BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2286—2291 (1969)

Separation Factors of Adjacent Rare Earths between the Aqueous and Resin Phases in the Presence of EDTA

Masaru Noguchi,[*1] Akashi Yoshifuji[*1] and Zenzi Hagiwara

Department of Chemical Engineering, Tohoku University, Sendai

(Received January 21, 1969)

In order to find the accurate separation factors of two adjacent rare earths between the aqueous and resin phases, measurements were performed at 30°C in the presence of EDTA and using Dowex 50W, X-8, 50—100 mesh. The following results were obtained under the same experimental conditions as were employed in ion-exchange system for the isolation of the rare earth series. The separation factors were 2.05 for Er-Tm, 1.88 for Dy-Ho, 1.61 for Y-Dy, 1.76 for Tb-Y, 1.30 for Eu-Gd, and 3.77 for Sm-Nd. In the Er-Tm separation factor, a fairly large discrepancy was observed between the calculated and experimental values. It is concluded from the experimental results that the separation factors of pairs of lanthanons should be directly measured.

A successful ion-exchange process[1] was first developed by the Reasearch Group of the Ames Laboratory, USAEC, in combination with a cation exchanger and using EDTA (ethylenediamine-*N,N,N',N'*-tetraacetic acid: H_4Y) as the eluant. In order to treat theoretically the elution system[2,3] of the rare earths with the EDTA eluant, it is

---

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

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

2) F. H. Spedding and A. H. Danne, "The Rare Earths," John Wiley, New York (1961).

3) Z. Hagiwara, *Bull. Japan Inst. Metals,* **4,** 311 (1965); Z. Hagiwara, *Asahi Glass Industry-Kogyo-Gijitsu-Shorei-Kai,* **9,** 183 (1963).

necessary to get precise information on the separation factors of the lanthanide elements in the presence of a chelating agent.

The separation factor (α) of adjacent rare earths, Ln_1 and Ln_2, is approximately expressed as the ratio of the two stability constants: $\alpha_{Ln_1}^{Ln_2} \cong K_{Ln_1Y}/K_{Ln_2Y}$ It is possible to calculate the α-value using the stability constants[4,5] measured at an ionic strength of 1/10 M. In the isolation of rare earths from each other, a dilute eluant such as approximately 0.015 M EDTA buffered with ammonium hydroxide (pH$\cong$8.5) is widely used. Therefore, it may be valuable to find more accurate separation factors of the lanthanide series suitable for a real system and to compare them with the calculated values. For the complete solution of the Eu-Gd pair, the minimum elution distance calculated by using $\nu=(1+\varepsilon N_0)/\varepsilon$ and $\varepsilon=\alpha_{Gd}^{Eu}-1=(K_{GdY}/K_{EuY})-1$ is quite different from the experimental results. The symbol ν indicates the minimum number of displacements of the mixed adsorption band necessary to carry out separation, while N_0 represents the mole fraction of the Eu component in the binary mixture of Eu and Gd being separated. Powell[6] indicated that the reason for this is the utilization of the separation factor unsuitable for the real exchange system, and that the Eu-Gd separation factor appears to be approximately 1.1.

The principal purpose of this research is to find the separation factor for pairs of adjacent lanthanons and to use them for analyzing the elution system of rare earth with EDTA.

Experimental

Materials Used. The rare earth 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, had high purities, greater than 99.9%. They were produced by the Shinetsu Chemical Industry Corp. Each oxide was dissolved with hydrochloric acid, and the rare earth ion was adsorbed in a resin bed of the hydrogen form in order to prepare the rare earth form. All the other chemicals used were of an analytical grade, and Dowex 50W, X-8, 50—100 mesh, was employed as the cation exchanger.

Experimental Procedures. An I.D.-22 mm Pyrex glass column containing Dowex 50W,X-8, 50—100 mesh was used for the elution experiment (Fig. 1). The resin was supported by a sintered glass disk.

Prior to the equilibrium experiment, a saturated form of the rare earth band was first prepared by passing the rare earth chloride solution through a Pyrex glass column involving a hydrogen form of Dowex 50W, X-8, 50—100 mesh; the column was then connected to the copper retaining bed (B-column). The latter was further connected to the C-column in the copper form. Using the 0.015 M EDTA buffered with ammonium hydroxide (pH$\cong$8.5) and the flow rate of 2 ml/min,

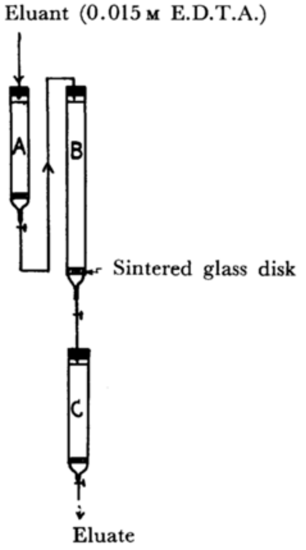

Fig. 1. Ion-exchange columns used for the preparation of rare earth type of resin containing ammonium and hydrogen.
Dimension of columns as hydrogen form of resin:
A: Rare earth adsorption bed (2.2×25 cm)
B: Copper retaining bed (2.2×50 cm)
C: Copper retaining bed (2.2×20 cm)
Resin used: Dowex 50W, X-8, 50—100 mesh
Flow rate: 2 ml/min

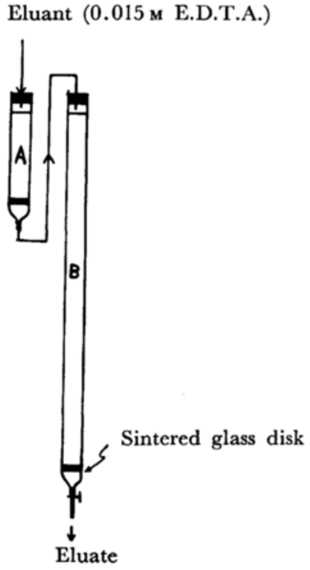

Fig. 2. Ion-exchange columns for the preparation of rare earth eluate.
Dimension of columns as hydrogen form of resin:
A: Rare earth adsorption bed (2.2×25 cm)
B: Copper retaining bed (2.2×100 cm)
Resin used: Dowex 50W, X-8, 50—100 mesh
Flow rate: 2 ml/min

---

4) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

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

6) E. Eyling, "Progress in the Science and Technology of the Rare Earths," Vol. 1, Pergamon Press, New York (1964).

Table 1. Composition of the aqueous and resin phases before equilibrium

Rare earth pair	Composition of resin phase (Equivalent fraction)				Composition of aqueous phase (mol/*l*)				
	Ln	Ln	NH_4	H	Ln	Y_f	Ln	NH_4	pH
Tm-Er	Tm	0.9101	0.0121	0.0783	Er	0.00082	0.01488	0.00353	2.00
Ho-Dy	Ho	0.8666	0.0344	0.0991	Dy	0.00143	0.01487	0.00575	2.05
Dy-Y	Dy	0.8779	0.0412	0.0809	Y	0.00138	0.01415	0.00610	2.23
Y-Tb	Y	0.9210	0.0312	0.0475	Tb	0.00169	0.01440	0.00650	2.21
Gd-Eu	Gd	0.8784	0.0559	0.0657	Eu	0.00193	0.01461	0.00745	2.41
Sm-Nd	Sm	0.8472	0.0547	0.0981	Nd	0.00250	0.01374	0.00997	2.59

Total concn. of anionic EDTA species: $Y_T = L_n + Y_f$ (mol/*l*)

the rare earth band was displaced to a distance corresponding to several band lengths. After the C-column had been completely displaced by the rare earth, the elution was stopped. The steady-state band of the rare earth in the C-column was then washed with a 60% ethyl alcohol solution and then dried. The dried resin was finally used for the experiments. By employing the above method, various rare earth forms of resins involving ammonium and hydrogen were prepared; they are listed in Table 1.

On the other hand, a rare earth solution containing ammonium and hydrogen was prepared by the column method, shown in Fig. 2. After making the rare-earth-saturated bed, it was eluted with the 0.015 M EDTA (pH≅8.5). After a movement proportional to approximately 3-4 band lengths, the rare earth fraction from the main column was collected for the equilibrium experiments. Several types of rare earth fractions prepared are listed in Table 1, in which the two symbols Ln and NH_4 express the total concentrations of rare earth and ammonium in the aqueous phase.

Equilibrium Experiment. After mixing definite portions of the prepared rare earth form of resin containing small amounts of ammonium and hydrogen with 300, 450, and 600 m*l* of the rare earth fraction, the mixtures were maintained at 30°C for 96 hr in a thermostat under occasional stirring. After equilibration, the resin was separated from the aqueous phase, and both phases were analyzed in order to find the separation factor in the presence of EDTA.

Analysis. The constituents in the resin were eluted with 2 M NaCl. The rare earth in the resin and aqueous phases was determined as a mixed oxide after precipitating the oxalate. Further, each rare earth in the mixed oxide was determined by spectrophotometry as well as by X-ray fluorescent spectrometry. The determination of ammonium was performed by the Kjeldahl method, and the excess of EDTA (Y_f), which was present in the uncombined form with rare earth, was determined volumetrically with a standard solution of $NdCl_3$, using an arzenoazo indicator [3-(2-arzono-phenylazo)-4,5-dihydroxy-2,7-naphthalene-disulfonic acid] and pyridine as the buffer solution.

Results and Discussion

The compositions of adjacent rare earths at equilibrium are given in Tables 2 to 7, in which the rare earths in both phases are expressed in the mole fraction:

$$m_{\mathrm{Ln}_1} + m_{\mathrm{Ln}_2} = 1, \quad m_{\overline{\mathrm{Ln}}_1} + m_{\overline{\mathrm{Ln}}_2} = 1$$

where the barred quantities refer to the resin phase, and the unbarred, the aqueous phase. The observed separation factors are also represented; these are found by the following relation:

$$\alpha_{\mathrm{Ln}_1}^{\mathrm{Ln}_2} = \left(\frac{m_{\overline{\mathrm{Ln}}_2}}{m_{\overline{\mathrm{Ln}}_1}}\right)\left(\frac{m_{\mathrm{Ln}_1}}{m_{\mathrm{Ln}_2}}\right)$$

whether or not a chelating agent is present in the system, the separation factor of the two adjacent rare earths is defined as the concentration ratio of these species in the resin and aqueous phases. The dimensionless separation factor is not affected by the selection of the concentration units. The average values of the separation factors for the two adjacent rare earths are tabulated in Table 8. The values calculated from the stability constants of the rare earth-EDTA chelates also appear in the same table.

In this study, the Er-Tm separation factor showed 2.05. This is too far from the value calculated using the stability constants ($\alpha_{\mathrm{Tm}}^{\mathrm{Er}} \cong K_{\mathrm{TmY}}/K_{\mathrm{ErY}}$). The $\alpha_{\mathrm{Tm}}^{\mathrm{Er}}$-value(7) at 60°C is 2.02 under almost the same experimental conditions at 30°C. Powell(8) pointed out that a linear relation is seen in the plot of the logarithm of the stability constants as a function of the ionic radius of rare earth from Gd through Lu (See Table 8). Considering a regular decrease in stability with an increase in the radius and the difference in cationic radius between the tripositive rare earth ions, one would speculate that the differences between $K_{\mathrm{Ln}_1\mathrm{Y}}/K_{\mathrm{Ln}_2\mathrm{Y}}$ and $K_{\mathrm{Ln}_2\mathrm{Y}}/K_{\mathrm{Ln}_3\mathrm{Y}}$ will be small. The differences in radius are 0.02 Å for Ho^{3+}–Er^{3+}, 0.01 Å for Er^{3+}–Tm^{3+}, and 0.01 Å for Tm^{3+}–Yb^{3+}. The following sequence can be estimated for pairs of elements from Ho through Yb:

$$\alpha_{\mathrm{Yb}}^{\mathrm{Tm}} < \alpha_{\mathrm{Tm}}^{\mathrm{Er}} < \alpha_{\mathrm{Er}}^{\mathrm{Ho}}$$

---

7) Z. Hagiwara, A. Banno and A. Kamei, *J. Inorg.* & *Nucl. Chem.*, submitted for publication (Feb., 1969).

8) J. E. Powell, *J. Chromatog.*, **29**, 210 (1967).

The α-value of 2.05 at 30°C is concluded to be reasonable on the basis of the following facts. The Er-Tm separation factor at 30°C can be calculated employing the thermodynamic quantities (ΔH°, ΔS° and ΔF°) obtained by a calorimetric study[9] of the formation of the rare earth-EDTA chelate

TABLE 2. ION EXCHANGE EQUILIBRIUM AND SEPARATION FACTOR (Tm-Er system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α^{Er}_{Tm}
	Tm-resin (meq.)	Er-soln. (ml)	Resin phase		Aqueous phase		
			Tm	Er	Tm	Er	
3-1	17.48	300	0.462	0.538	0.648	0.352	2.15
3-2	17.42	450	0.343	0.657	0.531	0.469	2.17
3-3	17.43	600	0.294	0.706	0.433	0.567	1.83

* Detail compositions are given in Table 1.

** Ratios of the two adjacent rare earths in both phases were determined by absorption method.

TABLE 3. ION EXCHANGE EQUILIBRIUM AND SEPARATION FACTOR (Dy-Ho system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α^{Dy}_{Ho}
	Ho-resin (meq.)	Dy-soln. (ml)	Resin phase		Aqueous phase		
			Ho	Dy	Ho	Dy	
5-1	16.20	300	0.449	0.551	0.611	0.389	1.93
5-2	16.13	450	0.337	0.663	0.487	0.513	1.87
5-3	16.23	600	0.269	0.731	0.405	0.595	1.85

* Detail compositions are given in Table 1.

** Determined by absorption method.

TABLE 4. ION EXCHANGE EQUILIBRIUM AND SEPARATION FACTOR (Y-Dy system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α^{Y}_{Dy}
	Dy-resin (meq.)	Y-soln. (ml)	Resin phase		Aqueous phase		
			Dy	Y	Dy	Y	
1-1	19.11	300	0.547	0.453	0.662	0.338	1.62
1-2	19.08	450	0.428	0.572	0.549	0.451	1.63
1-3	18.70	600	0.356	0.644	0.465	0.535	1.57

* Detail compositions are given in Table 1.

** Determined by X-ray fluorescent spectrometry.

TABLE 5. ION EXCHANGE EQUILIBRIUM AND SEPARATION FACTOR (Tb-Y system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α^{Tb}_{Y}
	Y-resin. (meq.)	Tb-soln. (ml)	Resin phase		Aqueous phase		
			Y	Tb	Y	Tb	
4-1	19.40	300	0.520	0.480	0.659	0.341	1.78
4-2	19.40	450	0.400	0.600	0.525	0.475	1.66
4-3	19.39	600	0.303	0.693	0.448	0.552	1.85

* Detail compositions are given in Table 1.

** Determined by X-ray fluorescent spectrometry.

---

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

Table 6. Ion exchange equilibrium and separation factor (Eu-Gd system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α_{Gd}^{Eu}
	Gd-resin (meq.)	Eu-soln. (ml)	Resin phase		Aqueous phase		
			Gd	Eu	Gd	Eu	
6-1	16.72	300	0.524	0.476	0.591	0.409	1.31
6-2	16.76	450	0.417	0.583	0.484	0.516	1.31
6-3	16.65	600	0.347	0.653	0.407	0.593	1.29

* Detail compositions are given in Table 1.
** Determined by absorption method.

Table 7. Ion exchange equilibrium and separation factor (Nd-Sm system)

Exp. No.	Sample* taken		Mole fraction of adjacent rare earths** at equilibrium (30°C)				α_{Sm}^{Nd}
	Sm-resin (meq.)	Nd-soln. (ml)	Resin phase		Aqueous phase		
			Sm	Nd	Sm	Nd	
2-1	17.91	300	0.440	0.560	0.748	0.252	3.78
2-2	17.88	450	0.306	0.694	0.619	0.381	3.68
2-3	17.89	600	0.226	0.774	0.528	0.472	3.84

* Detail compositions are given in Table 1.
** Determined by absorption method.

Table 8. Comparison of separation factors in presence of EDTA

Rare earth pair (Ln_1-Ln_2)	$\alpha_{Ln_1}^{Ln_2} \cong \frac{K_{Ln_1Y}}{K_{Ln_2Y}}$		$\alpha_{Ln_1}^{Ln_2}=\frac{m_{Ln_1}\, m_{\overline{Ln_2}}}{m_{Ln_2}\, m_{\overline{Ln_1}}}$ Observed mean value (30°C)	Ion	Radius (Å)
	Calcd Value*	Calcd value**			
Lu-Yb	2.00	1.82	—	Lu^{3+}	0.84
Yb-Tm	1.55	2.09	—	Yb^{3+} Tm^{3+}	0.85 0.86
Tm-Er	2.95	3.31	2.05	Er^{3+}	0.87
Er-Ho	1.86	1.74	—	Ho^{3+}	0.89
Ho-Dy	1.90	3.63	1.88	Dy^{3+}	0.91
Dy-Y	1.62	1.55	1.61	Tb^{3+}	0.92
Y-Tb	1.45	1.51	1.76	Gd^{3+} Eu^{3+}	0.94 0.96
Tb-Cd	3.63	4.79	—	Sm^{3+}	0.97
Gd-Eu	1.05	1.02	1.30	Pm^{3+}	0.98
Eu-Sm	1.62	1.38	—	Nd^{3+}	0.99
Sm-Nd	3.39	3.09	3.77	Pr^{3+} Ce^{3+}	1.00 1.02
Nd-Pr	1.62	2.04	—	La^{3+}	1.04
Pr-Ce	2.63	2.29	—	Y^{3+}	0.88
Ce-La	3.02	4.68	—	Sc^{3+}	0.68

* Stability constants measured by G. Schwarzenbach *et al.*,[5] are used.
** Stability constants measured by E. J. Wheelwright *et al.*,[4] are used.

(LnY) in solutions at 25°C and $\mu=0.1$.

$$\Delta F^{\circ}_{Er} = -\boldsymbol{R}T \ln K_{ErY} = \Delta H^{\circ}_{Er} - T\Delta S^{\circ}_{Er}$$
$$\Delta F^{\circ}_{Tm} = -\boldsymbol{R}T \ln K_{TmY} = \Delta H^{\circ}_{Tm} - T\Delta S^{\circ}_{Tm}$$

The above relation lead to the following form:

$$\log \alpha_{Tm}^{Er} = \log \frac{K_{TmY}}{K_{ErY}} = -\frac{(\Delta H^{\circ}_{Tm}-\Delta H^{\circ}_{Er})-T(\Delta S^{\circ}_{Tm}-\Delta S^{\circ}_{Er})}{2.303\boldsymbol{R}T}$$

Introducing $\Delta H^{\circ}_{Tm}=-1870$ cal/mol, $\Delta H^{\circ}_{Er}=-1708$ cal/mol, $\Delta S^{\circ}_{Tm}=79.1$ cal/mol per deg. and $\Delta S^{\circ}_{Er}=78.3$ cal/mol per deg., a value of 1.96 is obtained as the separation factor of the Er-Tm pair at 303°K. Further, the same treatment as above gives 1.91 as the α_{Tm}^{Er}-value at 333°K. The α_{Tm}^{Er}-values found experimentally at temperatures of 30°C and 60°C are in fair agreement with the calculated values.

The observed separation factor of 1.30 for Eu and Gd is greater than the calculated value; the former approaches 1.1,⁶⁾ as predicted from the results of the ion exchange elution of a mixture of Eu and Gd. On the other hand, slight differences in the separation factors for pairs of rare earths, such as Y–Dy, Tb–Y, and Nd–Sm, are observed between the calculated and experimental values. This may be attributed to the following facts: the α-measurement was performed at an ionic strength of *ca.* 0.015 M in order to get suitable values for the real exchange system, while the stability constants of the rare earth-EDTA chelates were determined at $\mu=0.1$. However, the difference in the separation factor due to the ionic strength may be insignificant between the adjacent rare earth pair. As may be clear from the stability constants of Ln-EDTA chelates,⁴,⁵,⁹⁾ fairly large differences have been reported in the literature. The accuracy in determining the stability constant is naturally limited to some degree by the very stable chealte formation. The above factors are considered to exert a serious effect on the calculation of the separation factor using the values of the stability constants.

It is convenient to calculate the separation factor by means of the difference in the stabilities of two adjacent rare earths. However, the experimental results show that the separation factor should be directly measured under conditions similar to those in the ion-exchange system employed for the elution.

The authors wish to thank Mr. Matsuji Sato for his X-ray fluorescent analysis.