The Enrichment of Lithium Isotopes by Ion Exchange Chromatography. III. The Influence of the Nature of the Solution Phase on the Separation Factor

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Single stage separation factors (α) for Li[6] and Li[7] have been determined in ion exchange systems containing various other cations and anions in the solution and resin phases. Dehydration of the lithium species in the resin phase may be the major contribution to the change in the isotopic separation factor. The hydrating tendency of the co-ions in the resin phase is directly related to the magnitude of the separation factor. The effect of coördination of the lithium species with EDTA also is discussed.

Introduction

The separation of isotopes by chemical exchange depends upon the fact that the isotopic species in the two phases should be dissimilar with respect to chemical bonding. In the ideal case, one compound should be strongly bonded having high vibrational frequencies and large frequency shifts upon isotopic substitution, while the compound in the other phase should be weakly bonded having low frequencies and small frequency shifts. The nature of the electronic structure of the lithium ion is such that it has little tendency to form coördination compounds in solution. The molecule with which lithium coördinates most strongly is water. The small lithium ions prefer to coördinate with smaller water molecules rather than with larger organic molecules. It has been shown in Part I of this series[2a] that a slight disruption of the hydration sheath around the lithium ion in one phase will account for differences in the isotopic separation factor. Glueckauf[2b] discussed these results from the standpoint of the equilibrium of lithium isotopes between a dilute and a concentrated aqueous solution.

The ability of certain ions to orient water molecules in solution is well known.[3] In the isotopic exchange reactions studied in this work, the lithium species involved are hydrated lithium ions. The high charge density of the lithium ion and its high heat of hydration indicate that the structure of the primary water sheath is very stable. Certainly, in the dilute solutions of the aqueous phase the lithium species is fully hydrated.

In the more concentrated solutions in the interior of highly crosslinked resins there will be association forces between the cations and the anion resin sites tending toward dehydration of the lithium ion. If the concentrated solutions in the interior of the resin contained additional ions which had great affinity for water, the competition for water would be increased and further dehydration of the lithium ion would be observed. Taube[4] and co-workers have demonstrated that the presence of hydrated cations in aqueous solutions in-

creases the separation factors for oxygen isotopes in water distillation. This indicates that there is additional bonding of the water molecules above that found in water alone. The strength of that bonding is at least partly dependent upon the magnitude of the primary hydration number of the cation involved.

The effect of anions in solution in cation exchange systems has been discussed very little.[5] For very dilute solutions the eluent anions in the resin phase would tend to be excluded and effects due to ion pairing, solvent breaking structure and steric hindrance should be insignificant. However, these effects may be significant for more concentrated eluents such as were used in this work. The concentration of the imbibed electrolyte in the resin phase may be high enough to cause a change in the lithium species.[6]

The effect of the anion should be more significant if the anion could coördinate with the cation. A coördination complex species involving anion ligands should have different ion exchange properties from that of the hydrated ion. Lithium forms anion complexes with several amino acids in basic solution. Martell and Calvin[7] summarize the work of Schwarzenbach, et al., who measured the stability constants of some of these lithium complexes. Nelson[8] has found that $LiEDTA^{-3}$ has anion exchange properties of Dowex 1 at pH 11 and that the alkali metals can be separated on an anion exchange column using this complexing agent.

To demonstrate the influence of various ions on the single stage separation factor for lithium isotopes separated on highly crosslinked ion exchange resins, two series of experiments were made; one series of experiments for the effect of cations and the other series for the effect of anions. The cations studied were NH_4^+, K^+, NH_3OH^+, Ca^{++}, Cu^{++}, Cr^{+++}, Al^{+++} and Th^{++++}, and the anions were OH^-, Cl^-, F^-, $HCOO^-$, SO_4^{--}, $Citrate^{--}$ and $Fe(CN)_6^{----}$. In the cation experiments all the anions were chloride, and in the anion experiments potassium and ammonium cations were used. The experiments performed with lithium ethylenediamine tetraacetate com-

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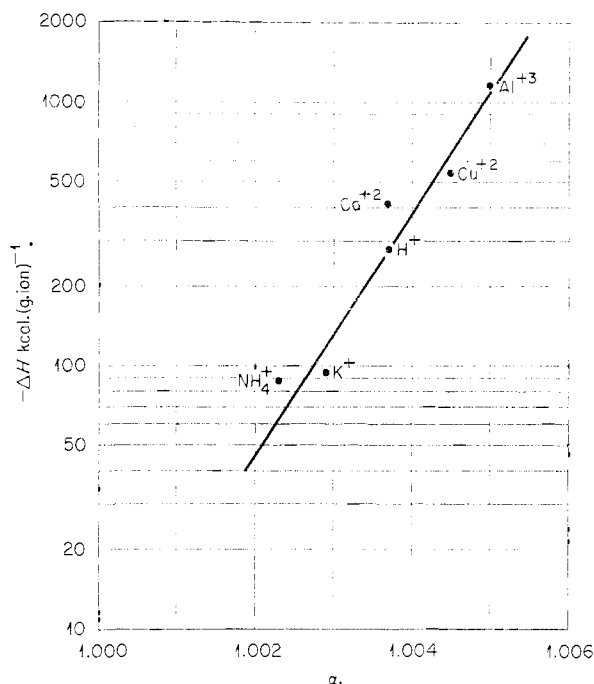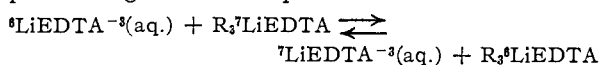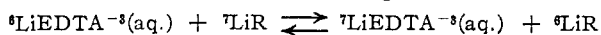
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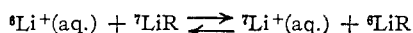
Fig. 1.—Alpha as a function of $-\Delta H$ for eluting cations.

plexes are given in the equilibria

$^6LiEDTA^{-3}(aq.) + R_3^7LiEDTA \rightleftharpoons$

$^7LiEDTA^{-3}(aq.) + R_3^6LiEDTA$

where R = an anion exchanger, Dowex 1-X10

$^6LiEDTA^{-3}(aq.) + ^7LiR \rightleftharpoons {}^7LiEDTA^{-3}(aq.) + {}^6LiR$

where R = cation exchangers Dowex 50-X2 and X8

$^6Li^+(aq.) + {}^7LiR \rightleftharpoons {}^7Li^+(aq.) + {}^6LiR$

where R = a cation exchanger containing imino-diacetate sites—Dowex Chelating Resin A-1,

Experimental

The ion exchange columns were conditioned by thoroughly washing the resin with a solution identical with the eluent to be used. The resin was then in the same cationic form as the cation content of the eluent. The same lithium band elution technique was used as described previously in Part I.[2a] Unless specified otherwise, all the resins used were Dowex 50-X16; dimensions of the columns and the mesh sizes of the resins varied in the cation experiments. For the anion experiments using potassium salts, the same resin column was used throughout the series. It was 21.5 mm. i.d. × 930 mm. long, packed with analytical grade 200–400 mesh resin. All eluents were 0.25 N. The resin columns used in the EDTA experiments are described in Table III. For the experiments done on the Dowex 1 and Dowex 50-X2 columns, the eluents were 0.25 M K₄EDTA. For the Dowex 50-X8 experiment, the eluent was 0.1 M K₄EDTA. The eluent used on the A-1 resin was 0.25 N NH₄Cl. The lithium samples collected after elution were processed by passing each sample through an ion exchange column to remove the eluent cation or anion which could have interfered with the isotopic mass analysis. The experimental techniques were the same as previously described.[2a,9]

Results and Conclusions

These experiments are summarized in Tables I, II and III. In Fig. 1 the values of α given in Table I are plotted against the logarithms of the heats of hydration[10] of the eluting cations. The

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results show that α for lithium isotopes increases as the degree of hydration of the eluting cation increases. This indicates that as the charge density of the cations in the concentrated solutions of the highly crosslinked resin phases increases, competition for the water available for hydration will become stronger. Consequently, the lithium ions may be partially dehydrated and a new lithium species formed. Interpenetration of the hydration spheres of the two cations involved may be the beginning of this dehydration, and it alone may account for small changes in the isotopic separation factor. Ion association and ion pair formation occurring at the resin sites may also account for some of the lithium ion dehydration.[11]

TABLE I
SUMMARY OF EXPERIMENTS TO DETERMINE THE EFFECT OF THE NATURE OF THE ELUTING CATION ON α

Eluting cation	Resin mesh size	Column dimensions, mm. × mm.	Flow rate, cm./sec.	Plates	α
NH₄⁺	50–100	26 × 1485	1.1 × 10⁻³	800	1.0023
K⁺	200–400	19 × 1085	1.6 × 10⁻³	500	1.0029
NH₃OH⁺	50–100	17 × 519	3.6 × 10⁻³	200	1.0033
H⁺	50–100	34 × 507	5.7 × 10⁻⁴	500	1.0037
Ca⁺⁺	200–400	12.5 × 1210	6.8 × 10⁻³	80	1.0037
Cu⁺⁺	200–400	12.5 × 1175	2.4 × 10⁻³	100	1.0045
Cr⁺⁺⁺	200–400	12.5 × 1175	3.9 × 10⁻³	100	1.005
Al⁺⁺⁺	200–400	12.5 × 973	8.5 × 10⁻³	100	1.005

TABLE II
SUMMARY OF EXPERIMENTS TO DETERMINE THE EFFECT OF THE NATURE OF THE ANION ON α

Anion	Sample break-through number	Flow rate, cm./sec.	Plates	α
		Potassium salts		
OH⁻	141	1.5 × 10⁻³	350	1.0037
Cl⁻	144	1.6 × 10⁻³	500	1.0029
F⁻	199	....	..	....
HCOO⁻	220	1.5 × 10⁻³	600	1.0028
SO₄⁻	223	1.2 × 10⁻³	700	1.0027
Fe(CN)₆³	257	1.4 × 10⁻³	1100	1.0027
		Ammonium salts		
Citrate		5.9 × 10⁻³	80	1.0029
Cl⁻		1.1 × 10⁻³	800	1.0023

TABLE III
SUMMARY OF EXPERIMENTS TO DETERMINE α IN PRESENCE OF EDTA

Resin	Mesh size	Column dimension, mm. × mm.	Flow rate, cm./sec.	Plates	α
Dowex 1-X10	−400	26 × 1490	1.3 × 10⁻³	190	0.9994
Dowex 50-X2	200–400	34 × 870	4.5 × 10⁻⁴	240	.9986
Dowex 50-X8	100–200	34 × 1150	7.1 × 10⁻⁴	440	.9977
Dowex chelating resin A-1	∼50	26.5 × 1030	1.4 × 10⁻³	140	.9996

Difficulty was encountered when an attempt was made to measure the separation factor in the presence of thorium ions. The distribution coefficient greatly favored thorium rather than lithium ions on the resin. Therefore, the number of plates available in the column for the lithium isotope separation was too small to make the calculations necessary to determine α. From our data it was found that as the charge density

(11) W. Pauli and E. Valko, "Electrochemie der Kolloid," Vienna, 1929.

of the eluting cation increases, the number of theoretical plates for the separation of lithium isotopes in a given column decreases. That is, the distribution coefficient so favors the eluting cations that very few sites are available to the lithium ions for the isotopic exchange. The number of theoretical plates for the different experiments in Table I is only meaningful for comparison when the resin mesh sizes and column dimensions are considered.

As shown in Table II, the effect due to different anions in the solution phase is essentially the same except for OH⁻ and possibly citrate. Anions tend to be excluded from the cationic resin phase; therefore, the coulombic attraction between imbibed eluent anions and the lithium ions in the resin should not be a major contribution toward a change in the lithum species in the resin and subsequent change in the isotopic separation factor. In this work it has been considered that the primary effect contributing to the change in the separation factor has been a hydration effect. Anions are generally hydrated less strongly than cations and their hydration numbers are small. Therefore anions would not compete strongly for hydration water. Hydroxyl ion may be an exception, perhaps, because it is more highly hydrated[12] than other anions, and it is an "order-producing" ion like most cations rather than an "order-destroying" ion like most anions.[13] Then too, the higher value for OH⁻ may be attributed to "localized hydrolysis" of the hydrated lithium ion by this anion in the resin phase.[14] Hydroxyl ion is a strong proton acceptor which could disrupt the water dipoles around the lithium ion by binding to protons of the hydration water, effectively causing dehydration.

The data in Table II show that both the number of plates and the sample break-through number increased as the charge on the anion in the eluent increased. This indicates that in this system the diffusion rates of lithium ions are affected by the anions in solution. The mechanism for this diffusion has not been established. For the highly crosslinked (×16) resins used in these experiments, the electrolyte penetration into the resin undoubtedly is small; but it may be sufficient to provide a means for increasing the lithium ion mobilities, according to the hypothesis of

R. Schlögl.[15] Schlögl suggests that cation mobilities can be increased by a free anion carrier which forms ion pairs with the cations and transports them more easily from site to site through the resin than when no anions are present. Richman and Thomas[16] also discuss this mechanism relative to self-diffusion. If this mechanism is applicable to our case, it is not evident whether or not the increase in the number of plates is due to the increase in ionic strength of the solutions or the nature of the anionic species. Evidently additional experiments are necessary to determine the effect of anions on diffusion and, subsequently, theoretical plate heights.

No value for the separation factor was found for the fluoride system. The insolubility of LiF caused a very flat elution curve which was unsuitable for making the plate calculations.

Table III summarizes the effect of EDTA complexing of the separation of lithium isotopes in several ion exchange systems. It was found in the progress of this work that when the ammonium salt of EDTA was used as an eluent, two lithium elution peaks occurred, both on cation and anion exchangers. It was impossible to determine isotopic separation factors in these systems because the peaks overlapped and the shape was such that no plate calculations could be made. This double peak effect was eliminated by using potassium EDTA instead of ammonium EDTA. The separation factors for all of these systems are less than one; that is, lithium-7 concentrates on the resin instead of lithium-6. For all other ion exchange systems which we have studied and which are reported in the literature, lithium-6 concentrates on the resin. The very small separation factor for the anion equilibrium is reasonable because the lithium complexes are essentially the same in both phases. For the equilibrium between the anion complex and the lithium cation on Dowex 50, a larger isotopic effect is found, as would be expected. The elution curves for these systems were asymmetric, indicating that the rate of exchange is slow. The isotopic effect here may be a kinetic rather than an equilibrium effect, and probably more than one equilibrium is involved. The separation factors shown in Table III are taken from the larger, more symmetrical part of the elution curve and represent the majority of individual assays. However, at the tail of the band where the elution curve is skewed, separations are much larger. Comparing resin column dimensions and the number of theoretical plates, it can be seen that plate efficiencies are poor.

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