Chromatographic Separation of Rare Earth Pairs by a Chelating Resin Having Bis(carboxymethyl)amino Groups

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Adsorption properties of rare earth elements toward a cross-linked polystyrene resin having bis(carboxymethyl)amino groups (CMA) have been studied. The selectivity sequence of the resin for a series of rare earth metals was in good accordance with that of the corresponding stability constants of diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid (DTPA) complexes. The chromatographic separation of La(III)/Pr(III), Nd(III)/Sm(III), and Y(III)/Gd(III) has been carried out by use of the present resin. The chromatographic conditions were empirically evaluated in terms of resolution (R_s), with varying column length, pH of the eluent, the flow rate and the column temperature.

Ion exchange chromatography has significantly contributed to the separation of rare earth elements.[1–4] In the conventional separation process, a cation-exchange resin and an aqueous solution of chelating reagent are employed as a stationary phase and a selective mobile phase, respectively.

Complexane-type reagents such as ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA),[1] *N′*-(2-hydroxyethyl)ethylenediamine-*N,N,N′*-triacetic acid (HEDTA)[5,6] and DTPA[7] are widely used as the selective reagent in a mobile phase due to their high separation factors for adjacent rare earths. However the solubilities for their protonated forms and the rare earth complexes are sometimes remarkably low. Therefore undesirable precipitation tends to take place during the column operations.[8,9] On the contrary, when we use a highly selective resin as a stationary phase, a simple buffer solution can be used as an eluent in place of valuable chelating reagents. In addition, the difficulty of extracting the rare earths as simple salts from the stable chelate compounds will be eliminated.

It has already been pointed out that selective resins including chelating resins[10,11] and reagent-impregnated resins[12] are effective for the separation of rare earth elements in the chromatographic systems. Takeda et al.,[11] demonstrated the chromatographic separation of several pairs of rare earths using polystyrene resins having functional groups structurally similar to EDTA and DTPA. Prior to experimentation, they have optimized the chromatographic conditions by computer simulation based on newly introduced thermodynamic parameters.

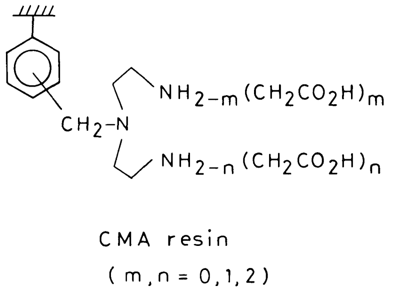

Fig. 1. Cross-linked polystyrene resin having bis-(carboxymethyl)amino groups.

We have developed the cross-linked polystyrene beads (macroreticular type) in which diethylenetriamine is linked uniquely through the secondary nitrogen.[13] Upon carboxymethylation of the aminated resin, we have obtained the chelating resin having bis(carboxymethyl)amino moieties (Fig. 1).[13,14] In this paper we have examined the adsorption selectivity of the CMA resin for a series of rare earth metals by measuring the distribution coefficient. The separation efficiency of the present resin has been evaluated by the separation factor derived from the distribution coefficients of the respective metal pairs. The mutual separation of several pairs of metals has also been carried out chromatographically under the optimum experimental conditions.

Experimental

Materials. A rare earth chloride solution was prepared by dissolving the corresponding oxide (99.9%, Japan Yttrium Co., Ltd.) in analytical grade hydrochloric acid. Other reagents were of analytical grade and were used without further purification. Chloromethylated polystyrene beads (Cl, 17.1%, 60—100 mesh) were kindly donated by Mitsubishi Chemical Co., Ltd. The resin matrix was a macroreticular (MR) type styrene-10%-divinylbenzene copolymer with the surface area and mean pore diameter, 7.3 $m^2\,g^{-1}$ and 720 Å, respectively.

Preparation of the Chelating Resin. The CMA resin was prepared by *N*-carboxymethylation of the dien-resin[13] in which diethylenetriamine (dien) is linked to the polystyrene resin uniquely through the imino nitrogen. Nitrogen analysis indicated that the CMA resin contains 1.65 mmol of the functional group per gram resin.[14]

Determination of the Adsorption Capacity. A batchwise technique was employed to determine the equilibrium adsorption capacity (amount of metal ion sorbed on one gram of dry resin) with the metal ion always being in excess over the ligand content. Typically, 500 mg of the dry resin (H^+ form) was added to 100 cm^3 of metal ion solution (0.025 mol dm^{-3}) of various pH. After shaking 2 days at 25 °C the equilibrium pH and the amount of metal ion remaining in the solution were determined. The capacity of the resin was calculated by the change in the metal concentration observed. The resin beads were packed in a glass column and washed thoroughly with water. The sorbed metal ion was liberated from the resin beads by elution with 20 cm^3 of 2 mol dm^{-3} hydrochloric acid and the metal ion in the eluent was analyzed. In most cases, a satisfactory material balance was observed between the metal ion liberated from the resin and that which remained in the solution.

Distribution Coefficients. The equilibrium distribution coefficient of the metal ion was determined under a batchwise procedure. A 500 mg batch of dry resin was immersed in 100 cm^3 of metal ion solution (0.001 mol dm^{-3}). The pH was adjusted with acetate buffer in the pH range 3.0—5.0, with hydrochloric acid below 3.0. After shaking 7 days at 25 °C, the equilibrium pH and the amount of metal ion remained in the solution were determined. The results are expressed as the distribution coefficient, K_d=amount of metal sorbed in one gram of the resin/amount of metal remaining in 1 cm^3 of the solution.

Column Separation of Metal Ion Mixture. A typical procedure is as follows; the resin beads were swollen with water and poured onto a glass column (ϕ 10 mm). An aqueous solution containing two kinds of rare earths of equal molar concentration was prepared. The pH of the solution was adjusted to 3.0 with 1 mol dm^{-3} glycine buffer. The metal ion solution was supplied to the column at a constant flow rate (0.25—1.00 cm^3 min^{-1}), and the sorbed metal ions were then eluted with a buffer solution (1 mol dm^{-3} glycine) of the pH ranging 0.8—2.0. The effluent was fractionated into 10 cm^3 portions and the amount of metal ion was determined.

Metal Analysis. The metal ion concentration was determined by a SEIKO ICP-atomic emission spectrometer, model SPS-1200A.

Results and Discussion

Equilibrium Adsorption Capacity. The capacity-pH profiles for La(III), Pr(III), and Sm(III) are given in Fig. 2. A similar trend was observed for other rare earth metals. The adsorption capacity apparently depends on the pH of the solution due to the competing protonation and complexation reactions of the functional group. The maximum capacity is approximately 1.4 mmol g^{-1} at pH higher than 4.9 irrespective of the metal ions examined. This value is close to the estimated ligand content (1.65 mmol g^{-1}). Hence the functional group in the CMA resin appeared to form 1:1 complexes with these metal ions in a similar manner to those of the EDTA complexes. The adsorbed metal ions can be quantitatively released from the resin on treatment with 2 mol dm^{-3} hydrochloric acid for regeneration.

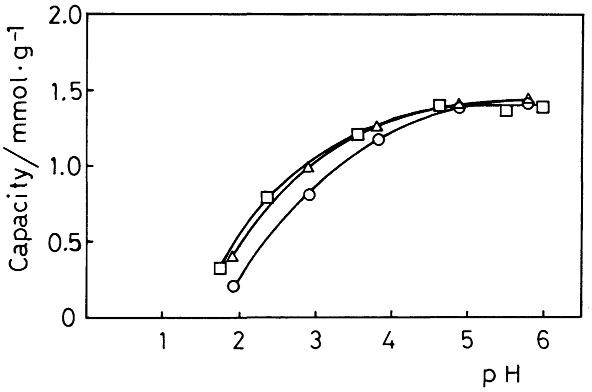

Fig. 2. Equilibrium adsorption capacity of the CMA resin for La(○), Pr(△), and Sm(□) as a function of pH (25 °C).

Distribution Coefficients. Distribution coefficients of the CMA resin for several rare earth metal ions were examined as a function of pH and the results are given in Fig. 3. The reaction of the CMA resin with a metal ions can be expressed as follows;

$$M^{n+} + RH_m \overset{K}{\rightleftharpoons} RH_{m-n}M + nH^+ \quad (1)$$

where R and M denote the resin group and the metal, respectively. The equilibrium constant of the above reaction should be given by

$$K = \frac{[RH_{m-n}M][H^+]^n}{[M^{n+}][RH_m]} \quad (2)$$

The distribution coefficient (K_d) of the metal ion between the resin phase and the aqueous phase is defined by

$$K_d = \frac{[RH_{m-n}M]}{[M^{n+}]} \quad (3)$$

From Eqs. 2 and 3, the following relationship can be obtained.

$$\log K_d = \log K + \log [RH_m] + n\text{pH} \quad (4)$$

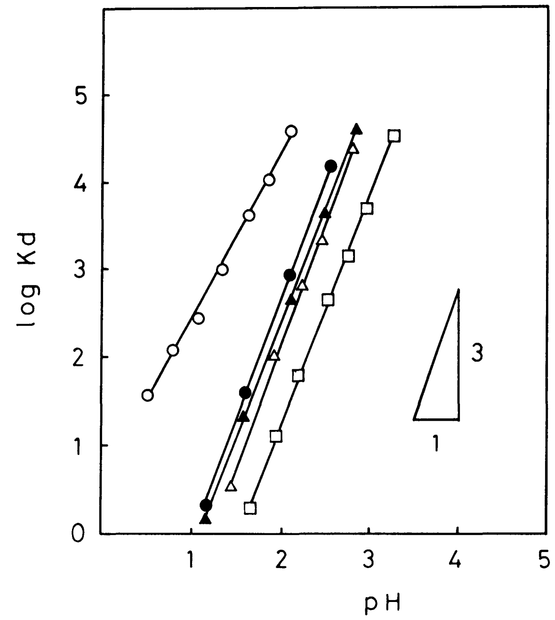

Fig. 3. log K_d of the CMA resin for several rare earth metal ions as a function of pH (25 °C). Sc(○), Y(△), La(□), Eu(●), and Yb(▲).

Equation 4 predicts that the plot of log K_d against pH gives a straight line of slope n under the condition where the amount of functional group is much larger than that of the metal ion. The slopes of the linear plots for the fourteen rare earth elements except Sc(III) were in the range from 2.7 to 3.0, which indicates that the adsorption of a rare earth metal ion is accompanied by the release of three protons. The slope for the Sc(III), 2.0, was smaller than that for other rare earth elements. In this case, some reaction mechanism other than those expressed in Eq. 1 may be involved.

Figure 4 shows the log K_d values at pH 1.6 for fifteen rare earth elements. The distribution coefficient apparently increased with decreasing ionic radius for the light rare earths (La—Sm), reached a maximum and then gradually decreased toward the heavy rare earths. Scandium, having the smallest ionic radius showed the highest affinity to the resin whereas yttrium occurred in the light rare earths. These trends are in good accordance with the stability constant sequence of the corresponding DTPA complexes where the gradual decrease in stability constant takes place for the heavy rare earths.[15] Therefore the selectivity of the resin can be attributed to the nature of a functional group which is structurally similar to DTPA.

Column Separation. The selectivity profile of the CMA resin (Fig. 4) suggests the possibility for mutual separation of light rare earths as well as Y from Sm—Dy. The separation efficiency of a metal ion pair is evaluated by the separation factor expressed by the ratio of distribution coefficients of individual metal ions 1 and 2.

$$S = K_{d1}/K_{d2} \tag{5}$$

In the present study, we chose the following pairs of rare earth metals, La(III)/Pr(III), Nd(III)/Sm(III), and Y(III)/Gd(III) for the chromatographic separation. The separation factors of the above three metal pairs calculated from the K_d values at pH 1.6 are 7.9, 2.3, and 3.0, respectively. Among them, the Nd/Sm pair seems to be most difficult to separate. The chromatographic separation was empirically characterized in terms of the resolution (R_s) of the species 1 and 2.

$$R_s = 2(t_{R2} - t_{R1})/(w_1 + w_2) \tag{6}$$

where t_{R1} and t_{R2} denote the retention time of the species 1 and 2, and w_1 and w_2 denote the band widths of 1 and 2, respectively.

Figure 5 shows the effect of pH of the eluent on the R_s for the separation of the three pairs of metal ions. It is said that the pH of the eluent is an important factor which affects the chromatographic separation.[16,17] The variation in R_s values with pH was not remarkable in the given pH range studied. When the pH is too low, the separation was unfavorable due to the small difference in the retention time, whereas the elution at higher pH lead to a significant band broadening. Therefore the most favorable pH for the separation of La(III)/Pr(III), Nd(III)/Sm(III), and Y(III)/Gd(III) were around 1.6, 1.2, and 1.2, respectively. In the present study we used 1 mol dm^{-3} glycine buffer as an eluent to keep the pH constant.

The effect of column length was examined for the separation of La(III)/Pr(III) (Fig. 5). Better resolution was attained with an increased column length, and a

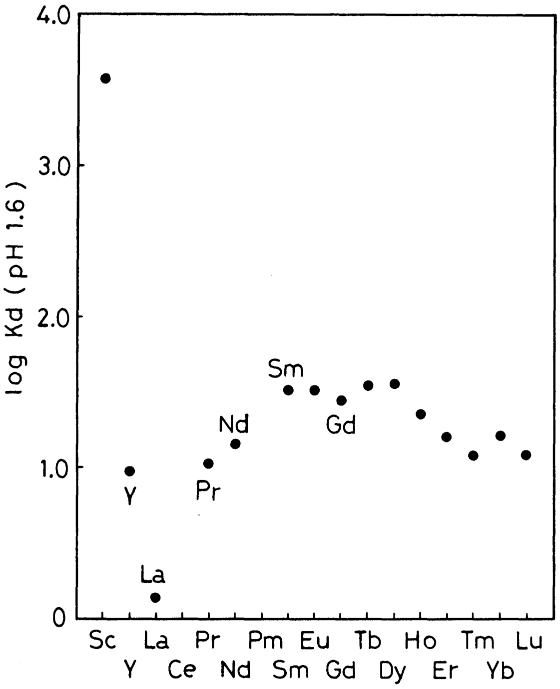

Fig. 4. Intercepts of the log K_d vs. pH plots at pH 1.6 for fifteen rare earth elements.

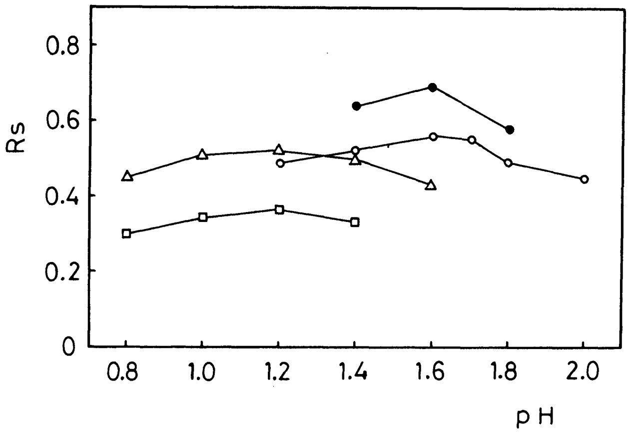

Fig. 5. Effect of pH of the eluent and the column length on the R_s for the separation of three pairs of metal ions. Column temperature: 25 °C. Flow rate: 0.5 cm^3 min^{-1}. ○: La/Pr, ϕ 1.0×14 cm, ●: La/Pr, ϕ 1.0×27 cm, △: Y/Gd, ϕ 1.0×14 cm, □: Nd/Sm, ϕ 1.0×14 cm.

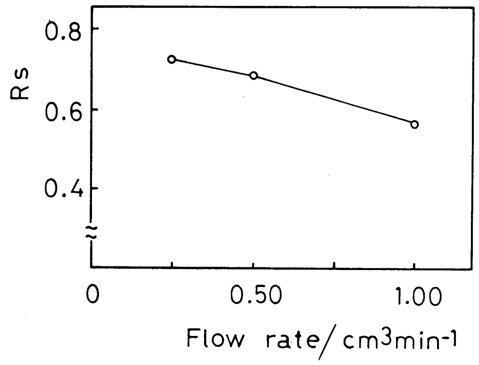

Fig. 6. Effect of the flow rate of the eluent on the R_s for the separation of La/Pr. Column temperature: 25 °C. Column size: ϕ 1.0×27 cm. The pH of the eluent: pH 1.6.

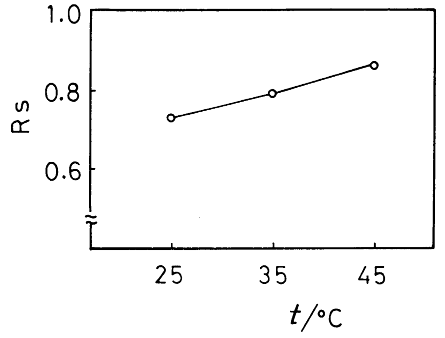

Fig. 7. Effect of the column temperature on the R_s for the separation of La/Pr. Column size: ϕ 1.0×27 cm. The pH of the eluent: pH 1.6. Flow rate: 0.25 cm^3 min^{-1}.

reduced flow rate (Fig. 6). An apparent improvement has also been attained by raising the column temperature from 25 to 45 °C (Fig. 7). The effect of temperature on the chromatographic separation may be attributed to two reasons. One is the increase of the separation factor. We have observed the increase of the retention times for La(III) and Pr(III) with increasing of the column temperature; the t_R values at 45 °C were about 1.20 and 1.24 times those at 25 °C for La(III) and Pr(III), respectively, leading to a better resolution. The second reason is the increase of the number of theoretical plates (N),[18] the N values of Pr(III) evaluated from the chromatograms were 61, 65, and 68 at 25, 35, and 45 °C, respectively. In the present study, all the column operations were carried out below 45 °C for practical reasons.

Figure 8 shows the chromatogram of the La(III)/Pr(III) pair at the optimized column condition. The degree of overlap of two peaks is less than 5% and the R_s value was found to be 0.86. Generally a separation is said to be "good" when R_s is >1.[19] For the separation of rare earth on a small scale, there are some reports in which R_s becomes larger than 1.[20,21] Considering the amount of metal ion in such as 1.2 mmol, the value 0.86 may be fairly good (Fig. 8).

It is interesting to consider a scale-up of these systems for productive purpose. Traditional ion-exchange systems where a chelating reagent is contained in the mobile phase essentially involve a restriction of solubility of the eluent. For example, the concentration of EDTA solution commonly used as an eluent is restricted due to the only moderate solubilities of the protonated EDTA or metal–EDTA com-

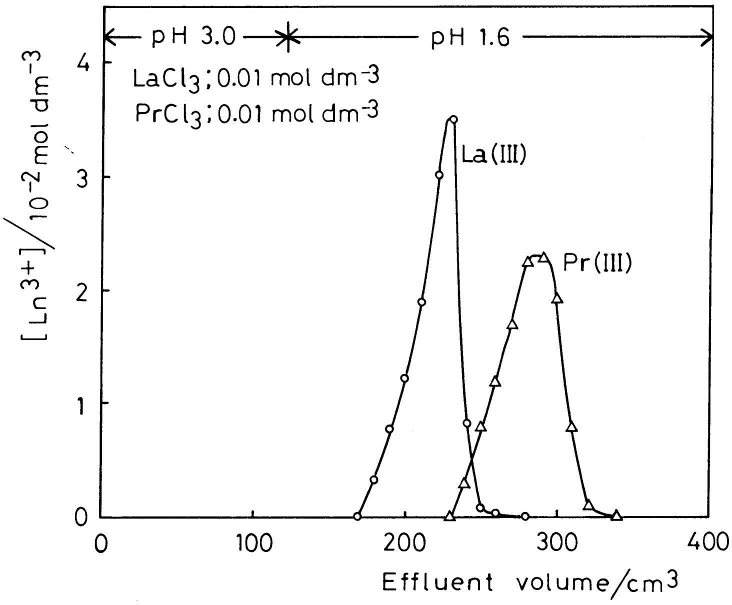

Fig. 8. Separation of La/Pr with the CMA resin. Column size: ϕ 1.0×27 cm. The pH of the eluent: pH 1.6. Flow rate: 0.25 cm^3 min^{-1}. Column temperature: 45 °C. Amount of the each metal ion: 1.2 mmol.

pounds. However, a chelating reagent is not always necessary in the present system, and hence the trouble due to precipitation during column operation can be eliminated. Figures 9, 10, and 11 show the separation chromatograms of the three pairs of metals. The amount of each metal ion is 10 mmol in all cases. The degree of overlapping of the two peaks for the separation of La(III)/Pr(III), Y(III)/Gd(III), and Nd(III)/Sm(III) were 1.1, 2.7, and 19.6%, respectively. In Fig. 9, about 95% of the loaded La(III) was collected in the fractions from 400 to 590 cm^3 of the eluate with the contamination by Pr(III) being less than 0.01%. In this experiment, the band ratio of ion-exchange zone to the metal loaded zone in the column is approximately 3 to 4 (0.75). Thus, highly purified La(III) was obtained in a reasonable yield in spite of the low band ratio. The maximum concentrations in the fractionated eluates are 8.5×10^{-2}, 4.8×10^{-2}, 9.4×10^{-2}, 5.2×10^{-2}, 8.0×10^{-2}, and 4.3×10^{-2} mol dm^{-3} for La(III), Pr(III), Y(III), Gd(III), Nd(III), and Sm(III), respectively.

A favorable separation has been realized under appreciably high loading using the CMA resin as the column stationary phase. In addition this system has advantages over the traditional ion-exchange systems where the chelating reagents are essentially required as the mobile phase. Thus, elution with only a buffer

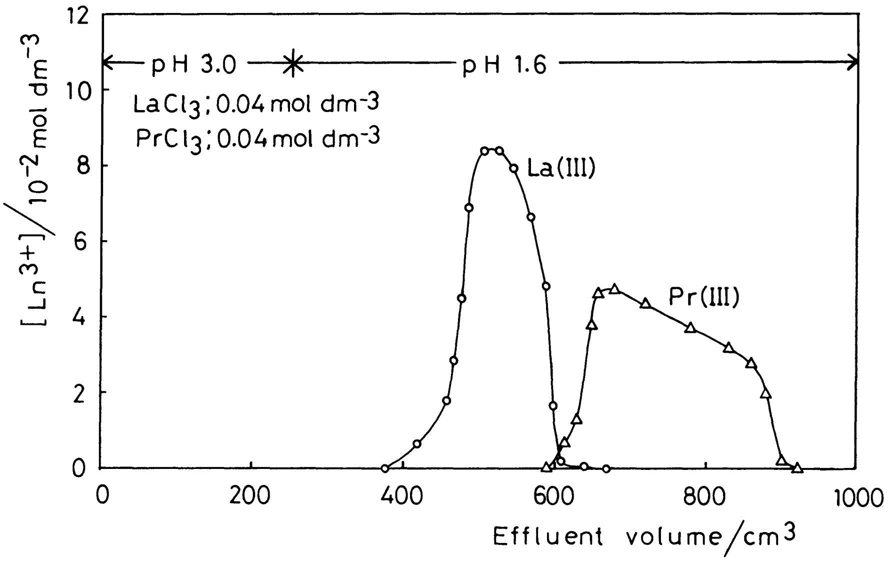

Fig. 9. Separation of La/Pr with the CMA resin. Column size: ϕ 1.0×95 cm. The pH of the eluent: pH 1.6. Flow rate: 0.25 cm^3 min^{-1}. Column temperature: 45 °C. Amount of the each metal ion: 10.0 mmol.

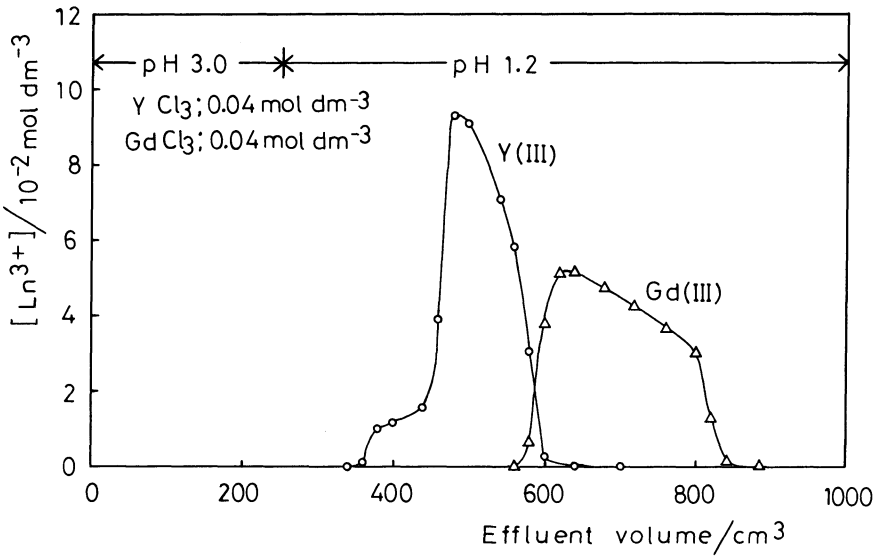

Fig. 10. Separation of Y/Gd with the CMA resin. The pH of the eluent: pH 1.2. Other conditions are the same as those given in Fig. 9.

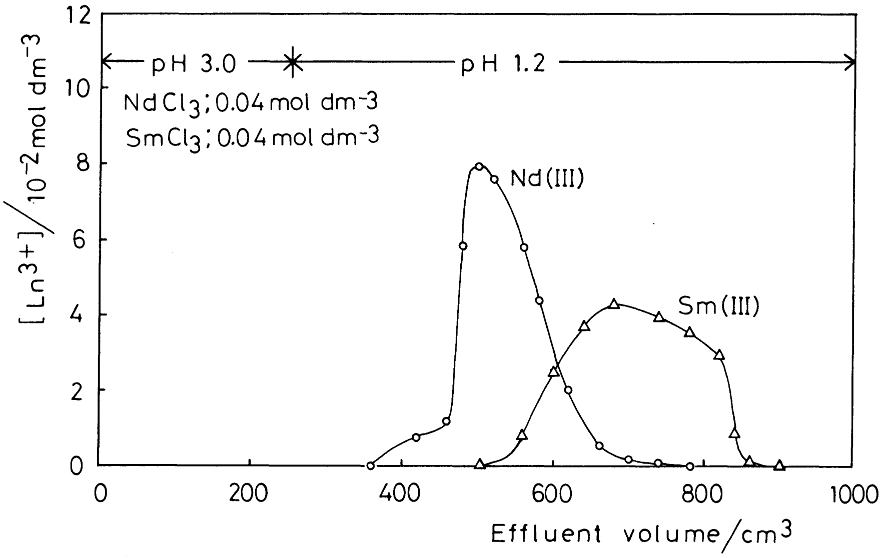

Fig. 11. Separation of Nd/Sm with the CMA resin. Conditions are the same as those given in Fig. 10.

solution may simplify the isolation procedure of metals from the eluates either by evaporation or precipitation as the oxalate or carbonate.

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