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Ion and lithium isotope selectivity of monoclinic antimonic acid

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Antimonic acid with the monoclinic structure, M-SbA, which had a high selectivity for the lithium ion among alkali metal ions, was prepared by extracting lithium ions from $LiSbO_3$ through ion exchange with protons and its lithium isotope selectivity has been studied. M-SbA underwent the reversible monoclinic-orthorhombic structural change upon desorption-sorption of lithium ions while it showed the irreversible monoclinic-cubic structural change upon sorption of sodium ions. Isotopically, M-SbA was a ^{6}Li-specific ion exchanger. The ^{7}Li-to-^{6}Li isotopic separation factor was slightly dependent on the kinds of counterion in the solution phase of the batch experiments and the maximum S value obtained at 25 °C was 1.025.

1. Introduction

Lithium is one of the elements whose isotopes, ^{6}Li and ^{7}Li, have potentially important applications in nuclear science and technology. ^{7}Li may be used as a coolant in nuclear fission reactors. In the future, lithium compounds rich in ^{6}Li will be required for the tritium breeder blanket in deuterium-tritium fusion power reactors.

Various methods for lithium isotope separation have been developed and evaluated [1]. Ion exchange chromatography is certainly a candidate for a large-scale enriched lithium isotope production. In this method, commercially available organic ion exchangers are usually used as column packing materials and lithium isotope effects on the order of 10^{-3} are obtained [2]. It is essentially important to achieve larger isotope effects in order to make a chromatographic separation system be of higher performance and more attractive.

Some inorganic ion exchangers and sorbents have high selectivity for one of the lithium isotopes. They include a sorbent prepared by extracting lithium ions from $LiMn_2O_4$ [3] and a sorbent prepared by extracting magnesium ions from Mg_2MnO_4 [4]. These sorbents have high selectivity for the lithium ion among alkali metal ions and showed lithium isotope effects one order of magnitude larger than those of organic ion exchangers did and could be column packing materials of chromatographic lithium isotope separation systems.

Antimonic acid with the monoclinic structure, hereafter designated as M-SbA, which is obtained by extracting lithium ions from $LiSbO_3$, may be another alternative to organic ion exchangers. The chemical formula of the pure M-SbA is expressed as $HSbO_3 \cdot 0.12H_2O$ [5]. Lithium ions are considered to be sorbed through ion exchange with protons, and thus M-SbA is an inorganic cation exchanger [6]. In this paper, we report on ion and lithium isotope selectivities of M-SbA.

2. Experimental

2.1. Preparation of M-SbA

M-SbA was prepared, referring to the method of Chitrakar and Abe [5]. The preparation procedure was briefly as follows. 1200 cm^3 of 1 M (M = mol/dm^3) lithium hydroxide solution was added to 40 cm^3 of 4 M antimony pentachloride solution. The resultant mixture solution was kept at 60 °C for two days, which yielded the precipitation of $LiSb(OH)_6$. The precursor of M-SbA, lithium antimonate with the orthorhombic structure ($LiSbO_3$), was obtained by heating the precipitation at 1100 °C for four hours. M-SbA was prepared in a chromatographic manner by extracting lithium ions from the precursor through ion exchange with protons using 11 M HNO_3 at room temperature. In the present study, we used M-SbA samples with the degree of lithium extraction of more than 98% and stocked in a silica gel desiccator for various experiments.

The identification of M-SbA and its precursor was performed by powder X-ray diffraction and subsidiarily by infra-red (IR) spectroscopy.

2.2. Ion selectivity

0.1 g of M-SbA was placed in 25.0 cm^3 of a NH_4OH-NH_4Cl buffer solution of pH = 9.18 containing alkali metal and magnesium ions at 1.0 mM at 25 °C. After

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equilibrium was attained between the ion exchanger and the solution phases, the ion exchanger was separated from the solution by filtration. The amount of ion sorbed was calculated from the concentration difference of the solution phase before and after the equilibrium. The distribution coefficient, K_d (cm^3/g), of each ion defined as,

$$K_d = \frac{\text{the amount of the ion sorbed per 1 g ion exchanger}}{\text{the amount of the ion remaining per 1 } cm^3 \text{ solution}}$$

was then estimated to evaluate the ion selectivity of M-SbA.

2.3. Ion uptake

The ion uptake was evaluated as the amount of that ion taken up from a solution with the metal ion concentration of 0.1 M. 0.1 g of M-SbA was placed in 10.0 cm^3 of the solution at a given temperature. After the equilibrium, the amount of ion taken up by the ion exchanger was calculated from the concentration difference of the solution phase before and after the equilibrium.

2.4. Lithium isotope selectivity

Experiments were conducted batchwise. 0.1 g of M-SbA was placed in 10.0 cm^3 of a 0.1 M lithium-containing solution at a given temperature. After equilibrium was attained between the ion exchanger and the solution phases, the ion exchanger was separated from the solution by filtration. The ion exchanger was then decomposed with conc. HCl containing potassium iodide (KI 1 g per HCl 50 cm^3) at 80 °C, referring to the method of Edstrand and Ingri [7]. About 15 cm^3 of the decomposing agent was required for 0.1 g of the lithium-sorbed M-SbA and it took about 20 h to complete the decomposition. 2 cm^3 aliquot of the resultant solution was placed on a cation exchange resin bed in the H^+ form packed in a chromatographic column and eluted with 0.5 M HCl. The portion of the effluent containing only lithium ions as cationic species (except for protons) was collected. After its volume was reduced by water evaporation, the collected portion of the effluent was passed through an anion exchange column, yielding a lithium hydroxide solution. To this solution was added an excess amount of hydriodic acid to obtain a lithium iodide solution. The lithium concentration of the solution was finally adjusted to 0.15 M and was subjected to mass spectrometry to determine the $^7Li/^6Li$ isotopic ratio of the ion exchanger phase. The chemical form of lithium in the solution phase was similarly converted to lithium iodide and was subjected to mass spectrometry. The isotopic ratio in the two phases were measured with the surface ionization technique on a Finnigan MAT 261 mass spectrometer [2, 4].

The ^{7}Li-to-^{6}Li isotopic separation factor, S, defined as,

$$S = (^7Li/^6Li)_{solution}/(^7Li/^6Li)_{M\text{-}SbA}$$

where $(^7Li/^6Li)_{solution}$ is the isotopic ratio in the solution phase and $(^7Li/^6Li)_{M\text{-}SbA}$ is that in the ion exchanger phase, was estimated to evaluate the magnitude of the lithium isotope effect under the given experimental conditions. The absolute value of $S - 1$ represents the magnitude of the lithium isotope effect, and by definition S is larger than unity when ^{6}Li is preferentially fractionated into the ion exchanger phase.

3. Results and discussion

3.1. Powder X-ray diffraction patterns

In Fig. 1, we show the powder X-ray diffraction (XRD) patterns of M-SbA, lithium-sorbed M-SbA, sodium-sorbed M-SbA and the precursor, $LiSbO_3$. The XRD pattern of our M-SbA (Fig. 1b) is identical with the one given in the literature [5] and so is the IR spectrum. The lithium-sorbed M-SbA retained the monoclinic structure (Fig. 1d) as long as the lithium uptake is small, but it changes its structure from the monoclinic one to the orthorhombic one (Fig. 1c), the structure $LiSbO_3$ possesses (Fig. 1a) [8], when the lithium uptake increases. This observation agrees with that reported by Kanzaki *et al*. [9]. The monoclinic-orthorhombic structural change is reversible; if lithium ions are re-extracted from the lithium-sorbed M-SbA with the orthorhombic structure through ion exchange with protons, the lithium-re-extracted M-SbA restores the monoclinic structure.

The sodium-sorbed M-SbA also retained the monoclinic structure (Fig. 1f) as long as the sodium uptake is small, but its structure changed to the cubic one (Fig. 1e), the structure of the cubic antimonic acid shows [10], when the sodium uptake is increased. Contrary to the lithium sorbed M-SbA, the sodium-sorbed M-SbA with the cubic structure does not restore the monoclinic structure, keeping the monoclinic one even if sodium ions are re-extracted from the sodium-sorbed M-SbA.

M-SbA is thus not very stable against metal ion uptake. We note however that M-SbA is stable at least for months in a silica gel desiccator.

3.2. Ion selectivity

In Fig. 2, we depicted ion selectivity of M-SbA expressed in terms of K_d values at 25 and 90 °C. M-SbA shows the high selectivity for the lithium ion among alkali metal ions as has been reported [5, 6] and is thus lithium-specific. This has been ascribed to the ion-sieve property of M-SbA [6]. The ion selectivity sequence at 90 °C agrees with the sequence obtained by pH titration at 30 °C [6]. The K_d value for the lithium ion of our M-SbA is 12300 cm^3/g at 25 °C and is equivalent to those of other lithium specific sorbents [3, 4, 11, 12]. The selectivity for the magnesium ion is very low compared to that for lithium ion in spite of the fact that the ionic radius of Mg^{2+} (71 pm) is very similar to that of Li^+ (73 pm) [13]. This indicates that the size of sorption sites is not the only determining factor of ion selectivity.

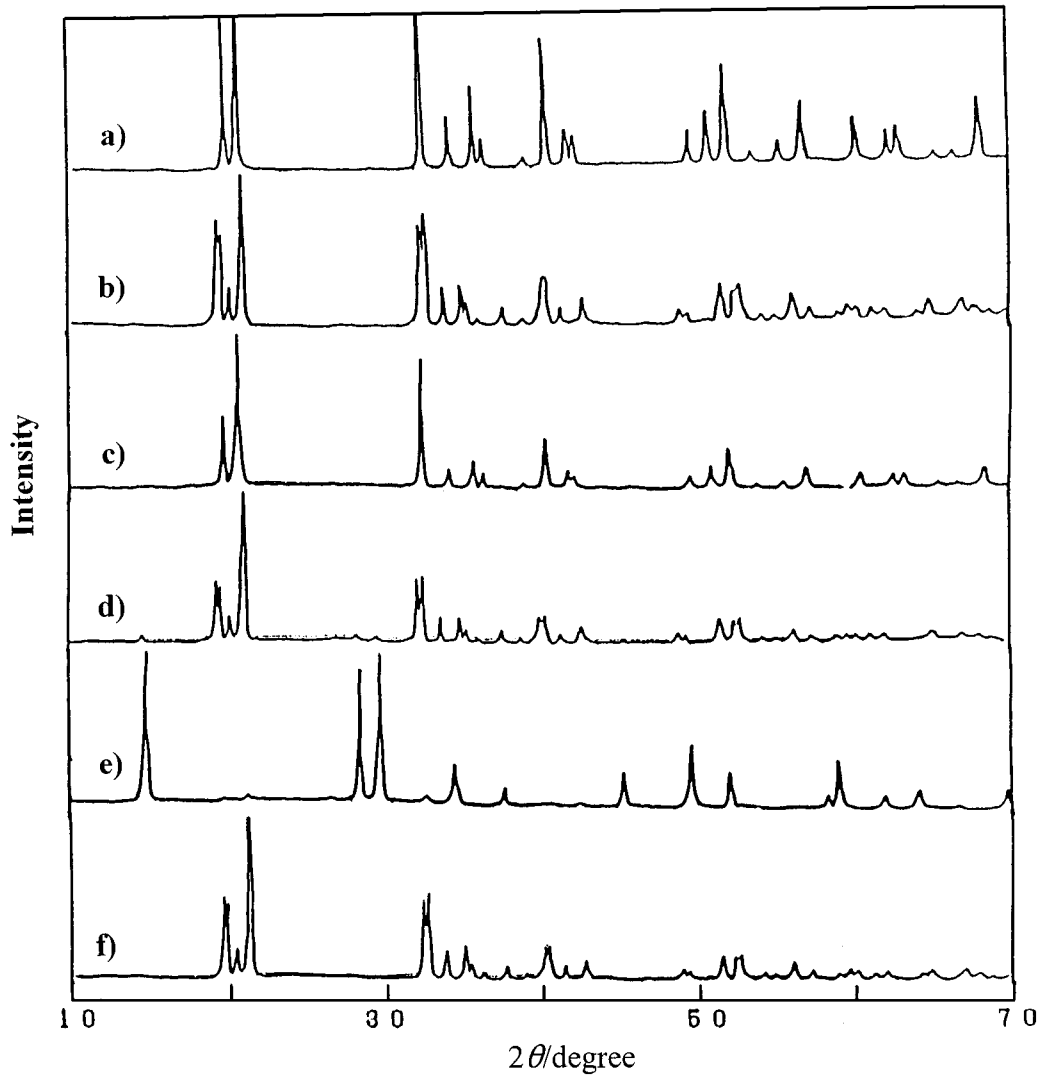

Figure 1 Powder X-ray diffraction patterns of $LiSbO_3$, M-SbA, Li-sorbed M-SbA and Na-sorbed M-SbA. (a) $LiSbO_3$; (b) M-SbA with no Li or Na ion uptake; (c) M-SbA with the lithium uptake of 5.74 mmol/g; (d) M-SbA with the lithium uptake of 2.29 mmol/g; (e) M-SbA with the sodium uptake of 2.53 mmol/g; (f) M-SbA with the sodium uptake of 1.11 mmol/g.

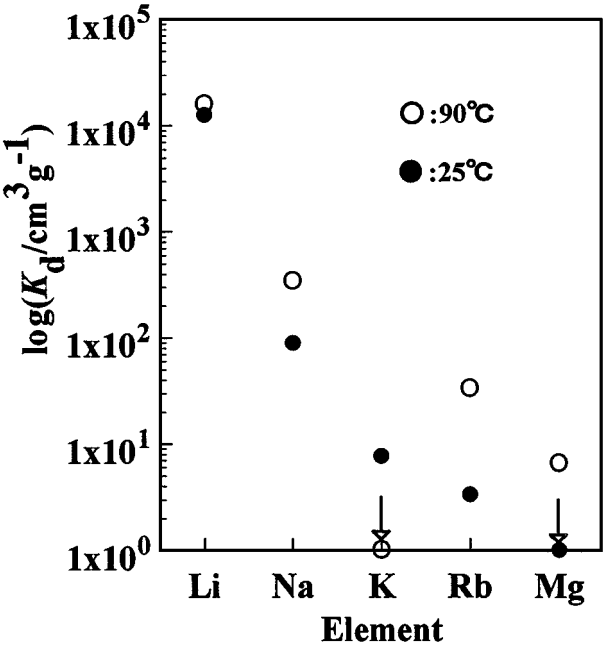

Figure 2 K_d values for alkali metal and magnesium ions. The symbols with an arrow denote that the data are located below the 1×10^0 line.

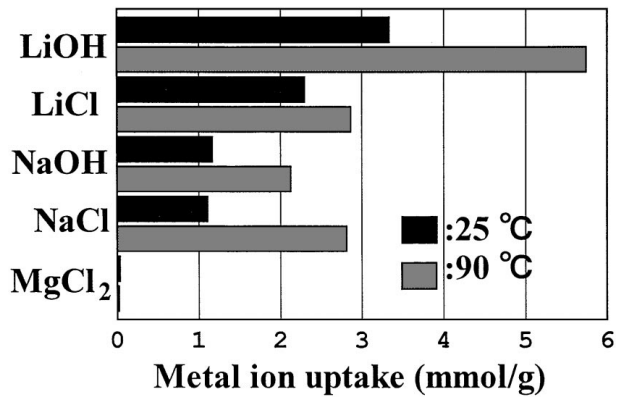

Figure 3 Metal ion uptake. A 0.1 g aliquot of M-SbA was immersed in 10 cm^3 of an aqueous solution containing 0.1 M metal ion.

3.3. Metal ion uptake

In Fig. 3, we show amounts of metal ions sorbed per 1 g of M-SbA under various conditions as histograms. Comparing at 25 °C, the lithium uptake is larger than the sodium uptake both for hydroxide and chloride systems. This is consistent with the results on ion selectivity

above. The maximum Li uptake of 5.74 mmol/g is observed for the LiOH solution at 90 °C. This is nearly equivalent to the value of the maximum exchange capacity of 5.78 mmol/g theoretically expected for pure $HSbO_3 \cdot 0.12H_2O$ assuming that lithium ions are sorbed solely through ion exchange with protons.

The sodium uptake from the NaCl solution at 90 °C is relatively large. The M-SbA sample after this sorption experiment had the cubic structure. It is known that the cubic antimonic acid is sodium specific among alkali metals [10]. This is probably the reason for the relatively high sodium uptake.

The magnesium uptake is extremely small despite the similarity in ionic radius between the magnesium and lithium ions [13]. This is consistent with the ion selectivity above. ^{1}H and ^{7}Li NMR studies [9] demonstrated that lithium ions are sorbed onto M-SbA in the dehydrated state up to half-capacity of exchange capacity, indicating that the size of sorption sites in M-SbA is about the size of the dehydrated lithium ion. The hydration enthalpy of the lithium ion is −503 kJ/mol [14] and this energy barrier is not high enough to prevent lithium ions from being sorbed onto M-SbA. On the other hand, the hydration enthalpy of the magnesium ion is −1908 kJ/mol [14]. This is probably high enough to keep magnesium ions in the solution phase, and thus the magnesium uptake is considerably small compared to that of the lithium ion. A similar difference between the magnesium and lithium ions was reported for the manganese-oxide-based lithium specific sorbent [15].

3.4. Lithium isotope selectivity

The results of batch experiments on lithium isotope selectivity are summarized in Table I. The *S* values listed have standard errors of $\pm 0.01 \sim \pm 0.02$. Every *S* value is larger than unity, meaning that M-SbA is isotopically ^{6}Li-specific and that stronger forces are acting on lithium ions in the solution phase than in M-SbA. Runs Li-1 and Li-2 were conducted to examine the reproducibility of the present experiments by repeating the whole process of experiment starting from the preparation of the precursor, $LiSbO_3$. The results assure the satisfactory high reproducibility of the experiments. A comparison of Runs Li-2 ∼ Li-5 indicates that the lithium isotope effect is slightly dependent on the kind of counterion in the solution phase, and the maximum *S* value of 1.025 was obtained for the lithium acetate solution at 25 °C. The *S* value of 1.020 obtained for the 0.10 M LiOH solution at 25 °C should be compared with those obtained for the other inorganic lithium-specific sorbents and organic ion exchangers under the similar experimental conditions. Three manganese-oxide-based sorbents prepared by extracting lithium or magnesium ions from manganese oxide frameworks showed *S* values of 1.007–1.015 [3, 4, 16]; a zirconium-phosphate-based sorbent had the *S* value of 1.009 [17]; and organic ion exchangers had values of 1.001–1.002 [2]. Thus M-SbA brings about a lithium isotope effect which is about ten times larger than those exhibited by organic ion exchangers and is larger than those of the other lithium specific sorbents so far examined. M-SbA thus seems superior to manganese-oxide-based sorbents as lithium isotope separator in terms of *S* value. It, however, has a serious drawback that it is very difficult to extract lithium ions sorbed on M-SbA; while lithium ions sorbed on manganese-oxide-based sorbents are easily extracted by dilute acids like dilute nitric acid, it is very difficult to extract lithium ions from M-SbA even by 11 M nitric acid without damaging the antimony oxide framework of M-SbA.

TABLE I Separation factor values obtained

Run no.	Original solution	Temp. (°C)	*S*
Li-1	0.10 M LiOH	25	1.020
Li-2	0.10 M LiOH	25	1.020
Li-3	0.10 M LiCl	25	1.020
Li-4	0.10 M $LiNO_3$	25	1.024
Li-5	0.10 M CH_3COOLi	25	1.025
Li-6	0.10 M LiOH	90	1.012
Li-7	0.10 M LiCl	90	1.011
Li-8	0.10 M CH_3COOLi	90	1.015
Li-9	1.0 M LiOH	25	1.022
Li-10	10 M LiOH	25	1.012

Table I also shows that a higher temperature results in a smaller value. This is qualitatively consistent with the prediction of the classical isotope effect theory [18]. A comparison of Runs Li-1, Li-9 and Li-10 reveals the effect of lithium concentration in the solution phase on *S* value. An extremely high lithium concentration of 10 M (Li-10) seems to result in a small isotope effect compared to low concentrations. Similar results were also observed for an organic ion exchanger [19].

Very recently, Inoue *et al*. [20] reported in a short note that monoclinic antimonic acid showed the separation factor value of 1.030 at room temperature. This value is larger than the values of 1.020–1.025 at 25 °C in the present study beyond the range of experimental errors. The reason for this discrepancy is at present unknown.

4. Conclusion

To summarize, we make the following statements:

1. M-SbA shows the high selectivity for the lithium ion among alkali metal ions. M-SbA changes reversibly its structure from the monoclinic one to the orthorhombic one with increasing lithium ion uptake. On the contrary, its structure changes irreversibly from the monoclinic one to the cubic one with increasing sodium ion uptake.

2. The magnesium ion uptake is considerably small compared to that of the lithium ion despite the similarity in ionic size between the two ions. This could be attributed to the large difference in hydration enthalpy between the two ions.

3. The maximum *S* value obtained at 25 °C was 1.025. This value is larger than those obtained for manganese-oxide-based lithium specific sorbents under similar experimental conditions. This is an advantage of M-SbA as lithium isotope separating agent over manganese-oxide-based sorbents, but it has a serious drawback that it is very difficult to extract lithium ions sorbed on it.

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