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Separation Factors for Several Lanthanon Pairs Obtained at 60°C in the Ion-Exchange System Involving EDTA

Zenzi HAGIWARA and Masaru NOGUCHI*[1]

Faculty of Engineering, Tohoku University, Aramaki, Sendai

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With a view to the accurate determination of the separation factors of adjacent rare-earth pairs between the aqueous and resin phases, measurements have been carried out at 60°C in the exchange system involving EDTA and Dowex 50W, X-8, 50—100 mesh. Under the same experimental conditions as were used for the isolation of the rare earths by ion exchange, the separation factors at 60°C were found to be 3.43 for Nd-Sm, 1.37 for Eu-Gd, 1.84 for Tb-Y, 1.54 for Y-Dy, 2.83 for Tb-Dy, 1.84 for Dy-Ho, and 2.02 for the Ho-Er and Er-Tm pairs. Further, the observed values were discussed from the viewpoints of both thermodynamics and the real elution of the rare earths by an ion-exchange column.

The isolation of individual rare-earth elements has been intensively performed by the cation-exchange method,[1,2] employing either ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (EDTA, H_4Y) or *N'*-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N'*-triacetic acid(HEDTA) as the eluant. In this case, elutions[3,4] at high temperatures brought about a preferable result for the separation of some lanthanon mixtures as compared to those at lower temperatures. Generally, an increase in the elution temperature gives a larger separation factor (α) and a smaller H.E.T.P. (height equivalent to a theoretical plate)[5-7] due to particle or film diffusion. These two terms are related to the evaluation of column efficiency in the ion-exchange process. The present authors, however, found experimentally that, in the separation of the rare-earth mixture, an increase in the temperature is not always effective for the improvement of α-value for special rare-earth pairs in the presence of a chelating agent. Therefore, a basic study of the temperature dependence of the separation factor is important. In order to make a theoretical treatment of the elution system involving rare earths and EDTA species at a high temperature, it is necessary to get precise information on the separation factors of two adjacent rare earths obtained at the same teaperature as the elution.

Previously, the present authors reported on the separation factors[8] for such adjacent rare-earth pairs as Sm–Nd, Eu-Gd, Tb–Y, Y–Ho, and Er–Tm in the presence of EDTA at 30°C; considerable differences were observed between the calculated values and those determined by experiment. The present study was undertaken in order to find more reliable separation factors for some lanthanon pairs at 60°C, (such factors are necessary for the analysis of a real elution system at the same temperature) and to compare them with the values calculated from the thermodynamic data. Further, with the aid of the experimental results obtained by the ion-exchange elution of the rare earths at 60°C, we determined whether or not the observed α-values at 60°C are correct.

Experimental

Materials Used. The rare earths were supplied in the form of oxides, such as Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Y_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, and Tm_2O_3, by the Shinetsu Chemical Industry Corp.; they all had high purities, greater than 99.99%. Each oxide was dissolved with a slight excess of hydrochloric acid under heating, and the rare-earth ions were adsorbed on a resin of the hydrogen form to prepare the rare-earth form. The other chemicals used were of an analytical grade; a Dowex 50W, X-8, 50—100 mesh was employed as the cation exchanger.

Experimental Procedures. Using the column method, various rare-earth forms of resins containing small amounts of hydrogen and ammonium were prepared. These preparations[8] have previously been described. Thus, the description of the methods is omitted

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*[1] Present address: Takefu Factory, Shinetsu Chemical Industry Corp.

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here. Throughout the experiments, Dowex 50W, X-8, 50—100 mesh was used. The following resins and solutions were prepared for the experiments:

Composition for the Rare-earth Forms of Resins (equivalent fraction).

Sm-resin: $\overline{\mathrm{Sm}}=0.8472$; $\overline{\mathrm{NH}_4}=0.0547$; $\overline{\mathrm{H}}=0.0981$.
Gd-resin: $\overline{\mathrm{Gd}}=0.8784$; $\overline{\mathrm{NH}_4}=0.0559$; $\overline{\mathrm{H}}=0.0657$.
Y - resin: $\overline{\mathrm{Y}}=0.9213$; $\overline{\mathrm{NH}_4}=0.0312$; $\overline{\mathrm{H}}=0.0475$.
Dy-resin: $\overline{\mathrm{Dy}}=0.8778$; $\overline{\mathrm{NH}_4}=0.0412$; $\overline{\mathrm{H}}=0.0809$.
Ho-resin: $\overline{\mathrm{Ho}}=0.8665$; $\overline{\mathrm{NH}_4}=0.0343$; $\overline{\mathrm{H}}=0.0991$.
Er-resin: $\overline{\mathrm{Er}}=0.8924$; $\overline{\mathrm{NH}_4}=0.0243$; $\overline{\mathrm{H}}=0.0833$.
Tm-resin: $\overline{\mathrm{Tm}}=0.9096$; $\overline{\mathrm{NH}_4}=0.0121$; $\overline{\mathrm{H}}=0.0782$.

Composition of the Rare-earth Solutions(mol/*l*)

Nd-soln.: $\mathrm{Y_f}=0.00250$; $\mathrm{Nd_T}=0.01374$; $\mathrm{NH_{4T}}=0.00997$; pH=2.59.
Eu-soln.: $\mathrm{Y_f}=0.00193$; $\mathrm{Eu_T}=0.01461$; $\mathrm{NH_{4T}}=0.00745$; pH=2.41.
Tb-soln.: $\mathrm{Y_f}=0.00169$; $\mathrm{Tb_T}=0.01440$; $\mathrm{NH_{4T}}=0.00650$; pH=2.21.
Y-soln.: $\mathrm{Y_f}=0.00023$; $\mathrm{Y_T}=0.01331$; $\mathrm{NH_{4T}}=0.00473$; pH=2.19.
Dy-soln.: $\mathrm{Y_f}=0.00143$; $\mathrm{Dy_T}=0.01487$; $\mathrm{NH_{4T}}=0.00575$; pH=2.05.
Ho-soln.: $\mathrm{Y_f}=0.00130$; $\mathrm{Ho_T}$;$=0.01449$; $\mathrm{NH_{4T}}=0.00503$; pH=2.13.
Er-soln.: $\mathrm{Y_f}=0.00082$; $\mathrm{Er_T}=0.01488$; $\mathrm{NH_{4T}}=0.00353$; pH=2.00.

The barred quantities refer to the composition of the indicated species in the resin, and the subscript quantities, to the concentrations of the indicated species in the aqueous phase. Further, the symbol $\mathrm{Y_f}$ represents the excess of anionic species of EDTA present in the uncombined form with the rare earth. Therefore, the total concentration of EDTA is equal to the sum of $\mathrm{Ln_T}$ and $\mathrm{Y_f}$, disregarding the presence of $\mathrm{Ln^{3+}}$ in the prepared rare-earth solutions. The resin and aqueous phases are expressed in the equivalent fraction and in moles per liter respectively.

Equilibrium Experiment. After mixing a definite amount of the prepared rare-earth resin containing small amounts of hydrogen and ammonium with a proper volume of the rare-earth solution, the resulting mixture was shaken for 96 hr in a constant-temperature bath kept at 60°C. After equilibration, the resin was separated from the aqueous phase, and the rare earths in both phases were determined in order to find the separation factor. The analytical procedures have been described in detail in the foregoing paper.[8]

Resutls and Discussion

The equilibrium compositions of the adjacent rare-earth pairs are listed in Table 1, in which the mole fraction is used as the concentration unit for the two phases. The observed α-values are also given in the same table; they are found from the relation:

$$\alpha^{\mathrm{Ln_1}}_{\mathrm{Ln_2}}=\left(\frac{m_{\overline{\mathrm{Ln}}_1}}{m_{\overline{\mathrm{Ln}}_2}}\right)\left(\frac{m_{\mathrm{Ln_2}}}{m_{\mathrm{Ln_1}}}\right) \qquad (1)$$

where $m_{\overline{\mathrm{Ln}}_1}+m_{\overline{\mathrm{Ln}}_2}=1$ (resin phase) and $m_{\mathrm{Ln_1}}+m_{\mathrm{Ln_2}}=1$ (aqueous phase). The $\mathrm{Ln_1}$ and $\mathrm{Ln_2}$ symbols represent adjacent rare-earth elements, and *m*, the mole fraction. The barred quantities refer to the resin phase, and the unbarred, to the aqueous phase. The average values of the separation factors obtained at 60°C are tabulated in Table 2, in which the α-values calculated from the

TABLE 1. EQUILIBRIUM COMPOSITIONS AND SEPARATION FACTORS FOR ADJACENT RARE-EARTH PAIRS AT 60°C

Exp. No.	Sample taken		Mole fraction of adjacent rare earth at equilibrium				$\alpha^{\mathrm{Ln_1}}_{\mathrm{Ln_2}}$	Ave. $\alpha^{\mathrm{Ln_1}}_{\mathrm{Ln_2}}$
			Resin phase		Aqueous phase			
	Ln-resin g	Ln-soln. *ml*	$\overline{\mathrm{Ln}}_1$	$\overline{\mathrm{Ln}}_2$	$\mathrm{Ln_1}$	$\mathrm{Ln_2}$		
2—4	5.00(Sm)	300(Nd)	0.542(Nd)	0.458(Sm)	0.264(Nd)	0.736(Sm)	3.30	$\alpha^{\mathrm{Nd}}_{\mathrm{Sm}}=3.43$
2—5	5.00(Sm)	450(Nd)	0.677(Nd)	0.323(Sm)	0.373(Nd)	0.628(Sm)	3.53	
2—6	5.00(Sm)	600(Nd)	0.761(Nd)	0.239(Sm)	0.479(Nd)	0.521(Sm)	3.46	
6—4	5.00(Gd)	300(Eu)	0.482(Eu)	0.518(Gd)	0.398(Eu)	0.602(Gd)	1.41	$\alpha^{\mathrm{Ed}}_{\mathrm{Gd}}=1.37$
6—5	5.00(Gd)	450(Eu)	0.583(Eu)	0.417(Gd)	0.507(Eu)	0.493(Gd)	1.36	
6—6	5.00(Gd)	600(Eu)	0.661(Eu)	0.339(Gd)	0.595(Eu)	0.405(Gd)	1.33	
4—4	5.00(Y)	300(Tb)	0.506(Tb)	0.494(Y)	0.363(Tb)	0.637(Y)	1.80	$\alpha^{\mathrm{Tb}}_{\mathrm{Y}}=1.84$
4—5	5.00(Y)	450(Tb)	0.634(Tb)	0.366(Y)	0.485(Tb)	0.515(Y)	1.84	
4—6	5.00(Y)	600(Tb)	0.726(Tb)	0.274(Y)	0.586(Tb)	0.414(Y)	1.87	
6—1	3.00(Dy)	180(Y)	0.462(Y)	0.538(Dy)	0.350(Y)	0.650(Dy)	1.59	$\alpha^{\mathrm{Y}}_{\mathrm{Dy}}=1.54$
6—2	3.00(Dy)	270(Y)	0.560(Y)	0.440(Dy)	0.459(Y)	0.541(Dy)	1.50	
6—3	6.00(Dy)	360(Y)	0.462(Y)	0.538(Dy)	0.360(Y)	0.640(Dy)	1.53	
5—4	5.00(Ho)	300(Dy)	0.563(Dy)	0.437(Ho)	0.413(Dy)	0.587(Ho)	1.83	$\alpha^{\mathrm{Dy}}_{\mathrm{Ho}}=1.84$
5—5	5.00(Ho)	450(Dy)	0.667(Dy)	0.333(Ho)	0.522(Dy)	0.478(Ho)	1.83	
5—6	5.00(Ho)	600(Dy)	0.739(Dy)	0.261(Ho)	0.604(Dy)	0.396(Ho)	1.86	
9—1	5.00(Er)	300(Ho)	0.526(Ho)	0.474(Er)	0.360(Ho)	0.640(Er)	1.97	$\alpha^{\mathrm{Ho}}_{\mathrm{Er}}=2.02$
9—2	5.00(Er)	450(Ho)	0.638(Ho)	0.362(Er)	0.464(Ho)	0.536(Er)	1.04	
9—3	5.00(Er)	600(Ho)	0.712(Ho)	0.288(Er)	0.547(Ho)	0.453(Er)	1.05	
3—4	5.00(Tm)	300(Er)	0.556(Tm)	0.443(Tm)	0.376(Er)	0.624(Tm)	2.08	$\alpha^{\mathrm{Er}}_{\mathrm{Tm}}=2.02$
3—5	5.00(Tm)	450(Er)	0.667(Tm)	0.333(Tm)	0.516(Er)	0.484(Tm)	1.88	
3—6	5.00(Tm)	600(Er)	0.740(Tm)	0.260(Tm)	0.575(Er)	0.425(Tm)	2.10	

Table 2. Comparison of separation factors for adjacent rare-earth pairs

Rare-earth pair Ln_1-Ln_2	Calcd $\alpha^{Ln_1}_{Ln_2}$ a) 298°K	Calcd $\alpha^{Ln_1}_{Ln_2}$ a) 333°K	Obsd $\alpha^{Ln_1}_{Ln_2}$ 303°K	Obsd $\alpha^{Ln_1}_{Ln_2}$ 333°K	$\alpha^{Ln_1}_{Ln_2}=K_{Ln_2Y}/K_{Ln_1Y}$ 298°K $\alpha^{b)}$	$\alpha^{Ln_1}_{Ln_2}=K_{Ln_2Y}/K_{Ln_1Y}$ 298°K $\alpha^{c)}$
La-Ce	1.78	1.77	—	—	3.02	4.68
Ce-Pr	2.09	2.00	—	—	2.63	2.29
Pr-Nd	1.95	1.81	—	—	1.62	2.04
Nd-(Pm)	1.8?	—	—	—	—	—
(Pm)-Sm	1.7?	—	—	—	—	—
Nd-Sm	3.00	3.15	3.77	3.43	3.39	3.09
Sm-Eu	1.32	1.51	—	—	1.62	1.38
Eu-Gd	1.51	1.75	1.30	1.37	1.05	1.02
Gd-Tb	3.08	3.43	—	—	3.63	4.79
Tb-Y	1.13	1.24	1.76	1.84	1.45	1.51
Y-Dy	2.59	2.32	1.61	1.54	1.62	1.55
Tb-Dy	2.92	2.87	2.83*	2.83*	2.35**	2.34**
Dy-Ho	1.82	1.77	1.88	1.84	1.90	3.63
Ho-Er	2.11	1.98	—	2.02	1.86	1.74
Er-Tm	1.97	1.91	2.05	2.02	2.95	3.31
Tm-Yb	2.21	2.06	—	—	1.55	2.09
Yb-Lu	1.48	1.43	—	—	2.09	1.82

* Calcd from the observed α-values of the Tb-Y and Y-Dy pairs.

? Estimated α-values using a value of K_{PmY} found graphically (Fig. 1) and the values of K_{NdY} and K_{SmY}.

** Found from the calcd. α-values of the Tb-Y and Y-Dy pairs.

a) Calcd from calorimetric data.[9]

b) Calcd from data of stability constants.[10]

c) Calcd from data of stability constants.[11]

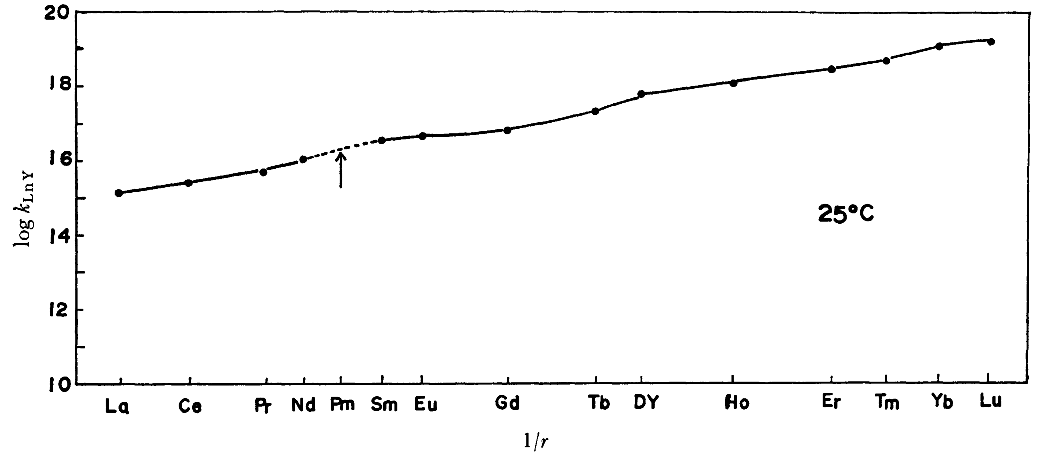

Fig. 1. Plots of stability constants of rare earth-EDTA chelates against the reciprocal value of the ionic radius.

Plots were made using data of Mackey *et al.*[9]

calorimetric data[9] of the formation of the Ln-EDTA chelates and from the ratio of the stability constants[10-11] are also given. The α-values at 30°C are given as well in order to compare the values at different temperatures.

The α-values in the second column in Table 2 were calculated using Eq. (4), which will be given below. The following relationships held, employ-

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[9] J. L. Mackey, J. E. Powell and F. H. Spedding, *J. Amer. Chem. Soc.*, **84**, 2047 (1962).

[10] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[11] E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Amer. Chem. Soc.*, **75**, 4196 (1953).

ing the thermodynamic quantities (ΔH°, ΔS°, and ΔF°):

$$\Delta F^\circ_{\mathrm{Ln}_1} = -\boldsymbol{R}T \ln K_{\mathrm{Ln_1Y}} = \Delta H^\circ_{\mathrm{Ln}_1} - T\Delta S^\circ_{\mathrm{Ln}_1} \quad (2)$$

$$\Delta F^\circ_{\mathrm{Ln}_2} = -\boldsymbol{R}T \ln K_{\mathrm{Ln_2Y}} = \Delta H^\circ_{\mathrm{Ln}_2} - T\Delta S^\circ_{\mathrm{Ln}_2} \quad (3)$$

The combination of the above equations leads to the following form:

$$\log \alpha^{\mathrm{Ln}_1}_{\mathrm{Ln}_2} = \log \frac{K_{\mathrm{Ln_2Y}}}{K_{\mathrm{Ln_1Y}}} = -\frac{(\Delta H^\circ_{\mathrm{Ln}_2} - \Delta H^\circ_{\mathrm{Ln}_1}) - T(\Delta S^\circ_{\mathrm{Ln}_2} - \Delta S^\circ_{\mathrm{Ln}_1})}{2.303\,\boldsymbol{R}T} \quad (4)$$

The α-values in the fourth column in Table 2 were calculated by means of the following relation[8]:

$$\alpha^{\mathrm{Ln}_1}_{\mathrm{Ln}_2} = \frac{K_{\mathrm{Ln_2Y}}}{K_{\mathrm{Ln_1Y}}} \quad (5)$$

As is shown in Table 2, the separation factors for the Nd-Pm and Pm-Sm pairs were calculated using a value of K_{PmY} found by interpolation of the data obtained by Mackey *et al.*[9] (Fig. 1).

In the present study, the temperature dependence of the separation factor is almost identical between the observed and calculated values except for the α-value for the Nd-Sm pair; the experimental results show that the effect of the temperature on α seems to be very small for such rare-earth pairs as Tb-Dy, Dy-Ho, Ho-Er, and Er-Tm. The α-values for the Dy-Ho, Ho-Er, and Er-Tm pairs obtained at 333°K are in good agreement with the calculated values obtained by introducing the thermodynamic data[9] into Eq.(4). On the other hand, the Er-Tm separation factor obtained at temperatures of 298 and 333°K by the use of Eq. (5) seems to be too high. A value of 2.83 for the Tb-Dy separation factor is indirectly found from the experimental data of 1.84 for $\alpha^{\mathrm{Tb}}_{\mathrm{Y}}$ and 1.54 for $\alpha^{\mathrm{Y}}_{\mathrm{Dy}}$; this is consistent with the calculated value of 2.87 at 333°K.

The $\alpha^{\mathrm{Y}}_{\mathrm{Dy}}$ found at 303°K is too low compared to the value of 2.59 at 298°K obtained by using Eq. (4); the former is rather close to the value obtained from the ratio of the two stability constants of the Ln-EDTA chelates. Further, the observed Tb-Y separation factors at both temperatures show fairly large discrepancies from the calculated values.

As a result of the analysis of the elution behavior of the rare-earth mixture containing Tb, Y, and Dy, the value of $\alpha^{\mathrm{Tb}}_{\mathrm{Y}}$ and $\alpha^{\mathrm{Y}}_{\mathrm{Dy}}$ obtained in this study may be concluded to be reasonable. In the temperature range from 25 to 60°C, the elution sequence of these elements with a solution of 0.015 M EDTA buffered with $\mathrm{NH_4OH}$ (pH=8.5) is: Dy→Y→Tb. In the elution of a mixture involving Dy, Y, and Tb through a copper-retaining bed with the aid of 0.015 M EDTA (pH=8.5), the rare-earth band arrived at a steady-state condition after travelling for a proper distance on the column. In such a state, the Tb-Y cut at the tail of the adsorption band is obviously sharper than the Dy-Y cut at the front. In other words, the inherent overlap region with Tb and Y is actually less than that with Dy and Y, as is to be expected from a comparison of the H.E.T.P./log α term. This fact supports the observed α-values for these pairs.

Using 0.015 M EDTA (pH=8.5) as the eluant, the following two elution experiments were carried out at 60°C with a flow rate of 10 m*l*/min (I.D. 22 mm-column). In one of the experiments, the rare-earth-sorption band with an equimolar mixture of Tb and Y (bed dimensions: 2.2×35 cm) was eluted down the retaining bed with Dowex 50 W, X-8, 50—100 mesh (2.2×90 cm). In the other run, the rare-earth band with an equimolar mixture of Dy and Y (bed dimensions: 2.2×70 cm) was eluted down the retaining bed (2.2×180 cm). In both runs, the length of the retaining bed is enough for the steady state to be attained during elution. The rare-earth eluates issuing from the column were analyzed to observe the change in the composition of the overlap region of the rare-earth band.

After a steady state had been established throughout the elution system by the displacement of the rare-earth band, the overlapping area with the two rare-earth components was fixed to a definite composition gradient; the shape of the boundary is independent of further elution distance. In this case, the following relationship[12] finally holds, if the ion exchange is regarded a countercurrent extraction: $\log R_n/R = n \log \alpha = (\log \alpha/\mathrm{H.E.T.P.})L$, where L is the distance between the two points on the resin; n, the number of theoretical plates, and α and R, the separation factor for the adjacent rare earths and their molar ratio respectively. Thus, the plateheight value can be found from the above relationship. Under the previously-described conditions, the H.E.T.P.-values are found to be 1.2 cm for the elution of the Tb-Y mixture and 2.0 cm for the elution of the Dy-Y mixture.

The length of the overlap region with 99.9% pure adjacent $\mathrm{Ln_1}$ and $\mathrm{Ln_2}$ products can be calculated from this relation:

$$L = \frac{6(\mathrm{H.E.T.P.})}{\log \alpha} \quad (6)$$

where the value of 6 as $\log R_n/R$ is found for the above conditions. Therefore, if any pure product is desired, it is necessary for the length of a sorption band of the rare earth in the column to exceed L. Taking H.E.T.P.=1.2 cm and $\alpha^{\mathrm{Tb}}_{\mathrm{Y}}=1.84$ at 60°C for the Tb-Y pair, L is equal to 27 cm, while a value of 28 cm was experimentally obtained. A good agreement is seen between them. In the case of the Dy-Y pair, taking H.E.T.P.=2.0 cm

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[12] J. E. Powell and H. R. Burrholder, *J. Chromatogr.*, **29**, 210 (1967).

and $\alpha_{\mathrm{Y}}^{\mathrm{Dy}}=1.54$ at 60°C, L is equal to 64 cm; this is near the observed value of 65 cm. In both calculations, the α-value was assumed to be constant throughout the whole mixed zone with rare earths.

One of the present authors deduced the following relationship[4] for film-diffusion control in ion exchange:

$$Z(X_{\mathrm{Ln}_2}) = H_f\left\{-\frac{\alpha}{\alpha-1}\ln X_{\mathrm{Ln}_2} + \frac{1}{\alpha-1}\ln(1-X_{\mathrm{Ln}_2}) - 1\right\} \tag{7}$$

where $Z(X_{\mathrm{Ln}_2})$ is the distance of the plane with the concentration of X_{Ln_2} from the gravity center of the rare-earth boundary involving Ln_1 and Ln_2, where α is the separation factor, and where H_f is the plate-height value due to film diffusion. The X_{Ln_2} symbol is expressed in the concentration unit of the equivalent fraction of the Ln_2 species, while both Z and H_f are expressed in centimeters. As Z is a function of X_{Ln_2}, the length of the rare-earth band required to get 99.9% pure products in a steady state can be calculated. The substitution of $\alpha_{\mathrm{Y}}^{\mathrm{Tb}}=1.84$ into Eq. (7) gives:

$$Z(X_{\mathrm{Tb}}) = H_f\{-5.04\log X_{\mathrm{Tb}} + 2.74\log(1-X_{\mathrm{Tb}}) - 1\} \tag{8}$$

Therefore, we obtain:

$$Z_1(X_{\mathrm{Tb}}) = -9.22\,H_f \quad \text{at } X_{\mathrm{Tb}} = 0.999$$

$$Z_2(X_{\mathrm{Tb}}) = 14.12\,H_f \quad \text{at } X_{\mathrm{Tb}} = 0.001$$

Thus, the length of the overlap region necessary for obtaining 99.9% Tb and Y products can be found by adding the absolute values of Z_1 and Z_2 at $H_f=1.2$ cm:*2

$$L = |Z_1| + |Z_2| = 28\ \mathrm{cm}$$

In the elution of the Y-Dy pair, when $\alpha_{\mathrm{Dy}}^{\mathrm{Y}}=1.54$ and $H_f=2.0$*2 are introduced into Eq. (7), the length of the band required to get 99.9% Y and Dy products is found to be 65 cm; this value is in excellent agreement with the value obtained in the elution experiments at a steady state. Therefore, it can be concluded that the α-values obtained for the Y-Dy and Tb-Y pairs in the exchange system with EDTA are satisfactory.

On the other hand, an increase in the temperature effects an increase in the Eu-Gd separation factor, as may be seen in Table 2. The α-value at 60°C was 1.37 in the presence of EDTA; this was lower than the value calculated from Eq. (4), while a vlue of 1.5 was obtained for the pair at 92°C by another study.[12] Considering the variation in α with the temperature, the observed value of 1.37 seems to be reasonable.

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*2 The H_f-values were found graphically by a curve-fitting method described in a previous paper.[4]