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Lithium isotope effects in water–dimethyl sulphoxide mixed-solvent ion-exchange chromatography

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ABSTRACT

Cation-exchange chromatography of lithium was successfully carried out to investigate the lithium isotope effects in water–dimethyl sulphoxide (DMSO) mixed-solvent ion-exchange systems at 25°C. The value of the separation factor minus 1 (ε) was $1.4 \cdot 10^{-3}$ to $2.2 \cdot 10^{-3}$; ε had a maximum value of $2.2 \cdot 10^{-3}$ when the molar fraction of water in the solution phase, x_{water}, was about 0.57, and decreased as x_{water} deviated from this value. A consideration based on a theory of isotope distribution between two phases indicated that DMSO was slightly preferentially fractionated into the ion-exchanger phase rather than into the solution phase.

INTRODUCTION

Studies on lithium isotope separation by ion exchange are old; the first use of an ion exchanger for this purpose is found in a publication by Taylor and Urey [1] in 1937. The topic, however, still draws continuing interest, in part because of the importance of the individual stable isotopes of lithium, ^{6}Li and ^{7}Li, in nuclear science and technology. The magnitudes of lithium isotope effects observed in aqueous ion-exchange systems, especially systems with commercially available organic ion exchangers, are in general small, of the order of 10^{-3} [2], and attempts to seek systems with larger isotope effects have been made. The use of inorganic lithium-specific adsorbents [3] and a cryptand resin [4,5] is one such attempt.

A second way to realize greater lithium isotope effects may be to use mixed solvents instead of water. The lithium isotope effects observed in ion-exchange systems mostly come from the difference in solvation state of lithium ions in the solution and the ion-exchange phases [6], and hence mixed solvents may increase (or, contrary to our intention, decrease) the effects if the mixing ratios of solvent differ between the two phases.

Nandan and Gupta [7] measured the magnitude of the lithium isotope effect in the ion-exchange system with a 50:50 (v/v) solvent mixture of water and dimethyl sulphoxide (DMSO) and reported that the effect is similar to that observed in the aqueous medium. They attributed this to the lack of the solvent fractionation in water–DMSO mixtures between the solution and the ion-exchange phases [8]. In spite of their non-affirmative conclusion, we carried out ion-exchange chromatographic separation of lithium isotopes in water–DMSO mixed solvents with the expectation of obtaining large lithium isotope effects compared with that in the aqueous medium. Our expectation was based on the experimental fact that the magnitude of the Gibbs free energy change upon lithium ion transfer from water to a water–DMSO mixture is very large [9], and consequently even a slight solvent fractionation between the solution and the ion-exchange phases may result in a large change in lithium isotope effect. In this paper, we report the results of chromatographic experiments on lithium isotope separation employing

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TABLE I

EXPERIMENTAL CONDITIONS

Ion exchanger = strongly acidic Toray TIN-100 ion-exchange fibre in the H^+ form; temperature = 25.0 ± 0.2°C; Ac = acetate ion.

Parameter	Run no.				
	LiAc1	LiAc2	LiAc3	LiAc4	LiAc5
Water/DMSO mixing ratio (v/v)	100:0	50:50	25:75	5:95	5:95
Ion-exchanger bed height (cm)	203.0	195.2	206.0	203.2	184.1
Operating manner	Band	Band	Band	Band	Breakthrough
Band length (cm)	48.0	50.1	37.2	40.2	–
Lithium acetate concentration in feed (mol/dm^3)	0.100	0.100	0.097	0.096	0.098
Potassium acetate concentration in eluent (mol/dm^3)	0.108	0.110	0.099	0.097	–
Flow-rate (cm^3/cm^{2}h)	12.61	6.02	6.18	1.85	12.64
Band velocity (cm/h)	2.75	1.06	1.30	0.34	1.85

lithium acetate (LiAc) as lithium salt and performed in water–DMSO mixed solvent media at 25°C.

EXPERIMENTAL

Reagents

The ion exchanger used was a highly efficient, cylindrical strongly acidic cation exchange fibre, Toray TIN-100, reinforced with polyethylene and manufactured by Toray. Its average size is 0.5 mm × 50 μm I.D. and its exchange group is the sulpho group. All the reagents used were of analytical-reagent grade and were used without further purification. Distilled water was used in every experiment.

Chromatographic process

Five chromatographic experiments were carried out; four operated in a band displacement manner and one in a breakthrough manner. Their experimental conditions are summarized in Table I. The mixing ratio of water and DMSO was varied from 100:0 to 5:95 (v/v). 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 *ca.* 200 cm.

In a band displacement chromatographic experiment, the ion exchanger packed in the column was first conditioned to the H^+ form in the usual manner by using a water–DMSO solution as solvent. A lithium feed solution (lithium acetate solution) was then fed to the column at a constant flow-rate to form a lithium adsorption band with an appropriate length. This band was eluted by an eluent containing potassium as the displacement ion for lithium ion. The effluent from the bottom of the column was collected and divided into small fractions (10 cm^3). 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.

The breakthrough experiment designed to examine the reproducibility of the lithium isotope effect in our experiments was performed in the usual way.

Analysis

The lithium and potassium concentrations in each fraction of the effluents were determined flame photometrically with a Daini Seikosha Model SAS-727 atomic absorption spectrometer.

For the feed solution and selected fractions of the effluent of each experiment, the ^{7}Li/^{6}Li isotopic ratio was measured, the procedure for which was the same as that in the previous paper [2] except for one point: when necessary, DMSO was separated from lithium by heating at about 150°C after the chemical form of lithium was converted from lithium acetate to lithium hydroxide. The lithium isotopic ratio measurements were performed with a double-filament thermal ionization technique on a Varian MAT CH-5 mass spectrometer. The relative standard deviation of a measurement was typically 0.1%.

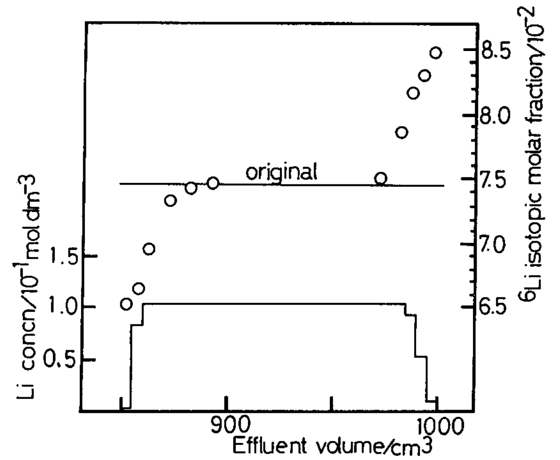

Fig. 1. Chromatogram and ^{6}Li isotopic molar fractions in run LiAc2. Experimental conditions are summarized in Table I. The solid step-like line denotes the total lithium concentration, the open circles the ^{6}Li isotopic molar fractions and the "original" line that in the feed solution. The ^{6}Li isotopic molar fraction in the feed was 0.07451.

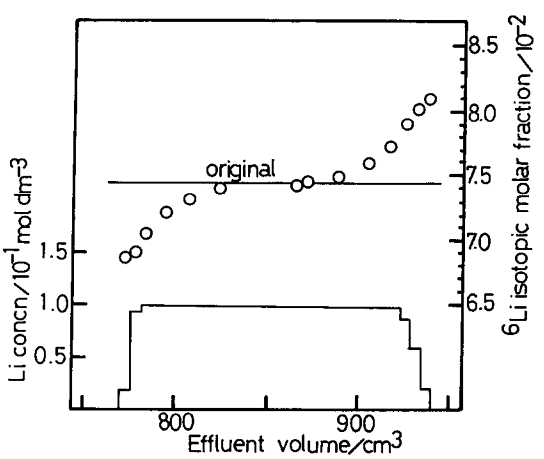

Fig. 2. Chromatogram and ^{6}Li isotopic molar fractions in run LiAc3. Experimental conditions are summarized in Table I. The solid step-like line denotes the total lithium concentration, the open circles the ^{6}Li isotopic molar fractions and the "original" line that in the feed solution. The ^{6}Li isotopic molar fraction in the feed was 0.07441.

RESULTS AND DISCUSSION

Examples of chromatograms and ^{6}Li isotopic molar fractions obtained are shown in Figs. 1 and 2. Fig. 1 presents the analytical results of run LiAc2 and Fig. 2 those of run LiAc3. In each figure, the solid step-like line represents the lithium concentration profile, the open circles the ^{6}Li isotopic molar fractions and the "original" line that of the feed solution. The chromatograms have satisfactorily sharp boundaries at both their ends, as is seen in the figures, and the band widths were virtually unchanged during the chromatographic operation. Thus, band displacement chromatography was realized in runs LiAc2 and LiAc3. Like the chromatogram of LiAc1 with the aqueous solvent, even that of LiAc4 with the 5:95 (v/v) water–DMSO mixed solvent had fairly sharp boundaries at both its ends, showing the realization of band displacement chromatography.

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

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

where [A] and $\overline{[\mathrm{A}]}$ denote the concentrations of isotope A in the external solution phase and in the ion-exchange phase, respectively. The ε value is calculable with experimentally determinable quantities by using the equation [10]

$$\varepsilon = \sum [\,|R_i - R_0|\,f_i]/[R_0(1 - R_0)Q]$$

The meanings of the symbols in the above equation are the same as those in the previous paper [2]. The ε values thus calculated are listed in Table II, together with the previous data [2,7]. All the values are of the order of 10^{-3}. The ε values of runs LiAc1, LiAc2 and LiAc3 are the averages of the ε values calculated by using the data in the front and rear parts of the chromatograms, while those of runs LiAc4 and LiAc5 are obtained only from the data in the front parts. The ε values of runs LiAc4 and LiAc5 are the same within experimental errors, and so are those of LiAc1 and Li09 in the previous paper [2], both suggesting satisfactorily high reproducibility of our chromatographic experiments.

In Fig. 3, ε is plotted against the molar fraction of water, x_{water}, in the water–DMSO mixed solvent in the solution phase. As can be seen, ε has a maximum at around $x_{\mathrm{water}} = 0.57$ (volume ratio of water to DMSO = 25:75) and decreases as x_{water} deviates from this value in either direction.

TABLE II

PREVIOUS AND NEW ε VALUES IN LITHIUM ACETATE SYSTEMS WITH WATER–DMSO MIXED SOLVENTS AT 25°C

Run no.	Water/DMSO ratio (v/v)	Ion exchanger	Lithium acetate concentration (mol/dm^3)	ε (× 10^{-3})	Ref.
LiAc1	100:0	Toray TIN-100	0.1	1.7	This work
Li05	100:0	Toray TIN-100	0.1	1.6	2
Li09	100:0	Asahi LS-6	0.1	1.0	2
	100:0	Dowex 50W-X8	0.2 (?)	1.3	7
LiAc2	50:50	Toray TIN-100	0.1	2.0	This work
	50:50	Dowex 50W-X8	0.2	1.5	7
LiAc3	25:75	Toray TIN-100	0.1	2.2	This work
LiAc4	5:95	Toray TIN-100	0.1	1.4	This work
LiAc5	5:95	Toray TIN-100	0.1	1.5	This work

In ion-exchange systems of the alkali metals, the overall isotope effect, which is the one experimentally obtained, is in general composed of four fundamental isotope effects, *i.e.* the one arising from phase change, a second originating from solvation state change, and the third and fourth effects accompanying complex formations (including ion associations) in the solution phase and in the ion-exchanger phase, respectively [11]. Since (1) no complex formation is expected to occur in the ion-exchanger phase in the present systems, (2) no appreciable lithium isotope effect accompanying complex formation between lithium ion and acetate ion in the solution phase was observed in an aqueous medium [2] and a similar situation is expected to hold in water–DMSO mixture media, and (3) the fundamental lithium isotope effect owing to phase change is generally considered to be small, the change in ε value observed in Fig. 3 must mostly come from the change in the solvation state of the lithium ion between the two phases. Based on a theory of isotope distribution between two phases [12], ln S can then be approximated as:

$$\ln S \simeq \ln f_{\mathrm{Li}} - \ln g_{\mathrm{Li}}$$

where f_{Li} and g_{Li} are the isotopic reduced partition function ratios [13] of the solvated lithium ion in the solution phase and in the ion-exchange phase, respectively. $f_{\mathrm{Li}} > g_{\mathrm{Li}}$ because $S > 1$, that is lithium ions are more strongly solvated in the solution phase than in the ion-exchange phase. Cations are more strongly solvated in DMSO than in water, and consequently the present results of the change in ε value indicate that DMSO is slightly more preferentially fractionated into the solution phase than water and that the degree of solvent fractionation is largest at around $x_{\mathrm{water}} = 0.57$.

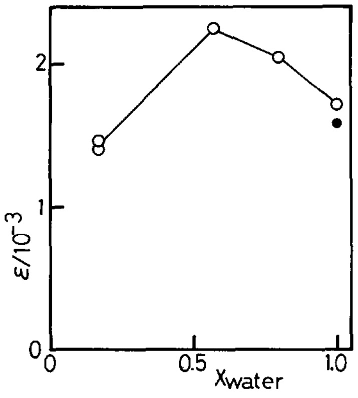

Fig. 3. The plot of ε (= $S - 1$) against molar fraction of water in the solution phase (x_{water}). (○) Present work; (●) from ref. 2.

Although Van Wart and Janauer [8] reported that in the ion-exchange systems of the Bio-Rad 50W-X8 resin in the Li$^+$ form with water–DMSO mixed solvent media, water is very slightly more preferentially distributed into the solution phase than into the ion-exchanger phase at 25°C, their results do not necessarily contradict ours. Firstly, we are dealing with different ion exchangers; they showed that even a change in the degree of cross-linking of the resin affects the solvent fractionation.

Secondly, in our chromatographic experiments, the ion exchanger in the lithium adsorption bands was not entirely in the Li^+ form but more or less in the mixed form of Li^+ and H^+, while their experiments were carried out with the resin in the complete Li^+ form, and with the Bio-Rad 50W-X12 resin in the H^+ form DMSO is slightly preferentially distributed into the solution phase for $x_{water} > 0.5$ [8]. Experimental errors involved in the determinations of DMSO and water [14] should also be pointed out. In any case, very accurate determination of DSMO and water in the two phases will be needed to clarify the correlation of the magnitude of the lithium isotope effect with the degree of solvent fractionation in the ion-exchange systems with water–DMSO mixed solvents.

The water–DMSO mixed solvent increased the ε value for the lithium isotopes, as is seen above. However, even the enhanced ε value is still much smaller than those obtained in the systems with a cryptand [4,5] and with lithium-specific adsorbents [3], and a continuing effort has to be made to search for mixed solvent systems with much larger lithium isotope effects.

CONCLUSION

The major findings of the present study are as follows.

(1) The ε values obtained were between $1.4 \cdot 10^{-3}$ and $2.2 \cdot 10^{-3}$ at 25°C.

(2) ε has its maximum value when the molar fraction of water in the solution phase, x_{water}, is about 0.57 and decreases as x_{water} deviates from this value.

(3) It was inferred that there is a slight solvent fractionation between the solution and the ion-exchange phases, and DMSO slightly prefers the latter to the former.

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