Technical Paper

Lithium Isotopic Fractionations in the Solvent Extraction by Ion-exchange-type Extractants with Different Ion Selectivity

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Abstract

Ion-exchange-type extractants showed lithium isotopic fractionations in the solvent extraction reaction, depending on their ion selectivity. The extractants having high Na⁺ selectivity, *calix[4]arene derivative* and *monensin*, showed high lithium isotope separation factors of 1.030 and 1.022, respectively.

Introduction

The study of isotope effects is important in the fields not only of industrial nuclear science but also of fundamental and geochemical sciences. There have been many studies on the isotopic fractionation properties of lithium isotopes in the chemical exchange reactions¹⁻³). We have studied lithium isotopic fractionations by two-phase chemical exchanges in different systems; ion exchange⁴) and liquid-membrane transport⁵). The lithium isotopic fractionations were found to be related closely to the ion selectivity of the exchangers or ionophores. The exchangers with high selectivity for sodium ions but not for lithium ions showed high separation factors for lithium isotopes⁴).

Solvent extraction is one of the promising methods for separating lithium isotopes economically. There have been several studies on the lithium isotopic fractionations in solvent extraction processes^{2,6,7}). Derivatives of *12-crown-4* and *15-crown-5* have shown high fractionation properties for lithium isotopes³). However, there has been no systematic study on the relation between ion selectivity and the lithium isotopic fractionation property in the solvent extraction system. The present paper describes the lithium isotopic fractionation properties of ion-exchange-type extractants with different selectivity for alkali metal ions.

Ion-exchange-types are advantageous for lithium isotope separation, since extraction processes can be easily controlled by adjusting the pH of the aqueous phase. The effect of ion selectivity of the extractant on its lithium isotopic fractionation property is discussed in terms of the coordination structure of lithium complex.

Experimental

*Thenoyltrifluoroacetone with tri-*n*-octylphosphine oxide (TTA + TOPO)* and *di-(2-ethylhexyl) phosphoric acid (D2EHPA)* were used as Li⁺ selective extractants^{7,8}), *monensin* and *25,26,27,28-tetrakis (carboxymethoxy) - 5,11,17,23-tetrakis (1,1,3,3-tetramethylbutyl) calyx -[4] - arene (tOct[4]CH₂COOH)* as Na⁺ selective ones^{9,10}), and *salinomycin* as K⁺ selective extractants¹¹). *Tetrakis[3,5-bis (trifluoromethyl)-phenyl] borate (TFPB)*, *tetrakis [3,5-bis (1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl) phenyl] borate (HFPB)*, and *benzoic acid with TOPO (BZA + TOPO)* were used as nonselective extractants^{12,13}). Reagents *TTA*, *TOPO*, *D2EHPA*, *sodium monensin*, *sodium salinomycin*, and *benzoic acid* were purchased from Wako Pure Chem. Ind. Ltd. and *NaTFPB* and *NaHFPB* from Dojindo Lab. Co. Sample *tOct[4]CH₂COOH* was synthesized by the method in the literature¹⁴).

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Extraction experiments were carried out using capped centrifuge cones. A solution containing 5 mM LiCl and 5 mM LiOH ($M = \text{mol dm}^{-3}$) was used as the aqueous phase. The organic phase was prepared by dissolving the extractant in CH_2Cl_2 to a concentration of 10 or 100 mM. Before the extraction studies, *monensin*, *HFPB*, and *TFPB* solutions were treated with a 0.05 M H_2SO_4 solution to transform proton type forms. Equal volumes (10 cm^3 each) of each phase were put together and intermittently shaken at 298 K. After equilibration, the aqueous solution was withdrawn and the lithium concentration was determined by atomic absorption spectrometry. The extractability of lithium was calculated by the decrease of lithium concentration relative to that of the starting solution. The lithium in the organic phase was back extracted by shaking with a 50 mM HCl solution (10 cm^3). The $^7\text{Li}/^6\text{Li}$ isotopic ratios were determined for both the aqueous solutions by a thermal ionization technique on a VG 336 mass spectrometer. The internal precision of isotopic ratio was less than 0.005 % and the external precision was less than 0.2%. The isotope separation factor (S) is defined as $S = (^7\text{Li}/^6\text{Li})_{\text{aq}} / (^7\text{Li}/^6\text{Li})_{\text{org}}$, where $(^7\text{Li}/^6\text{Li})_{\text{aq}}$ and $(^7\text{Li}/^6\text{Li})_{\text{org}}$ are isotopic ratios of the aqueous and organic phases in the forward reaction, respectively.

Results and Discussion

The results of lithium extractability and separation factor are summarized in **Table 1**. The lithium extractabilities increase with extractant concentrations for extractants (TTA + TOPO) and D2EHPA, but the separation factors are not dependent on the extractant concentration. **Table 1** indicates that the S value is strongly related to the ion selectivity of the extractant. The extractants (*monensin* and *tOct[4]CH₂COOH*) with high Na^+ selectivity have

markedly high separation factors (1.022 and 1.030, respectively) for lithium isotopes. The S values above unity indicate that the lighter isotope, ^6Li , is preferentially fractionated into the organic phase. *Salinomycin* with high K^+ selectivity show a relatively high separation factor (1.012). However extractants with high Li^+ selectivity show S values less than 1.003. The nonselective-type extractants also show small fractionations for lithium isotopes. In summary, the isotopic fractionation of extractant increases in the order: non-selective extractants, Li^+ -selective $< \text{K}^+$ selective $< \text{Na}^+$ selective extractants. This tendency is well correlated with that observed in the ion exchange reaction with inorganic ion exchangers⁴⁾.

In a previous paper⁴⁾, we introduced the ion-sieve radius (r_{is}) as a measure of pore size of the adsorbent; the r_{is} value corresponds to the radius of the alkali metal ions to which the adsorbent under consideration shows the highest selectivity. We assume that the same concept of ion-sieve size holds for the present system. The separation factors are plotted as a function of relative ion-sieve radius ($r_{\text{is}}/r_{\text{Li}}$, r_{Li} : ionic radius of Li^+) in **Fig. 1** for both the present data and the previous data on inorganic ion exchangers. The separation factors in both the systems lie on almost identical curve with the maximum at $r_{\text{is}}/r_{\text{Li}} = 1.5$, which corresponds to a sodium ion-sieve. This suggests that the lithium isotopic fractionation properties for both the systems are controlled mainly by the same factor, the ion-sieve size of the exchanger. The exchangers with sodium ion-sieve property may be able to make efficient use of the isotopic effect of dehydration, since they have a low selectivity for lithium ions and adsorb lithium ions in a less hydrated form.

The fractionation behaviors were analyzed in terms of solvent extraction process with isotope exchange reaction. The isotopic exchange reaction can be written as follows,

Table 1 Lithium Extractability and Lithium Isotope Separation Factors (S)

Extractant	Concentration of extractant/M	Lithium extractability/%	S
TTA + TOPO	0.01	14	1.000
	0.1	39	0.999
D2EHPA	0.01	15	1.003
	0.2	32	1.000
<i>Monensin</i>	0.01	49	1.022
<i>tOct[4]CH₂COOH</i>	0.01	54	1.030
<i>Salinomycin</i>	0.01	47	1.012
<i>HFPB</i>	0.01	23	1.000
<i>TFPB</i>	0.01	55	1.002
BZA + TOPO	0.01	14	1.002

Fig. 1 Plots on $\ln S$ as a function of relative ion-sieve radius. ●: present results, ○: results on the inorganic ion exchangers in the previous works.

where ${}^6\text{Li}(\text{aq})$ and ${}^7\text{Li}(\text{aq})$ are lithium isotopes in aqueous phase and ${}^6\text{Li}(\text{org})$ and ${}^7\text{Li}(\text{org})$ are those in organic phase. The equilibrium constant of equation 1 corresponds to the separation factor S . The equilibrium separation factor can be written using a reduced partition function ratio (RPFR) as $\ln S = \ln f_{\text{Li, aq}} - \ln f_{\text{Li, org}}^{15}$, where $f_{\text{Li, aq}}$ is the RPFR of hydrated lithium ions in the aqueous phase and $f_{\text{Li, org}}$ is that of the Li^+ complex in the organic phase. The RPFR value can be evaluated roughly from the knowledge of the totally symmetric vibration of the bond between the central lithium ion and the surrounding atoms, based on Bigeleisen-Mayer's simplifying formula¹⁵. The separation factor can be written as, $\ln S \cong B (k_{\text{A, hy}} n_{\text{hy}} - k_{\text{A, ex}} n_{\text{ex}})$, where B is a constant, $k_{\text{A, hy}}$ is the force constant for the totally symmetric stretching vibration of the hydrated lithium ion and n_{hy} is the hydration number. Notations $k_{\text{A, ex}}$ and n_{ex} are the relevant quantities of Li^+ complex in the organic phase. This shows that the difference in coordination structure between the hydrated lithium ion and the Li^+ complex influences significantly the isotopic fractionation behaviors.

The theoretical and experimental studies have shown that the $[\text{Li}(\text{H}_2\text{O})_4]^+$ cluster with tetrahedral coordination is the most stable in the aqueous phase^{16,17}. In the ($\text{TTA} + \text{TOPO}$) system, the formula for the extracted species has been shown to be $\text{Li}^+(\text{TTA}) - (\text{TOPO})_2$ with 4 coordination structure ($n_{\text{ex}} = 4$)¹⁸. Since its tetrahedral coordination structure resembles that of the $[\text{Li}(\text{H}_2\text{O})_4]^+$ cluster in the aqueous phase, the slight difference between $k_{\text{A, hy}} n_{\text{hy}}$ and $k_{\text{A, ex}} n_{\text{ex}}$ results in the low separation factor, as shown in **Table 1**. On the other hand, monensin has a 5-coordinated structure¹⁹ and the Li^+ -monensin complex is less stable than those of the 4-coordinated Li^+ complexes; therefore, $k_{\text{A, ex}} < k_{\text{A, hy}}$. The decrease of the force constant of the lithium complex in the organic phase may exceed the increase in the coordination number, which may bring about a considerable increase in the separation factor.

The present results suggest that the coordination structure in the exchange phase affects strongly the lithium

isotopic fractionation properties during the chemical exchange reaction.

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異なるイオン選択性の抽出剤（イオン交換型） による溶媒抽出時のリチウム同位体分別

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イオン交換型抽出剤は，リチウム溶媒抽出反応において，イオン選択性に依存してリチウム同位体分別作用を示した。ナトリウムイオン選択性を示すカリックス[4]アレーン誘導体，モネンシンが高いリチウム同位体分離係数（それぞれ 1.030, 1.022）を示した。