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Fractionation of Lithium Isotopes in Cation-Exchange Chromatography

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Abstract

Cation-exchange chromatography of lithium was carried out to investigate the lithium isotope effect in aqueous ion-exchange systems. The heavier isotope, ^{7}Li, was preferentially fractionated into the resin phase in every experiment conducted, and this result is consistent with the results of previous work. The value of the separation factor was 1.00089–1.00171 at 25°C. A comparison of lithium isotope effect with those of potassium and rubidium indicated that the isotope effect originating from hydration is larger than the effect due to phase change for lithium, while the opposite is the case with potassium and rubidium.

INTRODUCTION

Naturally occurring lithium consists of two stable isotopes, ^{6}Li and ^{7}Li, and each isotope plays an important role in nuclear science and industry. ^{7}Li could 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 (DT) fusion power reactors:

$$^{6}\text{Li} + n \rightarrow \text{T} + {}^{4}\text{He}$$

Various methods for lithium isotope separation have been developed, and their applicability to large-scale enriched lithium isotope production has been assessed (*1*). Ion-exchange chromatography is one such method. The first use of ion-exchangers for lithium isotope separation is found in a publication of Taylor and Urey (*2*) in 1937. In 1949, Glueckauf et al. (*3*) first applied synthetic organic ion-exchangers to lithium isotope separation. In a series of papers (*4–8*) between 1959 and 1965, Lee and coworkers examined the magnitude of the single-stage separation factor, S, as a function of several parameters such as resin structure, temperature, and nature of eluents by using the elution chromatographic technique. Band displacement chromatographic operation, which is considered to be the most effective for isotope separation among various chromatographic operations, was successfully applied to lithium isotope by Hagiwara and Takakura (*9*, *10*) for the first time. Fujine et al. (*11*, *12*) successfully carried out continuous displacement chromatography on a laboratory scale. Kakihana et al. (*13*) and Nandan and Gupta (*14*) investigated the lithium isotope effects in mixed solvent systems. The use of high-pressure ion-exchange displacement chromatography for lithium isotope enrichment was studied in China (*15*, *16*).

The main origin of lithium isotope fractionation in ion-exchange chromatography is said to be the difference in circumstances around lithium ions between the ion-exchanger phase and the external solution phase (*4*). In reality, separation factors experimentally observed are expected to be composed of some fundamental lithium isotope effects such as the effect due to hydration of lithium ion and one originating from lithium complex formation in the solution phase. There seem to be few papers which analyze the experimentally obtained separation factors in terms of fundamental lithium isotope effects.

In this paper we first report the results of experiments on column chromatographic separation of lithium isotopes carried out in the displacement chromatographic manner. We then analyze the separation factors obtained on the basis of a theory on isotope distribution between two phases (*17*). Finally, the results of the analysis are compared with the results of similar analyses on potassium (*18*) and rubidium (*19*, *20*), and a general discussion on isotope effects of the alkali metals in cation-exchange chromatography is presented.

EXPERIMENTAL

Ion-Exchangers and Reagents

The ion-exchangers used were a highly porous, strongly acidic cation-exchange resin, Asahi LS-6 (100–200 mesh), manufactured by Asahi

Chem. Ind. Co.; a highly efficient, strongly acidic cation-exchange fiber, Toray TIN-100, reinforced with polyethylene, manufactured by Toray Co.; and a porous, weakly acidic cation-exchange resin, Diaion WK-13 (65–170 mesh), manufactured by Mitsubishi Chem. Ind. Co. The ion-exchange fiber is a cylinder-shaped exchanger and its average size is 50 μmϕ × 0.5 mm. The exchange group of the two strongly acidic exchangers is the sulfo group (—$SO_3^-H^+$) and that of the weakly acidic exchanger is the carboxyl group (—COOH). The exchange capacities for lithium ion per 1 g exchanger in H^+ form (dried at 80°C and at 5 torr for 24 h) are 2.75 meq/g for LS-6, 3.12 meq/g for TIN-100, and 4.94 meq/g for WK-13.

All reagents used were of analytical-reagent grade and were used without further purification.

Chromatographic Process

Nine chromatographic experiments were carried out, one with the weakly acidic cation-exchange resin, four with the strongly acidic resin, and four with the strongly acidic ion-exchange fiber. A Pyrex glass column of 210 cm × 1 cm i.d. with a water jacket was used as the separation column in each experiment, so that the exchanger bed height was ~200 cm. Chromatography was operated in a band displacement manner whenever possible; otherwise, the reverse breakthrough operation was adopted.

In a band displacement chromatographic experiment, an ion-exchanger was first packed in the separation column and conditioned to the H^+ form. A lithium feed solution was fed to the column at a constant flow rate by a peristaltic pump to form a Li adsorption band with an appropriate length. This band was eluted by an eluent at a flow rate similar to that at which the Li solution was fed. Potassium, calcium, or strontium ion was used as the displacement ion for lithium ion. The effluent from the bottom of the column was collected and portioned into small fractions (5.2–8.0 cm^3) by a fraction collector. The temperature of the column was kept constant at 25.0 ± 0.2°C throughout the experiment by passing temperature-controlled water through the water jacket.

A similar experimental procedure was followed for each of the experiments operated in the reverse breakthrough manner except that the ion-exchanger was conditioned to the Li^+ form and replaced by K^+ or Ca^{2+}.

The experimental conditions of the nine experiments are summarized in Table 1. Some explanations on the Li feed solutions are necessary. Lithium chloride solutions (Runs Li01, Li03 and Li06) were prepared by dissolving lithium hydroxide and the equivalent amount (mole) of hydrochloric acid in pure water. Lithium lactate solutions (Li02 and Li07) were prepared by dissolving lithium hydroxide and lactic acid into pure water, with the mole ratio of Li^+ and the lactate ion being 1:2. Lithium acetate solutions (Li05

TABLE 1

Experimental Conditions[a]

Run	Cation-exchanger[b]	Resin bed height (cm)	Total capacity (eq)	Operating manner[c]	Li feed solution[d]	Eluent[d]	Flow rate (cm^3/h)	Band velocity (cm/h)
Li01	LS-6	200.8	0.144	Rev. bt.	0.120 *M* LiCl	0.053 *M* $CaCl_2$	8.33	1.15
Li02	LS-6	194.6	0.163	Band	0.098 *M* LiLc	0.050 *M* $SrLc_2$	7.09	0.83
Li03	WK-13	191.3	0.309	Rev. bt.	0.104 *M* LiCl	0.053 *M* $CaCl_2$	8.35	0.52
Li04	LS-6	193.5	0.189	Band	0.100 *M* LiOH	0.105 *M* KOH	8.99	0.98
Li05	LS-6	196.0	0.179	Band	0.100 *M* LiAc	0.055 *M* $SrAc_2$	7.18	0.83
Li06	TIN-100	196.0	0.073	Rev. bt.	0.120 *M* LiCl	0.106 *M* KCl	4.71	1.17
Li07	TIN-100	200.0	0.087	Band	0.104 *M* LiLc	0.114 *M* KLc	5.30	1.20
Li08	TIN-100	193.4	0.077	Band	0.104 *M* LiPh	0.101 *M* KPh	5.12	1.15
Li09	TIN-100	190.9	0.074	Band	0.107 *M* LiAc	0.094 *M* KAc	6.96	1.50

[a] Temperature = 25.0 ± 0.2°C for all experiments.

[b] LS-6 = strongly acidic cation-exchange resin with —SO_3^- exchange groups, 100–200 mesh, manufactured by Asahi Chem. Ind. Co.; WK-13 = weakly acidic cation exchange resin with —COO^- exchange groups, 65–170 mesh, manufactured by Mitsubishi Chem. Ind. Co.; TIN-100 = strongly acidic cation exchange fiber with —SO_3^- exchange groups, in cylindrical shape (50 μmϕ × 0.5 mm), reinforced with polyethylene, manufactured by Toray Co.

[c] Rev. bt. = reverse breakthrough.

[d] Lc = lactate ion, Ac = acetate ion, Ph = phosphate ion.

and Li09) were prepared similarly by using lithium hydroxide and acetic acid. The Li feed solution of Li08 was prepared from lithium hydroxide and phosphoric acid. The concentration of phosphoric acid was 0.085 mol/dm^3. The feed solution of Li04 was simply an aqueous solution of lithium hydroxide. All the effluents were prepared correspondingly.

Analysis

The lithium concentration in each fraction of the effluents was determined flame-photometrically by using a Daini Seikosha model SAS-727 atomic adsorption spectrometer after appropriate dilution with pure water. Potassium and strontium concentrations were also measured flame-photometrically, and calcium was determined by an atomic absorption method.

For the feed solution and selected fractions of the effluent of each experiment, the ^{7}Li/^{6}Li isotopic ratios were measured by a mass spectrometric method. The procedure for this was briefly as follows. For each fraction or the feed solution, an aliquot containing about 5×10^{-5} mol lithium was treated to prepare the sample for mass spectrometry (mass sample). The aliquot was passed through a chromatographic column packed with an anion-exchange resin (Dowex 1-X8) in the OH^- form. To the effluent from the column, which was, in fact, an aqueous LiOH solution, was added an aqueous HI solution, yielding a solution of lithium iodide, the best chemical species of lithium for lithium isotopic ratio measurements (*21*). This solution was evaporated to dryness to remove extra HI, and then pure water was added such that the concentration of LiI became about 0.05 *M* in the case of measurement with a Finnigan MAT 261 mass spectrometer or 0.15 *M* in the case of measurement with a Varian MAT CH-5 mass spectrometer and was subjected to the ^{7}Li/^{6}Li isotopic ratio measurement.

The ^{7}Li/^{6}Li isotopic ratio of a mass sample was measured with a double-filament (evaporation and ionization filaments) surface ionization technique on a Finnigan MAT 261 mass spectrometer at the National Defense Academy or on a Varian MAT CH-5 at Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology. 0.05 μmol Li with the MAT 261 or 0.75 μmol Li with the MAT CH-5 was loaded on an evaporation filament. Ionization was performed by passing a heating electric current through the ionization filament. After the ion beam intensities of ^{6}Li$^+$ and ^{7}Li$^+$ became sufficiently high (about 1 h from heating initiation), the ^{6}Li and ^{7}Li mass peaks were repeatedly recorded. The mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The measuring time was 40 min to 1 h, and hence the total time spent for one measurement was 1½ to 2 h. The ^{7}Li/^{6}Li ratio of a block was calculated by averaging all the peak-height ratios in the block, and that of the mass sample was calculated as an average of the ^{7}Li/^{6}Li ratios of the blocks. The ^{6}Li isotopic molar fraction of each feed solution was an average of 2 or 3 measurements, and that of each fraction was the result of one measurement.

RESULTS AND DISCUSSION

Chromatograms and ^{6}Li isotopic molar fractions of the nine experiments are shown in Figs. 1–9. In each figure the step-like line shows the Li concentration profile, the open circles are the ^{6}Li isotopic molar fractions, and the "original" line is the ^{6}Li isotopic molar fraction in the feed solution. It is clearly seen in the figures that the lighter isotope, ^{6}Li, is enriched in the rear parts of the chromatograms, that is, it is preferentially fractionated in the ion-exchanger phase, irrespective of the type of cation exchanger and the kind of counterion in the solution phase within the present experimental conditions. This trend of lithium isotopes in the present work is consistent with those reported by other researchers (*2–16*), but it is opposite to the trend found for potassium (*18*) and rubidium (*19*, *20*) isotopes under similar experimental conditions.

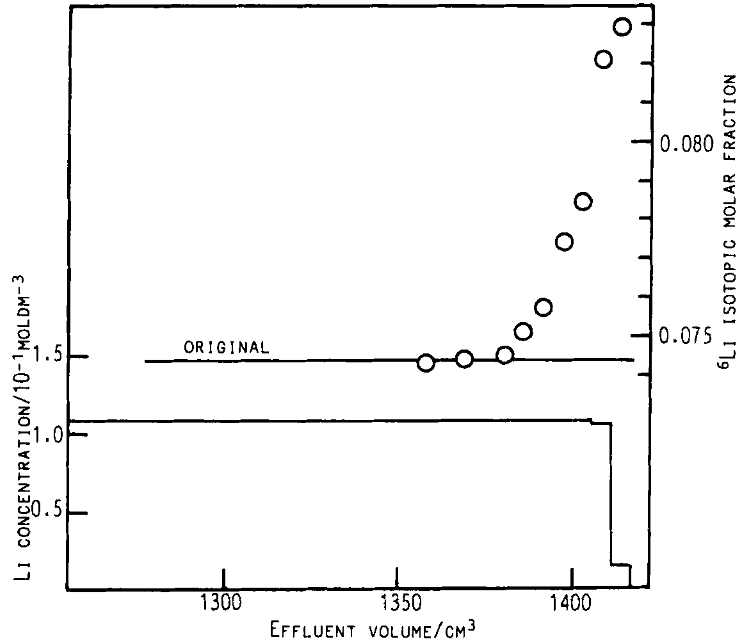

FIG. 1. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li01. Experimental conditions are summarized in Table 1.

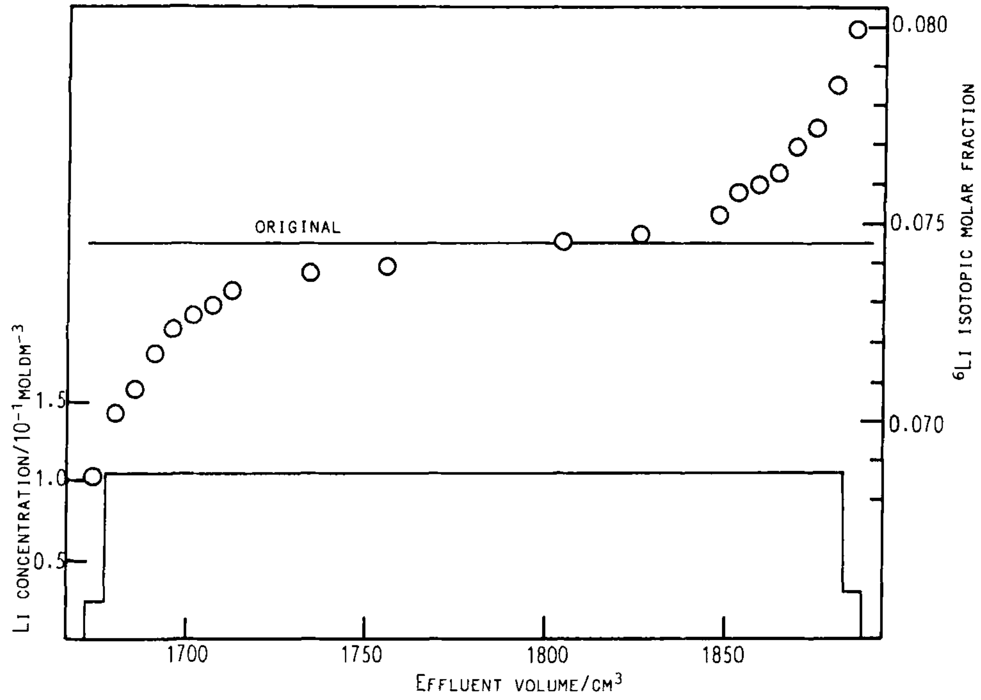

FIG. 2. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li02. Experimental conditions are summarized in Table 1.

A comparison of the experiments with the LS-6 resin (Runs Li01, Li02, Li04, and Li05) and those with the TIN-100 fiber (Runs Li06–Li09) reveals that the breakthrough points appeared much earlier in the experiments with the TIN-100 fiber than in the experiments with the LS-6 resin, despite the fact that the exchanger bed heights were similar in all experiments and that the exchange capacity of TIN-100 for Li is higher than that of LS-6. This difference is attributable to the difference in the packing state of the separation columns between the two exchangers. The TIN-100 fiber, being of cylindrical shape, is packed less closely in columns than the LS-6 resin with its spherical shape. In fact, the total exchange capacities of the columns packed with the LS-6 resin are much larger than those of the columns packed with the TIN-100 fiber (see the 4th column of Table 1). In addition, we found that resistance against the flows of feed solutions and eluents was much stronger for columns packed with LS-6 than for those packed with TIN-100.

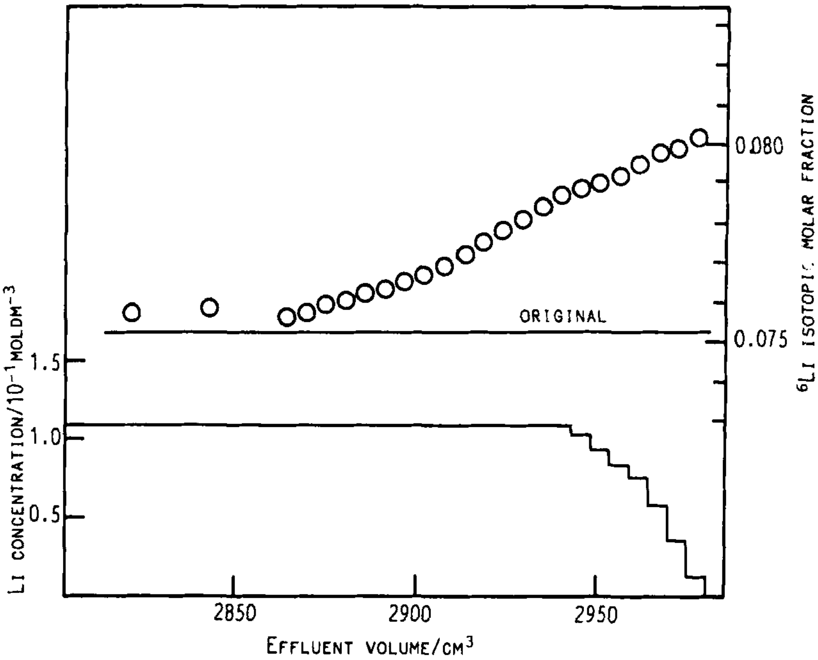

FIG. 3. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li03. Experimental conditions are summarized in Table 1.

Isotope Accumulation Profiles

It has been derived theoretically that, in the case of ideal displacement chromatography of two isotopes of an element, the ratio of the isotopic molar fractions of the two isotopes, say A and B, is to a good approximation an exponential function of the position in the adsorption band when isotope fractionation proceeds over a certain level (*22*). The accumulation curve in that case can be expressed as

$$R_A/R_B = (R_A^0/R_B^0) \exp [k^*(z - z_0)] \qquad (1)$$

where R_j (j = A, B) is the molar fraction of isotope j at position z in the adsorption band, R_j^0 is the molar fraction of j in the feed solution, z_0 is the position at which $R_j = R_j^0$, and k^* is a parameter which determines the sharpness of the slope of the isotope accumulation curve. From the viewpoint of practical isotope separation, a larger k^* value is preferable; when the S values are similar in two isotope separation systems, the system with a larger k^* value can achieve a higher maximum degree of enrichment

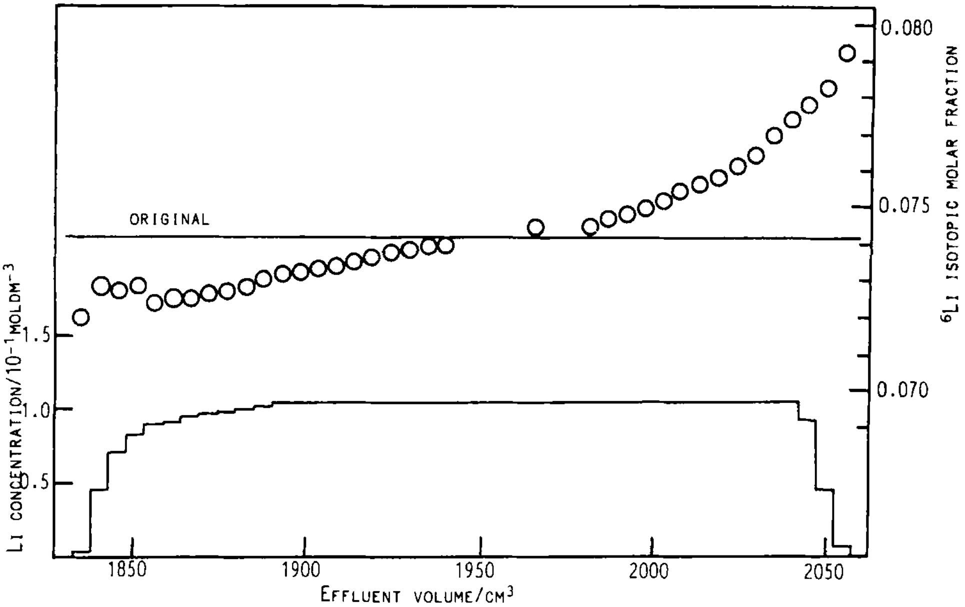

FIG. 4. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li04. Experimental conditions are summarized in Table 1.

than the other with a smaller k^* value for the same displacement distance. Differentiation of Eq. (1) with respect to z leads to

$$\delta \ln (R_A/R_B)/\delta z = k^* \tag{2}$$

The k^* value of an experiment can be determined by plotting $\Delta \ln (R_A/R_B)$ against Δz, using the chromatographic data.

The k^*s thus obtained for the present experiments are tabulated in the 4th and 5th columns of Table 2. Note that A = ^{7}Li and the direction of positive z is opposite to that of the effluent flows for the front parts, and A = ^{6}Li and the direction of positive z is the same as that of the effluent flows for the rear parts of the lithium adsorption bands, so that k^* is always defined as being positive. It can be pointed out from those data that for a common anion (counterion to Li^+) in the solution phase, the system with the strongly acidic cation-exchange fiber, TIN-100, in general shows a larger k^* than the system with the strongly acidic cation-exchange resin, LS-6 (Li01 vs Li06, Li02 vs Li07, and Li05 vs Li09), and that the lithium chloride system has the largest k^* value in both the LS-6 and TIN-100 systems and that the lithium acetate system follows next. The lithium hy-

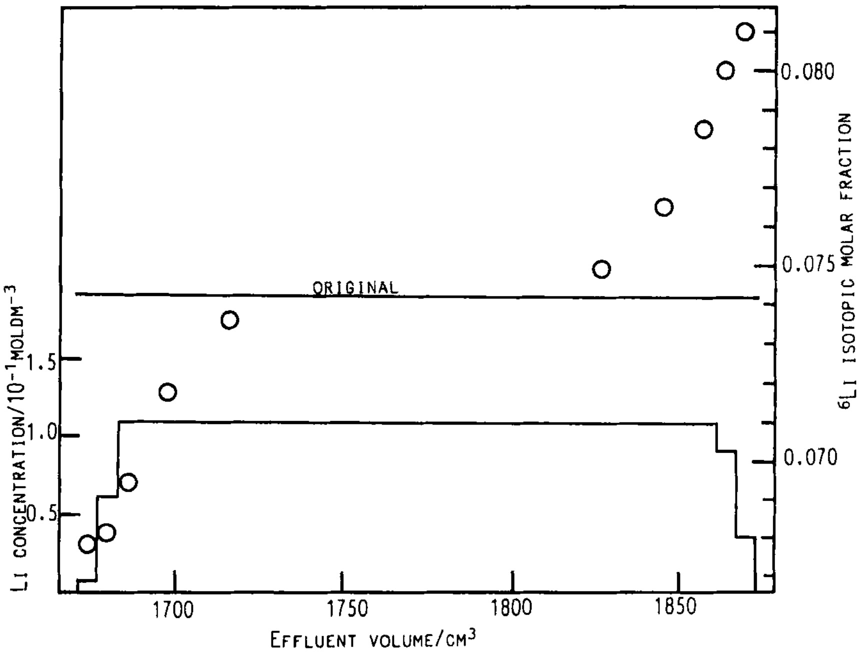

Fig. 5. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li05. Experimental conditions are summarized in Table 1.

droxide (Li04) and lithium phosphate (Li08) systems and the system with the weakly acidic resin (Li03) have very small k^* values.

Single-Stage Separation Factor

In order to compare the magnitudes of the lithium isotope effect observed in the present experiments, the single-stage separation factor, $S (= \epsilon + 1)$, for the ^{7}Li/^{6}Li isotopic pair, was calculated for each experiment. S is defined as

$$S = ([^7\mathrm{Li}]/[^6\mathrm{Li}])/([\overline{^7\mathrm{Li}}]/[\overline{^6\mathrm{Li}}]) \qquad (3)$$

where [A] and $[\overline{\mathrm{A}}]$ denote the concentrations of isotope A in the external solution phase and in the ion-exchanger phase, respectively. ϵ's are calculable by using the equation (*23*)

$$\epsilon = \Sigma[|R_i - R_0|f_i]/[R_0(1 - R_0)Q] \qquad (4)$$

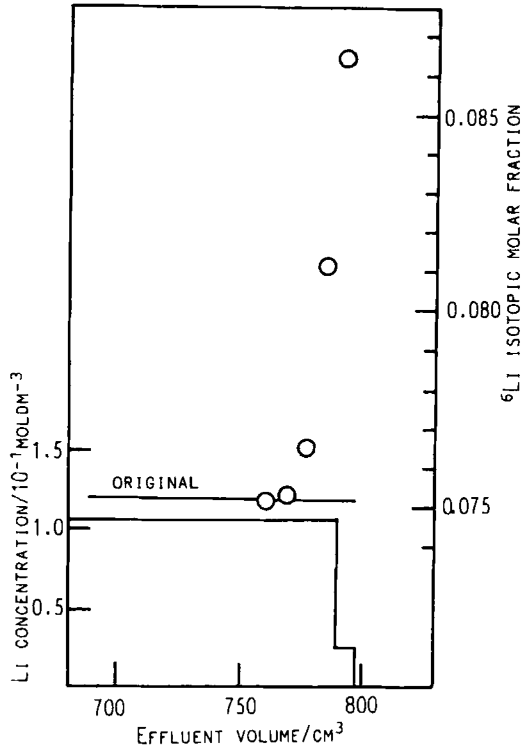

FIG. 6. Chromatogram of the ^{6}Li isotopic molar fractions of Run Li06. Experimental conditions are summarized in Table 1.

where R_0 is the ^{6}Li isotopic molar fraction in the feed solution, R_i is that in the ith fraction of the effluent, f_i is the amount of lithium in the ith fraction, Q is the total exchange capacity of the exchanger for lithium, and summation is taken over all the fractions that are enriched or depleted in ^{6}Li. The ϵ values thus calculated are listed on the last column of Table 2. They are in the range of 0.89 to 1.71×10^{-3}, the largest one being obtained for the lithium phosphate–TIN-100 ion-exchange fiber system.

The following qualitative observations can be made about the ϵ values obtained.

(1) For a common counterion to Li^+ in the solution phase, the system with TIN-100 shows a larger ϵ value than the system with LS-6 (Li01 vs Li06, Li02 vs Li07, and Li05 vs Li09). According to the work by Lee and Begun (*4*), this is attributable to the difference in degree of crosslinking between the two exchangers; that is, the

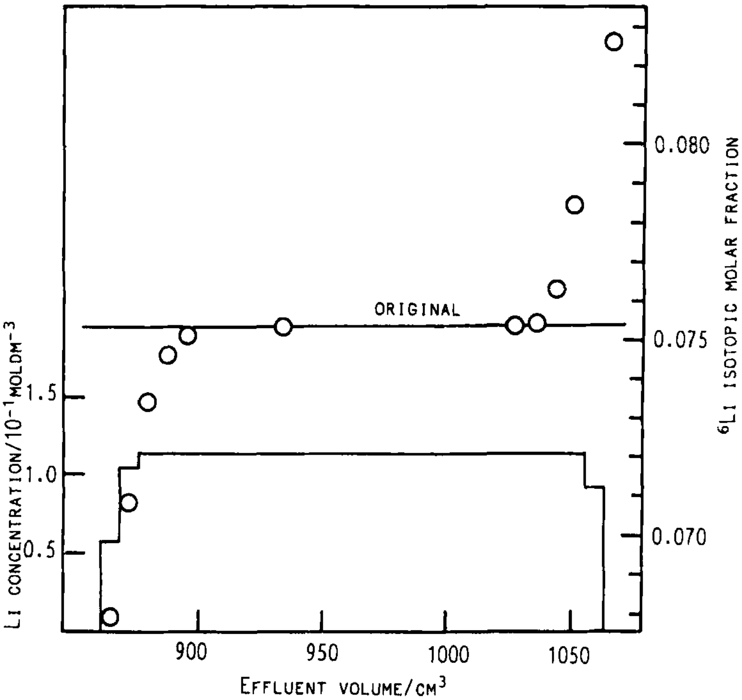

FIG. 7. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li07. Experimental conditions are summarized in Table 1.

work by Lee and Begun suggests that TIN-100 should have a higher degree of crosslinking than LS-6. Unfortunately, however, the manufacturers of these exchangers do not supply any data on this point.

(2) The acetate and chloride systems have similar ϵ values, but the lactate system shows a smaller ϵ value than do the other two for both LS-6 and TIN-100 exchangers.

The k^* and ϵ data suggest that the lithium acetate–ion-exchange fiber system is the most suited for lithium isotope separation of all the systems studied in this paper. Although the lithium phosphate–ion-exchange fiber system has the largest ϵ value, its isotope accumulation profile is unsatisfactory. The lithium chloride system, both with the strongly acidic and weakly acidic ion-exchangers, has the intrinsic drawback that band displacement chromatography is never realized, despite the ϵ values being equivalent to those of the lithium acetate system. The lithium lactate system is inferior to the lithium acetate system both in ϵ and k^* values, and the

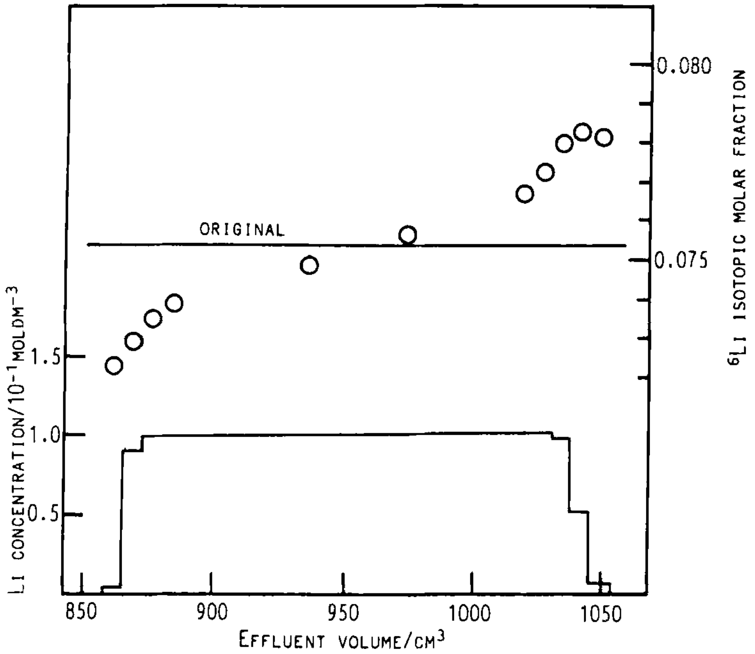

FIG. 8. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li08. Experimental conditions are summarized in Table 1.

lithium hydroxide system is equivalent to the lithium lactate system in ϵ value but is worse in k^* value.

Analysis of the Observed Lithium Isotope Effect on the Basis of an Isotope Two-Phase Distribution Theory

The theory on isotope distribution between two phases (*17*) correlates S with the isotopic reduced partition function ratios (RPFR's) (*24*) and the molar fractions of the species containing the isotopes of concern in a separation system. Based on the theory, S is in general expressed as

$$\ln S = \ln\left(\sum x_i f_i\right) - \ln\left(\sum \bar{x}_i \bar{f}_i\right) \qquad (5)$$

where x_i and f_i are the molar fraction and the RPFR of species i in the external solution phase, respectively, $\bar{x}_i$ and $\bar{f}_i$ are the same quantities in the ion-exchanger phase, and $\Sigma\ x_i = \Sigma\ \bar{x}_i = 1$. Symmetry numbers are neglected in the expressions of the RPFR's for simplicity.

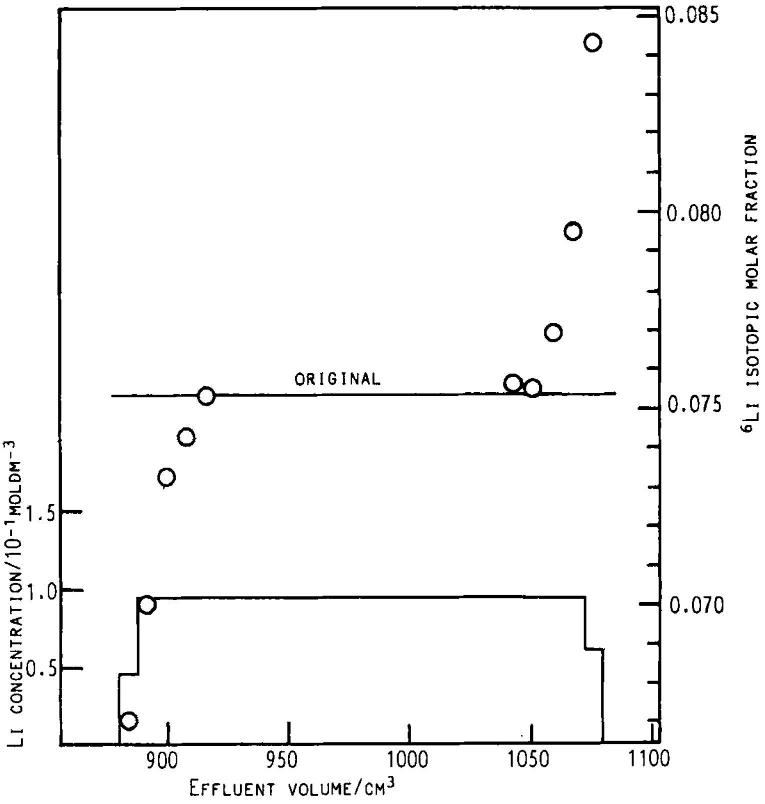

FIG. 9. Chromatogram and the ^{6}Li isotopic molar fractions of Run Li09. Experimental conditions are summarized in Table 1.

TABLE 2

k^* and ϵ Values Obtained

Run	Exchanger	Counterion in solution phase	k^* (front) (cm^{-1})	k^* (rear) (cm^{-1})	ϵ
Li01	LS-6	Cl^-	—	0.026	1.01×10^{-3}
Li02	LS-6	Lactate ion	0.016	0.022	0.89×10^{-3}[a]
Li03	WK-13	Cl^-	—	0.009	1.20×10^{-3}
Li04	LS-6	Hydroxide ion	0.002	0.011	0.90×10^{-3}[a]
Li05	LS-6	Acetate ion	0.019	0.023	1.01×10^{-3}[a]
Li06	TIN-100	Cl^-	—	0.033	1.64×10^{-3}
Li07	TIN-100	Lactate ion	0.024	0.024	1.50×10^{-3}[a]
Li08	TIN-100	$H_2PO_4^-$	0.005	0.005	1.71×10^{-3}[a]
Li09	TIN-100	Acetate ion	0.028	0.029	1.58×10^{-3}[a]

[a] Average of the two ϵ values obtained from the front and the rear parts of the band.

Runs Li01 and Li06

The simplest systems in the present study are those of Li01 and Li06 in which both the solution and the ion-exchanger phases can be regarded as strong electrolyte solutions and hence no complex formation nor ion-association is viable in either phase. Only the lithium species existing in the solution phase and in the exchanger phase are the simple hydrated ones, $Li^+(H_2O)_n$ and $Li^+(H_2O)_m$, where n and m are the hydration numbers in the former phase and in the latter phase, respectively. In this case, Eq. (5) is simplified to

$$\ln S = \ln f_{n,0} - \ln \bar{f}_{m,0} \tag{6}$$

[$S = S(\text{Li01})$ for Li01 or $= S(\text{Li06})$ for Li06; hereafter, such expressions as $S(\text{Li06})$ and $S_{\text{phase}}(\text{Li06})$ are abbreviated as S and S_{phase}, respectively, as long as it is clear which experiment we are discussing], where $f_{n,0}$ is the ^{7}Li-to-^{6}Li isotopic RPFR of $Li^+(H_2O)_n$ in the solution phase and $\bar{f}_{m,0}$ is that of $Li^+(H_2O)_m$ in the exchanger phase. By defining

$$S_{\text{hydra}} = f_{n,0}/f_{m,0} \tag{7}$$

and

$$S_{\text{phase}} = \bar{f}_{m,0}/f_{m,0} \tag{8}$$

Equation (6) is then rewritten as

$$\begin{aligned}\ln S &= \ln (f_{n,0}/f_{m,0}) - \ln (\bar{f}_{m,0}/f_{m,0}) \\ &= \ln S_{\text{hydra}} - \ln S_{\text{phase}} \end{aligned} \tag{9}$$

S_{hydra} is a part of the (overall) separation factor S, originating from a change in the hydration number from m to n in the solution phase. It is usually considered that n is larger than m (5). Therefore, $\ln S_{\text{hydra}}$ is positive. S_{phase} is a part of S due to the phase change, that is, the separation factor observed when the simple hydrated species, $Li^+(H_2O)_m$, is transferred from the solution phase to the exchanger phase. ln S(Li01) and ln S(Li06) are both positive and hence $\ln S_{\text{hydra}}(\text{Li01}) > \ln S_{\text{phase}}(\text{Li01})$ and $\ln S_{\text{hydra}}(\text{Li06}) > \ln S_{\text{phase}}(\text{Li06})$.

Run Li03

In the lithium chloride–weakly acidic cation-exchange resin system (Li03), the only viable Li species in the solution phase is the simple hydrated Li^+, but in the resin phase part of the lithium ions may form complexes and/or may be ion-associated with some of the —COO^- groups of the resin. By making no distinction between complex species and ion-associated species for the sake of mathematical simplicity, we regard them as one kind of lithium species and use the complex term. Equation (5) is then expressed, assuming an outer sphere complex, as

$$\ln S(\text{Li03}) = \ln f_{n,0} - \ln \{\bar{x}\bar{f}_{m,0} + (1 - \bar{x})\bar{f}_{m,1}\} \tag{10}$$

where $\bar{x}$ is the molar fraction of $Li^+(H_2O)_m$, $\bar{f}_{m,1}$ is the RPFR of the outer sphere complex, $Li^+(H_2O)_mL$ in the resin phase where L = —COO^+. Defining

$$\bar{S}_{\text{complex}} = \bar{f}_{m,1}/\bar{f}_{m,0} \tag{11}$$

Eq. (10) is rewritten as

$$\begin{aligned} \ln S(\text{Li03}) &= \ln (f_{n,0}/f_{m,0}) - \ln \bar{f}_{m,0}/f_{m,0}) \\ &\quad - \ln \{\bar{x} + (1 - \bar{x})(\bar{f}_{m,1}/\bar{f}_{m,0})\} \\ &= \ln S_{\text{hydra}} - \ln S_{\text{phase}} \\ &\quad - \ln \{\bar{x} + (1 - \bar{x})\bar{S}_{\text{complex}}\} \end{aligned} \tag{12}$$

$\bar{S}_{\text{complex}}$ is a part of the overall separation factor S due to complex formation in the resin phase. If we assume that ($\ln S_{\text{hydra}} - \ln S_{\text{phase}}$) of the weakly acidic resin WK-13 is the same as that of the strongly acidic resin LS-6, then

$$\begin{aligned} \ln \{\bar{x} + (1 - \bar{x})\bar{S}_{\text{complex}}\} &= \ln S(\text{Li01}) - \ln S(\text{Li03}) \\ &= -0.19 \times 10^{-3} \end{aligned} \tag{12'}$$

Since no data on the $\bar{x}$ value is presently available, we cannot estimate a definite value for $\bar{S}_{\text{complex}}(\text{Li03})$ on an experimental basis. However, it is apparent that -0.19×10^{-3} is the maximum value for $\ln \bar{S}_{\text{complex}}(\text{Li03})$. From Eq. (12'), $\ln \bar{S}_{\text{complex}}(\text{Li03}) = -1.9 \times 10^{-3}$ for $\bar{x} = 0.9$ and -9.5×10^{-4} for $\bar{x} = 0.8$.

In the above discussion we have assumed an outer sphere type complex between the hydrated lithium ion and the —COO^- group. It is also possible to assume an inner sphere type complex, $Li^+(H_2O)_{m-1}L$. In this case, Expression (13) is obtained instead of Eq. (12):

$$\ln S = \ln (f_{n,0}/f_{m,0}) - \ln (\bar{f}_{m,0}/f_{m,0}) - \ln \{\bar{x} + (1 - \bar{x})(\bar{f}_{m,1}/\bar{f}_{m,0}) \div (\bar{f}_{m,1}/\bar{f}_{m-1,1})\} = \ln S_{\text{hydra}} - \ln S_{\text{phase}} - \ln \{\bar{x} + (1 - \bar{x})\bar{S}_{\text{complex}}/\bar{S}_{\text{hydra}}\} \quad (13)$$

where

$$\bar{S}_{\text{hydra}} = \bar{f}_{m,1}/\bar{f}_{m-1,1} \quad (14)$$

$\bar{f}_{m-1,1}$ is the RPFR of $Li^+(H_2O)_{m-1}L$ in the exchanger phase, and $\bar{S}_{\text{hydra}}$ is a part of the separation factor obtained between the species $Li^+(H_2O)_mL$ and $Li^+(H_2O)_{m-1}L$ in the exchanger phase. If we anew define $\bar{S}_{\text{complex}}/\bar{S}_{\text{hydra}}$ as $\bar{S}_{\text{complex}}$, however, we can treat the inner sphere complex formation and the outer sphere complex formation as mathematically similar. As will be discussed in the next subsection, it is quite likely that the complex species formed in the exchanger phase in Li03 is an inner sphere complex rather than an outer sphere complex.

Runs Li05 and Li09

Contrary to the lithium chloride-weakly acidic cation-exchange resin system (Li03), the lithium acetate-strongly acidic ion-exchanger system (Li05 and Li09) is expected to have no complex species in the exchanger phase, but can have a complex species, $Li^+(H_2O)_nL$ ($L = CH_3COO^-$), in the solution phase [again, we assumed an outer sphere type complex, but a similar discussion is possible for the inner sphere type complex, $Li^+(H_2O)_{n-1}L$, as above]. Equation (5) is simplified for Runs Li05 and Li09 as

$$\ln S = \ln \{x f_{n,0} + (1 - x) f_{n,1}\} - \ln \bar{f}_{m,0} \quad (15)$$

[$S = S(\text{Li05})$ or $= S(\text{Li09})$], where x is the molar fraction of the simple hydrated species $Li^+(H_2O)_n$, and $f_{n,1}$ is the RPFR of the species $Li^+(H_2O)_nL$ in the solution phase. Defining

$$S_{\text{complex}} = f_{n,1} f_{n,0} \quad (16)$$

which represents a part of the separation factor originating from complex formation in the solution phase, Eq. (15) is rewritten as

$$\ln S = \ln (f_{n,0}/f_{m,0}) - \ln (\bar{f}_{m,0}/f_{m,0}) + \ln \{x + (1 - x)f_{n,1}/f_{n,0}\}$$

$$= \ln S_{\text{hydra}} - \ln S_{\text{phase}} + \ln \{x + (1 - x)S_{\text{complex}}\} \qquad (17)$$

A couple of stability constant values between lithium ion and acetate ion are reported in the literature (25). Calculation using these values and the value of the dissociation constant of acetic acid (25) shows that 14–20% of lithium exists as $Li^+(H_2O)_nL$ and the remaining as $Li^+(H_2O)_n$, depending on the stability constant value, under the present experimental conditions. Taking into consideration the existence of the ion-associated species, the x value is expected to be at most 0.80–0.86. Since ($\ln S_{\text{hydra}} - \ln S_{\text{phase}}$) of Li05 and Li09 is nothing but ln S(Li01) and ln S(Li06), respectively, it follows that $\ln S_{\text{complex}}(\text{Li05}) = 0$ and $\ln S_{\text{complex}}(\text{Li09}) = 0$. That is, there is no appreciable lithium isotope effect accompanying complex formation between lithium ion and acetate ion in the solution phase for each of the strongly acidic cation-exchangers.

Runs Li02 and Li07

The lithium lactate-strongly acidic exchanger system (Li02 and Li07) can be discussed similarly to the lithium acetate-strongly acidic exchanger system (Li05 and Li09). A comparison of the S values between Li01 and Li02 and between Li06 and Li07 reveals that $\ln \{x + (1 - x)S_{\text{complex}}\} = -0.12 \times 10^{-3}$ for Li02 and -0.14×10^{-3} for Li07. Thus, $\ln S_{\text{complex}}(\text{Li02})$ and $\ln S_{\text{complex}}(\text{Li07})$ are both negative. A S_{complex} value smaller than unity means that the sum of forces acting on a lithium ion is stronger in the simple hydrated lithium ion than in the complex species, and that complex formation of lithium ion with lactate ion in the solution phase reduces the overall separation factor, S. Unfortunately, we have at present no estimate for the x value, since no stability constant value between lithium ion and lactate ion is reported. If we tentatively assume 20% of lithium ions form complexes with lactate ions, then $S_{\text{complex}}(\text{Li02}) = 0.9994$ [$\ln S_{\text{complex}}(\text{Li02}) = 6.0 \times 10^{-4}$] and $S_{\text{complex}}(\text{Li07}) = 0.9993$ [$\ln S_{\text{complex}}(\text{Li07}) = 7.0 \times 10^{-4}$].

The result that $S_{\text{complex}} = 1$ for the lithium acetate system and $S_{\text{complex}} < 1$ for the lithium lactate system indicates that acetate ion and lactate ion coordinate Li^+ in different manners, despite the fact that both acids are carboxylic acids.

Run Li04

Equation (17) is also applicable to the lithium hydroxide-strongly acidic ion-exchange resin system (Li04). According to a study of the hydrolysis of lithium ion in aqueous solution (*25*, *26*), about 1.5% of lithium ions exist as LiOH and 98.5% as simple hydrated species in the solution phase under the present experimental conditions. Substituting the experimental data in Eq. (17), we derive $\ln \{x + (1 - x)S_{\text{complex}}\} = \ln S(\text{Li04}) - \ln S(\text{Li01}) = -0.11 \times 10^{-3}$. This result can be qualitatively interpreted in terms of RPFR's, showing that the RPFR of the simple hydrated lithium ion is larger than that of the hydrolysis product. The abundant existence of OH^- in the solution phase not only reduces the S value relative to that of Li01, but yields a much smaller k^* value than that of Li01, suggesting that it reduces the rate of lithium isotope exchange between the solution and the exchanger phases.

Run Li08

Equation (17) can also be used for the analysis of Run Li08. The existence of the complex species $LiHPO_4^-$ in an aqueous lithium-phosphoric acid solution has been reported and its formation constant measured (*25*). Calculation using the formation constant value of $LiHPO_4^-$ and the dissociation constant data of phosphoric acid show that the amount of this complex species in the solution phase is negligible under the present experimental conditions. Since phosphoric acid exists mainly in the form of $H_2PO_4^-$ and partly as H_3PO_4 under the experimental conditions, it is expected that a small part of the lithium ions are ion-associated with $H_2PO_4^-$ in the solution phase. The fact that the value of $S(\text{Li08})$ is only very slightly larger than that of $S(\text{Li06})$, i.e., $\ln S_{\text{complex}}(\text{Li08}) > 0$, indicates that the lithium isotope separation effect accompanying ion-association in the solution phase is small or that the amount of the ion-associated species is too small to cause a substantial increase in S value under the present experimental conditions.

Comparison of Lithium Isotope Effect with Potassium and Rubidium Isotope Effects in Cation-Exchange Chromatography

In Table 3 the lithium isotope effect observed in the present study is compared with the potassium and rubidium isotope effects obtained in previous papers (*18*, *20*) for systems of lithium chloride-LS-6 strongly acidic resin, lithium lactate-LS-6 resin, and lithium chloride-WK-13 weakly acidic resin. The isotope effects are expressed as ϵ per unit mass difference, $\epsilon/\Delta M$. A positive ϵ value means that the heavier isotope (^7Li, ^{41}K, or ^{87}Rb) is preferentially fractionated into the solution phase. As seen in Table 3,

TABLE 3

Separation Factors for Alkali Metals in a Few Ion-Exchange Systems at 25°C

Cation-exchange resin	Counterion to Li^+ in solution phase	$\epsilon/\Delta m$		
		$^7Li/^6Li$	$^{41}K/^{39}K$[a]	$^{87}Rb/^{85}Rb$[b]
Strongly acidic ($—SO_3^-$)[c]	Chloride ion	1.01×10^{-3}	-1.3×10^{-5}	-2.6×10^{-6}
Strongly acidic ($—SO_3^-$)[c]	Lactate ion	0.89×10^{-3}	-1.2×10^{-5}	-1.8×10^{-6}
Weakly acidic ($—COO^-$)[d]	Chloride ion	1.20×10^{-3}	-1.7×10^{-5}	-5.7×10^{-6}

[a] From Ref. 18.

[b] From Ref. 20.

[c] Asahi LS-6 cation-exchange resin.

[d] Diaion WK-13 cation-exchange resin.

the magnitude of ϵ is in the order of $\epsilon(Li)| > |\epsilon(K)| > |\epsilon(Rb)|$ for each of the counterion/resin combinations. This result is in qualitative agreement with what a theory of isotope effect (*24*) predicts. It is also seen that the direction of isotope enrichment in lithium systems is opposite to that of potassium and rubidium systems. As will be discussed below, this is mostly attributable to the difference in relative magnitudes of isotope separation effects due to hydration and phase change among the three alkali metals. Another observation from Table 3 is that for every alkali metal, $|\epsilon(Cl^-$-weakly acidic resin$)| > |\epsilon(Cl^-$-strongly acidic resin$)| > |\epsilon($lactate ion-strongly acidic resin$)|$.

Results of the analysis of the above systems based on the isotope two-phase distribution theory (*17*) are summarized in Table 4. $\ln S_{\text{hydra}} > 0$ is

TABLE 4

Comparison of Various *S*'s among Lithium, Potassium, and Rubidium[a]

Element	$\ln S_{\text{hydra}} - \ln S_{\text{phase}}$	Sign of $\ln S_{\text{complex}}$[b]	Sign of $\ln \bar{S}_{\text{complex}}$[c]
Li	1.01×10^{-3}	−	−
K	-2.5×10^{-5}	+	+
Rb	-5.2×10^{-6}	+	+

[a] For the definition of each kind of *S*, see the text.

[b] The complexing partner is the lactate ion.

[c] It is assumed that the $(\ln S_{\text{hydra}} - \ln S_{\text{phase}})$ of the weakly acidic resin is the same as that of the strongly acidic resin.

expected not only for lithium but also for potassium and rubidium (*27*). Then, from the result that (ln S_{hydra} − ln S_{phase}) is negative for K and Rb, ln $S_{\text{phase}} > 0$ can be concluded for K and Rb. Since there is no reason to distinguish between Li and the other two alkali metals concerning the sign of ln S_{phase}, ln $S_{\text{phase}} > 0$ is also expected for Li. The result that, while the heavier isotopes of K and Rb are preferentially fractionated in the resin phase, ^{7}Li is enriched in the solution phase is attributable to the difference in the relative magnitudes of ln S_{hydra} and ln S_{phase} between the light alkali and heavy alkali metals; $S_{\text{hydra}} > S_{\text{phase}} > 1$ for Li while $S_{\text{phase}} > S_{\text{hydra}} > 1$ for K and Rb. This is consistent with the well-known fact that lithium ions are hydrated very strongly but potassium and rubidium ions are not in aqueous solutions. When the hydrated lithium ion is adsorbed in the resin, it is deprived of part of the hydrating water molecules, resulting in a large lithium isotope effect. On the other hand, hydration of potassium and rubidium ions is very weak, and hence, when these ions are transferred from the solution phase to the resin phase, loss of part of the hydrating water molecules does not affect the hydration circumstances, and it results in small potassium and rubidium isotope effects.

ln S_{complex} is negative for Li and positive for K and Rb when the complexing partner is the lactate ion. As mentioned before, ln $S_{\text{complex}} < 0$ means $f_{n,1} < f_{n,0}$, which indicates that the sum of forces acting on Li^+ is stronger in the simple hydrated species than in the complex species. The different sign of ln S_{complex} for Li and for K and Rb suggests that the lithium ion forms a complex with the lactate ion in a manner different from the way in which potassium and rubidium ions form complexes. If isotope effects of hydration and complex formation are additive (*28*), the former ion is expected to form an inner sphere complex with the lactate ion while the latter ions form outer sphere complexes. (Since no complex formation of K^+ or Rb^+ with the lactate ion is reported, their complex species should actually be the ion-associated species.). It should be noted that complex formation between alkali metal ions and the lactate ion in the solution phase decreases the magnitude of the overall separation factor, *S*, for all the alkali metals examined.

The sign of the isotope effect due to the complex formation, $\bar{S}_{\text{complex}}$, in the resin phase of the weakly acidic resin (WK-13) is the same as that in the solution phase of the strongly acidic resin (LS-6) for each of Li, K, and Rb. Note that in the analysis it had been assumed that (ln S_{hydra} − ln S_{phase}) for the WK-13 resin is the same as that for the LS-6 resin. As in the case of the solution phase of the LS-6 resin, the complex formation of Li^+ with —COO^- in the resin phase is negative, indicating an inner sphere type complex formation, and those of K and Rb are positive, indicating outer sphere type complex formations. Despite the different sign of ln

$\bar{S}_{\text{complex}}$ for Li and for K and Rb, the complex formations in the resin phase increase the magnitude of the overall separation factor for all the alkali metals studied.

CONCLUSION

(1) The heavier isotope, ^{7}Li, was preferentially fractionated into the exchanger phase. This trend is independent of the type of cation-exchanger (weakly acidic resin, strongly acidic resin, or strongly acidic fiber) and the kind of lithium salts used in the feed solutions (chloride, acetate, lactate, hydroxide, and phosphate) within the range of the present experimental conditions.

(2) The ϵ values obtained were 0.89×10^{-3} to 1.71×10^{-3} at 25°C. The strongly acidic fiber gave a larger ϵ value than the strongly acidic resin for a common counteranion to Li^+ in the feed solution. This could be attributed to the difference in degree of crosslinking between the two cation-exchangers.

(3) For a common strongly acidic cation-exchanger, different counterions to Li^+ in feed solutions often yield different ϵ; the decreasing order of the ϵ value is ϵ(phosphate) $\geqq$ ϵ(chloride) = ϵ(acetate) > ϵ(lactate,) = ϵ(hydroxide). A slight dependence of ϵ value on the kinds of counterion seems to be due to the existence of complex and/or ion-associated species between the lithium ion and anions in the solution phase.

(4) The direction of isotope fractionation of lithium is opposite to that of potassium and rubidium. This is due to the fact that the isotope effect accompanying hydration is larger than the isotope effect due to the phase change for lithium, while the opposite is the case with potassium and rubidium.

(5) Complex formation has a different effect on the overall separation factor, S, of lithium system than on the potassium and rubidium systems. Complex formation of the lithium ion with the lactate ion in the solution phase decreases the S value, while that of potassium and rubidium ions increases S (the magnitude of ϵ decreases in all cases), indicating the difference in the type of complex formed between lithium and the other two alkali metals.

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