# ANION EXCHANGE BEHAVIOR OF RARE EARTH ELEMENTS IN POTASSIUM SULFATE MEDIUM

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Until recently, the most effective developments in ion exchange separation of rare earth elements have been made when cation exchangers and eluent systems consisting of organic complexing agents have been used. More recently, considerable effort has been made to exploit the use of anion exchange systems with inorganic eluents. Although strong base anion exchange resins do not adsorb the rare earths to any significant extent from mineral acid solutions[1-4], appreciable adsorption has been reported from other media. Pronounced uptake of rare earths from sodium triphosphate solution, adjusted to pH 1 to 9, on a strongly basic anion exchanger has been observed by SUBBARAMAN *et al.*[5]. The rare earths, in concentrated nitrate solutions, have also been found to adsorb sufficiently to permit the effective separation of complex mixtures of rare earth tracers[6]. Information has also been presented concerning the use of lithium chloride[7], sulfite[8], carbonate[9-11], thiocyanate[12] and sulfite, nitrite and thiosulfate[6] media.

Potassium sulfate does not appear to have attracted any attention for the separation of rare earths. Indeed, very little systematic work has been done with the rare earths in the anion exchange resin–sulfate or sulfuric acid systems. BUNNEY *et al.*[2] stated that yttrium, cerium and americium do not show any significant adsorption by Dowex 2 resin at any sulfuric acid concentration level. SAITO AND SEKINE[9] reported that a trace amount of ^{90}Y is slightly adsorbed on a strong-base anion exchange resin from ammonium sulfate and sulfuric acid systems. EDGE[13] has examined briefly the possible separation of some rare earths in dilute sulfuric acid solutions containing ethanol. However, little prospect of an effective anion exchange separation was expected for the neighbouring rare earths Nd and Pr. Thus, the more extensive investigation of the behavior of the whole series of rare earth elements in the sulfate medium, which would provide the basis for a better understanding of this system, appeared to be warranted.

## EXPERIMENTAL

### Resin

Anion exchanger, Dowex 1, X-8, 200 to 400 mesh, sulfate form. A commercial analytical grade Dowex resin was converted to the sulfate form before use. The converted resin was air-dried and stored in a large desiccator over a saturated solution of potassium bromide.

### Columns

Conventional glass tubes of 10 mm internal diameter, 600 mm long, packed at the

bottom with glass wool were used. The columns were filled with a slurry of 43 g of the dried resin and the top of the column was connected to a 500 ml dropping funnel through a rubber stopper. A bed height of 570 mm is usually obtained.

## Stock solution of metals

Stock solutions of the rare earths were prepared by dissolving the appropriate amount of the respective oxides (99.9 % purity) in a small amount of 3 $M$ sulfuric acid, evaporating to dryness and dissolving in 100 ml of deionized water to give approximately 2.5 mg rare earth metal per ml solution. A stock solution of cerium(III) was prepared by treating ceric oxide with small amount of 3 $M$ sulfuric acid, with occasional addition of an excess of hydrogen peroxide to reduce cerium(IV) to the tervalent state, and fuming to dryness. The residue was dissolved in water and diluted to a definite volume to give a concentration of 2.5 mg Ce per ml. The strength of the stock solutions was determined by titration with 0.001 $M$ EDTA, standardized previously with a zinc metal of primary standard using Xylenol Orange as indicator.

## Column procedure

Before starting the elution, the column should be pretreated with a sufficient volume of 0.01 $M$ potassium sulfate solution, of the same concentration as used for the elution. About 5 ml of a sample solution, adjusted to 0.01 $M$ in potassium sulfate, is allowed to run into the resin bed at room temperature. Sufficient time, usually 2 h must be allowed for the sample solution to run down the column. The weakly adsorbed rare earths are then eluted with 0.01 $M$ potassium sulfate solution at a flow rate of 10 ml per 60 $\pm$ 10 min. The effluent is collected in 10 ml fractions and each fraction titrated with 0.001 $M$ EDTA as described above.

To determine the void space of the column 0.01 $M$ potassium sulfate solution containing carrier-free [134]Cs was fed into the top of the column and allowed to pass through the column. The break-through point of the [134]Cs was detected by measurement of the activity of 1 ml fractions of the effluent with a well type gamma scintillation counter. After the activity of the effluent reached a constant level, the column was rinsed with 0.01 $M$ potassium sulfate solution until the effluent fraction showed no sign of [134]Cs activity. The two volumes, viz. that required for the break-through and that for the removal of the activity, were recorded. The two values thus obtained agreed well and gave 22.8 ml for the column used.

## RESULTS AND DISCUSSION

To investigate the column elution behavior of individual rare earths in the potassium sulfate medium ca. 4.8 mg of each rare earth was adsorbed on the head of the column and eluted with 0.01 $M$ potassium sulfate solution. Cumulative elution curves are plotted in Fig. 1.

It can be seen that there are considerable differences in the points of both break-through and complete elution among the individual rare earths, which should provide a basis for possible separations of some rare earth elements. The values of the respective distribution coefficients, $K_d$, for the rare earth elements, were calculated with the following equation:

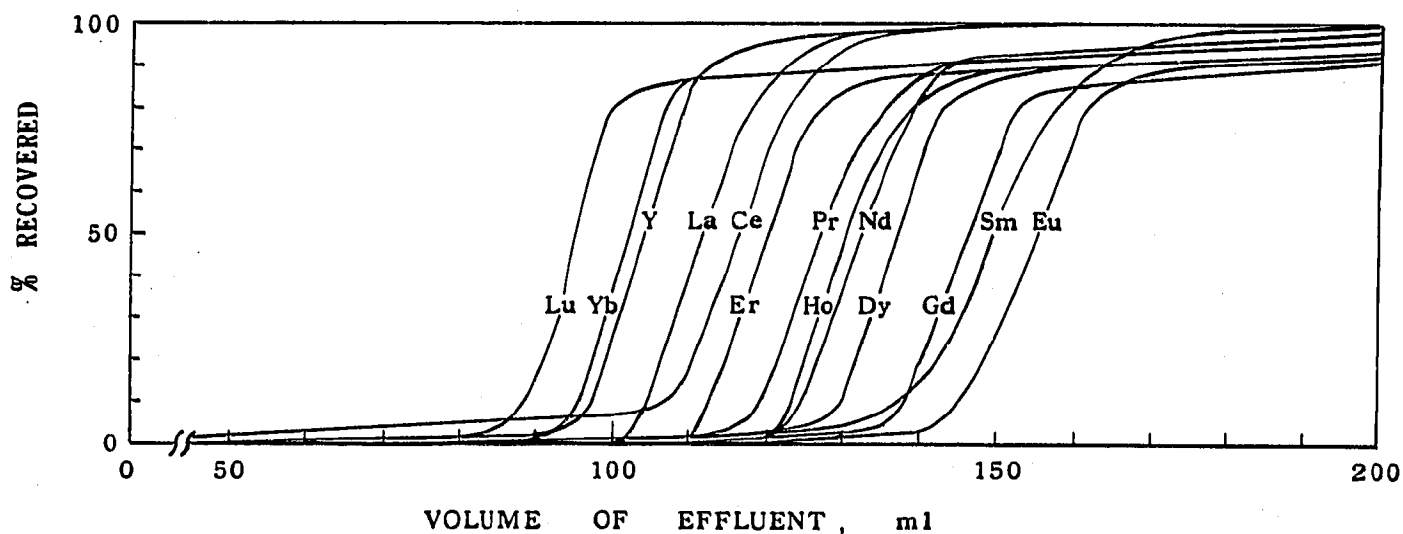$$K_d = \frac{U_{max} - U_0}{M}$$

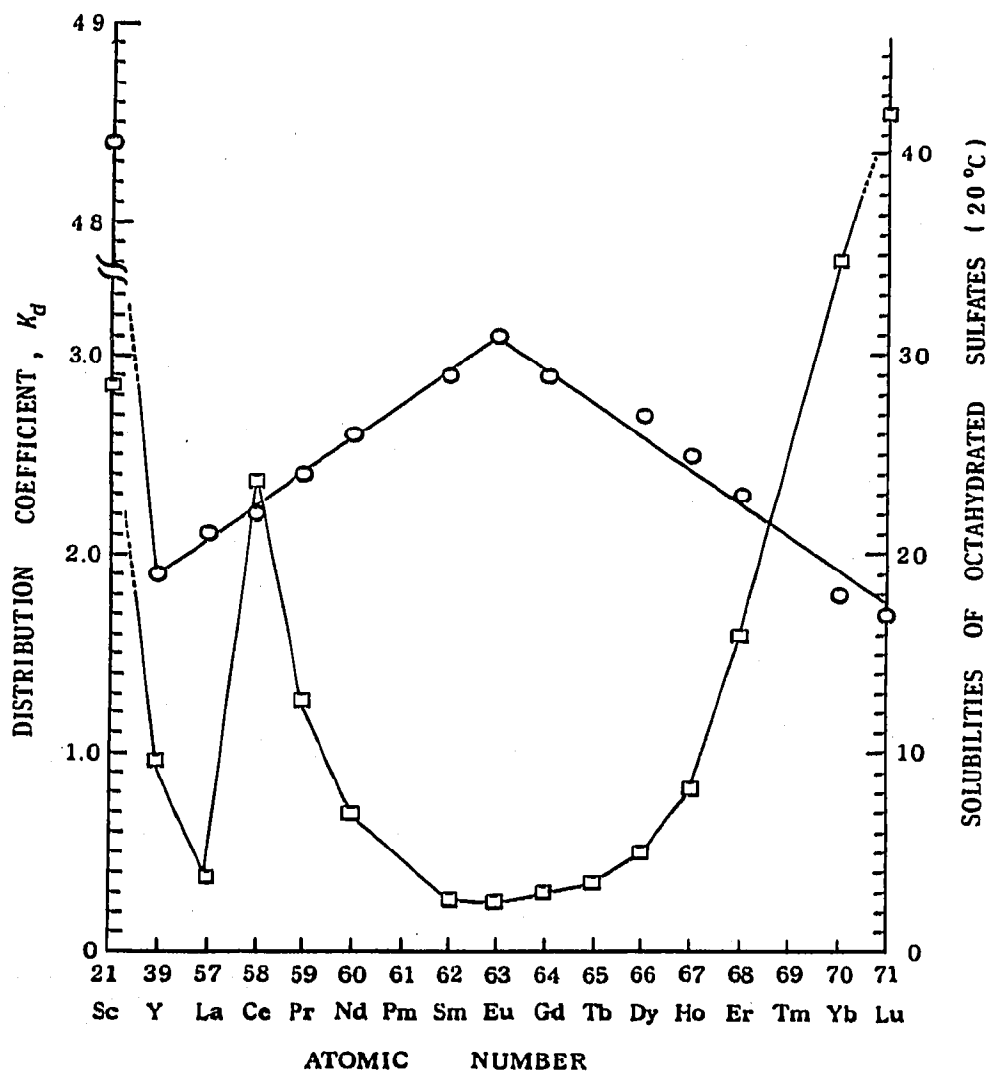Fig. 1. Cumulative elution curves for the rare earth elements.



Fig. 2. Distribution coefficients of the lanthanides as a function of the atomic number. □ : solubility data; O : distribution coefficient data.

where $U_{max}$ is the volume of the effluent when the concentration of respective rare earth reaches its maximum elution, $U_0$ the void space of the column, and $M$ the weight of the dried resin in the column. $K_d$ values thus calculated for 0.01 $M$ potassium sulfate medium are plotted in Fig. 2 as a function of atomic number.

Dependence of $K_d$ on the concentration of potassium sulfate was determined by a batch method for europium and scandium using the carrier-free radioactive isotopes [154]Eu ($T_{1/2} = 16$ years) and [46]Sc ($T_{1/2} = 85$ days), respectively. The result is shown in Fig. 3.
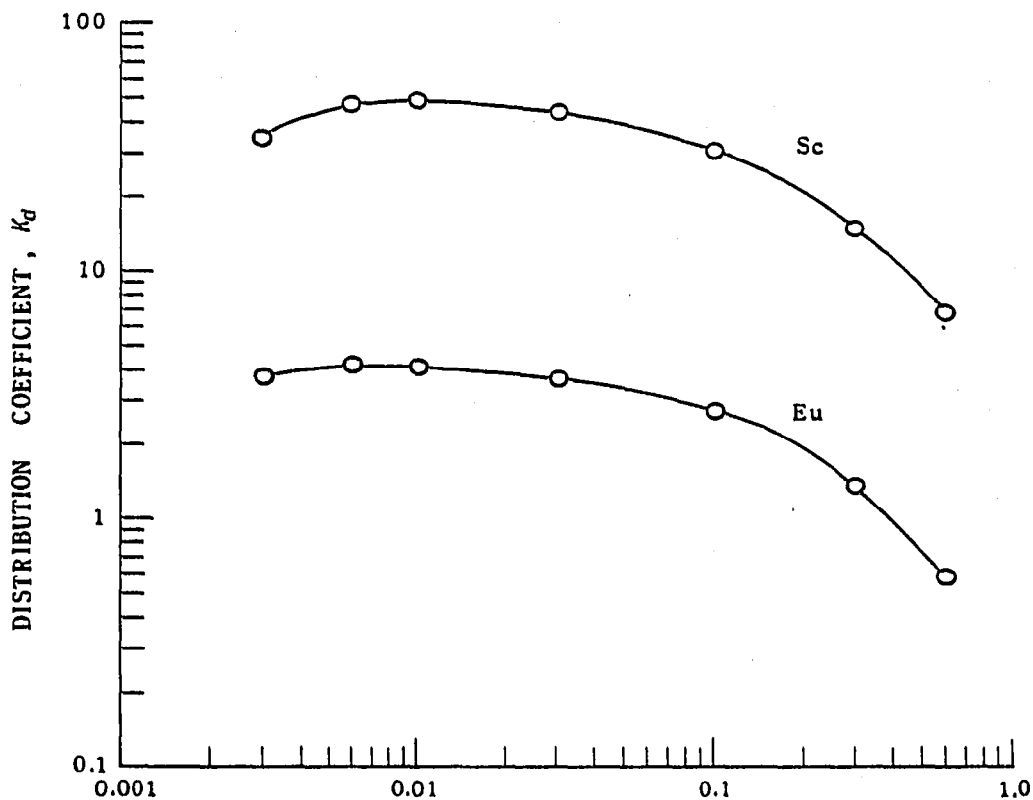
concentration of sulfate. This can be explained, easily, because the higher complexes occupy more fixed ionic groups per atom in the resin phase and are in competition with an increasing number of free sulfate ions.

As seen in Fig. 2 the distribution coefficient curve for lanthanides indicates a maximum in the vicinity of atomic number 63, europium. Similarly, the sequence of elution does not vary monotonically from lanthanum to lutetium; the retention volumes increase in accordance with the increase of the atomic number for the cerium group, while they decrease in the same direction for the yttrium group.

The position of yttrium in the elution sequence of rare earths in sulfate medium is of interest. As indicated in Fig. 2 the distribution coefficient of yttrium lies between that of thulium and ytterbium. Thus yttrium can be assigned an apparent atomic number of 69.5. This does not agree with the apparent atomic number ascribed to yttrium from the elution sequence in anion exchanger–EDTA system[15].

We would like to mention for comparison that the behavior of yttrium varies widely in cation exchange systems[16] with organic eluents; for example, yttrium elutes between Dy–Tb with EDTA, near Nd with DTPA, near Pr with HEDTA, near Eu with citrate at 10–20° and Dy–Ho with citrate at 87–100°, near Ho–Dy with lactate, and near Dy–Ho with thiocyanate[17].

It is also of interest to note that there is an apparent correlation between the values of the distribution coefficients and the solubilities of octahydrated sulfates[18] of the lanthanide elements (see Fig. 2). The solubility of sulfates of the type, $Ln_2(SO_4)_3 \cdot 8H_2O$, first diminishes within the cerium group, reaches a minimum at europium, and then increases with increase of atomic number. However, such correlation does not hold for scandium and lanthanum.

A similar correlation was found for the behavior of lanthanide elements in the system Amberlite IRA-400–aqueous solution of disodium ethylenediaminetetraacetate[15]. The distribution coefficients increase regularly within the cerium group, reaching a maximum at europium, and then decrease on going to higher atomic numbers. On the other hand the solubility of the complex salts, NaLnY, varies conversely showing a minimum in the vicinity of Sm–Eu. A similar relationship between the solubility of rare earth double salts and the adsorption by an anion exchange resin from nitrate solution has been observed by DANON[19]. Based on these observations one may conclude that the maximum affinity to the anion exchange resin corresponds to the minimum solubility. The different solubilities of the sulfates of the lanthanide elements in an alkali metal sulfate solution have been explained by the formation of complex compounds of the type $Me_3[Ln(SO_4)_3]$ or $Me[Ln(SO_4)_2]$, where $Me = Na^+$, $K^+$, $NH_4^+$ (ref. 16). The minumum solubility in the vicinity of Eu–Sm suggests that the possibility of predominance of neutral sulfato complexes of europium and samarium is greater relative to the other lanthanide elements, in the sulfate solution and that this will necessarily result in a greater uptake of europium and samarium on the anion exchanger, as stated before.

*Separation of rare earths*

The separation of all the rare earths cannot be achieved by a single elution with potassium sulfate as eluent, because the distribution coefficients for the rare earths do not vary in a simple way with increasing atomic number. However, the present anion exchange separation can easily be preceded by a double alkali sulfate precipitation,

which will, if properly handled, separate the light (La to Gd) and heavy (Tb to Lu) rare earths, according to temperature and the particular alkali sulfate employed for the precipitation. In the present anion exchange procedure, the conditions are favorable for the separation of certain selected pairs or groups of rare earths. It is obviously important in obtaining good separation of two elements that the separation factor, which is defined by the ratio of their distribution coefficients, $\alpha_2^1 = K_{d1}/K_{d2}$ should be large. In the sulfate medium described here, the separation factor for adjacent pairs of rare earths is not so high as that observed in other media coupled with cation exchangers, and shows a rather uniform value, averaging 1.08. The separation factor for the pairs, in which the atomic number differs by $n$, can approximately be given by $(1.08)^n$. For the pairs Ho–Y and Dy–Y, which are generally difficult to separate, $\alpha_Y^{Ho}$ and $\alpha_Y^{Dy}$ are 1.33 and 1.41, respectively, which is, in general, higher than the factors obtained for the cation exchanger-α-hydroxyisobutyrate system ($\alpha_{Ho}^Y = 1.56$, $\alpha_Y^{Dy} = 1.04$ at 87°) and lactate system ($\alpha_{Ho}^Y = 1.21$, $\alpha_Y^{Dy} = 1.14$ at 90°).

In Fig. 4 typical elution curves are shown for several pairs or groups of rare earth elements. Assuming the normal distribution for the elution curves of neodymium and europium, we calculated the total number of theoretical plates in the column employed, and obtained 341 for neodymium and 314 for europium by the procedure given by BEUKENKAMP et al.[20]. The effective height of the theoretical plate (EHTP) was estimated as 0.17 cm for neodymium and 0.18 cm for europium. Actually, one might expect the EHTP to be of the order of the diameter of the resin particles (about 0.07 mm for 200 mesh) under optimum conditions. The values obtained are about twenty times higher than the practical particle size. However, because of packing irregularities,
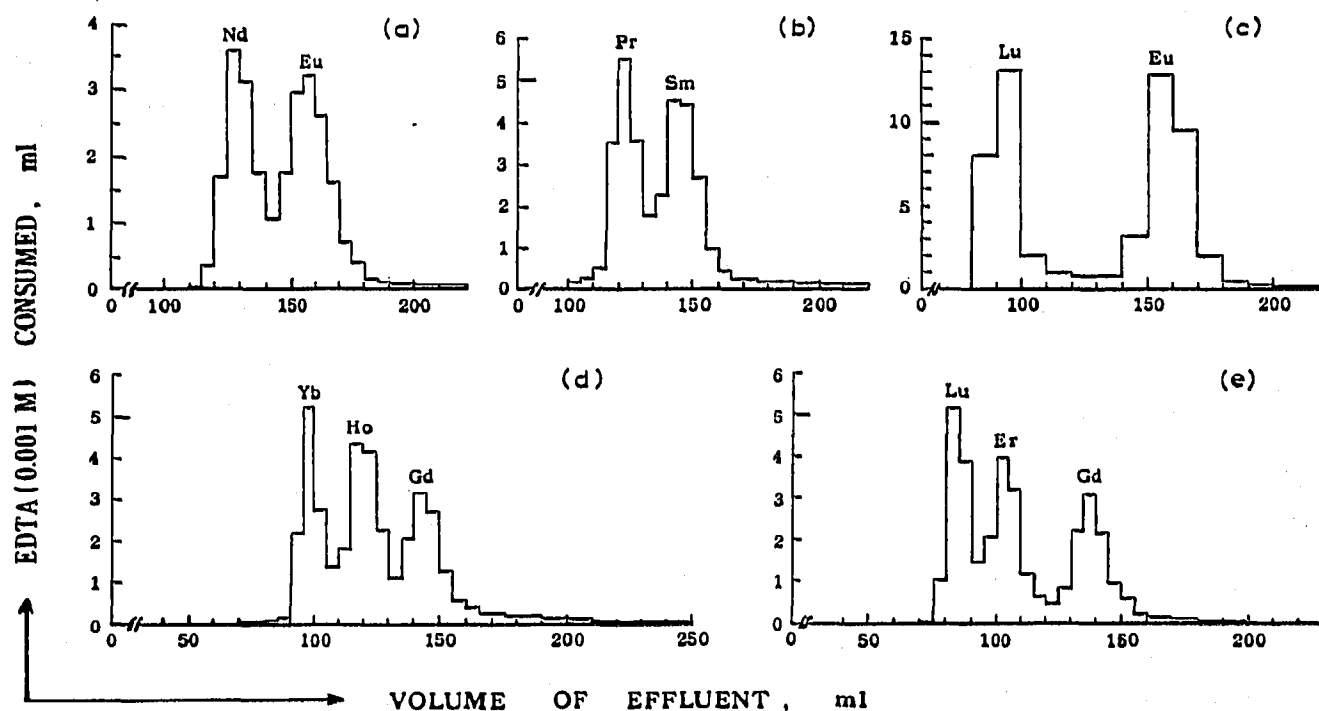


Fig. 4. Separation of selected pairs or groups of rare earth elements by elution with potassium sulfate solution. (a) Separation of neodymium and europium. (b) Separation of praseodymium and samarium. (c) Separation of lutetium and europium. (d) Separation of ytterbium, holmium and gadolinium. (e) Separation of lutetium, erbium and gadolinium.

channeling effects, and the need for extremely slow flow rates, ideal conditions are rarely realized in practice. Even in the excellent rare earth separations of KETELLE AND BOYD[21] the EHTP was approximately 0.1 cm[22], which is comparable to those obtained in the present separations. The total number of theoretical plates which are necessary to obtain a quantitative separation of neodymium and europium is $1.1 \cdot 10^3$, which corresponds to a column height of about 1.9 m. Likewise, a column height of about 8 m is required to separate quantitatively the adjacent pair, holmium and erbium. It is noteworthy that the rare earth-like element scandium has a distinctly high distribution coefficient compared to the rare earth elements (see Fig. 3). This should provide a promising procedure for the separation of scandium from other elements, because plenty of elements, as well as rare earths, have slight or no adsorption on anion exchange resins from sulfate or sulfuric acid medium.

SUMMARY

The anion exchange behavior of rare earth elements as well as scandium and yttrium in potassium sulfate medium was investigated. Rare earths and yttrium showed slight adsorption on the strongly basic anion exchange resin Dowex 1, X-8, from dilute potassium sulfate solution, while scandium was rather strongly adsorbed on the resin. The distribution coefficients of the rare earth elements were found to increase in a regular way from lanthanum to europium, reaching a maximum at europium and then decreasing with increasing atomic number. Although the system could not effect the separation of the whole of the rare earth elements in a single elution, the possibility of achieving effective chromatographic separation of selected pairs or groups of rare earth elements on a column, 57 cm long, was demonstrated.

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