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THE SEPARATION OF YTTRIUM FROM THE LANTHANIDES BY ION EXCHANGE WITH DIETHYLENETRIAMINEPENTAACETIC ACID AS ELUANT

I. SEPARATION OF YTTRIUM–ERBIUM MIXTURES

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SUMMARY

The elution of yttrium and erbium and the separation of yttrium–erbium mixtures on a sulphonated cation exchanger comprising 4–5 % divinylbenzene with 0.025 *M* diethylenetriaminepentaacetic acid (DTPA) solution was investigated at room temperature. The retaining ion was H^+ and the pHs of the eluting solutions were between 6.0 and 8.5. The composition of the lanthanide bands under equilibrium conditions was determined, the reactions involved were considered, and the height equivalent to a theoretical plate was determined as a function of the grain size. For the pH range studied, the leakage of $NH_4^+ + H^+$ into the lanthanide band was about 40 %. The mole fraction of erbium and yttrium in the resin band decreased with decreasing pH of the eluant. The concentration of Y^{3+} and Er^{3+} in the effluent increased from 38.5 and 39.6 mequiv./l at pH 6.10 to 51.0 and 49.8 mequiv./l at pH 8.15, respectively. The heights equivalent to a theoretical plate, in separations with resin particles of 20–50 and 52–100 mesh with all other conditions remaining constant, were 1.95 cm and 0.99 cm, respectively.

INTRODUCTION

Isolation of yttrium or of any individual lanthanide can be performed by ion-exchange methods using various complexing agents. Owing to complexation, the separation factors (α_{M1}^{M2}) between adjacent lanthanides are increased:

$$\alpha_{M1}^{M2} = \alpha'^{M2}_{M1} \times \frac{K_{M2Ch}}{K_{M1Ch}}$$

where α_{M1}^{M2} is the separation factor when using a complexant, α'^{M2}_{M1} is the separation factor without a complexant (nearly unity), and K_{MCh} is the stability constant of MCh.

Separations for analytical purposes (*i.e.* small quantities) are usually carried out by the elution development technique, while separations of larger amounts are achieved by the displacement development technique.

In industrial extractions, before starting the ion-exchange process, the mixture of the lanthanide oxides obtained from the raw material is usually separated into groups based on differences in the solubilities of their double sulphates[1,2]. The soluble fraction contains Y and the heavy lanthanides; in general, the yttrium content in this fraction is greater than 50 %, gadolinium, dysprosium and erbium about 10 % each, with smaller amounts of other elements of this group (Tb, Ho, Tm, Yb and Lu)[2].

The first separations of lanthanides by displacement development, using ammonium citrate as the complexing eluant and H^+ as the retaining ion, were investigated by SPEDDING AND POWELL[3,4]. They studied the NH_4^+ leakage into the lanthanide bed as a function of the pH of the eluant and found that it amounted to between 50 and 90 %, decreasing with an increase in the pH of the eluant. The maximum concentration of lanthanide in the effluent was 8.45 mequiv./l.

Following the experimental observation that polyaminoacetic acids give greater stability and larger differences in the stability constants between adjacent lanthanides, over a wide pH range, they began to be used as complexing eluants. The polyaminoacetic acids usually employed are ethylenediaminetetraacetic acid (EDTA)[5-8], N-hydroxyethylenediaminetriacetic acid (HEDTA)[9-11] and diethylenetriaminepentaacetic acid (DTPA)[12,13].

From the technological point of view, HEDTA and DTPA are more convenient eluants since their solubilities enable H^+ to be used as the retaining ion. Because of the low solubility of EDTA (0.04 % compared with 0.4 % for DTPA), the retaining ion employed is usually Cu^{2+}.

As the amount of lanthanides in the effluent is directly proportional to the eluant concentration, the chelating agents giving solutions of higher concentrations are preferable. With EDTA, even when the retaining ion is Cu^{2+}, the low solubility of Cu_2–EDTA restricts the eluant concentration to less than 0.015 *M* and limits the pH to the narrow range of 8.2–8.5. Another disadvantage is the difficult regeneration of EDTA or Cu^{2+} because of the high stability of the Cu_2–EDTA complex.

HEDTA is more soluble, but the moderate solubility of some of its heavy lanthanide complexes limits its concentration to 0.018 *M* at 25° in the separation of the yttrium group[9].

With DTPA, however, 0.025 *M* solutions may be used, its complexes are more stable[14], and in some cases $\alpha_{M_1}^{M_2}$ is more favourable. Separations using DTPA as eluant have recently been reported[12,13], but a theoretical description is lacking. The purpose of the present investigation was therefore to study the mechanism of separation by displacement development with DTPA as eluant. Because its main advantage is in the separation of yttrium from the heavy lanthanides, the mechanism of separation by displacement development of Y–Er mixtures was studied as representative of this group. The same mechanism should apply to the other lanthanides.

EXPERIMENTAL

Resin

The ion-exchange resins were Zeo-Karb 225, 4–5 % divinylbenzene (DVB) (Permutit Co.), a sulphonated polystyrene cation exchanger in the hydrogen form, 20–50 and 52–100 mesh.

Loading solutions.

Suitable amounts of yttrium and erbium oxides of analytical grade were dissolved in a slight excess of HCl and diluted to 2 l, giving solutions of pH 1.5–2.0. The loading on the basis of equivalents was 16.5 %. It was found that equilibrium conditions were achieved at this loading.

The eluant

0.025 *M* solutions of analytical grade DTPA were prepared and adjusted to the desired pH using NH_4OH.

Elution experiments.

The columns used were Pyrex tubes of 19 mm I.D., sealed at the bottom with sintered glass disks. The height of the resin bed was about 100 cm. Loading solutions were charged at a flow-rate of 1.5 cm of column length per min. After loading, the resin bed was washed with distilled water until it was free from chloride. The charged band was then eluted with the DTPA solution at room temperature. Experimental conditions are listed in Table I.

TABLE I

EXPERIMENTAL CONDITIONS

Experiment No.	*Grain size (mesh)*	*Charged elements*	*Composition of eluant*		
			pH	*Chy (mmole/l)*	NH_4y *(mequiv/l)*
1	20–50	Y^{3+}	8.55	25.2	87.7
2	20–50	50% Y^{3+} + 50% Er^{3+}	8.35	25.5	86.2
3	52–100	Er^{3+}	8.15	25.4	83.0
4	52–100	50% Y^{3+} + 50% Er^{3+}	8.20	25.8	84.9
5	52–100	50% Y^{3+} + 50% Er^{3+}	7.80	25.3	79.5
6	52–100	50% Y^{3+} + 50% Er^{3+}	7.10	25.5	75.6
7	52–100	50% Y^{3+} + 50% Er^{3+}	6.10	25.5	74.2

The experiments were performed at room temperature at an elution flow rate of 1.0 cm of column length per min. The effluent was collected in fractions of about 200 ml and analysed.

Analysis

Total ammonia in the eluant and in the effluent was determined by conventional distillation with NaOH.

Total DTPA in the eluant and uncomplexed DTPA in the effluent were determined with standard $ZnSO_4$ solution at pH 9 with Eriochrome Black T as indicator[15].

The molar concentration of Y^{3+}, Er^{3+}, or Y^{3+} + Er^{3+} in the effluent fractions is equivalent to the molar concentration of complexed DTPA, since the ratio between the lanthanides and DTPA in their chelates is 1 : 1.

The total concentration of DTPA in the effluent fractions was determined with standard $FeCl_3$ solution at pH 2 with sulphosalicylic acid as indicator[16]. From the difference between the total and uncomplexed DTPA, it was possible to calculate the molar concentration of the lanthanides.

In the mixed fractions, the sum of Y^{3+} + Er^{3+} was also determined gravimetrically by precipitation with oxalic acid and ignition to oxides[17]. Owing to the large difference between the molecular weights of Y_2O_3 and Er_2O_3, the percentages of each of them in the mixtures could be calculated from the chelometric and gravimetric determinations. This was possible for mixtures containing from 5 to 95 % of Y^{3+}.

RESULTS AND DISCUSSION

Reactions involved in the system

As mentioned above, the elution was performed using buffered ammonium–DTPA solutions of pH range 6.0–8.5. Within that range, Er^{3+} and Y^{3+} formed stable complexes with DTPA, their affinity for the ion exchanger was reduced, and NH^+_4, the eluting cation, was preferred. Thus, at the rear boundary of the absorbed band, the net reaction was:

$$\overline{M^{3+}} + nNH_4^+ + H_{5-n}DTPA^{n-} \rightleftharpoons \overline{3NH_4^+} + MDTPA^{2-} + (5-n)H^+ + (n-3)NH_4^+ \quad (1)$$

In the solution phase of the band, the following reactions occurred:

$$MDTPA^{2-} + H^+ \rightleftharpoons MHDTPA^- \quad (2)$$

$$MHDTPA^- + H^+ \rightleftharpoons MH_2DTPA \quad (3)$$

$$MH_2DTPA \rightleftharpoons M^{3+} + H_2DTPA^{3-} \quad (4)$$

$$H_{5-n}DTPA^{n-} + nH^+ \rightleftharpoons H_5DTPA \quad (5)$$

At the front edge, H_5DTPA was absorbed by the resin because of its amphoteric nature[18]:

$$\overline{2H^+} + H_5DTPA \rightleftharpoons \overline{H_7DTPA} \quad (6)$$

The reactions at the front edge were:

$$\overline{3H_7DTPA} + 2M^{3+} + 2H_2DTPA^{3-} \rightleftharpoons \overline{2M^{3+}} + 5H_5DTPA \quad (7)$$

$$\overline{H_7DTPA} + 2NH_4^+ \rightleftharpoons \overline{2NH_4} + H_5DTPA + 2H^+ \quad (8)$$

Elution curves and analysis of the lanthanide band

Flat-topped elution curves characteristic of displacement were obtained; as an example, that of experiment 4 (Table I) is given in Fig. 1. The lanthanide band was confined between resin beds in the form of NH^+_4 upward and H^+ downward. Unlike the occurrence usually observed in displacement development, the resin phase of the band contained NH_4^+ and H^+ in addition to the lanthanides. The compositions of the resin phase and of the effluent are given in Tables II and III.

The penetration of NH_4^+ and H^+ into the lanthanide band caused stretching of the band. After equilibrium was reached, the length of the stretched band

remained constant. It was possible to measure visually the lengths of the loaded and of the stretched bands, and these were in good agreement with the calculated values.

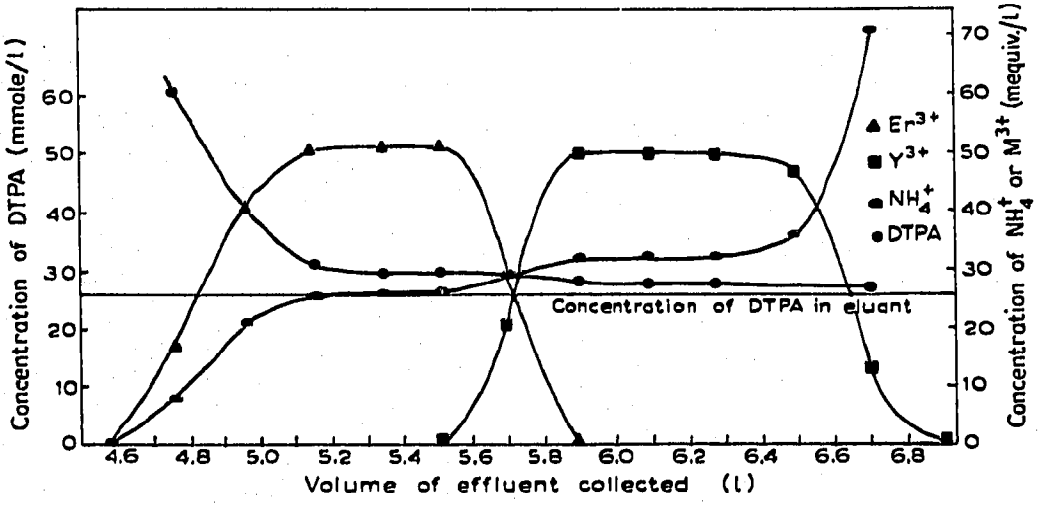

Fig. 1. Separation by displacement development of $Y^{3+} - Er^{3+}$ mixture (Experiment No. 4, Table I).

TABLE II

COMPOSITION OF THE AQUEOUS AND RESIN PHASES OF Y^{3+} AT EQUILIBRIUM

Experiment No.	*Aqueous phase*			*Resin phase (eq. fraction)*		
	Y^{3+} (*mequiv/l*)	NH_4^+ (*mequiv/l*)	*Chr* (*mmole/l*)	$\overline{Y^{3+}}$	$\overline{NH_4^+}$	$\overline{H^+}$
1	51.6	30.6	27.5	0.594	0.353	0.053
2	49.2	30.8	28.6	0.571	0.357	0.072
4	49.8	32.0	27.3	0.587	0.377	0.035
5	44.1	30.7	27.0	0.564	0.393	0.043
6	41.3	30.4	27.8	0.541	0.398	0.060
7	39.6	29.5	27.7	0.539	0.401	0.060

TABLE III

COMPOSITION OF THE AQUEOUS AND RESIN PHASES OF Er^{3+} AT EQUILIBRIUM

Experiment No.	*Aqueous phase*			*Resin phase (eq. fraction)*		
	Er^{3+} (*mequiv/l*)	NH_4^+ (*mequiv/l*)	*Chr* (*mmole/l*)	$\overline{Er^{3+}}$	$\overline{NH_4^+}$	$\overline{H^+}$
3	51.3	25.9	28.0	0.623	0.314	0.063
4	51.0	25.8	29.6	0.604	0.306	0.090
5	43.7	23.8	31.0	0.554	0.302	0.144
6	41.0	23.6	32.3	0.524	0.302	0.174
7	38.5	21.9	32.8	0.513	0.292	0.195

The band stretching of yttrium and erbium in the elution of the pure elements was the same, within experimental error, as that obtained from elution of their

mixtures. The average penetration of $NH_4^+ + H^+$ was 40 %, NH_4^+ being smaller in the case of Er, probably because of its higher stability constant ($\log K_{Er\ DTPA} = 22.74$, $\log K_{Y\cdot DTPA} = 22.05$). During elution, the tendency of reaction (1) to proceed to the right for yttrium exceeds that for erbium, consequently less NH_4^+ will appear in the Er-resin phase. The penetration of H^+ was larger for Er; because of the higher stability of Er-DTPA, the concentration of the uncomplexed erbium ions in the solution phase is smaller. Thus the tendency for reaction (7) to proceed to the right is greater in the case of yttrium than erbium and more H^+ will remain in the Er-resin phase.

The length of the band in the steady state depended on the pH of the eluant, since the penetration of $NH_4^+ + H^+$ was greater at lower pH. The length of the Y stretched band was 1.70 times that of the original band at pH 8.15, increasing to 1.85 times at pH 6.10; that of Er was 1.65 times longer at pH 8.15, increasing to 1.95 times at pH 6.10.

HAGIWARA AND ŌKI[10] reported that the penetration of $NH_4^+ + H^+$ with HEDTA as eluant was 7.5–60.7 % in the pH range 8.8–4.9, and the maximum concentration of the lanthanides was 36.9 mequiv./l. In our case, with DTPA as eluant, maximum concentrations of Y and Er higher than 50 mequiv./l were obtained. Higher concentrations were obtained in the pH range 8.2–8.5, which is preferable from a practical point of view.

Concentrations of NH_4^+ and M^{3+} in the resin phase were calculated from the analysis of the effluent fractions according to the following relation[4]:

$$\frac{[NH_4^+]}{\overline{NH_4^+}} = \frac{[M^{3+}]}{\overline{M^{3+}}} = \frac{NH_{4T}}{Q}$$

where $[NH_4^+]$ and $[M^{3+}]$ are concentrations in the effluent; $\overline{NH_4^+}$ and $\overline{M^{3+}}$ are equivalent fractions in the resin band; NH_{4T} it the total concentration of NH_4^+ in the eluant; and Q is the capacity of the resin.

In all the experiments, it was found that DTPA was more concentrated in the effluent than in the eluant by $[x]$ moles/l, indicating the presence of H^+ ions in the resin phase. The resin-phase H^+ concentration was calculated according to the following expression, since DTPA is bound to two SO_3H groups[18] ($[H^+] = 2[x]$):

$$\frac{2[x]}{\overline{H^+}} = \frac{NH_{4T}}{Q}$$

The sum of the cations in the effluent was in good agreement with the NH_4^+ concentration in the eluant.

$$[NH_4^+] + [M^{3+}] + 2[x] = NH_{4T}$$

Balance of the ions in the effluent against those in the eluant

The ions in the effluent were NH_4^+, H^+, MH_2DTPA, $MHDTPA^-$, $MDTPA^{2-}$, H_5DTPA, H_4DTPA^-, H_3DTPA^{2-} and H_2DTPA^{3-}.

The ions in the eluant were NH_4^+, H_3DTPA^{2-} and H_2DTPA^{3-}.

The following notation is used: Ch_T = total concentration of DTPA in the

eluant; NH_4T = total concentration of NH_4^+ in the eluant; and H_T = total concentration of H in the eluant. Molar concentrations of the ionic species in the effluent are indicated by brackets.

The ion balance is:

$$Ch_T = [H_5DTPA] + [H_4DTPA^-] + [H_3DTPA^{2-}] + [H_2DTPA^{3-}] + [MH_2DTPA] + [MHDTPA^-] + [MDTPA^{2-}] - [x]$$

$$[H_T] = 5[H_5DTPA] + 4[H_4DTPA^-] + 3[H_3DTPA^{2-}] + 2[H_2DTPA^{3-}] + 2[MH_2DTPA] + [MHDTPA^-]$$

$$NH_4T = [NH_4^+] + 3[MH_2DTPA] + 3[MHDTPA^-] + 3[MDTPA^{2-}] + 2[x]$$

$$[NH_4^+] = [H_4DTPA^-] + 2[H_3DTPA^{2-}] + 3[H_2DTPA^{3-}] + [MHDTPA^-] + 2[MDTPA^{2-}]$$

$$H_T = 5Ch_T - NH_4T$$

$$H_T = [H_T] - 7[x]$$

The concentration of H_T in the effluent is greater by $7[x]$ than that in the eluant, since DTPA is bound as $(RH)_2H_5DTPA$. This is in good agreement with the experimental results (Table IV) and shows that the H^+ ions in the lanthanide band originated from the retaining ion.

TABLE IV

THE BALANCE OF HYDROGEN IN THE EFFLUENT AND IN THE ELUANT

Experiment No.	H_T *in the eluant (mmole/l)*	$[H_T]$ *in the Y effluent*	$[H_T]+7[x]$	$[H_T]$ *in the Er effluent*	$[H_T]+7[x]$
1	38.3	55.3	39.2	—	—
2	41.3	63.0	41.3	—	—
3	44.0	—	—	62.9	44.7
4	44.1	51.7	44.2	71.2	44.6
5	47.0	66.2	48.3	87.5	47.6
6	51.9	97.3	51.2	96.9	49.3
7	53.3	66.4	54.0	103.6	52.5

Height equivalent to a theoretical plate values

The influence of the particle size of the resin on the efficiency of separation, with all other conditions constant, was studied.

The efficiency of separation and the shape of the boundaries depend on the height equivalent to a theoretical plate (HETP). The HETP is a function of the time of contact of the eluant with the resin and the rate of exchange of the species, and hence it depends upon the flow-rate, the concentration of the eluant, the particle size of the resin, and other operating conditions.

The mixed regions of Er–Y separations, performed on resins of particle size 20–50 mesh and 52–100 mesh, are represented in Figs. 2 and 3. The HETP was calculated by the following equation[6]:

$$\log r_m = \frac{\log \alpha_Y^{Er}}{HETP} L + \log r_0$$

where r_m = the ratio Y/Er at the rear edge; r_0 = the ratio Y/Er at the front edge; and L = the distance from the rear of the hindmost plate to the edge of the foremost plate being considered. Log α_Y^{Er} is 4.9 at room temperature.

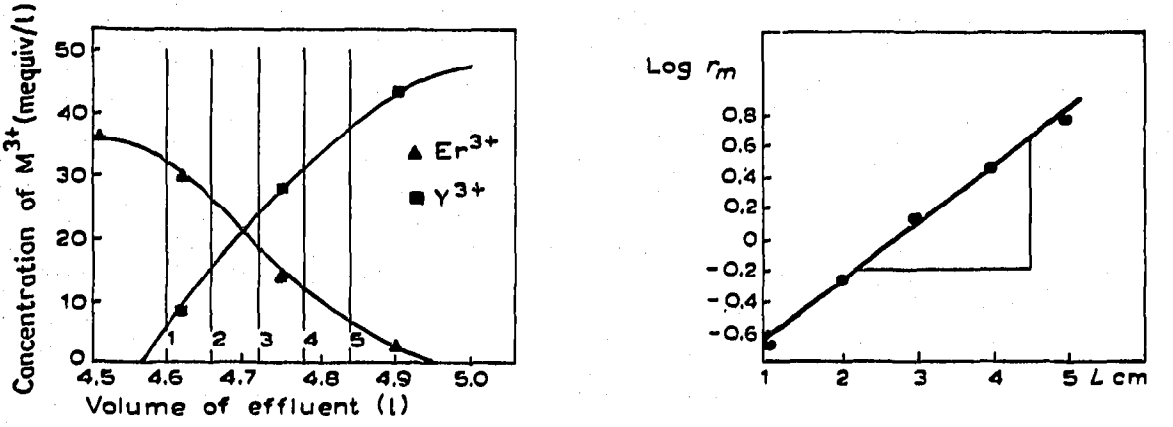

Fig. 2. Calculation of HETP from Experiment No. 2, Table I. (1 cm column length = 60 ml effluent.)

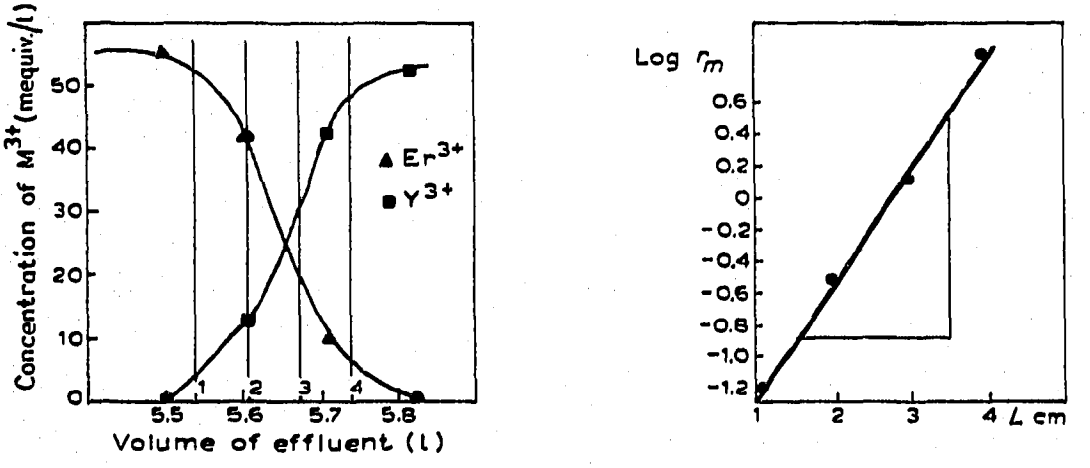

Fig. 3. Calculation of HETP from Experiment No. 4, Table I. (1 cm column length = 65 ml effluent.)

The HETP decreased from 1.94 cm to 0.99 cm with diminishing particle size. Thus, in the separations discussed, using a smaller particle is an important practical means of improving the separation without lengthening the time.

The great influence of the grain size on the HETP suggests that the described ion-exchange process with a DTPA eluant was controlled by particle diffusion as the rate-determining step.

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