Recovery of Highly-Purified Rare Earth Elements Using Newly-Synthesized Chelating Resins

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The chromatographic separation of rare earth elements was studied using newly-synthesized chelating resins which have EDTA (ethylenediaminetetraacetic acid) and DTTA (diethylenetriaminetetraacetic acid) pendant groups. The chromatography using EDTA- and DTTA-chelating resins gave excellent separation results, while the IDA-chelating resin was not satisfactory. The DTTA-type resin was especially effective, allowing highly purified rare earth elements to be recovered. The separation efficiency of each resin was attributed mainly to the difference in its complexing capability among rare earth ions. Prior to experimentation, the chromatographic conditions were assessed and optimized by computer simulation based on newly introduced equations. The simulation results were effective in the case of Pr^{3+}/Nd^{3+} for determining the experimental conditions. An analysis of the experimental results helped to elucidate the mechanism of the chromatographic separation while using the simulation results.

Lanthanum and cerium can be separated from other rare earth elements by a precipitation-filtration method; but the other 12 rare earth elements cannot be easily separated by such a simple chemical method. Many studies have been made on the separation of rare earth elements using solvent extraction and ion exchange.[1] In the field of analytical chemistry, it has been known that several organic ligands are capable of forming specific complexes with rare earth elements. Typical examples of such organic ligands are amine-*N*-polyacetic acids, such as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid). Their stability constants are as high as 5 to 20 in terms of a logarithmic value (log *K*).

Differences in the values of their stability constants among the rare earth elements are expected to be sufficiently large for chromatographic separation. Several studies have been conducted on the separation of rare earth elements with such chelating resins as iminodiacetate resin,[2,3] *N*-methyliminodiacetate resin[4] and nitrilophosphonic resin.[5]

The authors have previously reported on results regarding studies of the selective bromination of *m*-divinylbenzene (*m*-DVB).[6] A bromination method was developed by referring to the selective addition reactions of various amines to *p*-DVB.[7] Follow-up and industrial application studies of that reaction have been made.[8] An attempt was also successfully made to synthesize chelating resins with pendant groups that are structurally similar to EDTA and DTTA (diethylenetriaminetetraacetic acid).[9] This paper describes the excellent results of our investigation on the chromatographic separation of rare earth elements using the newly-prepared resins, and comparing them with the obtained results using a known IDA (iminodiacetic acid)-chelating resin.

Prior to experimentation, the separation conditions of the chromatography were assessed and optimized by a computer simulation based on newly introduced equations. Although various simulation methods were known, the method introduced in this study is characterized by its easy procedure for finding a solution. The simulation results help to elucidate the chromatographic separation mechanism of rare earth elements.

Experimental

Synthesis of Chelating Resins. The procedures for synthesizing the resins followed that of previous reports.[9]

An IDA-chelating resin was synthesized from a copolymer of *m*-divinylbenzene (*m*-DVB) with vinylbenzyl chloride (VBC).[10,11] The backbone structure of a resin must be suitably designed in order to develop a greater chelate-forming capability. This capability of a resin is considered to depend primarily on the stability constant of the pendant group and secondarily on the crosslinking and rigidity of the polymer chain. Notably, there is a larger steric hindrance against pendant groups adjacent to DVB units in a resin. The monomer sequences of copolymers (VBC/*p*-DVB and VBC/*m*-DVB) were calculated based on the probability theory[12] of radical polymerization (Table 1). The formation of DVB–DVB chains in a polymer is most important from the standpoint of polymer-chain rigidity. The DVB–DVB and DVB–VBC sequences are

Table 1. Sequence Distributions in Copolymers of DVB(M_1) Isomers with VBC(M_2)

Copolymer	A[a]	B[a]
$P_2\{M_1M_1\}$	1.7	0.8
$P_2\{M_1M_2\}$[b]	41.6	18.2
$P_2\{M_2M_2\}$	56.7	80.9
$P_3\{M_1M_1M_1\}$	0.13	0.07
$P_3\{M_1M_1M_2\}$[b]	3.2	1.5
$P_3\{M_2M_1M_2\}$	19.2	8.4

a) A and B are copolymers of VBC with *p*-DVB and *m*-DVB, respectively, where $[M_1]/[M_2]=0.118$. b) $P_2\{M_1M_2\}$ consists of both diads M_1M_2 and M_2M_1, and $P_3\{M_1M_1M_2\}$ both triads $M_1M_1M_2$ and $M_2M_1M_1$.

believed to cause a steric hindrance against chelation. The probability of a DVB–DVB sequence is 0.8% for *m*-DVB and 1.7% for *p*-DVB. *m*-DVB also gives a lower probability (18.2%) for DVB–VBC chain formation than *p*-DVB (41.6%). Thus, *m*-DVB was selected as the crosslinking agent. IDA groups could be introduced into the resin by the reaction of a copolymer of *m*-DVB and VBC (*m*-DVB/VBC by wt.=1:10) with diethyl iminodiacetate (IDAE), followed by hydrolysis. It took approximately 8 h for the reaction to be completed. The resin produced had a cation-exchange capacity of 4.3 meq g^{-1}.

An EDTA-chelating resin was synthesized by the amination of a copolymer [**II**] of *m*-(1,2-dibromoethyl)-styrene (*m*-DBS) [**I**] and *m*-DVB (*m*-DVB/*m*-DBS by wt.=2.5:7.5) with IDAE, followed by hydrolysis (Fig. 1). Amination while synthesizing an EDTA-chelating resin [**IV**] was not as easy as during IDA-chelating resin synthesis. One side reaction was the elimination of HBr from the 1,2-dibromoethyl group of a DBS unit, resulting in the formation of a double bond. The obtained resin had a cation-exchange capacity of 3.9 meq g^{-1}.

DTTA-chelating resin synthesis was performed by the preparation of a copolymer [**VI**] consisting of a monomer [V] and *p*-DVB (*p*-DVB/monomer [V] by wt.=2:8), followed by the *N*-carboxymethylation of the amino groups with bromoacetic acid (Fig. 2). Copolymer [**VI**] had an anion-exchange capacity of 6.2 meq g^{-1}. If conversion rates for the monomer [V] and *p*-DVB were both 100%, the anion-exchange capacity of the copolymer [**VI**] should be 7.5 meq g^{-1} at its maximum. The chelating resin [**VII**] obtained after *N*-carboxymethylation had a cation-exchange capacity of 5.1 meq g^{-1}.[9]

Separation Studies. Chelating Resins: Each of the chelating resins was classified between 100-mesh and 200-mesh with sieves. The classified resins were washed (twice with a 0.1 mol dm^{-3} aqueous NaCl solution and then with 0.1 mol dm^{-3} hydrochloric acid).

Reagents: Salts of rare earth elements, rare earth chlorides, were of commercially available grade (purity: 99.9% or higher). Each salt was weighed and dissolved in deionized water. Other reagents were of commercially available guaranteed grade.

Analysis: The concentrations of rare earth elements in a solution were determined by an automatic-recording luminescence spectrophotometer, manufactured by Shimadzu Corporation. The pH values of the solutions were measured with a pH meter (model HM-18B) and a glass electrode (model GST-155C9 manufactured by Toa Elec-

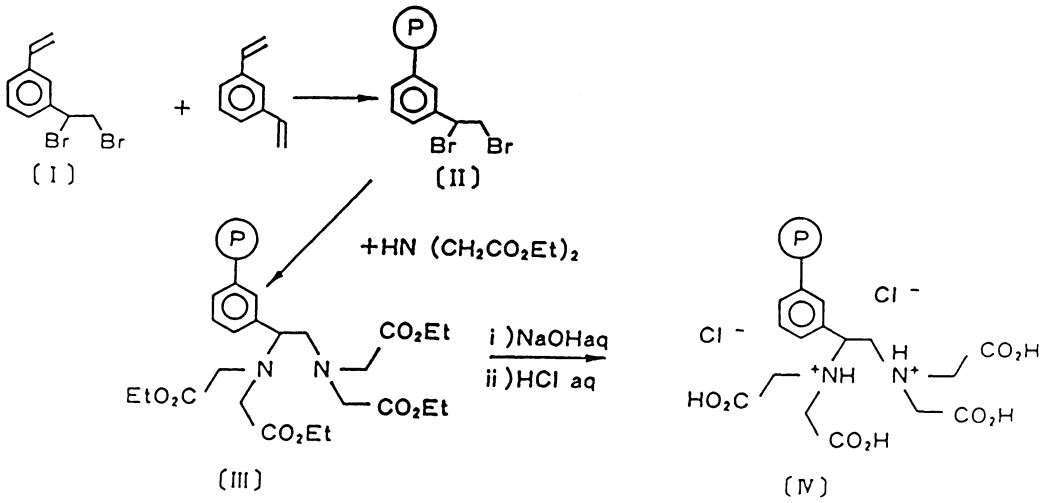

Fig. 1. Synthesis of EDTA-chelating resin.

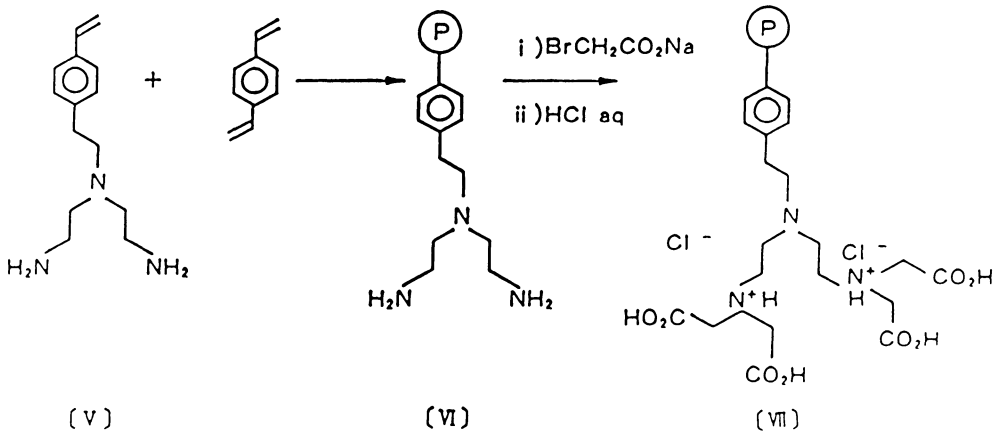

Fig. 2. Synthesis of DTTA-chelating resin.

Table 2. Rare Earth Ion Feed and Flow Rate for Each Separation Experiment

Figure No.	Rare earth feed		Flow rate
	Concentration (mol dm^{-3})	Amount (ml)	ml min^{-1}
5	44	125	14.6
6	34	106	17.3
7	29	120	14.1
8	19	120	12.7
9	19	120	12.5
10	25	120	12.7
11	25	347	9.32

tronics Ltd.).

Separation Procedure: Liquid chromatography was performed at 95 °C in a jacketed Pyrex column with an internal diameter of 10 mm and a length of 1 m (Figs. 5—10) or 2 m (Fig. 11). The concentration and amount of feed and the flow rate in each experiment are listed in Table 2. A chelating resin, which was converted to the OH^- form by an alkaline solution at pH=10, was embedded into this column. The resin bed was washed with de-ionized water to remove any remaining alkali from the column. A solution containing two rare earth elements at equal molar concentrations whose pH was adjusted using hydrochloric acid was fed into the column. Then, 0.1 mol dm^{-3} hydrochloric acid was added to the column and 2 cm^3 fractions of the eluate were collected by means of a fraction collector. The pH and concentrations of the rare earth elements were measured for each fraction.

Results and Discussion

Simulation of Separation for Determining the Experimental Conditions and Analyzing the Experimental Results. The equilibrium reactions involved in this chromatography consisted of the following two types: (i) Dissociation of amine-*N*-polyacetic acids fixed to a resin (acid-base reaction) and (ii) chelate formation of rare earth ions on the resin.

A well-known method for determining equilibrium is to introduce multidimensional equations using the equilibrium constant K. The equations give a plural of roots and it was generally hard to choose the correct root. An alternative method is to determine the concentrations in an equilibrium state by minimizing the Gibbs' free energy.[13,14] This method was more complicated, so both methods were unsuitable for the chromatography simulation.

Therefore, we devised a new method[15,16] in which each reaction was expressed as an addition reaction, and the "reduction potential strength" was used to evaluate the reaction thermodynamically. This method enabled the concentration of each chemical species to be readily determined for any equilibrium state of a system of plural reactions. Here, it is briefly explained.

In this study, a completely dissociated form of a resin-bound chelating group, denoted as R-$(COO^-)_n$, was adopted as an acceptor (Eq. 3) instead of a non-dissociated form, R-$(COOH)_n$. An addition of protons can generally be expressed as

$$\text{R-}(\text{COO}^-)_n + l\,\text{H}^+ \longrightarrow \text{R-}(\text{COO}^-)_{n-l}(\text{COOH})_l, \quad (1)$$

where n and l are integers safisfying $n \geqq l \geqq 1$. n=2 for an IDA type and n=4 for EDTA and DTTA types.

The addition of a rare earth ion to the acceptor can be expressed as

$$\{[\text{R-}(\text{COO})_n]^{n-}\}_m + \text{RE}^{3+} \longrightarrow \{[\text{R-}(\text{COO})_n]_m \cdot \text{RE}\}^- \quad (2)$$

where n=2 and m=2 for an IDA type. n=4 and m=1 for EDTA and DTTA types. The above two kinds of equations are referred to as individual reactions, where R-$(COO)_n{}^{n-}$ can be considered, apriori, to be suitable as an acceptor for both addends, H^+ and RE^{3+}, in the systems of this study. It was also reported[16] that amine-*N*-polyacetic acids such as EDTA complexed effectively with rare earth ions in an acceptor form as represented by Eq. 2. Taking advantage of the above expressions and reduction-potential strengths results in easier calculations and more definite determinations of the thermodynamics of a system involving plural exchange reactions, inclusive of the adsorption-desorption of rare earth ions and an acid-base reaction.

The protonation to a conjugate base and chelate formation are both generally expressed in a unified form:

$$\text{A} + \nu \cdot \text{X} \longrightarrow \text{D}. \quad (3)$$

where A is the acceptor of an addend X, D is an adduct and ν is the stoichiometric coefficient of an addend X. 'A' can refer to a carboxylate ion of an amine-*N*-polyacetic acid ligand; 'X' can refer to a rare earth ion or a proton and 'D' can be a complex of a rare earth ion with a carboxylate ion or a non-dissociated acid. The equilibrium relationship of Eq. 3 can be expressed as follows by using thermodynamic relations[17]:

$$\Delta\mu_x = \Delta\mu^\circ_{\text{D}} + \frac{RT}{\nu} \ln \frac{a_{\text{A}}}{a_{\text{D}}}. \quad (4)$$

Here, $\Delta\mu_x$ is termed the "reduction potential strength" and is defined by the chemical potential μ_x and standard chemical potential μ°_x as

$$\Delta\mu_x \equiv \mu^\circ_x - \mu_x. \quad (5)$$

$\Delta\mu^\circ_{\text{D}}$ is the "standard reduction potential strength" and is defined as

$$\Delta\mu^\circ_{\text{D}} \equiv \mu^\circ_x - \frac{(\mu^\circ_{\text{D}} - \mu^\circ_{\text{A}})}{\nu}. \quad (6)$$

Suppose that a system contains several kinds of

acceptor species A and N kinds of the addend X. The concentration ratio of an arbitrary adduct species D, which is a mixed-ligand complex of a given i-th species of A with L_j units of any j addend of X(j=1,2,⋯,N), to the remaining non-complexed i-th species can be expressed as Eq. 7[18]:

$$T_{i,Lj} = \exp\left(\frac{S_p - L_p}{RT}\right), \tag{7}$$

where

$$S_p = \sum_{j=1}^{N} \sum_{n_j=1}^{L_j} \nu_{i,n_j} \Delta\mu^\circ_{i,n_j} \tag{8}$$

and

$$L_p = \sum_{j=1}^{N} \sum_{n_j=1}^{L_j} \nu_{i,n_j} \Delta\mu_{i,n_j}. \tag{9}$$

Here, n_j is the stepwise number of additions of any addend j and L_j is the cumulative number of additions.

The introduced distribution function, Eq. 7, seems to be complicated, but it can be easily solved numerically since it always increases monotonously and leads to only one solution for any case.

Simulations were executed according to the following imaginary separation procedures: (1) An alkaline solution was supplied to a column packed with an EDTA-chelating resin, so as to dissociate amine-*N*-polyacetic acid groups of the resin; (2) An imaginary solution containing Nd^{3+} and Pr^{3+} was passed through the column and (3) the rare earth chelates were decomposed by supplying an acid solution. The first, second and third procedures are called "regeneration," "adsorption," and "development," respectively. Computations using an ECLIPS minicomputer manufactured by Data General Co., Ltd. were executed step-by-step for each imaginary plate formed by subdividing a packed column. In this procedure, Eq. 7 was repeatedly applied according to the reported treatment of multi-stage equilibrium.[19] The $\Delta\mu^\circ_{i,n_j}$ for rare earth ions and for H^+ are summarized in Tables 3(a)[20] and 3(c).[21] S_P for H^+ in Eq. 8 is shown in Table 3(b) and L_p is dependent on the concentrations of two addends (H^+ and RE^{3+}) in each plate of chromatography.

The results of simulated separation conditions in the chromatography can be summarized as follows:

1. A resin bed can be regenerated with an alkaline solution at pH>11.
2. A resin bed can be regenerated not only with a less alkaline solution but with a weakly acidic (pH>4) solution. It is hardly regenerated with a solution at pH<4.
3. Asorption bands can be developed at pH<2.
4. The concentrations of eluted rare earth ions are correlated positively with the acid concentration in the developing solution.

Table 3(a). $\Delta\mu^\circ_{i,n_j}$ for Protonation to the Conjugate Bases of Amine-*N*-polyacetic Acids

(kJ mol^{-1})

Amine-*N*-polyacetic acid	$\Delta\mu^\circ_{i,n_j}$[a]				
	n_j=1	n_j=2	n_j=3	n_j=4	n_j=5
IDA	44.0	14.3	—	—	—
EDTA	54.5	27.2	15.5	11.3	—
DTPA	59.9	49.0	20.4	15.0	10.8

a) The j refers to a proton and n_j to the stepwise number of the addition. Values of $\Delta\mu^\circ_{i,n_j}$ were calculated using the stepwise dissociation constants of the amine-*N*-polyacetic acids listed in Ref. 20.

Table 3(b). *S*-Potentials for Protonation to the Conjugate Base of Ethylenediaminetetraacetic Acid

(kJ mol^{-1})

L_j[a]	0	1	2	3	4
S_p	0	54.5	81.7	97.2	108.5

a) The j refers to a proton and L_j the cumulative number of additions.

Table 3(c). $\Delta\mu^\circ_{i,n_j}$[a] for a Complex Formation of Rare Earth Ions with Amine-*N*-polyacetic Acids

(kJ mol^{-1})

Rare earth ion	IDA	EDTA	DTPA
La^{3+}	33.5	88.4	114.0
Ce^{3+}	—	91.3	—
Pr^{3+}	39.4	93.9	124.9
Nd^{3+}	39.8	95.1	127.0
Sm^{3+}	40.6	98.0	130.7
Eu^{3+}	41.5	99.3	130.7
Gd^{3+}	40.2	99.3	131.6
Tb^{3+}	41.1	102.7	132.8
Dy^{3+}	41.9	104.8	134.1
Ho^{3+}	—	—	—
Er^{3+}	42.3	107.7	132.4
Tm^{3+}	42.7	110.6	131.1
Yb^{3+}	44.0	111.5	131.6
Lu^{3+}	—	113.1	—

a) The j refers to a rare earth ion. Values of $\Delta\mu^\circ_{i,n_j}$ were calculated using the stability constants of the rare earth ions listed in Ref. 21.

Examples of the simulation results, selected to determine a favorable experimental condition, are illustrated in Figs. 3 and 4.

When a solution has pH=10 (Fig. 3), the dissociation degree of EDTA groups within the resin is 83%. At pH=4 (Fig. 4) it is only 54%. In view of a reported observation,[16] it was originally expected that the rare earth ions could not be effectively adsorbed after a regeneration procedure at pH=4. However, it was predicted from simulation results that rare earth ions could be adsorbed when the solution was at pH=4 as well as at pH=10. At

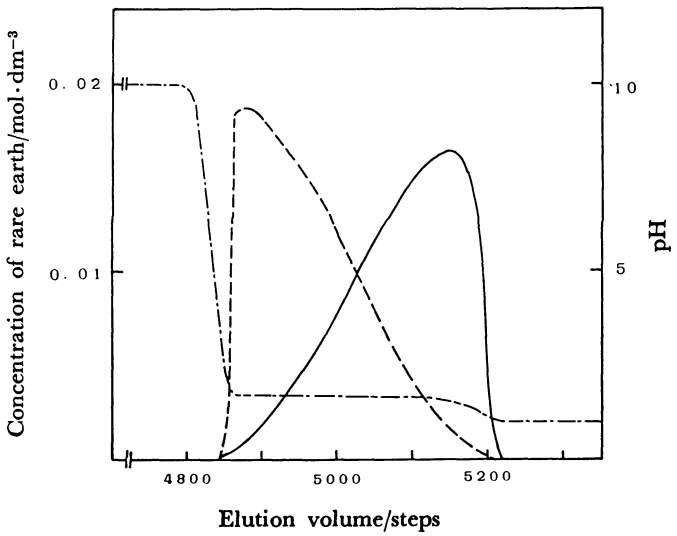

Fig. 3. Simulation of the separation of rare earth ions with EDTA-chelating resin. (The adsorption band is regenerated at pH=10 then developed with 0.1 mol dm^{-3} HCl.) ——: pH, ----: Pr^{3+}, ——: Nd^{3+}.

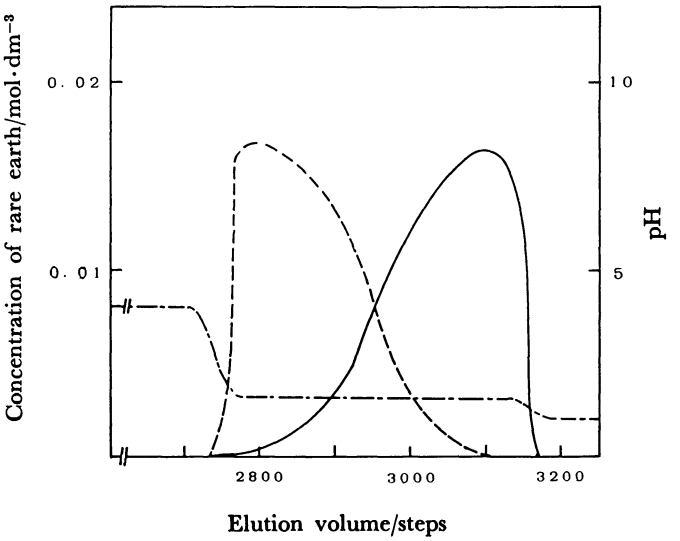

Fig. 4. Simulation of the separation of rare earth ions with EDTA-chelating resin. (The adsorption band is regenerated at pH=4 then developed with 0.1 mol dm^{-3} HCl.) ——: pH, ——: Pr^{3+}, ——: Nd^{3+}.

pH=4, two of the four carboxyl groups of an EDTA moiety were not dissociated. As a rare earth ion approaches the EDTA moiety, two nondissociated protons seem to be exchanged for a rare earth ion, allowing it to form a complex. The S_p of the second proton addition to the conjugate base of EDTA is 81.7 kJ mol^{-1} whereas the S_p of the complex formation of Pr^{3+} and Nd^{3+} with EDTA that are identical to the $\Delta\mu^{\circ}_{i,n_j}$ in these cases are as large as 93.9 and 95.1 kJ mol^{-1}. This might explain quantitatively why protons can be replaced by Pr^{3+} and Nd^{3+}.

The step number (the number of simulation calculations in which the imaginary solution phase is shifted downwards as the acid solution descends) at which rare earth ions begin to elute, is about 4840 when the adsorption band is initially regenerated at pH=10 (Fig. 3). The corresponding step number is 2750 when it is initially regenerated at pH=4(Fig. 4). It is noted that in the case of EDTA groups, the ratio of the dissociation degree at pH=10 to that at pH=4 is 1.5; also, the corresponding ratio of the step numbers for rare earth ions to start being eluted is 1.7. Thus, the former ratio does not agree with the latter ratio. It was then considered (on the basis of material balance) what determines the ratio of the step numbers for rare earth ions to start being eluted. The elution volume at the break-through point is defined by the resin volume and the rare earth ion concentrations in the solid and liquid phases.
That is,

$$V_f = \frac{C_{R,r}}{C_{R,s}} V_r \tag{10}$$

where V_f is the elution volume at the break-through point, V_r the resin volume, and $C_{R,r}$ and $C_{R,s}$ the rare earth ion concentrations in the solid and liquid phases. The ratio $C_{R,r}/C_{R,s}$ should be expressed by the proton concentrations in the respective regions as

$$\frac{C_{R,r}}{C_{R,s}} = \frac{[C_{H,r}]_B - [C_{H,r}]_F}{[C_{H,s}]_B}, \tag{11}$$

where $[C_{H,r}]_B$ and $[C_{H,s}]_B$ are the solid- and liquid-phase proton concentrations in the rare earth band and $[C_{H,r}]_F$ the solid-phase proton concentration in the front region. From Eqs. 10 and 11, the following equation is derived:

$$V_f = \frac{[C_{H,r}]_B - [C_{H,r}]_F}{[C_{H,s}]_B} V_r. \tag{12}$$

Calculations of V_f from Eq. 12 for regenerations at pH=10 and pH=4 give a value of 1.75 for the ratio of V_f. This value is almost equal to the value described above as the ratio of the step numbers for rare earth ions to start being eluted. The reason why the ratio of V_f at pH=10 to that at pH=4 is much larger than unity is that $[C_{H,r}]_F$ at pH=4 is almost three-times that at pH=10 while the $[C_{H,r}]_B$ at pH=4 is only two-times that at pH=10. $[C_{H,s}]_B$ does not change very much with the pH.

A rear boundary reaction is completed by bringing a sufficient amount of acid into contact with chelated rare earth ions. The acid concentration at the rear boundary is closely related to the liquid-phase concentration of rare earth ions in the adsorption band. The total concentration of the rare earth ions is about 110 mmol dm^{-3} when developed using 0.5 mol dm^{-3} hydrochloric acid whereas this concentration is about 20 mmol dm^{-3} with 0.1 mol dm^{-3} hydrochloric acid (Fig. 4).

The actual experimental conditions were set so that the pH of the regenerating solution was 10 and the acid concentration of the developing solution was 0.1 mol dm^{-3}.

Results of Experiments. A chromatographic separation of rare earth elements was carried out using each of the three different chelating resins under the computer-simulated conditions.

The result of a chromatographic separation of La^{3+} and Nd^{3+} with an IDA-chelating resin is shown in Fig. 5. The result was good, reflecting the large difference in the potential strengths of La^{3+} and Nd^{3+}, which is shown to be 6.3(kJ mol^{-1}) from Table 3(c). But Pr^{3+} and Nd^{3+} were slightly separated with IDA-chelating resin in Fig. 6. The result indicated that the difference $\Delta(\Delta\mu^\circ_{i,n_j})$ of the potential strengths $\Delta\mu^\circ_{i,n_j}$ between Pr^{3+} and Nd^{3+} with the IDA-chelating resin was small (see Table 4), as expected from the $\Delta(\Delta\mu^\circ_{i,n_j})$ with the corresponding acid (IDA) shown in Table 3(c).

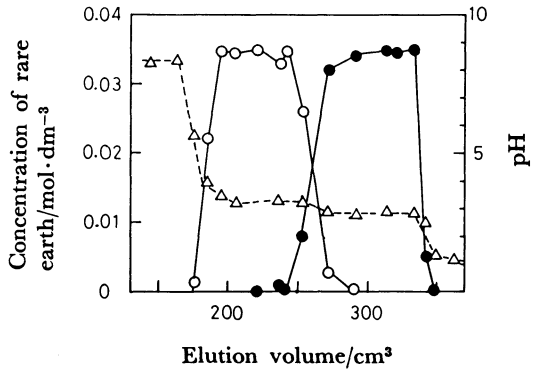

Fig. 5. Separation of La^{3+} and Nd^{3+} with IDA-chelating resin. △: pH, ○: La^{3+}, ●: Nd^{3+}.

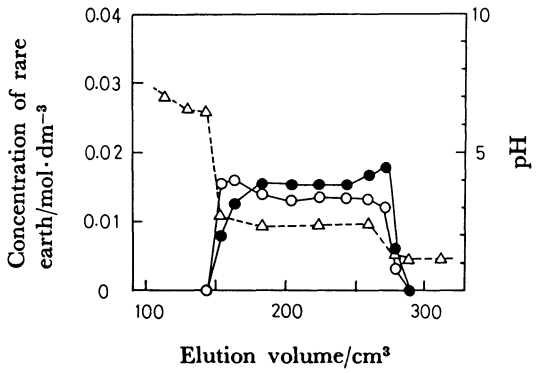

Fig. 6. Separation of Pr^{3+} and Nd^{3+} with IDA-chelating resin. △: pH, ○: Pr^{3+}, ●: Nd^{3+}.

Table 4. $\Delta(\Delta\mu^\circ_{i,n_j})$ for a Complex Formation of Rare Earth Ions with Chelating Resins

(kJ mol^{-1})

	IDA	EDTA	DTTA
Nd^{3+}/Pr^{3+}	0.17	0.88	0.92

Separation between Pr^{3+} and Nd^{3+} was more effectively attained with the EDTA-chelating resin prepared from m-DBS (Fig. 7). The potential difference $\Delta(\Delta\mu^\circ_{i,n_j})$ between both ions with the corresponding acid (EDTA) was 1.2 kJ mol^{-1}, larger than that of IDA (0.4 kJ mol^{-1}). Figure 8 shows even better separation result using the DTTA-chelating resin prepared from styrenetriamine monomer (V), than that using the EDTA-chelating resin. The potential difference of these ions with DTPA, whose structure is similar to DTTA, is 2.1 kJ mol^{-1} and is larger than that with EDTA. The potential-strength differences with the chelating resins observed in Fig. 6 to Fig. 8 (listed in Table 4) were all smaller than expected from the differences obtained with the corresponding amine-*N*-polyacetic acids. The reduction of the potential-strength differences is considered to be due to a steric hindrance of a polymer network to all the three acids and a chemical structure difference between DTPA and the resin-bound DTTA moiety. The other separation experiments for pairs of Eu^{3+}/Gd^{3+} and Ho^{3+}/Eu^{3+} with a DTTA-type resin gave the results shown in Figs. 9 and 10, respectively. The potential strength of Ho^{3+} is not

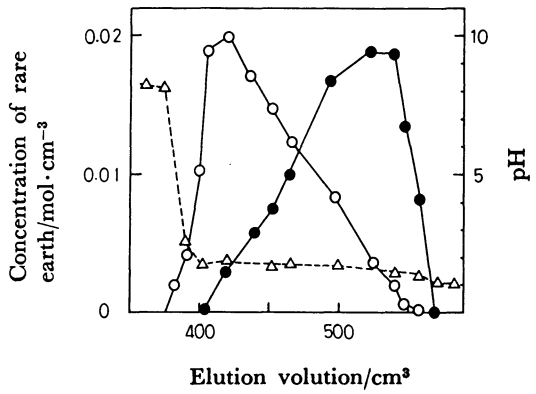

Fig. 7. Separation of Pr^{3+} and Nd^{3+} with EDTA-chelating resin. △: pH, ○: Pr^{3+}, ●: Nd^{3+}.

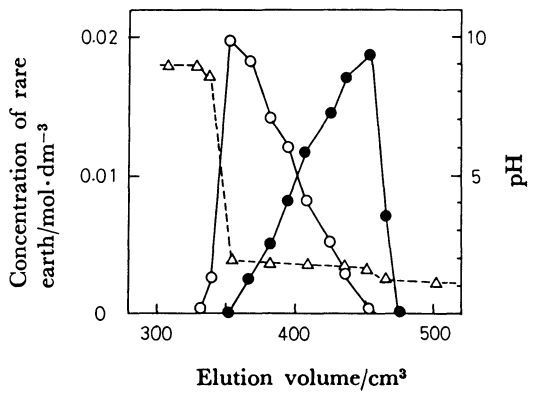

Fig. 8. Separation of Pr^{3+} and Nd^{3+} with DTTA-chelating resin. △: pH, ○: Pr^{3+}, ●: Nd^{3+}.

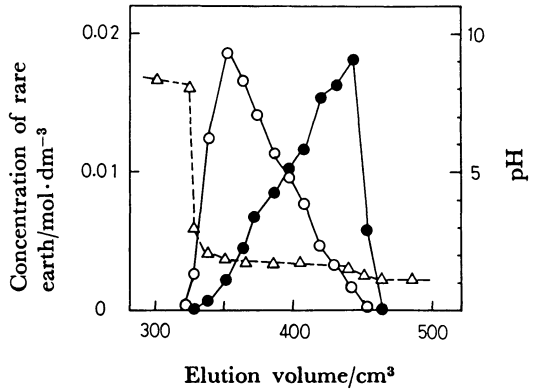

Fig. 9. Separation of Gd^{3+} and Eu^{3+} with DTTA-chelating resin. △: pH, ○: Gd^{3+}, ●: Eu^{3+}.

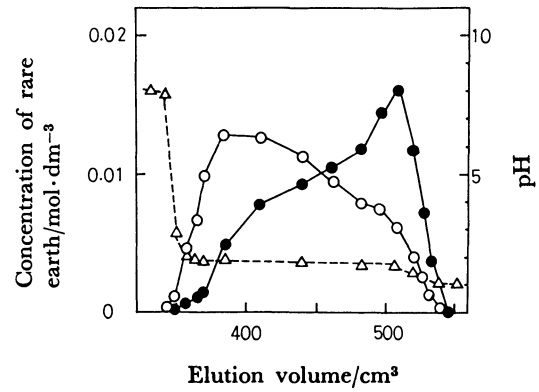

Fig. 10. Separation of Ho^{3+} and Eu^{3+} with DTTA-chelating resin. △: pH, ○: Ho^{3+}, ●: Eu^{3+}.

known and Fig. 10 is the first result of Ho^{3+} separation attempted with a DTTA-type chelate resin. The adsorbability of the Gd^{3+}/Eu^{3+} pair was contrary to that expected from the $\Delta(\Delta\mu^\circ)$ listed in the right column of Table 3(c). Several possible causes can be considered. The potential strengths of rare earth elements which have higher atomic numbers than Sm are similar to each other and no explicit tendency between the potential strengths and the atomic numbers has been observed for almost all amine-*N*-polyacetic acids. Moreover, structural distinction between DTPA and DTTA is necessary to be considered. Additional experimental results and theoretical considerations are necessary; these are presently being collected for our future reports.

Figure 11 shows the results using a longer separation column packed with a DTTA-chelating resin; the separation of Pr^{3+} and Nd^{3+} was further improved, compared with the shorter-column experiment shown in Fig. 8. Highly purified Pr^{3+} and Nd^{3+} could be recovered from almost half of the adsorption bands as well as from the neighborhoods of the front and rear boundaries. Comparing the results in Figs. 8 and 11, the volumes of the mixed-ion zone, where Pr^{3+} and Nd^{3+} were not fully (though

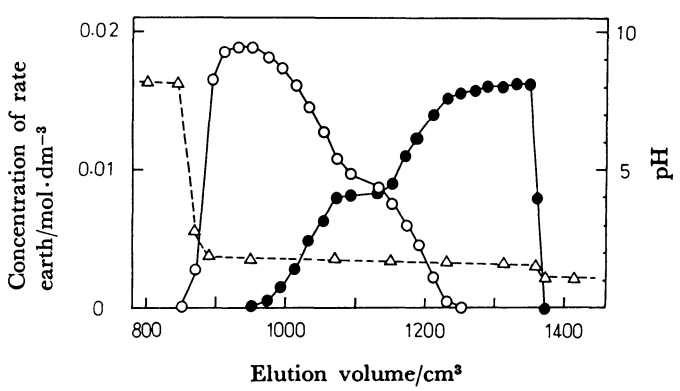

Fig. 11. Separation of Pr^{3+} and Nd^{3+} with DTTA-chelating resin. △: pH, ○: Pr^{3+}, ●: Nd^{3+}.

partially) separated from each other, were not much different. It is, thus, recognized that with a longer separation column, more fractions containing highly-purified rare earth ions can be recovered. In elution chromatography the concentrations of separated materials in effluents generally decrease with an increasing length of the separation column. The concentration of rare earth ions recovered in Fig. 11 was nearly equal to that in Fig. 8 due to displacement chromatography. The fractions from 850 to 1370 cm^3 of the elution volume (Fig. 11) were analyzed by an Argon-plasma spectrometer to determine the purity of each constituent. Two fifths of the fractions had purity values ranging from 99.99 to 99.999%. Near the rear boundary, the purity of Nd^{3+} ions seemed to be higher than 99.999% since it tended to be higher in a later fraction; however, no accurate analytical value greater than 99.999% was obtained in the measurement. An analysis of kinetics is indispensable for any discussion of chromatography and results always strongly depend on the speed of adsorption-desorption or ligand exchange. In this study, the height of an imaginary plate used in the simulation was converted to the volume of the effluent under the experimental conditions by comparing the separation profiles.

Conclusion

The separation of rare earth ions was studied with synthesized amine-*N*-polyacetic acid type chelating resins.

(1) Satisfactory separation results were obtained in experiments by displacement chromatography using EDTA- and DTTA-chelating resins.

(2) Highly-purified rare earth ions could be recovered more efficiently using a longer separation column.

(3) Systems comprising five equilibrium reactions were analyzed using the concept of reduction potential strength and a novel distribution function. A prediction made on the basis of

simulation results matched the results of separation experiments in the case of Nd^{3+}/Pr^{3+} with good precision.

(4) The step number at which rare earth ions began to elute depended on the pH of the regenerating solution; the total concentration of the rare earth ions depended on the acid concentration of the developing solution.

(5) Several rare earth ions could be separated using a DTTA-chelating resin most efficiently. However, much remains to be done before quantitatively discussing the observed differences in $\Delta(\Delta\mu^\circ)$ between the chelating resins and the corresponding amine-*N*-polyacetic acids.

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