

## SEPARATION OF THE RARE EARTHS BY ANION EXCHANGE IN WATER-SOLVENT MIXTURES IN THE PRESENCE OF $\alpha$ -HYDROXYISOBUTYRIC ACID\*

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Separation of the lanthanide and actinide elements on a cation exchange resin using an  $\alpha$ -hydroxycarboxylic acid as a complexing agent has long been established in analytical chemistry but very little work had been reported using anion exchangers until the studies of HOLM, CHOPPIN AND MOY<sup>1</sup>. They found that the lighter elements in either series were less adsorbed than the heavier from aqueous solutions of glycolate, lactate and isobutyrate, but separation factors were generally not as great as for analogous cation exchange. Adsorption was lowest in isobutyrate solutions with distribution coefficients falling below a value of ten.

The work of KORKISCH<sup>2</sup> and others has demonstrated that the addition of miscible non-aqueous solvents can greatly increase the uptake of metal ions on to an anion exchange resin. The present experiments were conducted primarily to determine the degree of adsorption and the separation factors of the rare earths from various solvent mixtures containing  $\alpha$ -hydroxyisobutyric acid as a complexing agent and to assess the system for analytical separations. Barium and strontium were included in the work and observations made of a few other elements.

### EXPERIMENTAL

#### *Materials*

All experiments were carried out by column elution at room temperature ( $\sim 23^\circ$ ) using AG Dowex 1X4, 100–200 mesh anion exchange resin. The chloride form was dried overnight at slightly over  $100^\circ$ , weighed and quantitatively transferred to a column. Commercial 10 ml burettes with polypropylene wool inserted to serve as a support for the resin were conveniently used. The resin was changed to the hydroxide form with 1–2 M NaOH, rinsed until the effluent was neutral, and then converted completely to the isobutyrate form by passing a dilute solution of  $\alpha$ -hydroxyisobutyric acid through the resin bed. For good performance the resin in a column was soaked overnight in the appropriate solvent mixture and stirred thoroughly before using to remove trapped air bubbles. Most of the work was carried out with 500 mg portions of resin; bed dimensions were approximately 6 mm  $\times$  57 mm.

The  $\alpha$ -hydroxyisobutyric acid was supplied commercially (Aldrich Chem. Co., Milwaukee) as pure white crystals and used without further treatment. Superior

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\* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

grade organic solvents were used as received from various suppliers. All elution mixtures were prepared by adding the organic solvent to the required percentage volume of aqueous mixture and then cooling to room temperature before bringing to volume. No pH adjustments were made.

### *Procedure*

An aliquot of a dilute nitric acid stock solution containing microgram amounts of the elements of interest was taken to dryness and redissolved in 1 to 2 ml of the appropriate solvent mixture with gentle warming. The solution was then allowed to flow very slowly on to an equilibrated column. As the elution was continued the flow rate was increased to collect effluent fractions of 10 ml in about 45–60 min.

The elution of most elements was determined by emission spectrographic examination of effluent fractions by the copper spark method<sup>3</sup>. Samples were evaporated to dryness, the organic matter volatilized, then redissolved in hydrochloric acid and brought to volume. Aliquots were evaporated on the flat ends of copper electrode pairs and sparked under standard conditions. The spectra were photographed in appropriate wavelength regions. Americium was determined by counting the gamma activity using a well-type scintillation counter with a sodium iodide crystal. Curium was added to columns with the americium and its elution position estimated after alpha counting by subtracting the activity due to the americium from the gross alpha counts.

Elution curve maxima were approximated from visual examination of spectral line intensities and from radioactive assays. Distribution coefficients were calculated from the expression  $K_d = V/M$ , where  $V$  is the volume in ml that has passed through the column at the elution curve peak, corrected for the first volume of interstitial liquid displaced, and  $M$  is the mass of resin in grams.

### RESULTS

Adsorption of the rare earths was most sensitive to changes in water content of a solvent mixture. Figs. 1, 2 and 3 summarize the results of experiments made to determine the variation of distribution coefficients with proportion of aqueous content in mixtures of methanol, ethanol and isopropanol. The overall concentration of  $\alpha$ -hydroxyisobutyric acid was maintained at 0.0125 molar. Acidity of solutions ranged from pH 3.0 in 100% aqueous solutions to approximately pH 4.0 in solutions of high alcohol content. Elution of the lanthanides was in the order of increasing atomic number, in agreement with the results of HOLM *et al.*<sup>1</sup>. The ratio of distribution coefficients, or separation factor, between two adjacent members of the series was nearly constant in all mixtures and as a rule became less with increasing atomic number. In methanol solutions the separation factors averaged about 3.5 for Ce–La and about 1.8 for both Pr–Ce and Nd–Pr, then generally gradated from 1.4 for Eu–Sm to 1.2 for Lu–Yb. About the same degree of separation was found in ethanol and somewhat less in isopropanol mixtures. Irregularities within each family of distribution curves shown did not exceed the experimental error. Adsorption of the heavier rare earths from solutions containing less than 25% water was too great for their practical determination by column elution. It would seem likely that an extension of the adsorption curves shown would give acceptable estimates of the higher values.

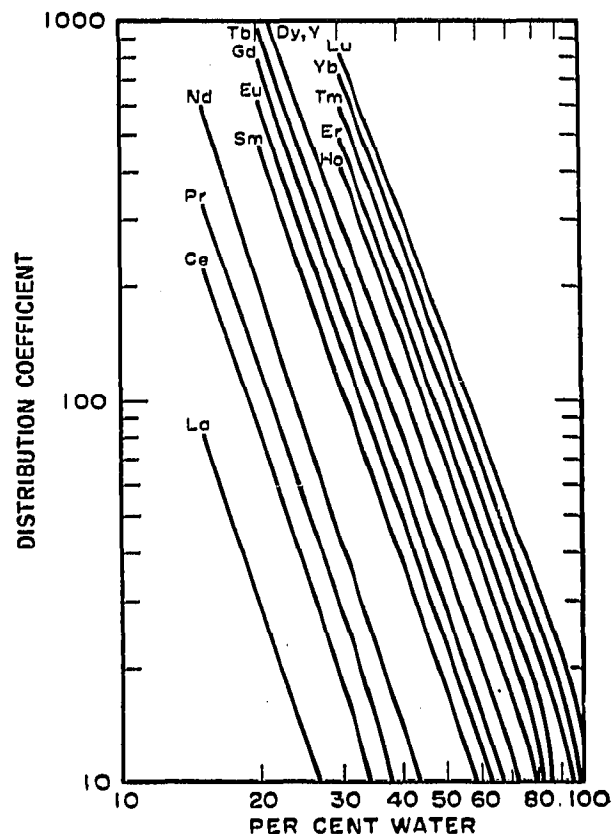
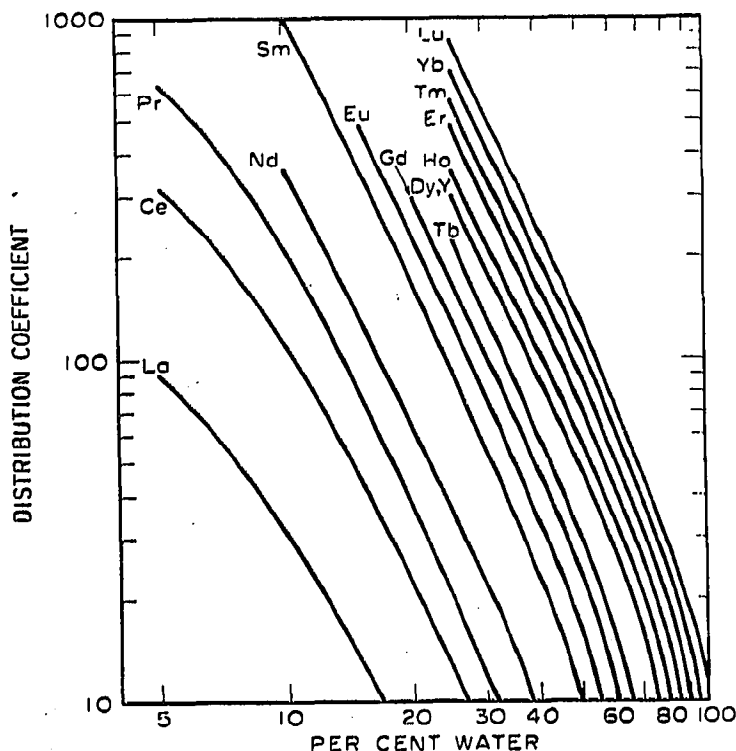


Fig. 1. Variation of distribution coefficient with aqueous content of methanol mixtures; 0.0125  $M$   $\alpha$ -hydroxyisobutyric acid. Dowex 1X4, 100-200 mesh resin.

Fig. 2. Variation of distribution coefficient with aqueous content of ethanol mixtures; 0.0125  $M$   $\alpha$ -hydroxyisobutyric acid. Dowex 1X4, 100-200 mesh resin.

No general attempt was made to measure distribution coefficients that fell below a value of ten.

A comparison of rare earth adsorption in nine different solvents containing a constant proportion of water and complexing agent is given in Fig. 4. As much as a thirtyfold increase in distribution coefficients was found between the least effective solvent, *n*-propanol, and the most effective, dioxane, but no significant differences were observed in separation factors between members of the lanthanide series.

Increasing the concentration of  $\alpha$ -hydroxyisobutyric acid in a solvent mixture produced higher distribution coefficients but did not appreciably affect separation factors of the lanthanides heavier than cerium. Adsorption behavior similar to that shown in Fig. 5 for the rare earths in a 25% aqueous methanol medium can be expected in other solvent mixtures. The elution curves in 0.005  $M$  solutions of the complexing agent were not as reproducible as those in higher concentrations.

The results of experiments made to establish the elution positions of americium and curium are given in Fig. 6. Americium was eluted first with an average separation factor of 1.28. This value was less than that commonly attained by cation exchange and by anion exchange in nitrate systems<sup>4,5</sup>.

Approximate distribution curves for scandium in the three solvents tested are also shown in Fig. 6. Scandium elution curves were somewhat more difficult to reproduce experimentally than those of the lanthanides.

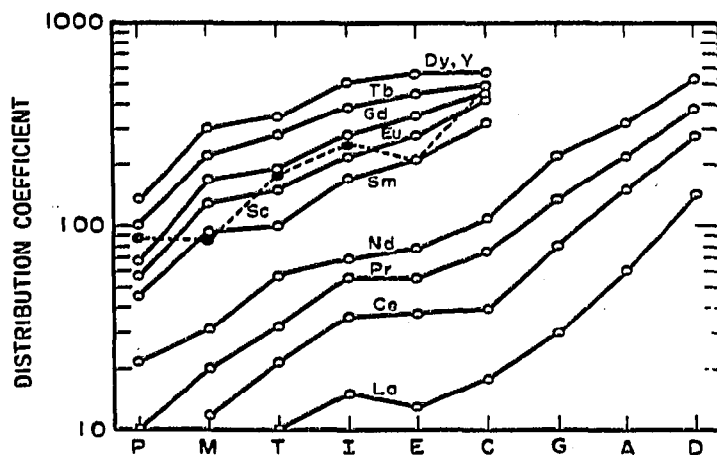
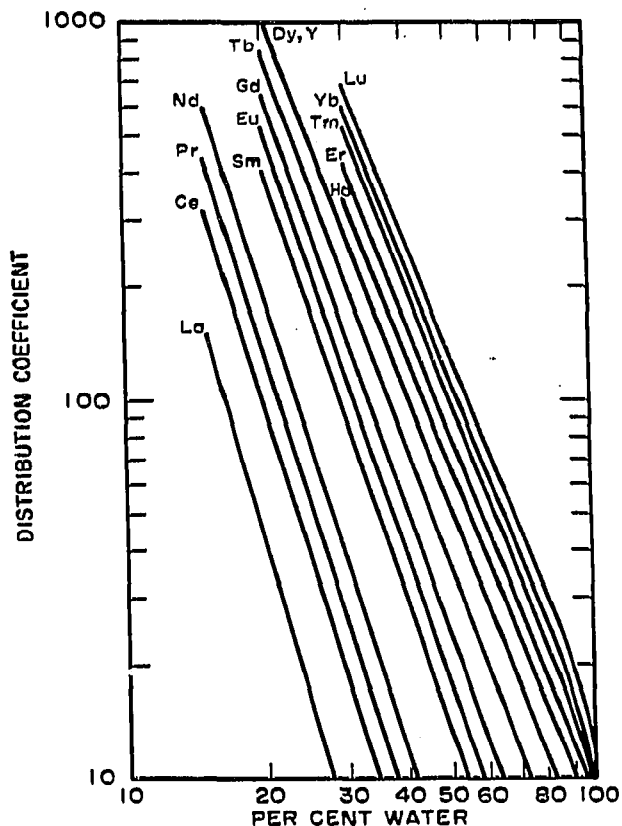


Fig. 3. Variation of distribution coefficient with aqueous content of isopropanol mixtures;  $0.0125 M$   $\alpha$ -hydroxyisobutyric acid. Dowex  $1X_4$ , 100–200 mesh resin.

Fig. 4. Adsorption of the rare earths from several solvent mixtures containing 25% water and  $0.0125 M$   $\alpha$ -hydroxyisobutyric acid. Dowex  $1X_4$ , 100–200 mesh resin. P = *n*-Propanol, M = methanol, T = tetrahydrofuran, I = isopropanol, E = ethanol, C = cellosolve (ethylene glycol monoethyl ether), G = diethylene glycol monomethyl ether, A = acetone, D = P-dioxane.

Strontium and barium were included in all experiments. Neither element was adsorbed from any of the solvent mixtures, thus permitting their ready separation from the rare earths. In other tests, both U(VI) and Fe(III) were easily separated from the non-adsorbed elements since both ions were strongly retained by the resin and could not be removed from a column by washing with water. No general survey of the anion exchange behavior of other metal ions in the isobutyrate system has yet been made but it would seem likely to offer a potential for further separations that would be useful in analytical chemistry.

#### APPLICATION AND DISCUSSION

Several column elution experiments were carried out to explore the application of the system to macro separations. In the examples given below the samples were weighed, dissolved in nitric acid and taken to dryness to remove the free acid. The nitrates were placed in a solution of the required amounts of alcohol and water with gentle warming, then an excess of the solid complexing agent was added. Larger samples often precipitated if the carboxylic acid was added before diluting to a concentration of about 4 mg/ml. The rare earths were readily soluble in aqueous methanol

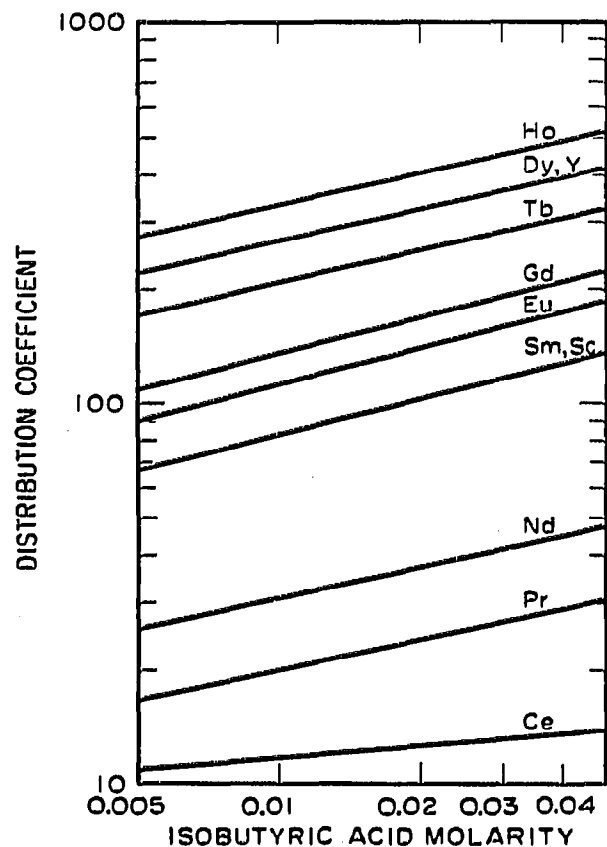


Fig. 5. Variation of distribution coefficient with concentration of  $\alpha$ -hydroxyisobutyric acid in 25% aqueous solutions. Dowex 1X4, 100-200 mesh resin.

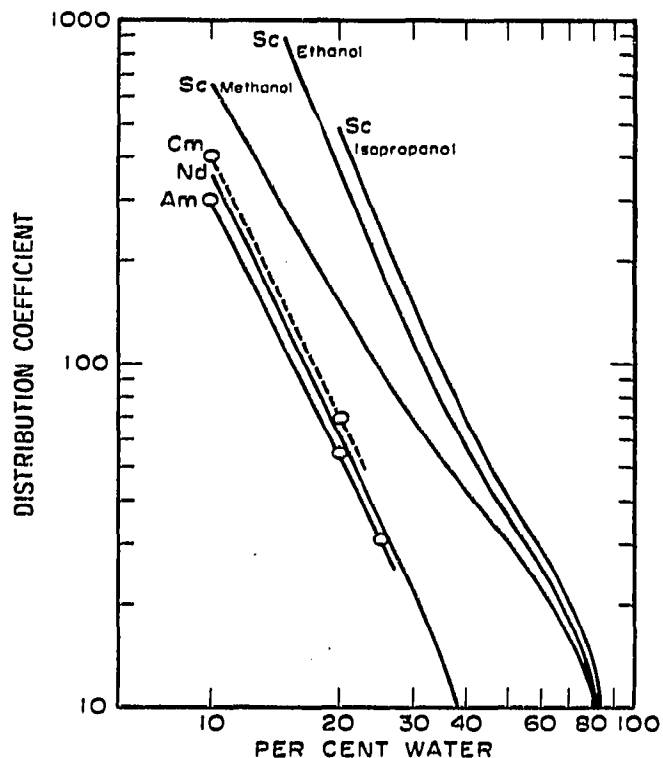


Fig. 6. Variation of distribution coefficients of Am and Cm with aqueous content of methanol mixtures compared to Nd. Approximate Sc values in three solvent mixtures are also shown. All solutions 0.0125 M in  $\alpha$ -hydroxyisobutyric acid. Dowex 1X4, 100-200 mesh resin.

but the solutions were added to a column without undue delay because some of the heavier members of the group and yttrium tended to precipitate during overnight standing.

### Lanthanide fractionation

Although separation factors between adjacent members of the series do not permit their mutual isolation in macro amounts, the distribution data given in Figs. 1-3 and 5 may be conveniently applied to fractionations within the group by

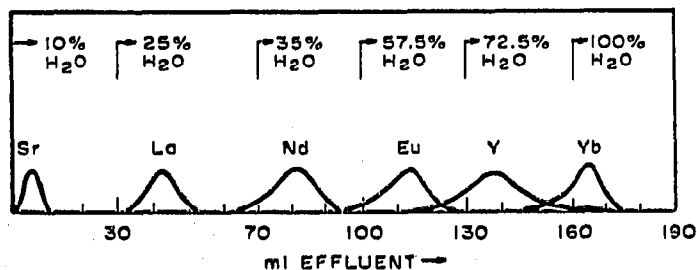


Fig. 7. Elution of 1 mg each of Sr, La, Nd, Eu, Y and Yb with methanol-water mixtures in the presence of 0.02 M  $\alpha$ -hydroxyisobutyric acid. Dowex 1X4, 100-200 mesh resin column, 10 mm  $\times$  70 mm.

gradient elution. An example is shown in Fig. 7. The elution curves were drawn from spectrographic analysis of effluent fractions after adding to a column a mixture of 1 mg each of La, Nd, Eu, Y and Yb plus a non-adsorbed element, Sr. The resin bed was 10 mm in diameter and about 70 mm in length. All mixtures, except the final water wash, were maintained at 0.02 *M*  $\alpha$ -hydroxyisobutyric acid.

#### *Trace element analysis*

Ion exchange-spectrographic methods currently used at this laboratory usually require a sample weight of from 0.1 to 1 g for adequate detection of trace impurities. During evaluation of the isobutyrate system it was experimentally found that rare earth samples weighing 100 mg could be adsorbed without difficulty on a column from solutions containing 4 mg/ml but precipitation in the column usually occurred when the sample weight was increased to 500 mg and the solution made several times more concentrated. The separation of added rare earth impurities from the heavier members of the series was consequently examined using 100 mg samples. Analysis of effluent fractions showed that trace amounts of the elements La through to Tb could be isolated from macro erbium samples before any appreciable breakthrough of the matrix. Dysprosium and Y could be qualitatively detected. The eluate was a 60% aqueous methanol solution, 0.02 *M* in  $\alpha$ -hydroxyisobutyric acid, and the resin bed measured approximately 20 mm in diameter and 90 mm in length. Similarly, La to Eu could be isolated from a yttrium matrix with a 50% methanol eluant. Conditions for separating impurities from other matrices may be chosen from the distribution data given in Figs. 1-3 and 5. Once prepared, a column may be used indefinitely since the adsorbed rare earths are easily removed by washing with water.

These separations permit the emission spectrographic detection of p.p.m. amounts of the separated impurities and complement anion exchange adsorption from nitric acid-methanol mixtures which has been used for analysis of the lighter rare earths<sup>6</sup>. Sensitivities of the spectral lines used for analysis by the copper spark method have been reported<sup>7</sup>.

#### ACKNOWLEDGEMENTS

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#### SUMMARY

Adsorption of the rare earths and a few other elements on to an anion exchange resin from mixed solvents containing  $\alpha$ -hydroxyisobutyric acid has been investigated. Elution of the lanthanides was in the order of increasing atomic number. Separation factors between adjacent members of the series were essentially independent of solvent composition and somewhat less in value than analogous cation exchange. Some applications of the system using macro samples have been illustrated.

## REFERENCES

- 1 L. W. HOLM, G. R. CHOPPIN AND D. MOY, *J. Inorg. Nucl. Chem.*, 19 (1961) 251.
- 2 J. KORKISCH, *Progress in Nuclear Energy, Series 9*, Vol. 6, Pergamon, Oxford, 1966, p. 1.
- 3 M. FRED, N. H. NACHTRIEB AND F. S. TOMKINS, *J. Opt. Soc. Am.*, 37 (1947) 279.
- 4 W. KRAAK AND W. A. VAN DER HEIJDEN, *J. Inorg. Nucl. Chem.*, 28 (1966) 221.
- 5 J. HINES, M. A. WAHLGREN AND F. LAWLESS, *Conf. Anal. Chem., Gallinburg, 1962, 6th, TID-7655*, p. 247.
- 6 J. P. FARIS AND J. W. WARTON, *Anal. Chem.*, 34 (1962) 1077.
- 7 J. P. FARIS, *Conf. Anal. Chem., Gallinburg, 1962, 6th, TID-7655*, p. 193.

*J. Chromatog.*, 26 (1967) 232-238