

Enrichment of Lithium Isotopes by Ion Exchange Chromatography

Influence of Exchange Functional Group on Separation Factor

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ISOTOPIC SEPARATION FACTORS, α , (${}^6\text{Li}/{}^7\text{Li}$) resin/ $({}^6\text{Li}/{}^7\text{Li})$ aqueous, were measured for lithium isotopes on ion exchange materials to determine the influence due to the functional groups in the resin on the separation factor. The magnitude of the separation factor will give a qualitative measure of bonding differences between the lithium ion species in the resin and solution phases. From these data, isotope separation by chemical exchange may be better understood. Also, isotope separation by ion exchange may be a useful tool for studying the structure of ions in solution.

Recent cation exchange experimentation has been done to a large extent on sulfonated polystyrene-divinylbenzene copolymers because of their superior properties in performance. In previous work (6, 7, 8) these exchangers were used almost exclusively. Weakly acidic cation exchangers, both organic and inorganic, have interesting properties which may enhance lithium isotopic separations. The organic exchangers studied included resins with carboxylic, phosphonous, and phosphonic acid groups. Bregman (2) has discussed the selectivities of alkali metal ions on weakly acidic exchangers. The selectivity order as compared to the order for sulfonic acid resins is reversed, which indicates that the lithium ion species in weakly acidic resins is not the same as the species in strongly acidic resins. Therefore, the separation factor for lithium isotopes enriched on weakly acidic exchangers may be different.

Many inorganic exchangers behave somewhat like clay minerals with respect to ion exchange (5). Some, especially the silicates, suffer degradation in strongly acidic solutions, while others have ion exchange properties comparable to sulfonic acid resins (1). Differences in the natural abundances of lithium isotopes in their ores suggest that inorganic exchangers may have selective properties for the separation of these isotopes by ion exchange (3).

The prior history of lithium isotope separation by ion exchange has been reviewed (8). The ion exchange materials used, other than Dowex 50, were Zeo Karb H.I. and Decalso. Merz (9) has separated lithium isotopes on zirconium phosphate with a separation factor of about 0.99998 (4).

EXPERIMENTAL

Amberlite IRC-50 (Rohm and Haas Co.) has carboxylic acid exchange groups on an acrylic polymer lattice. Duolite CS-100 (Chemical Process Co.) is a carboxylated phenolic resin. Zeo Karb (Permutit Co.), a sulfonated coal, has sulfonate, carboxyl, and hydroxyl functional groups. Decalso (Permutit Co.) and zirconium phosphate (Minnesota Mining and Manufacturing Co.) are precipitated gel-type inorganic exchangers. Decalso is a sodium aluminosilicate, and the zirconium phosphate contains exchangeable hydrogen ions. Bio-Rex 62 and 63 (Bio-Rad Laboratories) are phosphonous and phosphonic acid cation exchangers, respectively. They have a styrene-divinylbenzene lattice. The "fines" in the resins were removed by repeatedly slurring the resin in distilled water, allowing it to settle, and decanting the finer particles. Weakly acidic resins which exchange hydrogen ions with difficulty were neutralized with ammonium hydroxide and allowed to stand overnight in an excess of base. The resins were converted to the same cationic form as the eluent by passing a moderately concentrated salt solution through a wide bed of resin. Reagent grade chemicals were used. The resins were then washed with water and the eluent to be used until the effluent concentration was the same as the eluent. The experimental techniques were those used previously (6, 7, 8) and experimental conditions are summarized in Table I.

RESULTS AND CONCLUSIONS

The performance on the exchangers listed in Table I was good only with the Bio-Rex and Dowex resins. For the others the number of plates in the columns was low and the elution curves were rather asymmetric, indicating slow rates of equilibrium. The separation factors determined on carboxylate resins IRC-50 and CS-100 and on Zeo Karb are comparable to the separation factor (1.0023) for lithium isotopes separated on Dowex 50-x16 in the ammonium form.

Of the ion exchangers studied in this work, the aluminosilicate exchanger, Decalso, produced the largest separation factor for lithium isotopes. A comparison of cation capacities and water contents for six exchangers— NH_4^+ ,

Table I. Summary of Separation of Lithium Isotopes on Ion Exchangers Having Different Functional Groups

Exchanger	Mesh Size	Column Dimensions, I.D. \times Length, Mm.	Flow Rate, Cm./Sec.	Eluent	No. of Plates	α
IRC-50	100	15 \times 630	4.9×10^{-3}	0.1N NH_4Cl	80	1.0020
CS-100	270	19 \times 1190	2.5×10^{-3}	0.1N NH_4Cl	100	1.0026
Zeo Karb	80-270	15 \times 570	1.1×10^{-3}	0.1N NH_4Cl	70	1.0023
Decalso	200-270	12.5 \times 1125	8.8×10^{-3}	0.25N NH_4Cl	80	1.0047
Zirconium phosphate	30	24 \times 1150	4.4×10^{-3}	0.25N HCl	55	1.0016
Bio-Rex 62	200-400	21.5 \times 1260	2.8×10^{-3}	0.25N NH_4Cl	480	1.0005
Bio-Rex 63	200-400	21.5 \times 1210	1.4×10^{-3}	0.25N NH_4Cl	1000	1.0003
Dowex 50-16x	50-100	26 \times 1485	1.1×10^{-3}	0.25N NH_4Cl	816	1.0023

Li^+ , and K^+ forms of Decalso and Dowex 50-x16—indicates qualitatively that the lithium ions contain less coordinated water in Decalso than in Dowex 50-x16. If the magnitude of the separation factor is dependent upon the differences in the degree of hydration of the lithium ion species in the two phases, which was the assumed model for the quantum mechanical estimation of α previously proposed (8), the higher value of 1.0047 for Decalso is reasonable.

The separation factor for lithium isotopes separated on zirconium phosphate was determined to be 1.0016. This value is not very different from the majority of the values found for other exchangers, but it does not compare with the value reported by Merz (4, 9). The conditions of the two experiments were considerably different. Perhaps the large difference in flow rates is the chief factor contributing to the discrepancy. Since the rate of exchange between lithium ions on zirconium phosphate and lithium ions in solution is slow (1), a fast flow rate could eliminate any isotopic separation. A difference in the procedures for preparing the zirconium phosphate could possibly produce precipitates that have divergent ion exchange properties toward lithium isotopes.

Very little is known about the structural homogeneity and ion exchange properties of the phosphonous and phosphonic acid resins. Therefore, it is difficult to explain the separation factors measured on these resins. Phosphonic acid resins have bifunctional groups. For the separation of lithium isotopes on Dowex Chelating Resin A-1, which has bifunctional groups, the separation factor was also an order of magnitude smaller than the factors determined for monofunctional exchangers (6). Whether this is characteristic of bifunctional groups is unknown. The separation factor on phosphonous acid resin was considerably larger than the factor for phosphonic acid resin, but much smaller than those found for other monofunctional exchangers. The only conclusion that can be made

for the experiments performed on the Bio-Rex resins is that since the separation factors are small, the lithium ion species in the resin phase, more than likely, are not dehydrated in the primary hydration sphere.

SUMMARY

Carboxylic acid resins and inorganic exchangers produce separation factors for lithium isotopes which are comparable to the factors observed for sulfonic acid resins. However, column efficiencies are not as good as those for sulfonic acid resins. The separation factors on phosphonous and phosphonic acid resins are an order of magnitude smaller than the factors for other exchangers. It is postulated that the degree of hydration of the lithium ion in the resin phase will determine the magnitude of the separation factor, and any mechanism that will dehydrate that ion will increase the factor.

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Properties and Potential Uses of Sodium Cellulose Acetate Sulfate, A New Water-Soluble Cellulose Derivative

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WATER-SOLUBLE cellulose esters have been known for many years; however, in contrast to water-soluble cellulose ethers, the esters seem to have attracted little or no commercial interest.

This article describes a new type of water-soluble cellulose ester which has commercial potentialities. This derivative is a sodium cellulose acetate sulfate, conveniently referred to as SCAS.

The sulfating of cellulose to produce a water-soluble derivative is by no means a new reaction. In 1894, Stern (8)

prepared a cellulose disulfate simply by dissolving cellulose in cold sulfuric acid. In 1928, Fulnegg (3) prepared a less-degraded product by allowing cellulose to react with chlorosulfonic acid dissolved in pyridine. During the past 10 years, several new methods for sulfating cellulose without degrading it excessively have been patented. Most of these patents (4-7) suggest alcohols and other sulfuric acid-miscible organic solvents as diluents for the reactants. Recently, at Eastman Kodak Co., a method (1, 2) was found for simultaneously sulfating and acetylating cellulose.