithium isotope, separation factor

1 Introduction

Lithium chemicals are widely used in lots of product such as high energy storage lithium battery, heat-resistant glass, surface acoustic wave filter, and drug medicine of manic-depressive. Lithium isotopes also are essential to operate a nuclear power plant. The lithium element consists of two stable isotopes, ^6Li and ^7Li , in the natural state. The heavier isotope, ^7Li , is used in the form of $^7\text{LiOH}$ in order to control the pH of boric acid solution injected as cooling water into the reactor core of the nuclear power generation. The lighter isotope, ^6Li , is considered for the tritium breeder blanket of nuclear fusion generation which is currently under development.

The demand of lithium chemicals is increasing yearly. Seawater is considered as a vast source of lithium, although the lithium concentration in seawater is as low as about 0.17 mg dm^{-3} . Several studies on lithium recovery from seawater have been done.[1-3] A novel ion-exchanger, $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$, has been developed, which is the most suitable to date for lithium recovery owing to its high selectivity toward lithium ions, its large adsorptive capacity and its high chemical stability.[4] Since the adsorbent uptakes not only lithium ions mainly but also slightly other elements of sodium, potassium, magnesium and calcium ions from seawater, the recovered lithium solution, which is obtained by desorption of lithium from the adsorbent with acid solution, contains these minor elements. Thus, it is necessary to eliminate such impurities from the lithium solution in order to obtain a highly-pure lithium compound. $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ shows a unique ion-exchange behavior with smooth Rb^+/Na^+ and Rb^+/K^+ exchanges while no Rb^+/Li^+ exchange in an alkali metal chloride solution.[5] In our previous paper, we reported ion-exchange property of $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ which is obtained by acid-treatment of the precursor,

$\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$, and demonstrated that the niobate can uptake only sodium and potassium ions from a matrix of lithium chloride solution by a batch method.[6]

In the present study, we report purification of a lithium solution by chromatography with the niobate, and it is discussed with the result of the pH dependence of selectivity for alkali metal ions by batch experiments. We also report lithium isotope selectivity of the niobate and chromatographic lithium isotope separation. Some inorganic ion-exchangers have been reported to have relatively high separation factors for lithium isotope,[7-12] and the lithium isotope fractionation of ion-exchanger has been often discussed in relation to the affinity toward alkali metal ions. An ion-exchanger with high affinity to Li^+ and/or Na^+ tends to have a large S value.[7,9,10] From the unique ion exchange behavior of $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$, we can expect that it shows high lithium isotope fractionation effect, since it has high affinity not only for K^+ ions but also for Na^+ ions.

2 Experimental

2.1 Materials

Niobate crystal, $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$, was prepared by a heating method similar to that in the literature.[6] The starting material, $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$, was prepared by heating a stoichiometric mixture of Rb_2CO_3 (>97%, Wako Chem. Co. Ltd.) and Nb_2O_5 (99.9%, Wako Chem. Co. Ltd.) at 1200 °C for 24 hours. The as-prepared $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ was crushed and sieved in size from 63 to 300 μm . The sieved sample (600 g) was acid-treated with a 10 M HNO_3 solution (3 dm^3) for 16 hours. The acid-treatment was carried out four times in order to extract Rb^+ ions completely to form $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ by $\text{Rb}^+/\text{H}_3\text{O}^+$ exchange. After the acid treatment, the solid was washed thoroughly with deionized water and dried at 70 °C. X-ray diffraction (XRD) patterns of the starting material $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and the final product $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ agreed with those in the previous paper.[6] The XRD patterns were measured using a RINT 2100 (Rigaku Co. Ltd.).

2.2 Distribution Coefficient (K_d)

100 mg of the ion-exchanger, $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$, ground in an agate mortar was immersed in 10 cm^3 of a mixed solution of 1 mM ($M = \text{mol dm}^{-3}$) XCl and XOH ($\text{X} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$) with various ratio of Cl^-/OH^- . After intermittent shaking for 2 days, the K_d values were calculated as:

$$K_d (\text{cm}^3 \text{ g}^{-1}) = \frac{\text{metal ion uptake (mmol g}^{-1})}{\text{metal ion concentration (mmol cm}^{-3})}$$

Each metal ion concentration in the supernatant solution was determined by atomic absorption spectrophotometry (AAS) using a AAnalyst 300 (Parkin Elmer Co. Ltd.). The metal ion uptake was calculated from the residual ion concentration of the solution. The pH of the solution after adsorption was measured by a pH meter.

2.3 Column Chromatography for Purification of Lithium Chloride Solution

An $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ (70.4 g of dry weight) slurry was packed in the full space of a chromatographic glass column (10 mm in diameter and 500 mm in length). The bed volume of niobate was 39 cm^3 . This paper defines the bed volume as one BV . A feed solution which contains 3290, 236 and 72 mg dm^{-3} of Li^+ , Na^+ and K^+ , respectively, was prepared by dissolving LiCl , NaCl and KCl in deionized water. A 15 dm^3 of the feed solution was passed downward through the column at a flow rate of 11.8 $\text{cm}^3 \text{ h}^{-1}$ (space velocity = 0.30 h^{-1}) at 25 °C with a peristaltic pump. The effluent was collected by every 10 cm^3 fractions using an automatic sample collector. The metal ion concentrations in selected fractions were measured by a usual method for Li^+ and by a standard addition method for Na^+ and K^+ . The pH in the selected fractions was also measured by pH meter.

2.4 Lithium Isotopic Separation Factor (S)

The lithium isotopic separation factor, S , was measured by a batch method. The niobate (0.28, 0.46 or

1.00 g) was immersed in 10 cm³ of a mixed solution of 0.03 M LiCl and 0.07 M LiOH, shaken intermittently for 3 days at 25 °C and then filtered. The *S* value was calculated using the following equation:

$$S = \frac{(^7\text{Li}/^6\text{Li})_{\text{solution}}}{(^7\text{Li}/^6\text{Li})_{\text{solid}}}$$

where $(^7\text{Li}/^6\text{Li})_{\text{solution}}$ and $(^7\text{Li}/^6\text{Li})_{\text{solid}}$ are the lithium isotopic ratios in the solution and solid phases, respectively. The $(^7\text{Li}/^6\text{Li})_{\text{solid}}$ can be calculated from the lithium isotopic ratios and the lithium ion concentrations of the solution before and after the ion-exchange reaction. The lithium ion uptake was calculated from the residual ion concentration of the solution which was measured by AAS. The *S* value was actually calculated using the following equation:

$$S = \frac{\alpha(1 + \alpha)C_0 - \alpha(1 + \alpha_0)C}{\alpha_0(1 + \alpha)C_0 - \alpha(1 + \alpha_0)C}$$

where α_0 and C_0 are $^7\text{Li}/^6\text{Li}$ isotopic ratio and lithium ion concentration, respectively, before adsorption and α and C are those after adsorption. To determine the $^7\text{Li}/^6\text{Li}$ isotopic ratio by surface ionization mass spectrometry, the starting solution and the filtrate were converted to LiOH solution by passing through a column of anion-exchange resin (Amberlite CG-400, Organo Co. Ltd.), and then to LiI solution by addition of HI solution to the LiOH solution. The lithium isotopic ratio was measured using a VG336 with a wide flight tube (V.G. Co. Ltd.). The relative standard deviation of the $^7\text{Li}/^6\text{Li}$ measurement was less than 0.11 %.

2.5 Chromatography for Lithium Isotope Separation

A chromatographic column was prepared as in the section 2.3. The Li⁺ exchanged band was formed at the top of the bed by passing down 0.05 M CH₃COOLi (240 cm³) at a flow rate of 12 cm³ h⁻¹ at 25 °C with a double-plunger pump. After rinsing out the liquid in the column with deionized water, 0.1 M HNO₃ was then fed at the flow rate of 12 cm³ h⁻¹, to elute the exchanged lithium ions. The eluate was collected by every 5 cm³ fractions. The lithium ion concentrations of the fractions were measured by AAS. The $^7\text{Li}/^6\text{Li}$ isotopic ratios of the fractions were measured by inductively-coupled plasma mass spectrometry (ICP-MS) with a SPQ9000 (Seiko instruments Inc.) after the eluate was diluted by 0.5 µg dm⁻³ of lithium ion concentration with 0.1 M HNO₃. The isotopic ratios were corrected using the factor which was obtained from the isotopic ratios of the feed solution measured by both the surface ionization mass spectrometry and ICP-MS.

3 Results and Discussion

3.1 Ion-exchange Property

Table 1 Distribution coefficient (K_d) for alkali metal ions.

Solution	log K_d / cm ³ g ⁻¹					pH after equilibrium adsorption	Reference
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺		
A	0.8	2.8	4.3	3.3	0.9	-	5
B	1.1	3.1	3.9	3.6	1.4	3.04	This work
C	1.3	3.9	5.1	3.7	1.3	3.47	This work
D	5.0	3.1	4.1	4.1	2.1	7.32	5
E	5.9	3.4	4.0	3.4	1.8	10.7	This work

A: 1mM LiCl + 1mM NaCl + 1mM KCl + 1mM RbCl + 1mM CsCl. B: 1mM LiOH + 1mM NaCl + 1mM KCl + 1mM RbCl + 1mM CsCl. C: 1mM LiOH + 1mM NaOH + 1mM KOH + 1mM RbCl + 1mM CsCl. D: 1mM LiOH + 1mM NaOH + 1mM KOH + 1mM RbOH + 1mM CsOH. E: 1mM LiOH + 1mM NaOH + 1mM KOH + 1mM RbOH + 3mM CsOH.

The K_d values for alkali metal ions of $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ at different pH values are given in Table 1. The K_d value for Li^+ changes drastically with pH, showing the lowest value among alkali metal ions at pH of less than 3, whereas the highest at pH of 10.7. In contrast, the K_d values for Na^+ , K^+ and Rb^+ are markedly high irrespective of pH. The K_d value for Na^+ is similar to that for Rb^+ at the same pH, and the K_d for K^+ is higher than those for Na^+ and Rb^+ . The K_d for Cs^+ shows a low value irrespective of pH due to the fact that Cs^+ ions rarely exchange with lattice protons, but only with hydroxyl groups on the surface of $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$. [6] The selectivity is thus in the order of $\text{Li}^+ \gg \text{K}^+ > \text{Na}^+$, $\text{Rb}^+ \gg \text{Cs}^+$ at pH of more than 7.3 and of $\text{K}^+ \gg \text{Na}^+$, $\text{Rb}^+ \gg \text{Li}^+$, Cs^+ at pH of less than 3.5. This result suggests that $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$ uptakes Na^+ , K^+ and Rb^+ much more selectively than Li^+ and Cs^+ , when the pH of the mixed aqueous solution is low.

3.2 Purification of Lithium Chloride Solution

Figure 1 shows break through profiles of Li^+ , Na^+ , K^+ and a pH change in the chromatography of a lithium chloride solution containing minor amount of NaCl and KCl . The dashed lines in the figure indicate the concentrations of Li^+ , Na^+ and K^+ ions in the feed solution. The Li^+ concentrations in effluent solutions are almost the same as that of the feed solution through the column experiment, indicating that Li^+ ions are hardly adsorbed to the niobate.

The Na^+ and K^+ ions in the feed solution can be effectively removed by passing through the niobate column although their concentrations are markedly lower than the Li^+ concentration. The Na^+ concentration is 0.014-0.032 mg dm^{-3} at $BV < 198$ and the K^+ concentration is 0.025-0.10 mg dm^{-3} through the column study (up to BV of 382). This indicates that more than 99.98 % Na^+ and more than 99.8 % K^+ can be removed effectively from the LiCl solution by only passing through the niobate column. The Na^+/Li^+ and K^+/Li^+ mole ratios (1.7×10^{-6} in average and 2.8×10^{-6} in average, respectively) of the effluent solution are lower than those ($\text{Na}^+/\text{Li}^+ = 4.0 \times 10^{-6}$, $\text{K}^+/\text{Li}^+ = 4.0 \times 10^{-6}$) of a commercial LiCl of special reagent grade (99.9%, Wako Chem. Co. Ltd.).

The Na^+ concentration increases steeply at around 200 BV and is nearly constant at $BV > 280$. The pH change correlates well with the change of Na^+ concentration; the pH value increases steeply from 1.9 to 2.7 at BV around 200. Accordingly the breakthrough point of Na^+ can be detected by monitoring the pH of effluent solution without measuring Na^+ ion concentrations of fractions. It is noticeable that the Na^+ concentration (273 mg dm^{-3} in average) of the effluent at $BV > 280$ is higher than that (234 mg dm^{-3}) of the feed solution. The molar concentration difference of Na^+ is 1.70 mmol dm^{-3} (39 mg dm^{-3}), which is close to

Figure 1 Break through profile of Li^+ , Na^+ , K^+ and pH change. Ion concentrations of Li^+ , Na^+ and K^+ of feed solution are 3290, 236 and 72 mg dm^{-3} , respectively, and indicated by dashed line, respectively.

the decreasing value of K^+ molar concentration, $1.84 \text{ mmol dm}^{-3}$ (72 mg dm^{-3}). This correlation suggests that the exchanged Na^+ ions are excluded from the site due to Na^+/K^+ exchange since the niobate has the highest selectivity for K^+ among alkali metal ions at $pH < 3.5$. The presence of Na^+/K^+ exchange subsequent to the H^+/Na^+ exchange reaction is also supported by analysis of the metal ion distribution of the bed. The upper and lower parts (2 g each) of the bed were sampled after the chromatographic operation and the Na^+ and K^+ contents of these samples were determined by AAS after dissolved in a mixed solution of HF and HNO_3 while heating at 90°C , followed by adding an oxalic solution (Table 2). The K^+ ions are exchanged mainly in the upper part of bed but hardly in the lower part. Conversely, the Na^+ ions are exchanged rarely in the upper part and mainly on the lower part. These results indicate that the K^+ ions are exchanged preferably to both the lattice protons and Na^+ ions, and the exchanged Na^+ ions are excluded from the site by Na^+/K^+ exchange. The excluded Na^+ ions may be exchangeable to the lattice protons just below the K^+ adsorption band.

Table 2 Na^+ and K^+ contents of niobate after the chromatographic operation.

	Na^+ content / mmol g^{-1}	K^+ content / mmol g^{-1}
Upper part	0.392	1.52
Lower part	1.53	0.002

3.3 Fractionation Property for Lithium Isotopes

Lithium uptakes and isotopic separation factors for the ion exchanger, $(H_3O)_8Nb_{22}O_{59}$, are given in Table 3. The lithium uptake increased with a decrease of the amount of immersed niobate on the batch experiment. The S values are 1.017-1.026, depending on Li^+ uptake. All of the S values are larger than 1, similar to those of inorganic ion-exchangers so far reported.[7-12] Thus the lighter isotope, 6Li , is preferentially taken up on $(H_3O)_8Nb_{22}O_{59}$, and the heavier isotope, 7Li , is enriched in solution phase.

Table 3 Lithium isotopic separation factors.

Li^+ uptake / mmol g^{-1}	S
0.69	1.026
1.40	1.019
2.20	1.017

The lithium isotope selectivity of an ion-exchanger has been often explained from a correlation with affinity toward alkali metal ions: an ion-exchanger with high affinity to Li^+ and/or Na^+ tends to have a large S value.[7,9,10] For instance, monoclinic antimonite acid with a large S value of 1.020 has high affinity for Li^+ . [8] Cubic antimonite acid with a large S value of 1.024 has high affinity for Na^+ and low for Li^+ and K^+ . [9] Zirconium phosphate with a NASICON structure has relatively large S value, with high affinity for Li^+ and Na^+ , and low for K^+ . [10,11] The present niobate may be the first example that shows relatively large S value with the highest selectivity for K^+ ions among alkali metal ions.

The lithium ion concentration profile and lithium isotopic ratio, $^7Li/^6Li$, in elution chromatography are shown in Figure 2. A good chromatogram with clear boundary is obtained in the front part of the lithium elution band, but a slightly nonideal chromatogram with an unclear boundary is obtained in the rear part. The lithium isotopic ratio in the front part is higher than that (12.4) of the isotopic ratio of feed solution, while it is lower in the rear part. The result that 7Li is enriched in the front part of the adsorption band, 6Li

Figure 2 Lithium concentration profile and $^7Li/^6Li$ isotopic ratio of chromatography (band operation). Feed solution: $0.05 \text{ M CH}_3\text{COOLi}$, 240 cm^3 , $12 \text{ cm}^3 \text{ h}^{-1}$. Eluent: 0.1 M HNO_3 , $12 \text{ cm}^3 \text{ h}^{-1}$. $^7Li/^6Li$ isotopic ratio of feed solution is 12.4, and indicated by dashed line.

in the rear part, correlates well with the result of the batch experiment, where ^6Li is preferentially exchanged with the niobate. ^6Li may retain in exchanger phase for a longer time than ^7Li . The maximum and minimum isotopic ratios of the fractions are 15.0 and 11.2, respectively. The lithium isotopic ratio in the rear part increases again after the minimum value. Since the boundary of the band is not so clear as that in the front part, the displacement process may not be ideal due to the slow pore diffusion of Li^+ ions.

The elementary separation factor, S' , can be estimated from the lithium concentration profile and isotopic ratios in Figure 2 using the following equation:[13]

$$S' = 1 + \frac{\sum |R_i - R_0| f_i}{QR_0(1 - R_0)}$$

where R_0 and R_i are the isotopic mole fractions of ^6Li in the inflow and the i th effluent fraction, respectively.; f_i the amount of lithium in the i th fraction.; Q the total exchange capacity of the niobate. The summation is taken over all the fractions where ^6Li were enriched or depleted. The Q value was evaluated as 59 mmol from the experimental value of ion-exchange capacity, 0.84 mmol g^{-1} , which was determined using a $0.05 \text{ M CH}_3\text{COOLi}$ solution. The S' value was calculated from the front part of the elution curves, assuming that the $^7\text{Li}/^6\text{Li}$ ratio varies linearly between observed values. The S' value was 1.0047; this was much smaller than that of batch experiment given in Table 3, as in the case of α -titanium phosphate granulated with polyvinyl chloride.[14] The reason may be that the actual Q value during the elution is much smaller than that derived from the ion exchange capacity, because the ion exchange capacity estimated from the pH titration curve is markedly small in the present elution condition (0.1 M HNO_3).[6]

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