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Lithium Isotope Separation using Cation Exchange Resin and Cross-linkage Effect on Isotope Fractionation

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We have studied on the lithium isotope separation by the chromatographic techniques using cation exchange resin. We observed the isotope fractionation by cation exchange reaction. The lithium-6 was enriched in the resin side. The isotope fractionation coefficient was confirmed to depend on the cross-linking degree of cation exchange resin, and to increase linearly with the cross-linking degree. From the result of the chemical shifts by NMR spectrometry, we deduced that the cross-linkage effect on the isotope fractionation is caused by the dehydration from the lithium aqua complex ion.

Keywords: lithium isotope, isotope separation, isotope exchange reaction, cation exchange resin, isotope effect, cross-linkage, NMR.

1. Introduction

Tritium is used as fusion fuel, but natural abundance among hydrogen isotopes is too low. Thus, the tritium must be produced artificially. The ^{6}Li(n,α)T reaction is a most well-known tritium breeding method. For the effective breeding the tritium, the enrichment of lithium-6 is necessary, since the natural ratio of lithium-6 is about 7.5%. On the other hand, the enriched lithium-7 is required for the pH control chemical of the primary coolant in the PWR [1]. The enriched lithium isotopes are supplied by the chemical exchange using amalgam, since the amalgam lithium isotope separation method has the high isotope separation factor [2]. However, recently the new lithium isotope separation method of mercury free is required. One of candidates of the lithium isotope separation substituting for the amalgam method is a cation exchange method. The lithium isotope separation methods using a cation exchange reaction is not a novel method. The first lithium isotope separation was demonstrated by using the cation exchange reaction by Tayler and Urey [3]. And then, many studies on lithium isotope separation by using a cation exchange reaction has been performed. The separation factors obtained in the cation exchange reactions have wide-range values. The higher separation factors were generally obtained in the case of using inorganic cation exchanger than in the case of using organic cation exchange resin [4-6]. Many researchers are exploring the cation exchanger with the higher separation factor. Resins with macrocyclic ligands such as crown ethers become studied in search of higher separation factor [7-9]. However, above mentioned system has difficult tasks, such as expensiveness of macrocyclic ligands, and low ion exchange rate, i.e., high height equivalent to a theoretical plate. Lithium isotope separation factors in many system are summarized in Tables of Ref. [10] very well. From the standing points of engineering chromatography, usage of organic cation exchange resin is generally appropriate. In the case of using the organic cation exchange resin, it was reported that the separation factors by using the cation exchange resin depend on their cross-linking degree [4]. In this report, it is indicated that this cross-linkage effect is related to the hydration of lithium ion. It was reported that the degree of cross-linkage is evaluated by the chemical shift of ^{6}Li NMR [11]. While, in the case of using inorganic cation exchanger, the lithium isotope fractionation was reported to be related to the chemical shift of the ^{7}Li NMR [6]. In this report, it was discussed that the isotope fractionation is related with the dehydration of the lithium ion in the solid phase.

In the present study, the lithium isotope separation by the cation exchange chromatography was investigated. The cross-linkage effect on the isotope fractionation was discussed by using the ^{7}Li NMR spectrometry. From obtained results, we suggest the lithium isotope separation by using cation exchange resin with high cross-linking degree.

2. Experimental

2.1 Cation Exchange Resins

The cation exchange resins used in the present study were Dowex series (Dow Chemical Co.,(Bio Rad)), Diaion series (Mitsubishi Chemical Co.), and SQS(Asahi Kasei Co.). All resins we used were the styrene-divinylbenzene type strongly acidic cation exchange resins with sulfo groups. Both the gel type and the porous type resins were included in the used resins.

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2.2 Chromatography

Each cation exchange resin was filled in a glass column, 1 cm ID and 1 m of length. The conditioning of the column filled with cation exchange resin was carried out by following methods; first, the 400 cm^3 of 1 M (mol/dm^3) NaOH solution was flowed in the column, next about 1 dm^3 of 1 M HCl solution was flowed, last the deionized water was flowed until the acidity of effluent water changed into neutral. The cation resin in the column was conditioned to H$^+$ type resin by above treatments. The 120 cm^3 of 0.5 M lithium acetate solution was fed into the conditioned column packed with cation exchange resin at a constant flow rate of 8 cm^3/min. The lithium was eluted by flowing the 0.5 M potassium acetated solution at a constant flow rate of 5 cm^3/min. The concentration of lithium in the eluted solutions was measured by a flame analysis. The isotope ratio of lithium in the eluted samples was determined by a thermal ionization mass spectrometry.

2.3 NMR Analysis

Each cation exchange resin was pretreated using a small glass column packed with the cation exchange resin by successive flowing 1M HCl solution and deionized water. 0.5 M lithium acetate solution was fed into this column in order to adjust the resin to the Li$^+$ type. Then, the Li type resin was rinsed with deionized water. After that, we obtained the resin used for ^{7}Li NMR measurement. This adjusted resin is put into a 10 mm OD glass NMR sample tube. 1.7 M butyl-lithium in hexane is used as reference. The small NMR sample tube of 5mm OD enclosing the reference was set into the above mentioned large diameter sample tube. The ^{7}Li NMR spectrometry was conducted using a Varian FT-NMR XL 300.

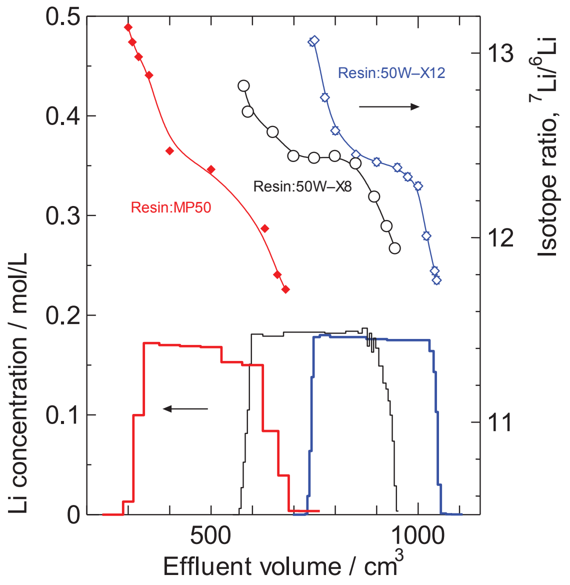

Fig.1 Example of the chromatograms and the lithium isotope fractionation curves by the lithium cation exchange chromatography. 50W-X8 and 50W-X12 are similar gel type cation exchange resins except for the degree of cross-linkage; X8 and X12 mean 8% and 12% of cross linking degree, respectively. MP-50 is the macro-porous equivalent to 50W resin.

3. Results and Discussion

Three examples of the chromatogram and the lithium isotope fractionation are shown in Fig. 1. The chromatograms and the isotope fractionation curves are similar form, and the adsorption amounts are different. From the isotope fraction curves, we confirmed that the lithium-6 is enriched in the resin phase. The isotope exchange reaction we used for the chromatography is as follow;

$$^7\mathrm{Li}^+ + \mathrm{CH_3COO}^6\mathrm{Li} \leftrightarrows {}^6\mathrm{Li}^+ + \mathrm{CH_3COO}^7\mathrm{Li}. \qquad (1)$$

The above isotope exchange equilibrium reaction is found to be biased toward the right-hand side, since lithium ion binds with the cation exchange resin. The degree of isotope separation is evaluated by the separation coefficient, ε. The separation coefficient is defined as the subtraction 1 from the separation factor on single stage. In other words, the separation coefficient means the off degree from 1 of the isotope exchange equilibrium constant. The separation coefficient of the chromatography was calculated by following equation using the chromatogram and the isotope fractionation curve,

$$\varepsilon = \frac{\sum C_i V_i (R_0 - R_i)}{Q R_0 (1 - R_0)} , \qquad (2)$$

where C_i, V_i, and R_i are the lithium concentration, the

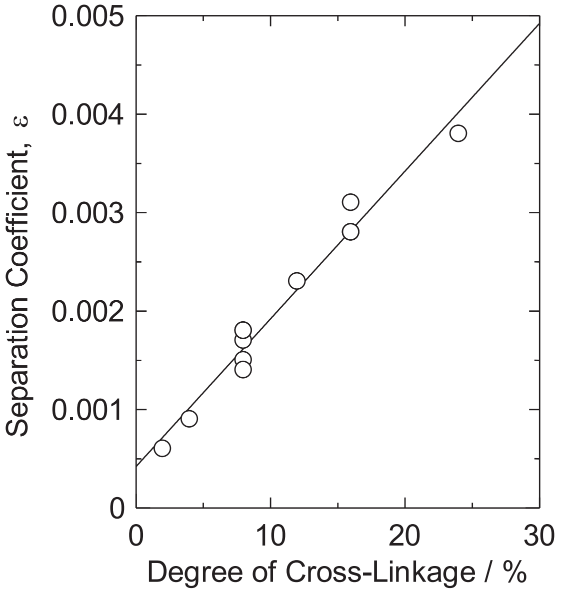

Fig.2 Cross-linkage effect of cation exchange resin on isotope fractionation.

volume, and the isotope abundance, $R = r\ (1+r)$, in the sample fraction i, respectively. r is the isotope ratio. R_0 is the original isotope abundance. Q is the adsorption amount. The relationship between the calculated separation coefficient and the cross-linking degree of the used resin is shown in Fig. 2. We can see that the separation coefficient have a linear relationship to the degree of cross-linkage. This result shows that the separation coefficient can be raised by increasing the degree of cross-linkage of resin. It was also confirmed that the separation coefficient is not dependent on the gel type resin or the porous type resin.

The chemical shift of ^{7}Li NMR spectrum in each resin was evaluated. The relationship between the chemical shift and the degree of cross-linkage is shown in Fig. 3. We can confirm that the chemical shift is linearly related to the degree of cross-linkage, and that the resin with the higher cross-linkage degree makes the ^{7}Li spectrum shift to the lower frequency, this shift is called as the high magnetic field shift. The high magnetic field shift means that the electron density around the lithium nucleus increases with the increase in the degree of cross-linkage. This phenomenon can be explained by the hydration of lithium ion. The lithium ion is well-known to be hydrated and to exist as the aqua complex ion in the aqueous solution. Although the lithium ion is fully hydrated in the aqueous solution, the dehydration from the lithium aqua complex ion occurres in the cation exchange resin because of the hydrophobicity of the resin. Since the sulfonate anion of cation exchange resin can get closer toward the lithium ion in the case of removing the hydration water surrounding the lithium ion, the closing sulfonate anion is deduced to supply the negative electron around the lithium nucleus. The number of hydrated water molecules around lithium ion in the resin with the higher degree of cross-linkage is lower [12], because the resin with the higher degree of cross-linkage has generally higher hydrophobicity [13].

The dependence of the separation coefficient on the degree of cross-linkage can be also explained by the hydration and the dehydration of lithium ion in the cation exchange resin. The lithium ion in the isotope exchange reaction (1) is not a bare lithium ion but a hydrated lithium ion. Since some hydrated water molecules are removed if the lithium ion binds the cation exchange resin, the isotope exchange reaction is occurred in the hydration and dehydration reactions in the time of the adsorption and desorption reactions. The reaction (1) is replaced with the following reaction adding the hydration and dehydration reactions.

$$\begin{aligned} &R^{-}\ {}^{7}Li(H_2O)_n^{+} + CH_3COO^{6}Li(H_2O)_m \\ &\leftrightarrows R^{-}\ {}^{6}Li(H_2O)_n^{+} + CH_3COO^{7}Li(H_2O)_m, \qquad (3) \end{aligned}$$

where R is resin, and n < m. The heavier isotope is enriched in the side of the chemical form with the stronger binding force [14]. Since the hydration bonding is strong, the lithium-7 is enriched in the lithium acetate with the more number of hydrated water molecules which exits in aqueous solution, and the lithium-6 is enriched in the less hydrated water molecules which exits in the resin phase. The results of isotope fractionation shown in Fig. 1 consists of the above explanation. The separation coefficient becomes larger if the difference of the chemical condition in the isotope exchange reaction is larger. Thus, the separation coefficient becomes larger in the case of using the resin with the higher degree of

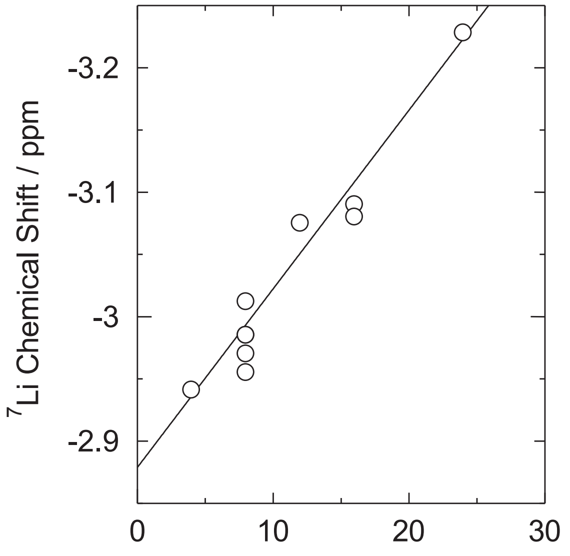

Fig.3 Relationship between cross-linkage of cation exchange resin and chemical shift of ^{7}Li NMR.

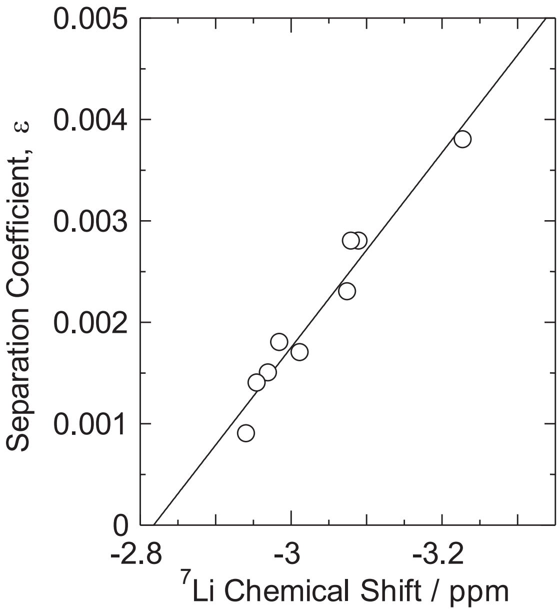

Fig.4 Relationship between ^{7}Li Chemical shift and and isotope fractionation.

cross-linkage, since the difference between m and n in the reaction (2) becomes larger on account of the dehydration from the lithium acqua complex ion in the resin. Ooi *et al*. theoretically indicate that the dehydration reaction of lithium ion has a high separation coefficient [15]. It is summarized the cross-linkage effect on the isotope fractionation in the cation exchange reaction is due to the dehydration reactions in the resin. Since the degree of dehydration in the resin is estimated by the chemical shift of ^{7}Li NMR spectrum, it may be better to make the connection between the isotope fractionation and the chemical shift as shown in Fig. 4. The dehydration is dependent on the chemical properties of the resin such as the hydrophobicity. Therefore, we expected that the high separation coefficient can be obtained by increasing the hydrophobicity of the resin. The increasing the degree of cross-linkage of the resin is one of the relatively-easy methods.

4. Conclusion

The lithium isotope separation was carried out by the chromatography using the cation exchange reaction. We confirmed that the ^{6}Li is enriched in the cation exchange resin phase. The cross-linkage effect on the lithium isotope fraction was confirmed. The high isotope fractionation can be obtained with using the cation exchange resin with high cross-linking degree. This cross-linkage effect can be explained by the dehydration from the lithium aqua complex ion in the resin. We proposed the using the resin with the high hydrophobicity to obtain the high separation coefficient.

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