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The Ion Exchange of a Mixture of Er and Tm with HEDTA

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Under experimental conditions similar to those in the elution system of the rare earth with a dilute HEDTA eluant, the Er-Tm separation factor has been found in the system of HEDTA and Dowex 50W, X-8, 50—100 mesh. The values for this pair, 1.57 at 25°C and 1.63 at 60°C were in agreement with the values calculated from the stability constants of the rare earth-HEDTA chelates. Further, an equimolar mixture of Er and Tm has been eluted with a 0.015M HEDTA solution buffered with ammonium hydroxide. Under the present experimental conditions, the adsorption band of each rare earth reached a steady state after it had moved down through the hydrogen-retaining bed to a distance several times the initial band length. Several series of experimental data were used for analyses of the adsorption band from the point of view of rate theory. It was concluded that the present ion-exchange process with a HEDTA eluant was controlled by film diffusion as the rate-determining step. The plate-height values were also found to be functions of the flow rate.

In the ion-exchange separation of the rare-earth series on a commercial scale, EDTA[1] (ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid, H_4Y) and HEDTA[2] [*N*′-(2-hydroxyethyl)-ethylenediamine-*N*,*N*,*N*′-triacetic acid, H_3Ch] eluants buffered with ammonium hydroxide has been employed with marked success. In order to make a theoretical treatment of the elution system of the rare earth by HEDTA complexation, it is necessary to find an accurate separation factor for adjacent rare-earth pairs and to understand the mechanism of the separation of the rare-earth group under steady-state conditions.

In connection with the above ion-exchange

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[1] J. E. Powell and F. H. Spedding, *Trans. Met. Soc. AIME*, **215**, 457 (1959).

[2] J. R. Morton and D. B. James, *J. Inorg. Nucl. Chem.*, **29**, 2997 (1967).

system, the formation of the H_5Ch^{2+}-band[3] during elution was studied; the adsorption isotherm was also discussed in detail. Theoretical treatments[4] of the ion-exchange column involving the rare-earth band with dilute HEDTA were made in order to clarify the elution mechanism of the rare-earth species. Further, one of the present authors previously reported the separation factors[5] for adjacent rare-earth pairs, such as Er-Tm, Dy-Ho, Y-Dy, Tb-Y, Eu-Gd and Sm-Nd, in the presence of EDTA, significant differences were then found in them between the values calculated from the stability constants of the rare earth-EDTA chelates and the measured values. Thus we arrived at the conclusion that, except in special cases, the separation factor should be measured experimentally under conditions similar to those in a practical elution system containing a mixture of rare earths.

One of the purposes in this work is to find the Er-Tm separation factor in the presence of HEDTA at different temperatures, and to use these values for analyzing the elution system involving the Er-Tm pair. Another purpose is to analyze the elution system of a rare-earth mixture under steady-state conditions so that a comparison of both dilute and concentrated eluants can be made.

Separation Factor for the Er-Tm Pair in the Presence of HEDTA

The separation factor (α) of an adjacent rare-earth pair (Ln_1-Ln_2) in the presence of a chelating agent, such as EDTA (H_4Y) or HEDTA (H_3Ch), can be estimated using the values of the stability constants of the Ln-chelates.

In the ion-exchange system involving adjacent rare-earths and HEDTA, the main exchange reaction is written by:

$$\overline{Ln_1}^{3+} + Ln_2Ch \rightleftarrows \overline{Ln_2}^{3+} + Ln_1Ch$$

where the barred symbols refer to the resin phase, and the unbarred symbols, the aqueous phase. The exchange quotient (or selectivity coefficient) is expressed by:

$$K' = \frac{[\overline{Ln_2}^{3+}][Ln_1Ch]}{[\overline{Ln_1}^{3+}][Ln_2Ch]} \tag{1}$$

where the brackets represent the concentrations of related species. In the elution system with a dilute eluant of HEDTA buffered with ammonium hydroxide, the following species are present in the aqueous phase of the rare-earth band:

$LnCh^0$, Ln^{3+}, NH_3^+, H^+, H_3Ch, H_2Ch^-, HCh^{2-}, Ch^{3-}.

Whether a chelating agent is present in the system or not, $\alpha_{Ln_2}^{Ln_1}$ is defined as the concentration ratio of the two elements:

$$\alpha_{Ln_2}^{Ln_1} = \frac{[\overline{Ln_{1T}}][Ln_{2T}]}{[Ln_{2T}][Ln_{1T}]} \tag{2}$$

where the T's indicate the total concentrations of indicated rare earths in both phases. Since the rare earth is present as the tripositive ion in the resin, Eq. (2) is expressed in this form:

$$\alpha_{Ln_2}^{Ln_1} = \frac{[\overline{Ln_1}^{3+}][Ln_{2T}]}{[Ln_2^{3+}][Ln_{1T}]} \tag{3}$$

Considering the presence of Ln^{3+} and $LnCh^0$ as the Ln-species, we have:

$$\alpha_{Ln_2}^{Ln_1} = \frac{[\overline{Ln_1}^{3+}]\{[Ln_2^{3+}]+[Ln_2Ch]\}}{[Ln_2^{3+}]\{[Ln_1^{3+}]+[Ln_1Ch]\}} \tag{4}$$

Introducing $[LnCh]=K_{LnCh}\,[Ln^{3+}][Ch^{3-}]$ into (4), we have:

$$\alpha_{Ln_2}^{Ln_1} = \frac{[\overline{Ln_1}^{3+}][Ln_2^{3+}]\{1+K_{Ln_2Ch}[Ch^{3-}]\}}{[\overline{Ln_2}^{3+}][Ln_1^{3+}]\{1+K_{Ln_1Ch}[Ch^{3-}]\}} \tag{5}$$

In the above expressions, K_{LnCh} indicates the stability constant of LnCh and the brackets represent the molarities of the indicated species. As $[Ln^{3+}]$ is very small compared with [LnCh], we have:

$$\alpha_{Ln_2}^{Ln_1} = \frac{[\overline{Ln_1}^{3+}][Ln_2^{3+}]K_{Ln_2Ch}}{[\overline{Ln_2}^{3+}][Ln_1^{3+}]K_{Ln_1Ch}} = K_{Ln_2}^{Ln_1}\frac{K_{Ln_2Ch}}{K_{Ln_1Ch}} \tag{6}$$

When the exchange quotient, $K_{Ln_2}^{Ln_1}$, is almost equal to unity, one obtains the following approximation:

$$\alpha_{Ln_2}^{Ln_1} \cong \frac{K_{Ln_2Ch}}{K_{Ln_1Ch}} \tag{7}$$

Surls and Choppin[6] studied the ion-exchange equilibrium between Ln^{3+} and the hydrogen form of Dowex 50 using radioactive Ln-nuclides and perchloric acid; they observed no difference in the distribution coefficient ($K_d=[\overline{Ln}^{3+}]/[Ln^{3+}]$) between the adjacent rare earths. Consequently, $K_{Ln_2}^{Ln_1}$ is approximately equal to unity. According to their study, the mean K_d-values of 2.20×10^5 and 2.22×10^5 were obtained for the Er-H and Tm-H systems respectively. It can be decided from these data that K_{Tm}^{Er} is approximately equal to unity.

In the presence of HEDTA, the Er-Tm separation factor is expressed by Relation (7):

$$\alpha_{Tm}^{Er} \cong \frac{K_{TmCh}}{K_{ErCh}} \tag{8}$$

It may be said qualitatively that $\alpha_{Ln_2}^{Ln_1}$ in the system containing a chelating agent is independent of the composition of the aqueous and resin phases and

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3) Z. Hagiwara and H. Ōki, This Bulletin, to be published.

4) Z. Hagiwara, *J. Inorg. Nucl. Chem.*, **31**, 2933 (1969)

5) M. Noguchi, A. Yoshifuji and Z. Hagiwara, This Bulletin, **42**, 2286 (1969).

6) J. P. Surls, Jr., and G. R. Choppin, *J. Am. Chem. Soc.*, **79**, 855 (1957).

of the type of exchanger, and that the $\alpha^{Ln_1}_{Ln_2}$-value is decided only by the ratio of the stability constants of the Ln-chelates. However, it is recommended the α-values should be measured directly, for the reason described in the previous paper.[5] In the present work, the α-values were measured at 25 and 60°C using the batch method and their temperature dependency was investigated.

Experimental

1) Experimental Method for Determining the Separation Factor. *Preparation of Aqueous Phase.* Erbium and thulium were eluted separately using a 0.015 M HEDTA eluant buffered with ammonium hydroxide (pH=7.5) and using a hydrogen-retaining bed with Dowex 50W, X-8, 100—200 mesh. The elution conditions were the same as those in Exp. No. 12 and 13 in the previous paper;[7] the rare-earth eluates from the exchange column were employed as the aqueous phase in the equilibrium experiments. As the composition of the Er-eluate obtained by this elution was almost identical with that of the Tm-eluate, it was very easy to prepare aqueous solutions having different ratios of Er to Tm but without any other notable change in constituents.

Preparation of the Rare Earth and Ammonium Types of Resins. By passing the load solutions, such as $ErCl_3$, $TmCl_3$ and NH_4Cl, into an ion-exchange column containing Dowex 50W, X-8, 50—100 mesh in the hydrogen form, the erbium, thulium, and ammonium types of resins were prepared.

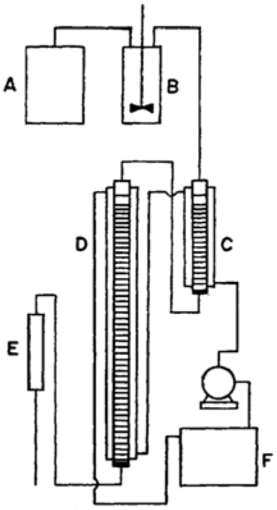
Equilibrium Experiment. A total of about 5 g of the prepared resins was taken; for weighing, the ammonium and Ln-types of resin were taken into the required portions, so that the constituents in the resin phase would become a 0.8 equivalent fraction of the sum of $\overline{Er}^{3+}$ and $\overline{Tm}^{3+}$ and a 0.2 equivalent fraction of $\overline{NH_4}^{+}$. Further, the ratio[*1] of Er to Tm in the resin was adjusted to give a α^{Er}_{Tm}-value of approximately 1.6, as was to be expected from the α^{Er}_{Tm}-values in Table 3. After the resin mixture (5 g) had been equilibrated with a total volume of 300 m*l* of the erbium and thulium eluates at a constant temperature of either 25°C or 60°C for 48 hr in a thermostat, the two phases were separated and analyzed.

Analytical Method. The analytical methods employed for the determination of the various species present in the two phases were the same as those given in the literature,[4] while the rare-earth mixtures were determined spectrophotometrically using a Shimadzu QR-50 spectrophotometer and a 1.00-cm cell. The samples of the rare-earth oxides obtained from the two phases were placed in a volumetric flask and dissolved with a slight excess of 1 M $HClO_4$ under heating. After dilution to a definite volume, the resulting solutions were analyzed at the following wavelengths:

Rare earth	λ (mμ)	Slit width (mm)	Molecular absorption coefficient (*l*/mol·cm)
$ErClO_4$	379.0	0.0240	6.55
$TmClO_4$	683.0	0.0135	2.50

A 1.00-cm quartz cell was used.

2) Experimental Method of the Elution of the Er-Tm Mixture. As the experimental method[4] for the elution at 60°C has already been reported, only the outline will be given here. In the experiments, 22-mm I.D. columns made of Pyrex glass jacketed with 60-mm-I.D. columns were used. At the bottom of each column, a sintered glass disk was fixed in order to support the resin bed containing Dowex 50W, X-8, 50—100 mesh. The column was kept at a certain temperature by circulating water through the jacket columns from the thermostat. The jacket column with an equimolar mixture of Er and Tm was connected to the main column containing the hydrogen form of Dowex 50W, X-8, 50—100 mesh. The connection was made by the aid of a vinyl tube, whose outside was covered with shielding material. In elution, the HEDTA eluant (0.015 M) was first passed through the pre-heater equipped with a stirrer; here the solution temperature was raised in order to remove any dissolved air. Then the eluant entered the top of the rare-earth adsorption column. The eluate from the retaining column was cooled through the condenser and collected into small fractions by means of a fraction collector. The experimental apparatus is represented in Fig. 1.



A Eluant
B Preheater
C R.E. Adsorption column
D Retaining column
E Cooler
F Thermostat

Fig. 1. Schematic representation of apparatus.

Results and Discussion

Separation Factor for the Er-Tm Pair. The compositions of the two phases at equilibrium

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[7] Z. Hagiwara and H. Ōki, *J. Inorg. Nucl. Chem.*, to be published.

[*1] If the composition of the aqueous phase employed for the equilibrium experiment is known, the ratio of Er to Tm in the resin can be determined on the assumption that $\alpha^{Er}_{Tm} \cong 1.6$ (see Table 3).

TABLE 1. COMPOSITION OF THE AQUEOUS AND RESIN PHASES AT EQUILIBRIUM (25°C)

Exp. No.	Aqueous phase (mmol/l)						Resin phase (eq. fraction)					α^{Er}_{Tm}
	Er_T	Tm_T	(Er_T+Tm_T)	NH_{4T}	Ch_T	pH	$\overline{Er^{3+}}$	$\overline{Tm^{3+}}$	$(\overline{Er^{3+}}+\overline{Tm^{3+}})$	$\overline{NH_4^+}$	$\overline{H^+}$	
E-3-1	0.96	7.83	8.79	4.92	15.20	3.29	0.1094	0.6551	0.7645	0.1741	0.0614	1.36
E-3-2	1.95	6.81	8.76	5.03	15.11	3.29	0.2418	0.5216	0.7634	0.1739	0.0627	1.62
E-3-3	3.28	5.40	8.68	5.09	15.02	3.30	0.3805	0.3805	0.7610	0.1752	0.0637	1.65
E-3-4	5.01	3.71	8.72	5.03	15.07	3.31	0.5206	0.2409	0.7615	0.1732	0.0653	1.60
E-3-5	6.76	1.98	8.74	5.29	15.14	3.33	0.6424	0.1160	0.7584	0.1749	0.0668	1.62

Ave.: 1.57

TABLE 2. COMPOSITION OF THE AQUEOUS AND RESIN PHASES AT EQUILIBRIUM (60°C)

Exp. No.	Aqueous phase (mmol/l)						Resin phase (eq. fraction)					α^{Er}_{Tm}
	Er_T	Tm_T	(Er_T+Tm_T)	NH_{4T}	Ch_T	pH	$\overline{Er^{3+}}$	$\overline{Tm^{3+}}$	$(\overline{Er^{3+}}+\overline{Tm^{3+}})$	$\overline{NH_4^+}$	$\overline{H^+}$	
E-4-1	0.99	8.10	9.09	4.72	15.35	3.25	0.1021	0.6428	0.7449	0.1812	0.0740	1.30
E-4-2	1.95	7.12	9.07	4.72	15.34	3.24	0.2371	0.4922	0.7293	0.1791	0.0916	1.76
E-4-3	3.30	5.71	9.01	4.72	15.29	3.25	0.3802	0.3737	0.7539	0.1817	0.0643	1.76
E-4-4	4.95	4.00	8.95	4.73	15.23	3.25	0.5225	0.2325	0.7550	0.1853	0.0597	1.82
E-4-5	6.93	1.97	8.90	4.75	15.19	3.30	0.6451	0.1199	0.7650	0.1806	0.0544	1.53

Resin: Dowex 50W, X-8, 50—100 mesh

Ave.: 1.63

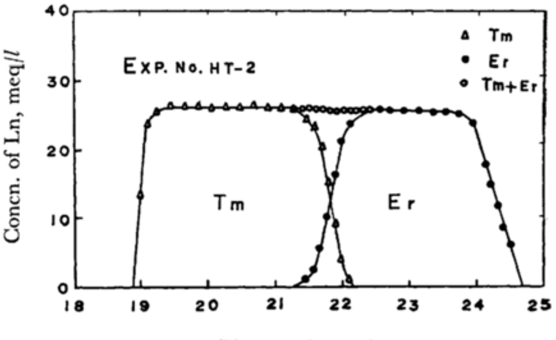


Fig. 2. Elution curve of the Er-Tm pair under a steady state condition.

are listed in Tables 1 and 2. The α^{Er}_{Tm}-values were calculated by the use of Eq.(2):

$$\alpha^{Er}_{Tm} = [\overline{Er_T}][Tm_T]/[\overline{Tm_T}][Er_T]$$

Table 1 and 2 indicate that when the total composition of rare earths in the resin and aqueous phases shows an almost constant value [see (Er_T+Tm_T) and $(\overline{Er^{3+}}+\overline{Tm^{3+}})$], the variation in α with the Er/Tm ratio and temperature is not remarkable. The average α^{Er}_{Tm} -values were 1.57 at 25°C and 1.63 at 60°C. The stability constants of the Ln-HEDTA chelates have been found by several investigators. Introducing these data into Eq.(8), the Er-Tm separation factors were calculated as tabulated in Table 3, in which the agreement is excellent with the α^{Er}_{Tm}-values calculated from the data of Spedd-

TABLE 3. CALCULATED VALUES OF THE Er-Tm SEPARATION FACTOR IN THE PRESENCE OF HEDTA

Investigator	Method	Measured condition		log K_{ErCh}	log K_{TmCh}	$\alpha^{Er}_{Tm}=\frac{K_{TmCh}}{K_{ErCh}}$
Spedding et al.[8]	pH-titration	$\mu=0.1$	(25°C)	15.17	15.38	1.62
	polarograph	$\mu=0.1$	(25°C)	15.4	15.5	1.3
Moeller and Ferrus[9]	pH-titration	$\mu=0.1$	(15°C)	15.45	15.66	1.62
			(20°C)	15.45	15.64	1.58
			(25°C)	15.42	15.59	1.48
			(30°C)	15.41	15.62	1.62
			(35°C)	15.46	15.72	1.82
			(40°C)	15.42	15.69	1.86
Powell and Mackey[10]	Hg-electrode	$\mu=0.1$	(20°C)	15.61	16.00	2.45

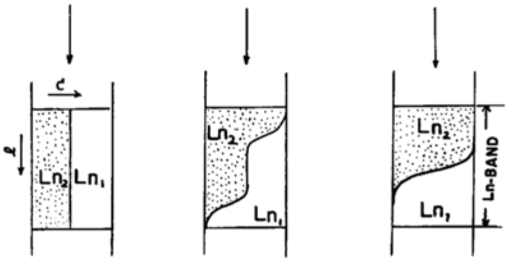
TABLE 4. EXPERIMENTAL CONDITIONS USED FOR THE ELUTIONS OF EQUIMOLAR MIXTURE OF Er AND Tm

Exp. No.	Composition of eluant			Elution temp. °C	Flow rate cm/min	Dimention of bed		Band length*
	$\widetilde{Ch}_T$ mol/l	$\widetilde{NH}_{4T}$ mol/l	pH			Rare Earth bed cm	Retaining bed cm	
HT-2	0.01502	0.03096	7.44	60	0.53	2.2×18.0	2.2×85.2	4.7
HT-4	0.01500	0.03092	7.44	60	1.58	2.2×18.0	2.2×85.9	4.8
HT-5	0.01500	0.03050	7.43	60	2.11	2.2×18.0	2.2×85.9	4.8
HT-6	0.01500	0.03075	7.47	60	2.63	2.2×18.0	2.2×85.9	4.8
HT-9	0.01500	0.04248	9.04	60	1.58	2.2×17.3	2.2×85.9	5.0
RT-1	0.01500	0.03076	7.43	25	1.05	2.2×17.6	2.2×85.5	4.9

* Band length=length of retaining bed used/length of rare earth bed
Resin: Dowex 50W, X-8, 50—100 mesh
I.D.-22 mm-column

ing[8] and Moeller.[9] The α-value calculated from the data of Powell and Mackey[10] seems, however, to be too large. In spite of measurements at different ionic strengths, the $\alpha^{\mathrm{Er}}_{\mathrm{Tm}}$-value observed at 25°C is in good agreement with that calculated Spedding's data.[8]

Elution Results. After the break-through of rare earth, the total concentration of the rare earth in the eluate was plotted against the eluate volume. As may be seen in Fig. 2 (Exp. No. HT-2), the total amount of Er and Tm in the eluate was kept almost constant; an elution curve with a flat top for each element was obtained over a fairly wide range of eluate volume. After the rare-earth band had been moved down the hydrogen-retaining bed a distance corresponding to about 5 band lengths,[*2] a steady state was reached. In such a steady state, the mixed rare-earth boundary with Er and Tm has a pattern with a definite gradient of composition; further progress in the separation of these species can not be expected by increasing the elution distance. The elution curves obtained under different flow rates did not differ from the elution curve shown in Fig. 2. However, tailing and channelling were increased to some degree with the increase in the flow rate.



(a) (b) (c)

Fig. 3. Change in the composition of rare earth during the ion exchange process.

When the rare-earth-saturated band containing equimolar adjacent rare earths (Fig. 3-a) is displaced down the hydrogen-retaining bed with the HEDTA eluant buffered with ammonium hydroxide in the beginning of the elution step, ammonium and hydrogen ions in the eluant leak through the rare-earth band until the band expands to its equilibrium band length. During this early step, Ln_1 and Ln_2 begin to be separated at the boundary, the degree of separation is gradually increased, as Fig. 3-b shows. However, the analysis of the exchange system on the basis of the rate theory seems to be difficult in this step, because complicated phenomena are still occurring in the rare-earth band, with Ln, NH_4, H, and HEDTA species included in both phases. With further progress in elution, a steady state is finally attained, as may be seen in Fig. 3-c, in which the composition of the Ln_1-Ln_2 boundary has been fixed to a definite gradeint, as has been mentioned above. Under steady-state conditions (Fig. 3-c), all the other species except the rare earths are considered to be distributed homogenously over the entire range of the band. This may be explained by the fact that, after the attainment of a steady state, the exchange system is finally fixed by the composition of the eluant itself, as has been illustrated in a previous paper.[7] In other words, when the composition of the eluant and the exchange constants related to the system are known, all the constituents in the resin and aqueous phases of each pure rare-earth band formed during elution can be calculated as functions of the eluant composition on the assumption of a true equilibrium for the ion-exchange

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8) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *J. Am. Chem. Soc.*, **78**, 34 (1956).

9) T. Moellor and R. Ferrus, *J. Inorg. Nucl. Chem.*, **20**, 261 (1961).

10) J. E. Powell and J. L. Mackey, *Inorg. Chem.*, **1**, 418 (1962).

[*2] The minimum number of displacements (ν) of the mixed rare-earth band needed to carry out separation is about 2.1 using the relation of $\nu=(1+\varepsilon N_0)/\varepsilon$, where N_0 is the mole fraction of Er in the mixture of Er and Tm being separated, and where N_0 and ε are 0.5 and 0.63 respectively in this run. Therefore, the value of *ca.* 5 band lengths (see Table 4) is enough to realize a steady-state elution.

process. The effective separation of rare earths by ion exchange is based mainly on differences in K_{LnCh} between the lanthanons. However, these differences are not very large between the adjacent rare-earth pairs. Further, significant differences in such exchange constants as $K_{\mathrm{NH_4}}^{\mathrm{Ln}}$ and $K_{\mathrm{H}}^{\mathrm{Ln}}$ cannot be expected between the adjacent pairs. Considering only the presence of rare earth as the cationic species in the rare-earth band, and taking only the reaction of Eq. (1) as important, the $\mathrm{Ln_1}$-band can be assumed to be displaced by $\mathrm{Ln_2}$(see Fig. 3-c; $\mathrm{Ln_1}$=Tm and $\mathrm{Ln_2}$=Er in this study).

Analysis of the Ion-Exchange System by the Rate Theory. For an elution system involving the rare earths under steady-state conditions, the analysis on the basis of the rate theory[4,11,12] is possible using the experimental data related to the mixed region with adjacent rare earths.

In the ion-exchange process, the rate of particle and film-diffusion may be expressed by the following relation.[13] For particle-diffusion control, we have:

$$\left(\frac{\partial \bar{X}_i}{\partial t}\right)_Z = \frac{\bar{D}}{0.071 r_0^2}(\bar{X}_i^* - \bar{X}_i) \tag{9}$$

and for film-diffusion control:

$$\left(\frac{\partial \bar{X}_i}{\partial t}\right)_Z = \frac{3D}{2\delta r_0}(C_i - C_i^*) \tag{10}$$

The r_0 and δ symbols indicate the radius of the resin particle and the film thickness respectively, while $\bar{D}$ and D express the self-diffusion or interdiffusion coefficient in the resin and aqueous phases. The symbol C_i represents the concentration of species i in the interstitial solution, and $\bar{X}_i$, the amount of species i in the resin per unit volume of the resin bed. The asterisks refer to equilibrium; for example, C_i^* denotes the concentration of the interstitial solution in equilibrium with $\bar{X}_i$. The symbol Z represents the distance from a reference point in the column.

From Eqs. (9) and (10), the following relations can finally be deduced. When particle diffusion is the rate-limiting step, one obtains:

$$Z(x_{\mathrm{Ln_2}}) = H_p\left\{-\frac{1}{\alpha-1}\ln x_{\mathrm{Ln_2}} + \frac{\alpha}{\alpha-1}\ln(1-x_{\mathrm{Ln_2}}) + 1\right\} \tag{11}$$

where:

$$H_p = v_b r_0^2/14\bar{D}$$

For film-diffusion control, one obtains:

$$Z(x_{\mathrm{Ln_2}}) = H_f\left\{-\frac{\alpha}{\alpha-1}\ln x_{\mathrm{Ln_2}} + \frac{1}{\alpha-1}\ln(1-x_{\mathrm{Ln_2}}) - 1\right\} \tag{12}$$

where:

$$H_f = 2\delta r_0 v_b \bar{X}/3DC$$

In Eqs. (11) and (12), $Z(x_{\mathrm{Ln_2}})$ indicates the distance of the plane with a concentration of $x_{\mathrm{Ln_2}}$ from the gravity center of a rare-earth boundary containing $\mathrm{Ln_1}$ and $\mathrm{Ln_2}$, and α is the separation factor. The symbol v_b represents the linear velocity for the movement of the rare-earth band; $\bar{X}$, the total amount of species in the resin phase per unit volume of bed, and C, the total concentration of counter ions. Further, H_p and H_f indicate the plate height due to particle diffusion and film diffusion. Using Eqs. (11) and (12), the plots of $x_{\mathrm{Ln_2}}$ with respect to Z give the shape of the boundary in a steady state.

In particle-diffusion control, the shapes of the boundary with $\mathrm{Ln_1}$ and $\mathrm{Ln_2}$ are represented in Fig. 4, in which some relationships between $x_{\mathrm{Ln_2}}$ and Z may be seen at the α-values of 1.2, 1.5, 2, and 3 on the assumption that H_p=0.5 cm. For film-diffusion control, similar relations are represented

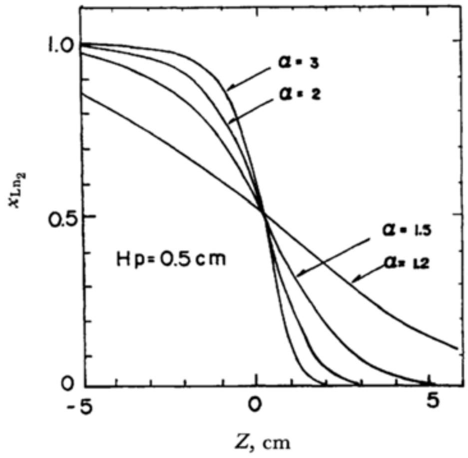

Fig. 4. Relationship between $x_{\mathrm{Ln_2}}$ and Z in particle-diffusion control.

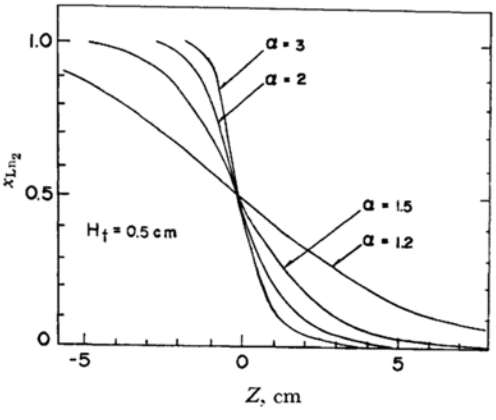

Fig. 5. Relationship between $x_{\mathrm{Ln_2}}$ and Z in film-diffusion control.

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in Fig. 5. As may be clear from the above figures, under steady-state conditions, the concentration gradient of the mixed region is decided by the value of either H_p or H_f as well as by the α-value, and a sharp boundary can be expected if we decrease the plate height. In general, some leakage of Ln_2 is observed in film-diffusion control and some tailing of Ln_1 in particle-diffusion control.

Employing the experimental data obtained in the elution of the Er-Tm mixture, the analysis of the overlap region in a steady state was performed on the basis of the rate theory. The following values were used as the Er-Tm separation factors in a system with HEDTA:

$$\alpha^{\mathrm{Er}}_{\mathrm{Tm}} = 1.57 \text{ at } 25°\mathrm{C};\ \alpha^{\mathrm{Er}}_{\mathrm{Tm}} = 1.63 \text{ at } 60°\mathrm{C}$$

Introducing them into Eq. (12), we obtain the following equations:

for 25°C-elution:

$$Z(x_{\mathrm{Er}}) = H_f\{-6.34 \log x_{\mathrm{Er}} + 4.04 \log (1-x_{\mathrm{Er}}) - 1\} \tag{13}$$

and for 60°C-elution:

$$Z(x_{\mathrm{Er}}) = H_f\{-5.96 \log x_{\mathrm{Er}} + 3.66 \log (1-x_{\mathrm{Er}}) - 1\} \tag{14}$$

where $Z(x_{\mathrm{Er}})$ indicates the distance of the plane with a concentration of x_{Er} from the gravity center of the Er-Tm overlap region. The dimensions of x_{Er} and Z are expressed in the equivalent fraction and in centimeters respectively. Further, the separation factor is assumed to be constant throughout the Er-Tm overlap zone. The plate-height contribution due to film-diffusion can be found from the cruve-fitting method using Eqs. (13) and (14); the experimental data are represented graphically in Figs. 6 and 7. As the figures show, most of the experimental data fall on the theoretical line. On the contrary, the elution results in this study cannot be explained with the aid of Eq. (11). It is obvious that the elution system of the rare earth with a dilute HEDTA, such as 0.015M as the total anionic species of HEDTA ($\widetilde{\mathrm{Ch}}_T$) and with

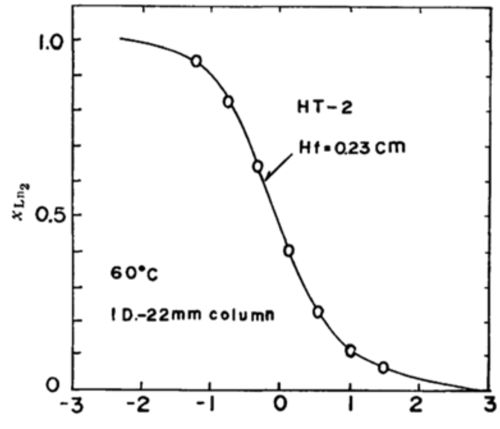

Fig. 6. Relation between x_{Er} and Z in film-diffusion control.

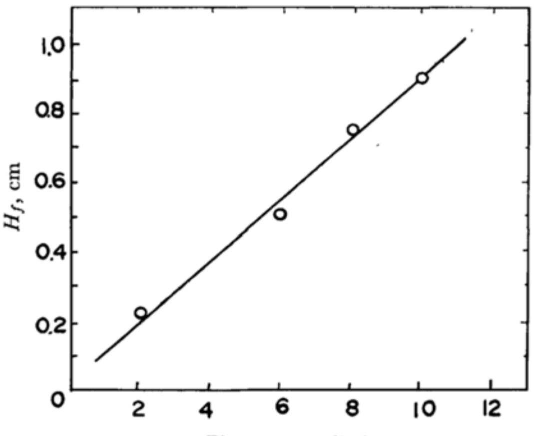

Fig. 8. H_f *versus* flow rate.
temp. 60°C I.D.-22 mm jacket column

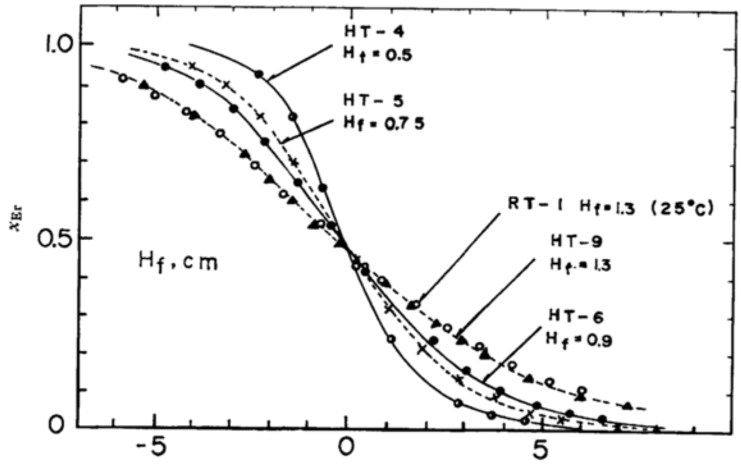

Fig. 7. x_{Er} *versus* Z in film-diffusion control.

TABLE 5. H_f-VALUES AS A FUNCTION OF FLOW RATE

Exp. No.	Elution temp. (°C)	Flow rate* ml/min	H_f cm
HT-2	60	2.0	0.23
HT-4	60	6.0	0.50
HT-5	60	8.0	0.75
HT-6	60	10.0	0.90
HT-9	60	6.0	1.30
RT-1	25	4.0	1.25

* I.D. 22 mm-Jacket column
Eluant composition:
$\widetilde{\text{Ch}}_T=0.015$ mol/l; $\widetilde{\text{NH}}_{4T}=0.031$ mol/l.
except for HT-9
$\widetilde{\text{Ch}}_T=0.015$ mol/l; $\widetilde{\text{NH}}_{4T}=0.042$ mol/l.
for HT-9.

a moderate crosslinked resin (X-8) is mainly controlled by film-diffusion as the rate-determining step. The plots of H_f *versus* the flow rate are shown in Fig. 8, where a linear relation may be observed. Also, the detailed values of H_f obtained in the elution at 25° and 60°C are tabulated in Table 5. The elution temperature affects the plate-height value as well as the separation factor. Since a smaller value of the plate height is obtained with an increase in the temperature, the separation efficiency in the ion-exchange process is improved by elution at high temperatures. Generally, film diffusion, particle diffusion, and particle size all contribute to the plate height. The contribution of the last two is, however, very small in the present exchange system, and film-diffusion plays the most important role for the rate-determining step. As may be seen in Table 5, the plate-height value by film diffusion at 60°C becomes smaller than that at 25°C; this is because the diffusion rates of various species in the Nernst film layer increase with a rise in the temperature.

Summary

1) The separation factors for the Er-Tm pair were found to be 1.57 at 25°C and 1.63 at 60°C in the system with HEDTA and Dowex 50W, X-8.

2) Under various experimental conditions, elutions of an equimolar mixture of Er and Tm were carried out at 25° and 60°C using a 0.015M HEDTA eluant buffered with ammonium hydroxide; a steady state was established through the rare-earth band.

3) The elution system of the rare earth under steady-state conditions was analyzed on the basis of the rate theory; the present exchange system was thereby confirmed to be controlled by film-diffusion the rate-determining step.

4) By raising the elution temperature, the separation efficiency was increased; this was because of the decrease in the plate-height value as well as because of the increase in the separation factor itself.