Experimental

The experimental procedure and calculation methods were the same as or involved obvious modifications of those previously described.[3,4] The solutions contained 18.0 millimoles of sulfur dioxide and 1.0 millimoles of S^{35}-labeled thionyl chloride in every case, together with various added amounts of mixed catalysts. Exchange was followed by withdrawing periodic vapor samples, predominantly sulfur dioxide, from the solutions, contained in pressure stopcock-equipped bombs. Although this procedure may quite possibly have resulted in a significant progressive drain on hydrogen chloride concentration from the solutions involving this material, the non-observance of evidence for any effect on the exchange rates of the presence of this component did not make modification of the procedure seem worthwhile. It may be noted that the effect looked for, namely, the occurrence of any interaction between the catalyst and hydrogen chloride, would presumably have tended to minimize loss of the material.

In three of the aluminum chloride–tetramethylammonium chloride experiments a white flocculent precipitate appeared whose composition we did not succeed in establishing. It did not appear to be simply the complex itself precipitating out, however. Possibly traces of moisture left on the glass in these experiments, done early in the research, may have caused a slight hydrolysis of aluminum chloride to insoluble hydroxide. It seems unlikely that any hydrogen chloride so produced would affect the exchange rates, considering the results of the experiments involving this material. The effect of aluminum hydroxide is uncertain. In any case, it is to be observed that, except in one instance, the results of these precipitate-containing experiments are in general conformity with those anticipated and are in accord with those where no precipitate appeared. In subsequent experiments, however, considerably greater pains were taken to ensure the absence of moisture.

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CORVALLIS, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The Enrichment of Lithium Isotopes by Ion-exchange Chromatography. I. The Influence of the Degree of Crosslinking on the Separation Factor

BY D. A. LEE AND G. M. BEGUN

RECEIVED SEPTEMBER 18, 1958

Single stage separation factors have been determined for Li^6 and Li^7 between aqueous lithium ions and lithium ions on sulfonated polystyrene-divinylbenzene copolymers of various degrees of crosslinking. A band elution technique on an ion-exchange column was used. The single stage separation factor, α, (Li^6/Li^7)resin/(Li^6/Li^7)aqueous, was determined according to the method of Glueckauf from the elution curve and isotopic assays. Variations in α (1.0006 to 1.0038) with the degree of crosslinking can be explained by a simple concept of partial "dehydration" of lithium ions in the resin phase. Assuming a model for the lithium ion species in the two phases, the magnitude of α can be estimated quantum mechanically.

The enrichment of lithium isotopes on ion-exchange media has been reported by several workers. Taylor and Urey[1] were first to demonstrate the separation of lithium isotopes on a hydrated sodium aluminum silicate ion exchanger called "Decalso." Using the Rayleigh distillation formula, they calculated α, defined in this paper as (Li^6/Li^7)resin/(Li^6/Li^7) aqueous, to be 1.022 for a multiple extraction of lithium from a LiCl solution using successive small quantities of the zeolite. Sessions, Kibbey, Roberts and Blanco[2] repeated Taylor and Urey's experiments but were unable to reproduce their results. For the batch-type multiple extraction experiment using LiCl solution *vs.* Na^+-Decalso, no significant enrichment was found. For Li^+-Decalso *vs.* NaCl solution, α was estimated to be 1.0058 ± 0.0098. In two column experiments α was determined to be 1.0055 in one and 1.0038 in the other. Glueckauf, Barker and Kitt[3] used Zeo Karb H.I. in an ion-exchange column to obtain a partial separation of lithium isotopes. They concluded that the enrichment factor for this system was considerably smaller, perhaps tenfold less, than 1.022 as obtained by Taylor and Urey. Gross[4] separated lithium isotopes on a 10% cross-linked Dowex 50 column. From Gross' data Jury[5] calculated α to be 1.0065. Blanco, Kibbey, Land and Roberts[6] made fifteen successive batch equilibrations of lithium form Dowex 50W with an aqueous solution of LiCl. The separation factor was determined to be 1.0027 with a 95% confidence range of 1.0015 to 1.005. Studier, Brody and Mech[7] from their column elution data obtained an α of 1.0025 using Dowex 50. Menes, Saito and Roth[8] obtained an α of 1.002 also using Dowex 50. Bregman[9] discussed the effect of several variables on the selectivity of cation exchange resins for monovalent ions. These variables were: structure of the resin, nature of the acidic functional group, mole fraction of the exchange cations in the resin phase, resin capacity, external ionic strength and temperature. Whether these variables have any effect on the separation of isotopes is unknown. The purpose of this work was to establish the magnitude of α for lithium isotopes on ion-exchange materials with various degrees of crosslinking. Some of the other variables will be reported in subsequent papers.

Experimental

The ion-exchange columns used for these studies were generally from 50 to 150 cm. long and 1.5 to 3.5 cm. i.d. The ion-exchange materials were usually 50 mesh or finer. A band elution technique was used in all of the experiments. For each experiment, the resin column was saturated with

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[1] T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, **5**, 597 (1937); **6**, 429 (1938).

[2] R. I. Sessions, A. H. Kibbey, J. T. Roberts, R. E. Blanco, Oak Ridge National Laboratory Report CF-53-6-241 (June 1, 1953).

[3] E. Glueckauf, K. H. Barker and G. P. Kitt, *Disc. Faraday Soc.*, **7**, 199 (1949).

[4] J. H. Gross, AECD-2952 (Nov. 29, 1950).

[5] S. H. Jury, Oak Ridge National Laboratory Report CF-52-8-218 (Aug. 15, 1952).

[6] R. E. Blanco, A. H. Kibbey, J. I. Land and J. T. Roberts, Oak Ridge National Laboratory Report CF-53-11-47 (Nov. 4, 1953).

[7] M. H. Studier, J. K. Brody and J. I. Mech, "Summary Report of Chemistry Division," July 1, 1953–March 31, 1955, ANL-5450, p. 23.

[8] F. Menes, E. Saito and E. Roth, "Proceedings of the International Symposium on Isotope Separation," North-Holland Publishing Co., Amsterdam, Netherlands, 1958, p. 227.

[9] J. I. Bregman, *Ann. N. Y. Acad. Sci.*, **57**, 125 (1953).

the same cation as used in the eluent. To the top of this column was added a band of saturated lithium resin. The lithium was moved through the column with a suitable eluent. All chemicals used were reagent grade. The eluate was collected as a measured volume by an automatic sampling device. Lithium concentration in the samples was determined by flame spectrophotometry. After the lithium content of a sample was determined, the solution remaining was evaporated to dryness and any organic material was destroyed with nitric acid. The lithium was converted to the iodide by the addition of hydroiodic acid and evaporation to dryness. This step was repeated just before placing the sample into the mass spectrometer, since LiI is very hygroscopic and decomposes to the hydroxide and carbonate in moist air. Mass analyses were determined with a modified Nier-type, 60 degree mass spectrometer.

Calculations.—An elution curve was obtained by plotting the concentration of lithium in the samples against the sample number or elution volume. From the elution curve the number of theoretical plates was calculated according to Glueckauf.[10] Either one of two equations was used

$$N' = 2\pi(C_{\max}\bar{v}/m)^2 \qquad (1)$$

$$N' = 2\bar{v}v_e/\bar{v} - v_e = 8(\bar{v}/\beta)^2 \qquad (2)$$

where N' = number of theoretical plates from the center of the original band to the bottom of the column; $C_{\max}$ = concentration of solute at the maximum peak height of the elution curve; $\bar{v}$ = peak elution volume (or sample number at the peak); $m = \int_0^\infty C\,d\bar{v}$ = area under the elution curve; and for equation 2, v_e = the elution volume where the concentration is $C = C_{\max}/e = 0.368C_{\max}$; β = the band width at the concentration $C = C_{\max}/e$. Equations 1 and 2 give identical results for perfectly symmetrical curves. Equation 2 was simpler to use.

The calculation of α from the elution curve and assay data was made according to a method described by Glueckauf.[11] The data were plotted on probability paper where the abscissa was a probability scale and the ordinate was a linear scale. The log of the local separation coefficient (log of the Li^6/Li^7 assay ratio x the natural abundance Li^7/Li^6 ratio) was the ordinate and the fraction of the eluted mixture ($\Delta m/m$) was the abscissa. This gave a linear plot. The slope of this line had the value $\sqrt{N'} \times \delta$, where N' was the number of theoretical plates in the column and δ was the separation factor (α) minus one. A typical plot is shown in Fig. 1.

Results and Discussion

It is known from ion-exchange studies that selectivity is dependent upon hydrated ion size[12] and that the degree of crosslinking in ion-exchange resins controls the accessibility of the interior of the resins to ions of different sizes. Gregor and Bregman[13] have studied the effect of crosslinking on the selectivity characteristics of sulfonated polystyrene-divinylbenzene copolymers. For resins of very low crosslinking, the selectivity values approach unity. As the crosslinking increases (divinylbenzene content 8 to 24%), the molality of the ions in the resin phase increases.[14] The resultant closer association between the cations and the fixed resin anionic groups will tend to strip the cation of hydration water. This dehydration is manifest to the largest extent in highly hydrated ions such as lithium. Each different hydrated species formed in this way may be expected to have a somewhat different vibrational zero point energy. If these zero point energy differences are sufficiently large, different separation factors should be observed when each species is equilibrated with an aqueous solution of lithium ions.

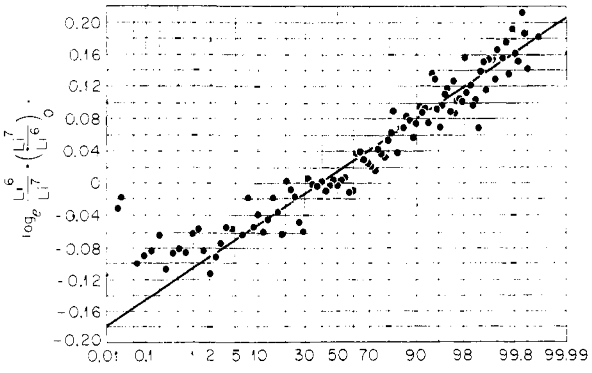

Fig. 1.—Li^6–Li^7 separation on Dowex-50-X16 eluted with 0.25 N NH_4Cl.

The influence of the degree of crosslinking on the selectivity of the lithium isotopes was investigated in two series of experiments using the sulfonated polystyrene-divinylbenzene copolymers Dowex 50 —2x, 4x, 8x, 12x, 16x and 24x. The first series of experiments were made with 4x, 8x, 12x, 16x and 24x using HCl as an eluent. The experimental conditions and results of these experiments are shown in Table I. The second series of experiments were made using 2x, 4x, 8x and 16x Dowex 50 with NH_4Cl as an eluent. These data are also given in Table I. It was found that the separation factor increased as the degree of crosslinking increased. The increase using H_3O^+ as an eluting agent is greater than for NH_4^+, especially in resins of high crosslinking. This may be due to greater competition for water in the resin phase between H_3O^+ and Li^+ than between NH_4^+ and Li^+, and subsequently more dehydration of the Li^+.

The data presented for Dowex 50 resin offer an interesting series for examination. In order to try to understand the increase in isotopic separation with increasing crosslinking, the two phases involved must be examined. In the aqueous phase the lithium ion may be regarded primarily as $Li^+(H_2O)_4$. There are, of course, other water molecules which interact weakly and the four water molecules in the primary solvation shell are constantly exchanging with solvent water. The resin phase is somewhat harder to picture. The concept that the resin phase also contains hydrated Li^+-$(H_2O)_n$ ions which are attracted, largely electro-statically, to the active groups of the resin offers a reasonable model. It has been shown that as the crosslinking is increased, the amount of water present in the Dowex 50 type resin is decreased. Values are given for hydration of Dowex 50 resin by Myers

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[10] E. Glueckauf, *Trans. Faraday Soc.*, **51**, 34 (1955).

[11] E. Glueckauf, *ibid.*, **54**, 1203 (1958).

[12] G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947).

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TABLE I

SUMMARY OF DOWEX 50 EXPERIMENTS TO DETERMINE THE EFFECT OF CROSSLINKING ON α

Cross-linking	Mesh size	Column dimension, mm. × mm.	Eluent	Flow rate, cm./sec.	Lithium loading, mg.	Plates N'	$\frac{(Li^6/Li^7)res.}{(Li^6/Li^7)aq.}$ (α)
4x	200–400	15 × 650	0.1 N HCl	2.3×10^{-3}	16	1000	1.0010
8x	50–100	34 × 542	.3 N HCl	9.4×10^{-4}	58	730	1.0016
12x	200–400	19 × 1100	.3 N HCl	2.0×10^{-3}	176	500	1.0027
16x	50–100	34 × 507	.3 N HCl	5.7×10^{-4}	115	460	1.0037
24x	100–200	15 × 1650	.3 N HCl	3.4×10^{-3}	87	138	1.0038
2x	50–100	34 × 492	.25 N NH_4Cl	7.9×10^{-4}	95	533	1.0006
4x	50–100	26 × 1498	.25 N NH_4Cl	1.0×10^{-3}	368	538	1.0010
8x	50–100	34 × 494	.25 N NH_4Cl	8.0×10^{-4}	59	637	1.0018
16x	50–100	26 × 1485	.25 N NH_4Cl	1.1×10^{-3}	360	816	1.0023

and Boyd[15] and by Argersinger, Davidson and Bonner.[16]

Water contents of 7.2, 6.6 and 4.5 moles per equivalent of Li^+ resin are reported for 12, 16 and 24% D.V.B. Dowex 50 resin, respectively.

Glueckauf and Kitt[17] have shown that at least one of the water molecules is associated with the active sulfonate group of the resin so that the maximum number of water molecules available to the lithium ion would be one less than the numbers given above. For resins with high crosslinking (24x) this number would be in the range of 3–4 water molecules available per lithium ion. Thus, the resin phase may be pictured as $[Li^+(H_2O)_n][R]^-$ where n is a number between 3 and 4.

Assume that the equilibrium involved is

$$^6Li^+(H_2O)_4 + {}^7Li^+(H_2O)_3R^- \rightleftharpoons {}^7Li^+(H_2O)_4 + {}^6Li^+(H_2O)_3R^-$$

Now as a first approximation Bigeleisen and Mayer's[18] central ion formula may be used to evaluate the partition function ratios of the two species. This is (omitting the symmetry numbers)

$$Q^7/Q^6 = 1 + \frac{\Delta M \times m}{24M^2} u^2 n$$

M = mass of the central atom, m = mass of the surrounding atom (oxygen in this case), $u = hc\omega/kT$, where ω is the symmetrical breathing frequency in cm.$^{-1}$ and n equals the number of surrounding atoms. Using n equal to 4 and 3, a choice must be made for ω in the two cases. Since the symmetrical vibrational frequency has not been observed for lithium ions in aqueous solution, no firm assignment can be made. However, the data of Feder[19] on O^{18} isotope effects does allow one to estimate roughly a figure for the symmetrical breathing frequency of Li^+ surrounded by four H_2O molecules. This number is approximately 166 cm.$^{-1}$.

To estimate the shift in frequency for the lithium hydrates when n is reduced from 4 to 3, an analogy can be made with the shift in the breathing frequency in going from $SO_4^=$ to SO_3 (981 to 1069 cm.$^{-1}$). This is roughly a 10% frequency shift. Using these criteria for selecting assumed frequencies, the list shown in Table II was made and the equilibrium constants were calculated. Omega is the frequency when Li^+ is surrounded by 4 water molecules and ω' the value when Li^+ is surrounded by 3 water molecules.

TABLE II

PARTITION FUNCTION RATIOS AT 300°K.

ω (cm.$^{-1}$)	ω' (cm.$^{-1}$)	$(Q^7/Q^6)_{H_2O}/(Q^7/Q)^6_{resin}$
160	170	1.0056
160	180	1.0019
160	190	0.9980
170	180	1.0065
170	190	1.0026
170	200	0.9985
180	190	1.0075
180	200	1.0034
180	210	0.9991
200	220	1.0051
200	230	1.0004
200	240	0.9956

The value 1.0034 in Table II gives fairly good agreement with the separation factor of 1.0038 measured for 24x Dowex 50 resin.

It is obvious that the calculation of the separation factor is entirely dependent upon the assumed hydrated species and their breathing frequencies and that in the absence of actual spectral data concerning these frequencies positive conclusions cannot be drawn. The use of the central ion formula in this case is an approximation. The calculation does, however, show that it is possible to account for the magnitude and direction of the separation effect by the concept of "dehydration" of the lithium ion in the resin phase. It is certainly true that the model is much too simple since it is probable that the ion-exchange sites are not all identical and that in the same resin particle there will be a variation of the degree of localized cross-linking. In a resin of high crosslinking some of the sites may contain fully hydrated lithium ions while others will contain partially dehydrated lithium ions.[20] This difficulty can be overcome by a statistical approach in which average properties are calculated. This does not seem worthwhile unless spectral data become available. The basic concepts, however, would remain unchanged.

Acknowledgments.—We would like to acknowledge the helpful suggestions given by Drs. George

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Boyd and W. H. Fletcher; also, the assistance of Cecil Lynn and Martha Childs in performing the flame spectrophotometer analyses and LiI sample preparations, Otto Briscoe and Joel Thomason for making mass spectrometer assays and the laboratory help of summer student participants Shirley Johnson Raines and Tony Mason.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENTS OF INORGANIC CHEMISTRY, THE AUSTRALIAN NATIONAL UNIVERSITY, AND THE UNIVERSITY OF ADELAIDE]

The Resolution of the Tris-(thio-oxalato)[1] Complexes of Co(III), Cr(III) and Rh(III)

BY FRANCIS P. DWYER AND ALAN M. SARGESON[2]

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The tris-(thio-oxalato) complexes of Co(III), Cr(III) and Rh(III) have been separated into the optical isomers through the calcium *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salts. As anticipated from the similarity of the bonding of oxygen and sulfur to chromium, the complex with this metal racemized rapidly in solution and in the solid state. The Co(III) and Rh(III) complexes showed no significant loss of rotation in the solid state in several weeks nor in aqueous solution at 90° in 10 min. All were decomposed by light. Though the Fe(III) compound has the magnetic moment (2.35 B.M.) indicative of spin-pairing, attempts at resolution were fruitless.

In contrast with the trisoxalato metal complexes little investigation has been made of the analogous tristhio-oxalato complexes. From resolution[3] and racemization studies[4,5] and the rates of exchange[6] with oxalate ion the trisoxalato complexes fall into two roughly defined categories: those that are inert and easily resolved, (Co(III), Cr(III), Rh(III), Ir(III), and those that exchange rapidly and whose resolution has not been achieved[3] or is in dispute,[3] (Al, Ga, Fe(III), Ru(III), Mn(III)).

Because of the generally stronger bonding of sulfur to transition metals, which can be ascribed in part to double-bonding, enhanced optical stability might be anticipated in the tristhio-oxalato complexes of Co(III) and Fe(III), though not with Cr(III) because of the well known preference of this metal for oxygen. The Fe(III) complex, which might be expected to be spin-paired, is of particular interest since the reported resolution of the spin-free trisoxalato ion[7] has never been substantiated.

The bisthio-oxalato complexes with Ni(II) and Pd(II), and the tris complexes of Co(III) and Rh(III) have been described by Jones and Tasker.[8,9] A brownish purple iron(II) complex of indefinite composition was also isolated[9] as the anilinium salt (possibly a bis-complex).

In the present work the Cr(III) complex has been obtained by warming an aqueous mixture of potassium thio-oxalate and hexa-(urea)-chromium(III) chloride. The dark greenish brown potassium salt separated on the addition of calcium bromide. Because of the rather rapid hydrolysis of the thio-oxalate ion and slow reaction with simple hydrated chromium salts, poor yields result when these are employed in the synthesis. For the same reason efforts to prepare the tristhio-oxalatoiridates(III) and ruthenates(III) from potassium aquopentachloroiridate(III) and the corresponding ruthenium chloro complex were not successful. The case of replacement of the ammonia groups in hexamminecobalt(III) chloride by the thio-oxalate ion is surprising. All of the thio-oxalato complexes decomposed slowly in the dark and quite rapidly in the light. For satisfactory analytical results the analyses had to be done on very freshly prepared material.

The Fe(III) complex prepared from iron(III) nitrate and isolated as the dark purplish-brown potassium barium salt decomposed especially easily in the light. The rapid photoreduction of the trisoxalato-ferrate(III) ion is well known. The sparingly soluble tris-(ethylenediamine)-cobalt(III) trisdithio-oxalato-ferrate(III) salt was more stable. The moment of the latter substance (2.35 B.M.) showed that the Fe(III) anion was spin-paired.

Resolution of the Co(III), Rh(III) and Cr(III) complexes has been effected through the calcium *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salts, $[\mathrm{Ca(Co\ en_2\ (NO_2)_2][M(C_2O_2S_2)_3]}$. The substitution of barium ion or magnesium ion for calcium ion allowed only a poor separation of the diastereoisomers because of unsuitable solubilities. Partial resolution could be effected by the use of active tris-(ethylenediamine)-cobalt(III) ion but the low solubility of both diastereoisomers is a disadvantage. Efforts to resolve the iron(III) complex were fruitless. This is due to its low stability with respect to reduction, and thence complete decomposition.

Unlike its trisoxalato analog the cobalt complex did not racemize appreciably in solution at 90° in 10 min. nor in the solid state over some weeks in the dark. The chromium compound lost its activity in ten hours in solution or in the solid state. Tristhio-oxalatorhodate(III) like the trisoxalato compound was optically stable.

Experimental

All rotations were measured at 20° in a 1 dm. tube.

***l*-Potassium Barium Tristhio-oxalatocobaltate(III) 5-Hydrate.**—Potassium thio-oxalate was prepared by the

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(1) The name thio-oxalato is used in *Chemical Abstracts*. A more precise name that defines the positions and number of the S atoms would be *sym*-dithio-oxalato.

(2) The Australian National University, Canberra, A.C.T., Australia.

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