Lithium Isotope Effects in Cation Exchange Chromatography of Lithium Lactate in Water-Dimethyl Sulfoxide and Water-Acetone Mixed Solvent Media

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Lithium isotope separation by ion exchange displacement chromatography of lithium lactate in water-dimethyl sulfoxide (DMSO) and water-acetone mixed solvent media at 25 °C was explored. In both the water-DMSO and water-acetone system, the single stage isotope separation factor (S) was a convex function of the mixing ratio of the solvents in the external solution phase; S had its maximum value of 1.00254 at water:DMSO = 25:75 v/v and 1.00182 at water:acetone = 75:25 v/v. Strong correlations of S with solvent partitions between the solution and the exchanger phases were found in both systems, which was qualitatively explainable by considering the lithium isotope distributions between the two phases based on the fundamental lithium isotope effects and the relative affinities of water, DMSO and acetone towards the lithium ion.

1. Introduction

Lithium isotope separation is an old but still attractive research theme, due in part to the usefullness of the individual stable isotopes of lithium, ^{6}Li and ^{7}Li, in nuclear fusion and fission science and technology. Ion exchange chromatography is one of the most intensively studied and most promising methods of separating lithium isotopes [1]. Commercially available organic ion exchangers are usually used as column-packing material and water as solvent, and this way lithium isotope effects on the order of 10^{-3} are achieved. A way to realize larger lithium isotope effects in chromatographic systems may be to use solvents other than water and/or mixed solvents.

Kakihana et al. [2] studied lithium isotope effects in methanol-water and acetone-water mixed solvent systems and found that the single stage separation factor (S) increased with increasing organic portion of the mixed solvents. On the contrary, Ciric and Pupezin [3] reported that S decreased as the ratio of the organic component increased in ethanol-water, glycol-water and dioxane-water mixtures.

Since the lithium isotope effects in ion exchange systems originate mostly from the difference in the solvation of the lithium ions between the solution and the exchanger phases [4], it seems important to examine the fractionation of the solvent between the two phases. The above two studies [2, 3] lack data on this fractionation. Nandan and Gupta [5] reported that, compared to S in aqueous medium, S is large in methanol-water mixtures, is nearly unchanged in acetone- and dimethyl sulfoxide (DMSO)-water mixtures and is small in an isopropanol-water mixture. Unfortunately, their experimental points are too scanty to draw any decisive conclusions. Gupta [6] summarized the S values in mixed solvent media then available and discussed them from the standpoint of free energy changes.

In a previous paper [7], we reported that the magnitude of the lithium isotope effect observed in cation exchange chromatography of lithium acetate in water-DMSO mixed solvents had a maximum at the volume ratio 25:75 of water and DMSO and decreased as the solvent mixing ratio deviated from this value in either direction. However, our study lacked information on the solvent fractionation between the two phases. In the present work we carried out ion exchange displacement chromatographic lithium isotope separation experiments in water-DMSO and water-acetone mixed solvents using lithium lactate as lithium salt,

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and in addition we measured solvent fractionation between the solution and the ion exchanger phases. On this basis, we discuss the correlation of the lithium isotope effects in ion exchange systems in mixed solvent media with the phase-fractionation of the solvents.

2. Experimental

2.1. Reagents

The ion exchanger, manufactured by Toray Co., was a highly efficient, strongly acidic cation exchange fiber, Toray TIN-100, reinforced with polyethylene. The grains were cylindrical, 500 μm in length and 50 μm in diameter. The exchange group was the sulfo group ($-SO_3^-$) and the exchange capacity was 3.12 meq per g (dried at 25 °C below 2 torr for 24 hours). All the reagents used were of analytical-reagent grade and were used without further purification. Distilled water was used as pure water throughout this study.

2.2. Chromatographic Experiments

2.2.1. Chromatographic Process

Nine chromatographic experiments were carried out, eight operated in the band displacement manner and one in the breakthrough manner. The experimental conditions are summarized in Table 1. The separation column (Pyrex glass, length 210 cm, I.D. 1 cm) had a jacket. The temperature was kept at 25.0 ± 0.2 °C by circulating temperature-controlled water through the jacket. In the experiments operated in the band manner, lithium was introduced as lithium lactate and displaced by potassium ions. The volume ratio of water/DMSO was varied from 100:0 to 5:95, and that of water/acetone from 100:0 to 25:75. Run DM05BT, the only experiment operated in the breakthrough manner, was designed to check the reproducibility of the lithium isotope effect.

The experimental procedure was as follows: In a band displacement experiment, the ion exchanger packed in the column was first brought in the usual manner into the H^+ form in the solvent specified in Table 1. After washing the conditioning agent out with the pure solvent, lithium lactate solution was fed to the column to form the lithium adsorption band. The band was then eluted by potassium lactate in a solvent of the same composition as that of the feed solution. The effluent was collected and divided into fractions. The lithium and potassium concentrations, the pH and the $^7Li/^6Li$ isotopic ratios of the fractions were measured.

The breakthrough experiment (DM05BT) was performed in the usual way.

2.2.2. Chemical and Isotopic Analyses

The lithium and potassium concentrations were determined flame photometrically with a Daini Seikosha Model SAS-727 atomic absorption spectrometer. In case of the water-acetone system, an aliquot of the fraction was first evaporated to dryness to avoid any possible influence of acetone on the lithium determi-

Table 1. Experimental conditions [a].

Run	DM05BT	DM05	DM25	DM50	DM100 [b]	AC25	AC50	AC75	AC100
Solvent volume ratio									
water : DMSO [c]	5:95	5:95	25:75	50:50	100:0				
water : acetone						25:75	50:50	75:25	100:0
Operational manner [d]	b.t.	band	band	band	band	band	band	band	band
Exchanger bed height (cm)	164.3	203.8	85.2	195.2	200.0	180.4	168.5	185.0	193.7
Band length (cm)		41.6	28.6	49.3	48.5	44.6	64.7	45.5	60.7
Concentration of Li lactate feed (mol dm^{-3})	0.0950	0.102	0.100	0.100	0.104	0.0862	0.0908	0.0931	0.0913
Concentration of K lactate eluent (mol dm^{-3})		0.100	0.100	0.101	0.114	0.0749	0.0803	0.0821	0.0852
Flow rate ($cm^3\ cm^{-2}\ h^{-1}$)	5.43	4.92	6.14	5.78	6.75	12.0	16.1	11.1	12.8
Band velocity (cm h^{-1})	1.07	0.87	1.01	1.07	1.20	2.70	3.35	1.77	2.32

[a] Temperature: 25.0 ± 0.2 °C. – [b] From [7]. Designated as Run Li08 therein. – [c] DMSO: Dimethyl sulfoxide. – [d] b.t.: breakthrough operation; band: band operation.

nation, and pure water was added to the evaporated residue so that the lithium concentration fell within the range of 0.5–5.0 μg/cm^3. Similarly, the potassium concentration was adjusted so that it became between 2.5 and 25 μg/cm^3. As for the water-DMSO system, an aliquot was diluted with pure water. A preliminary experiment showed that the influence of DMSO on the lithium and potassium determinations was negligible.

The procedure for the preparation of samples for mass spectrometry was as follows: Aliquots containing about 5×10^{-5} or 1.5×10^{-4} mole lithium first underwent anion exchange in a chromatographic column, in order to change the counterion of lithium ion from lactate to hydroxide. The effluent from the column was evaporated to dryness and was kept at 150 °C until the organic component of the mixed solvent was eliminated completely. To the evaporated residue (lithium hydroxide) a hydroiodic acid solution with an excess amount of iodide ion was added, yielding a lithium iodide solution. This solution was evaporated to dryness to remove excess hydroiodic acid. Finally, the residue was dissolved in pure water so that the lithium concentration became 0.05 M or 0.15 M (1 M = 1 mol/dm^3).

The procedure for the ^{7}Li/^{6}Li isotopic ratio measurements on the samples thus prepared has been described in [4, 7]. The measurements on the 0.05 M samples were made with a Finnigan MAT 261 mass spectrometer, and those of the 0.15 M samples with a Varian MAT CH-5 mass spectrometer. The relative standard deviation of a measurement was typically 0.1%.

2.2.3. Estimation of the Single Stage Separation Factor

The single stage separation factor, S $(=\varepsilon+1)$, for the ^{7}Li/^{6}Li isotopic pair is defined as

$$S = ([^7\mathrm{Li}]_{\mathrm{sol}}/[^6\mathrm{Li}]_{\mathrm{sol}})/([^7\mathrm{Li}]_{\mathrm{exc}}/[^6\mathrm{Li}]_{\mathrm{exc}}), \quad (1)$$

where $[\mathrm{A}]_{\mathrm{sol}}$ and $[\mathrm{A}]_{\mathrm{exc}}$ denote the concentrations of isotope A in the external solution and in the ion exchanger, respectively. If in the middle stretch of the band the isotopic composition has remained that of the feed solution, as was the case in our experiments, ε can be evaluated with the equation [9]

$$\varepsilon = \sum [|R_i - R_0| f_i]/[R_0(1-R_0)Q], \quad (2)$$

where R_0 is the ^{6}Li isotopic mole fraction in the feed solution, R_i that in the i-th fraction of the effluent, f_i the amount of lithium in the i-th fraction, Q the total exchange capacity of the exchanger bed for lithium, and the summation is taken over the fractions that are enriched or depleted in ^{6}Li. ε of a band displacement experiment is in principle calculable from the analytical results of either the front or the rear part of the band.

2.3. *Solvent Fractionation Experiments*

2.3.1. Water-DMSO

The same type of ion exchange fiber as used in the above experiments was packed in a short column (Pyrex glass, length 30 cm, I.D. 1 cm) with a water jacket. The ion exchanger and the solution phases were equilibrated with each other with respect to both lithium and solvent by feeding about 1 dm^3 of a 0.100 M lithium salt solution with a given water:DMSO mole ratio. The column temperature was kept at 25.0 ± 0.2 °C. After the equilibrium was attained, the column was emptied and the exchanger phase was separated from the solution phase first by filtration with suction and then by centrifugation with a Kubota KS-8000 centrifuge. The centrifugal separator was run with 2000 rpm (840 g) for 20 minutes, which was chosen because it was found in preliminary experiments that the weight ratio of the ion exchanger phase before and after centrifugation did not change between 1500 and 2500 rpm (470 and 1300 g) for the centrifuging period of 20 minutes. Pepper et al. [10] reported that the centrifugal force had an insignificant effect on the weight losses of wet sulphonated polystylene resins between 225 and 530 g even for that resin with its very low degree of cross-linking of 2%.

The water content in the solution phase was determined by Karl Fischer's method with a Hiranuma model AQV-55 aquacounter. The amount of solution used for one measurement was about 0.05 g. The water content in the exchanger phase was determined in a similar way by directly placing about 0.05 g of the exchanger wet with the mixed solvent into the titration cell of the aquacounter. The water contents thus determined were corrected for the moisture in the air.

The DMSO contents in the two phases were determined by the redox titration method reported by Rao [11]: DMSO was first oxidized by potassium dichromate in a sulfuric acid solution, and then the residual unreacted dichromate was estimated with ammonium iron(II) sulfate using N-phenylanthranilic acid as indicator. A blank experiment was carried out under identical conditions without DMSO. The final DMSO content was calculated from the difference in the titer values of the two titrations. In order to obtain results with high accuracy, it was important to prepare potassium dichromate and N-phenylanthranilic acid immediately before their uses and to apply a minimal amount of the indicator. An aliquot containing about 0.05 mole of DMSO was employed in a measurement.

The measured water and DMSO contents in the two phases yielded the fractionation factor of the solvents, K_d^w, defined as

$$K_d^w = (y_w/y_d)/(x_w/x_d)\,, \tag{3}$$

where y_w and y_d are the mole fractions of water and DMSO in the ion exchanger phase, respectively, and x_w and x_d are those in the solution phase. By definition, $K_d^w > 1$ when water is preferentially fractionated into the ion exchanger phase.

2.3.2. Water-Acetone

Solvent with a given water: acetone mole ratio was first put at the bottom of a desiccator where the desiccating agent is usually placed. About 0.5 g of the exchanger in the Li^+ or H^+ form, dried at 80 °C and below 1 torr for 24 hours in a vacuum drying apparatus, was put on a porcelain dish, and the dish was placed in the desiccator above the solvent. The desiccator was then thermostatted at 25.0 ± 0.2 °C in a water bath, was connected to a vacuum pump, and was evacuated below 1 torr to remove the atmospheric components. After the evacuation, a valve between the desiccator and the pump was closed, and thus the solvent absorption onto the ion exchanger commenced. The desiccator was kept for three days to equilibrate the solution and the exchanger phases with respect to the solvent (a preliminary experiment showed that this time was sufficient for the equilibration). After equilibrium was attained, the water and acetone contents of the two phases were determined.

The water contents in the two phases were determined in the same manner as used for water-DMSO.

The acetone content in the solution phase was determined by first oxidizing acetone to acetate ion by iodine and then back titrating unreacted iodine with sodium thiosulfate using a starch solution as indicator [12]. About 1 g of the solution was employed for a measurement. The acetone content in the ion exchanger phase was calculated from the weight difference of the exchanger before and after the solvent absorption and its water content.

The fractionation factors for the water-acetone system, defined as

$$K_a^w = (y_w/y_a)/(x_w/x_a)\,, \tag{4}$$

where y_a and x_a are mole fractions of acetone in the ion exchanger phase and in the solution phase, respectively, were calculated by using the water and acetone contents in the two phases.

3. Results and Discussion

Examples of the obtained chromatograms are depicted in Figs. 1 and 2. It is seen that the lighter isotope, ^{6}Li, is more strongly retained in the ion exchanger than ^{7}Li. This tendency was common to all the experiments. Ohtaki et al. [13] reported for the water-ethanol system, that the preference of the Dowex 50 resins for sodium isotopes (^{23}Na and ^{24}Na) changes with the solvent mixing ratio, but such crossover phenomena were not observed in the present study.

3.1. Isotope Separation Factors

The presently obtained ε values, together with data from [7] are listed in Table 2. The ε values of Runs DM50, DM100, AC25, AC50, AC75 and AC100 are the means of the two ε values obtained from the front and rear parts of the chromatograms whereas those of Runs DM05BT, DM05, DM25 are obtained from only one part of the chromatograms. All the values were on the order of 10^{-3}, ranging from 1.47×10^{-3} to 2.54×10^{-3}. The following may be extracted from the table:

1) In the water-DMSO system, ε has a maximum at about water: DMSO = 25:75 v/v and decreases as the solvent mixing ratio deviates from this value in either direction. This tendency is independent of the kind of lithium salt used (lactate or acetate).

2) Likewise, ε has a maximum as a function of the solvent mixing ratio in the water-acetone system, but this time at around water: acetone = 75:25 v/v.

3) The change in ε with varying solvent mixing ratio is larger in the water-DMSO system than in the water-acetone system.

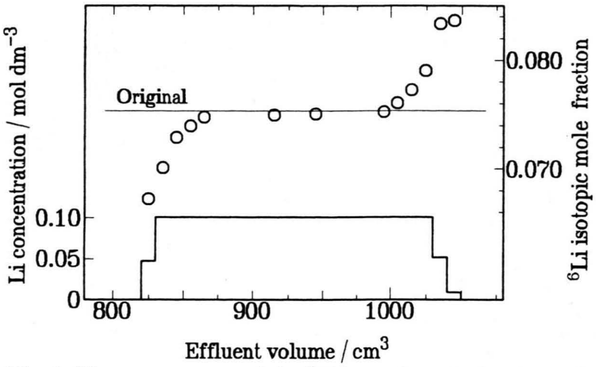

Fig. 1. Chromatogram and the ^{6}Li isotopic mole fractions of Run DM50 (volume ratio water:DMSO = 50:50). The experimental conditions are summarized in Table 1. The solid step-like line is the lithium concentration profile and the empty circles denote the ^{6}Li isotopic mole fractions. The ^{6}Li isotopic mole fraction in the feed solution was 0.07537.

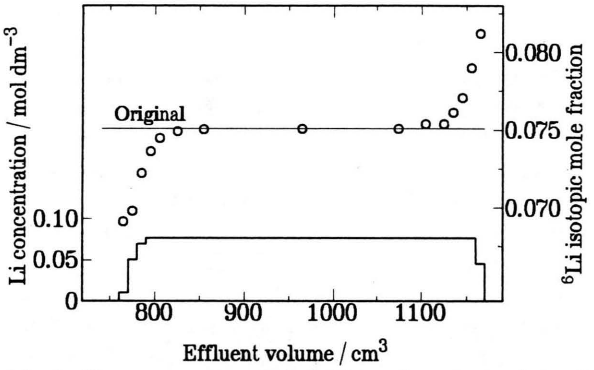

Fig. 2. Chromatogram and the ^{6}Li isotopic mole fractions of Run AC50 (volume ratio water:acetone = 50:50). The experimental conditions are summarized in Table 1. The solid step-like line is the lithium concentration profile and the empty circles denote the ^{6}Li isotopic mole fractions. The ^{6}Li isotopic mole fraction in the feed solution was 0.07510.

3.2. *Solvent Fractionation between Solution and Ion Exchanger Phases*

The results of the solvent fractionation experiments between the external solution and the ion exchanger phase are summarized in Tables 3 and 4. In Figs. 3 A and B, the mole fraction of water in the exchanger phase, y_w, is plotted against the mole fraction of water in the solution phase, x_w, for water-DMSO and water-acetone systems, respectively.

In the water-DMSO system, water is slightly preferentially distributed into the solution phase for $x_w > 0.6$, and for $x_w < 0.6$ the TIN-100 ion exchanger shows no preference. This is different from the results by Van

Table 2. Obtained ε values.

Run no.	Organic component		Counter-ion of lithium	$\varepsilon \times 10^3$	Ref.
	Kind	Weight%			
DM05BT	DMSO	95.4	lactate	2.07	*
DM05	DMSO	95.4	lactate	2.02	*
DM25	DMSO	76.8	lactate	2.54	*
DM50	DMSO	52.5	lactate	1.84	*
DM100	DMSO	0.0	lactate	1.49	*
	DMSO	95.4	acetate	1.4	[7]
	DMSO	76.8	acetate	2.2	[7]
	DMSO	52.4	acetate	2.0	[7]
	DMSO	0.0	acetate	1.7	[7]
AC25	acetone	70.4	lactate	1.51	*
AC50	acetone	44.2	lactate	1.76	*
AC75	acetone	20.9	lactate	1.82	*
AC100	acetone	0.0	lactate	1.47	*

* This work.

Table 3. Results of water-DMSO fractionation experiments with TIN-100 in the H$^+$ form at 25 °C.

Li salt [a]	Solution phase [b]		Exchanger phase [b]		K_d^w [c]
	water	DMSO	water	DMSO	
LiCl	89.1	10.9	80.7	19.3	0.511
	77.4	22.6	65.4	34.6	0.550
	62.3	37.7	55.7	44.3	0.759
	48.4	51.6	43.5	56.5	0.822
	37.0	63.0	33.6	66.4	0.862
	24.3	75.7	25.0	75.0	1.038
	17.3	82.7	16.9	83.1	0.970
	4.71	95.3	4.70	95.3	0.998
Li acetate	46.1	53.9	41.6	58.4	0.835
Li lactate	46.6	53.4	41.5	58.5	0.815

[a] Lithium concentration = 0.100 mol dm^{-3}.
[b] Given in weight percent.
[c] For definition see (3).

Table 4. Results of water-acetone fractionation experiments with TIN-100 at 25 °C.

Li salt	Form of ion exchanger	Solution phase [a]		Exchanger phase [a]		K_a^w [b]
		water	acetone	water	acetone	
none	H$^+$	11.9	88.1	31.0	69.0	3.32
		28.3	71.7	47.1	52.9	2.26
		36.7	63.3	49.4	50.6	1.69
		47.0	53.0	51.6	48.4	1.20
		56.8	43.2	63.0	37.0	1.29
		65.9	34.1	66.6	33.4	1.03
		74.5	25.5	77.0	23.0	1.14
		78.8	21.2	85.3	14.7	1.58
		91.7	8.35	96.1	3.87	2.27
0.100 M Li lactate	Li$^+$	55.3	44.7	60.0	40.0	1.21

[a] Given in weight percent. – [b] For definition see (4).

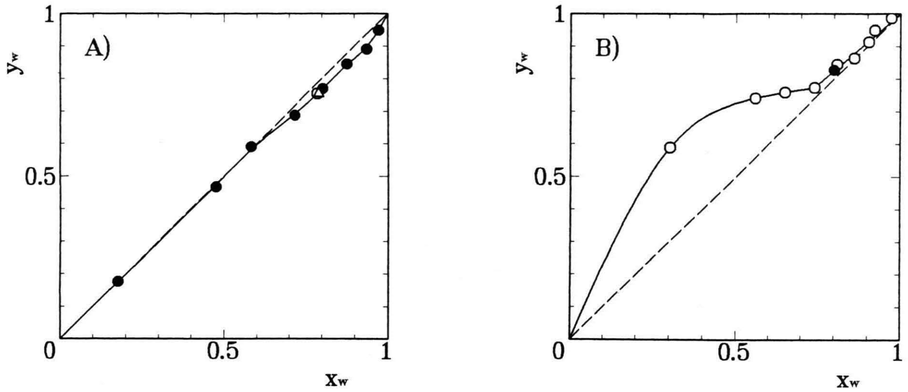

Fig. 3. Solvent selectivities of TIN-100 ion exchange fiber at 25 °C. x_w and y_w are mole fractions of water in the external solution phase and in the ion exchanger phase, respectively. A) Water-DMSO mixtures with the exchanger in the Li^+ form. The full circles denote the results with LiCl, the empty circle that with lithium acetate and the empty triangle that with lithium lactate. B) Water-acetone mixtures. The empty circles denote the results with the exchanger in the H^+ form and without any solute in the solution phase and the full circle the result with the exchanger in the Li^+ form and with 0.10 M lithium lactate in the solution phase.

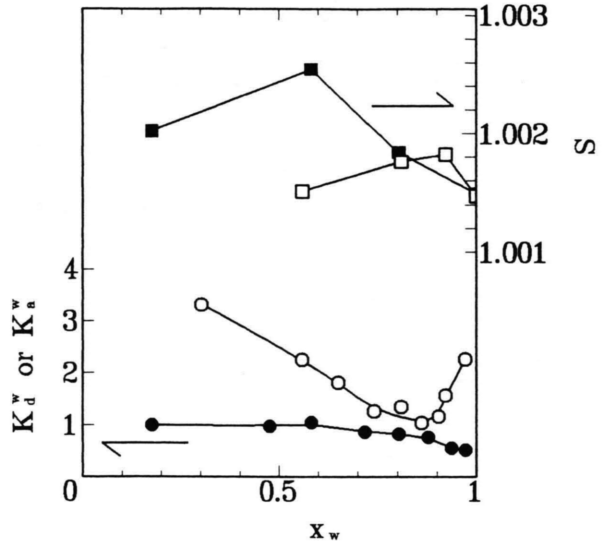

Fig. 4. Isotope separation factors S and solvent fractionation factors K as functions of the mole fraction of water in the solution phase. Full boxes: S in the water-DMSO system; empty boxes: S in the water-acetone system; full circles: K_d^w; empty circles: K_a^w.

Wart and Janauer [8]. They reported that DMSO was slightly preferentially fractionated into the solution phase of Bio-Rad 50W-X8 and -12X resins at 25 °C. Our results on water-DMSO show that contrary to the assumption made in [7], the solvent selectivity of the ion exchanger does not necessarily correlate with the lithium isotope effect the exchanger shows.

Table 3 and Fig. 3A also show that the kind of lithium salt does not influence the solvent partition between the two phases within the experimental range investigated.

The fractionation factor K_d^w of the water-DMSO system is slow and convex function of x_w and seems to have a broad peak at around $x_w = 0.582$ (weight ratio (w/w) of water: DMSO = 24.3 : 75.7).

Contrary to the water-DMSO system, in the water-acetone system, water is clearly preferentially fractionated into the ion exchanger phase, which is especially obvious for $x_w < 0.7$ (see Table 4 and Figure 3B). This result agrees with that summarized in [6]. No significant difference in the solvent partition pattern was observed between the experiments with TIN-100 in the H^+ form and without lithium salt in the solution phase, and the experiment with TIN-100 in the Li^+ form and 0.1 M lithium lactate in the solution phase.

K_a^w of the water-acetone system is always larger than unity, is a concave function of x_w and has a relatively clear minimum at about $x_w = 0.862$ (water: acetone = 66.0 : 34.0 w/w). Compared to K_d^w, K_a^w varied widely as a function of the solvent mixing ratio in the solution phase.

3.3. Correlation of Isotope Separation Factor with Solvent Fractionation

In order to examine how the isotope separation factor in mixed solvent systems correlates with the solvent fractionation factor, we provided Figure 4. In this figure, S's in the water-DMSO and water-acetone system and K_d^w and K_a^w are plotted against x_w. In the water-DMSO system, S and K_d^w show similar x_w dependences; both S and K_d^w are convex functions of x_w and have peaks at around $x_w = 0.58$. In the water-acetone system, S is a convex function of x_w while K_a^w is a concave function, the extrema of both functions coinciding at about $x_w = 0.86$. These correlations show that the lithium isotope effects in ion exchange systems with mixed solvents are strongly dependent on the difference in the solvent mixing ratios in the solution and ion exchanger phases. They can qualitatively be explained on the basis of the affinities of the solvents towards the lithium ion and the theory of isotope distribution between two phases [14], as follows.

In ion exchange systems of the alkali metal ions, the overall isotope effect, which is the one experimentally obtained, is composed of four fundamental isotope effects [15], the first arising from the phase change, the second from the difference in the solvation state of the ion between the solution and ion exchanger phases, and the third and fourth from complex formation (including ion association) in the solution and ion exchanger phase, respectively. Among the fundamental isotope effects, the one due to the phase change is usually considered to be small, although it is significant for the potassium [15] and rubidium [16] isotopes. The isotope effects accompanying complex formations are generally of paramount importance for metals other than the alkali metals, as exemplified by the cases of the alkaline earth metals [17–19] and uranium [20]. In the cases of the alkali metals, however, they are not the major contributors to the overall isotope effect. The alkali metal ions do not or very little form complexes with anions, and although ion associations may occur to some extent, they usually do not result in large isotope effects, as exemplified by the case of lithium ion in aqueous solution [4]. Thus the major contributor to the overall lithium isotope effect in the present chromatographic experiments must be the isotope effect due to the difference in the solvation state of the lithium ion in the solution and ion exchanger phase. We consider only this effect in the following.

In the present study, S was always larger than unity, which means that the ^{7}Li-to-^{6}Li isotopic reduced partition function ratio [21], f, of the solvated lithium ion in the solution phase (f_{sol}) is larger than in the exchanger phase (f_{exc}); $f_{sol} > f_{exc}$; $S = f_{sol}/f_{exc}$ [14]. The affinities towards the lithium ion are in general in the order DMSO > water > acetone [22]. If a higher affinity means that the solvent exerts a stronger force on the lithium ion, which is not universally but generally the case [23], f decreases in the order: lithium ion coordinated by DMSO > hydrated lithium ion > lithium ion coordinated by acetone, assuming the same solvation number. The largest S value is then expected for the largest K_d^w value in the water-DMSO system and for the smallest K_a^w value in the water-acetone system. The strong correlations between S and K_d^w and between S and K_a^w in Fig. 4 are consistent with the above reasoning and can thus be explained on the basis of the relative affinities of the solvents towards the lithium ion and of the lithium isotope distribution between the two phases caused by the fundamental lithium isotope effects.

Lastly, it is also noted in Fig. 4 that a small variation in K_d^w caused a large change in S, while a wide variation in K_a^w resulted in only a small change in S. This may indicate that, whereas DMSO can directly interact with the lithium ion and thus affect its solvation state largely, being able to exist in its first solvation sphere in the water-DMSO mixed solvents, acetone cannot enter the first solvation sphere in the water-acetone mixtures, existing only in the second or outer spheres and hence influencing only little the solvation state of the lithium ion. This picture is also consistent with the relative affinities of the solvents towards the lithium ion.

4. Conclusions

To summarize, we make the following statements:

1) In cation exchange displacement chromatography at 25 °C of lithium lactate in water-DMSO mixtures, ε for the lithium isotopes took on its maximum at water:DMSO = 25:75 v/v. In water-acetone mixtures it took on its maximum at water:acetone = 75:25 v/v. The range of the ε values was from 1.49×10^{-3} to 2.54×10^{-3} in the water-DMSO systems and from 1.47×10^{-3} to 1.82×10^{-3} in the water-acetone systems.

2) DMSO was slightly fractionated into the ion exchanger phase for $x_w > 0.6$, while for $x_w < 0.6$ the ion exchanger showed little solvent selectivity. On the contrary, acetone preferred the solution phase, which tendency was especially clear in the region of $x_w < 0.7$.

3) Strong correlations were found between the isotope separation factor and solvent fractionation factor both in the water-DMSO system and in the water-acetone system. In the water-DMSO mixtures, the larger K_d^w was, the larger S was. In the water-acetone mixtures, a smaller K_a^w resulted in a larger S. These facts were qualitatively explainable by considering the lithium isotope distribution between the two phases based on the fundamental lithium isotope effects and the relative affinities of the solvents towards the lithium ion.

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