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Chromatographic Selectivity of Rare Earth Elements on Iminodiacetate-Type Chelating Resins Having Spacer Arms of Different Lengths: Importance of Steric Flexibility of Functional Group in a Polymer Chelating Resin

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Three types of chelating resins containing iminodiacetic acid homologues (IDA resins) with spacer arms of different lengths were prepared and examined as the column stationary phase for ion chromatography. The chromatographic retention behavior of rare earth elements (REEs) on the IDA resins was evaluated with respect to a capacity factor (k') to elucidate the selectivity profile of the resins. The k' values for a series of REEs on the IDA resins were compared with the chelate formation constants (K_{ML}) of the corresponding free ligands of analogous structure. Selectivity of the chelating resins having longer spacer arms between the ligand group and the polymer matrix showed a better correlation with the corresponding monomeric ligands in solution. This trend has been attributed to the increase in steric flexibility of the ligand group by the presence of the spacer arm.

Ion chromatography (IC) and high-performance liquid chromatography (HPLC) have been widely applied to the determination and speciation of metal ions.¹ In these procedures, several types of ion exchangers coupled with various complexing reagents have been employed. However, metal separation using chelating resins as a selective stationary phase is rather limited. Even in the use of a chelating resin as a stationary phase, complexing reagents have been applied as a mobile phase to improve the separation efficiency.^{2,3} When the stationary phase is highly selective, separation can be achieved simply by elution with a

mineral acid, which offers a great advantage for the following detection and isolation procedures.

In our recent publications, we reported the chromatographic separation of rare earth elements (REEs) using a chelating resin having a nitrilotriacetate (NTA) group.^{4,5} In this resin, the NTA group is located remote from the polymer matrix due to the presence of a spacer arm. A favorable separation of a series of REEs was attained with the NTA resin column simply by elution with nitric acid. A good correlation was found between the capacity factor (k') and the formation constant (K_{ML}) of the corresponding NTA complex.⁶ This result suggests that the spacer arm plays an important role in attaining favorable separation. Attention has been directed to the importance of the spacer arm in the chelating resins;⁷ however, the relationship between selectivity and ligand flexibility has not been investigated in detail.

In the present study, we have prepared three kinds of iminodiacetic acid homologue (IDA) resins having spacer arms of different lengths. Their chromatographic retention behavior for a series of REEs was examined in order to understand the role of the spacer arm to the ligand flexibility and the resin selectivity.

EXPERIMENTAL SECTION

Synthesis of the Ligands. The synthetic scheme of lysine-*N*-acetic acid is shown in Figure 1. Chloroacetic acid (94.5 g, 1

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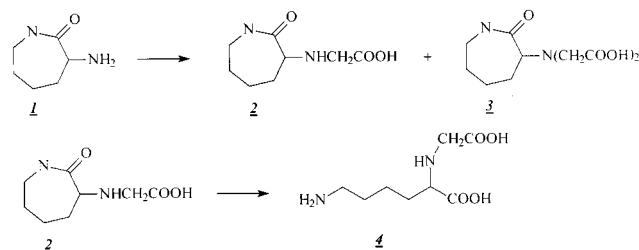


Figure 1. Synthetic scheme of lysine-*N*^ε-acetic acid (ligand for IDA resin III).

mol) in 200 mL of water was neutralized with sodium hydroxide (40.0 g, 1 mol) in 400 mL of water at a temperature below 5 °C. To this solution was added α -amino- ϵ -caprolactam (1; 128.2 g, 1 mol), and the resultant solution was stirred at 40 °C for 12 h. The reaction solution was kept basic (pH 9.5–10) by addition of 2 M sodium hydroxide solution. The solution was then acidified to pH 2 with concentrated hydrochloric acid, and the water was evaporated off. The white residue contains α -amino- ϵ -caprolactam-*N*^ε-acetic acid (2) and α -amino- ϵ -caprolactam-*N*^ε,*N*^ε-diacetic acid (3). Recrystallization of the product from an aqueous ethanol solution (EtOH:H₂O = 4:1) gave 112.8 g of (2) as the first crop. Yield 60.6%.

This compound (74.5 g, 0.4 mol) was hydrolyzed by refluxing the crystals with 400 mL of 6 M potassium hydroxide solution. The solution was then acidified to pH 2.6 with 70% perchloric acid. The precipitate of potassium perchlorate was filtered off. After allowing the filtrate to stand in a refrigerator, crystals of lysine-*N*^ε-acetic acid (4; 53.5 g) were obtained in 65.5% yield.

The structures of these ligands were confirmed by the ¹H and ¹³C NMR spectra.

Preparation of the IDA Resins. The cross-linked poly(glycidyl methacrylate) (GMA gel, 10 (μ m) and chloromethylated poly(styrene-divinylbenzene) (PS-CH₂Cl gel, 60% cross-linked, 10 (μ m) obtained from Hitachi Chemical Co., Ltd., were used as the base matrixes for the preparation of the chelating resins. The synthetic scheme is shown in Figure 2. The introduction of IDA to GMA gel was carried out as follows: The GMA gel beads (5 g) were added to an aqueous solution (100 mL) containing 4 (25 mM). The mixture was adjusted to pH 11 and then kept at 50 °C for 24 h. The resin beads were filtered, washed with 2 M hydrochloric acid and water, and then dried. The procedure for introducing IDA into the PS-CH₂Cl gel was based on the previous report.^{4,5} The adsorption capacities for Cu(II) were determined to be 450, 410, and 220 μ mol/g for IDA resins I, II, and III, respectively. The IDA resins were packed into a chromatographic column of 4.6 mm i.d. \times 125 mm for IDA resins I and III and 4.6 mm i.d. \times 40 mm for IDA resin II using the slurry packing technique.

Chemicals and Solutions. An atomic absorption spectrometry grade of the REE solutions and a superpure grade of 61% nitric acid were purchased from Kanto Chemical (Tokyo, Japan). Chlorophosphonazo III was purchased from Dojin Chemical Laboratories Ltd., (Kumamoto, Japan). Reagents for synthesis of IDA resins were obtained from Wako Pure Chemical Industry (Osaka, Japan) and Tokyo Kasei Kogyo (Tokyo, Japan). Pure water was obtained from a Milli-Q system (Nihon Millipore, Tokyo, Japan).

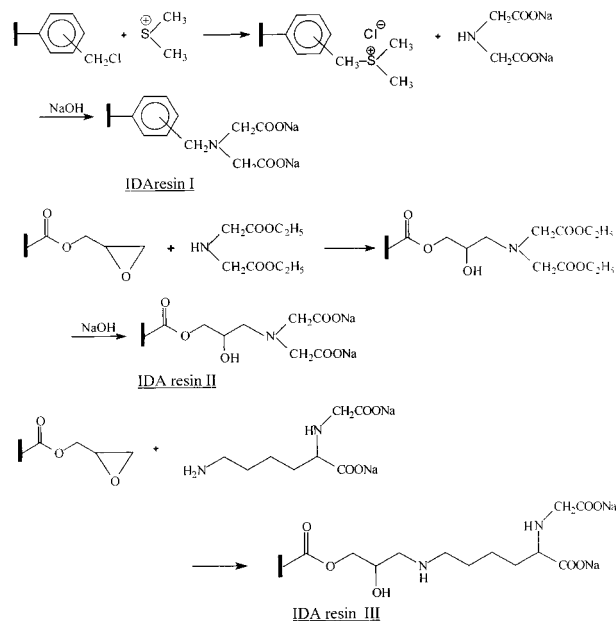


Figure 2. Synthetic scheme of IDA resins.

Apparatus. Model IC7000 (Yokogawa Analytical Systems, Inc., Tokyo, Japan) was used in the chromatographic experiments. Unless otherwise mentioned, the operation was carried out under the following conditions: The flow rate of the mobile phase was 1.0 mL/min, the column oven temperature was 40 °C, and the injection volume was 0.05 mL. In the postcolumn derivatization, the effluent from the column was mixed with chlorophosphonazo III solution (50 mg/L in 20 mM nitric acid) to give the dye compound. The produced dye compound was detected colorimetrically at 660 nm.

RESULTS AND DISCUSSIONS

Preparation of the Chelating Resins. The selectivity of a chelating resin is mainly attributed to the nature of the ligand group. However, because the ligand group is fixed on the bulky polymer matrix, the complex formation of a chelating resin tends to be different from that observed in a homogeneous reaction. We synthesized lysine-*N*^ε-acetic acid by the chemical modification of ϵ -aminocaprolactam (Figure 1), and the ligand was introduced into GMA gel (Figure 2). The chelating resin III thus obtained involves an iminodiacetate homologue as the metal binding site which is located spatially remote from the polymer matrix due to the presence of a spacer arm. For comparison, we also prepared chelating resins I and II by the reaction of IDA with chloromethylated polystyrene and GMA gel, respectively. In these cases, the iminodiacetate group is introduced into the polymer matrix through the imino nitrogen. As shown in Figure 2, the ligand moieties of the IDA resin I and II are structurally rather similar to benzyliminodiacetate (Bz-IDA) and *N*-(hydroxyethyl)iminodiacetate (HIDA), respectively. The location of the metal binding site of the three chelating resins relative to the polymer backbone differs, depending on the length of the spacer arm.

Correlation of the Selectivity of IDA Resins and the Chromatographic Retention Behavior. The reaction of the

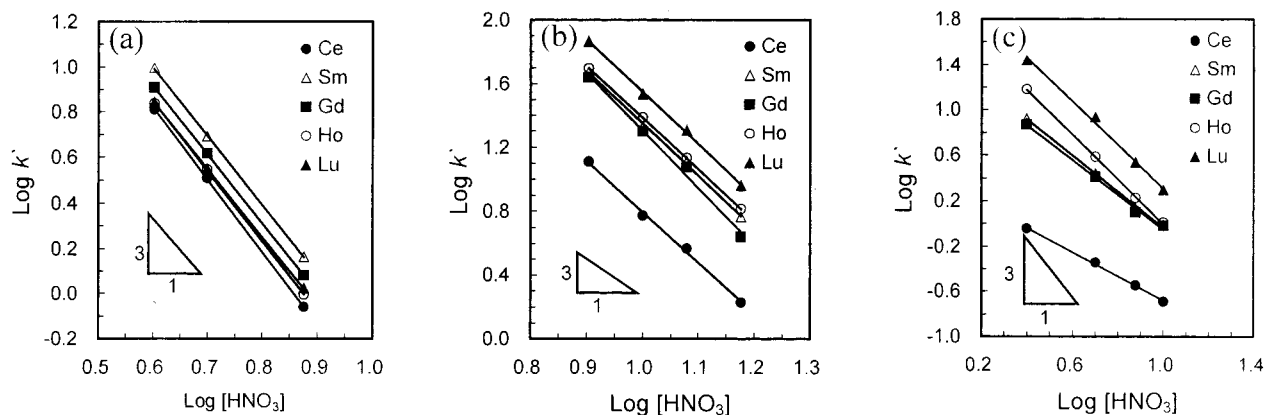
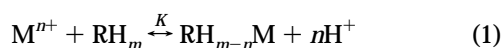


Figure 3. Plot of $\log K'$ of IDA resins **I** (a), **II** (b), and **III** (c) vs $\log [\text{HNO}_3]$. Column size: 4.6 mm i.d. \times 125 mm (IDA resins **I** and **III**), 4.6 mm i.d. \times 40 mm (IDA resin **II**). Column temperature, 40 °C, Mobile phase: nitric acid, 1.0 mL/min. ●, Ce; △, Sm; ■, Gd; ○, Ho; ▲, Lu.

chelating resin with the REE can be expressed as follows:



where M and RH_m denote the REE and the chelating resin in a protonated form, respectively. The equilibrium constant K is given by

$$K = [\text{RH}_{m-n}\text{M}][\text{H}^+]^n / [\text{M}^{n+}][\text{RH}_m] \quad (2)$$

The distribution constant (K_d) of the metal ions between the stationary phase and the mobile phase is given by the ratio of the metal ion concentration in two phases.

$$K_d = [\text{RH}_{m-n}\text{M}][\text{M}^{n+}] = K[\text{RH}_m]/[\text{H}^+]^n \quad (3)$$

The capacity factor (k') of the metal ions in the chromatographic system is defined using the K_d value and the volume ratio of the stationary phase (V_s) and the mobile phase (V_m).⁶

$$k' = K_d[V_s]/[V_m] = K_d C \quad (4)$$

where C is the ratio of V_s and V_m .

From eqs 2 and 4, the following relationship can be obtained.

$$\log k' = \log K + \log[\text{RH}_m] - n \log[\text{H}^+] + \log C \quad (5)$$

Equation 5 predicts that the plots of $\log k'$ vs the proton concentration give a straight line with a slope of $-n$ under the conditions where the amount of the functional group is in large excess relative to that of the REE.

Retention Behavior of IDA Resins. The retention behavior of five REEs on the present chelating resins was examined using nitric acid as the mobile phase. The void volume was calculated from the retention time of the magnesium ion. Figure 3 shows the relationships between the concentration of nitric acid and k' of the five REEs for the present IDA resins. Linear relationships were obtained with slopes ranging from 3 to 3.20 (Figure 3a) and 3.17 to 3.28 (Figure 3b) for the IDA resins **I** and **II**, respectively. These values suggest that three protons are released upon

retention of a REE according to eq 5. Because the IDA moiety has two dissociative protons, the REE complexes with IDA resins **I** and **II** are supposed to be $\text{M}^{3+}(\text{L}^{2-})(\text{LH}^{-})$ or $\text{M}^{3+}(\text{LH}^{-})_3$. Although the presence of these types of complexes with trivalent metal ions has been suggested in the commercially available IDA resins,⁸ formation of the $\text{M}^{3+}(\text{LH}^{-})_3$ complex requires a rather high ligand density and a favorable orientation of the IDA groups. The ligand density is rather low in the present resins; therefore, complexation of the type $\text{M}^{3+}(\text{LH}^{-})_3$ may be unlikely. Thus, retention of the metals such as the $\text{M}^{3+}(\text{L}^{2-})(\text{LH}^{-})$ is very likely to occur.

Similarly, linear correlation was obtained for the IDA resin **III**, where the slope ranges from 1.07 to 1.96 (Figure 3c). This indicates that two protons are released upon adsorption of REE ions, except for Ce(III) (slope 1.07). Thus, a 1:1 complex formation of the type $\text{M}^{3+}(\text{L}^{2-})\text{A}^{-1}$ is likely to occur where A^{-1} is an anion. Because the retention behavior did not change remarkably with the use of perchloric acid in place of nitric acid, the anion appears to act as a simple counterion to retain the electroneutrality. For Ce(III) (and maybe La(III) as well), the chemical species of the complex may be $\text{M}^{3+}(\text{LH}^{-})(\text{A}^{-1})_2$. The ionic radii of Ce(III) and La(III) are larger than that of the other REEs; therefore, the affinity between the metal and IDA is generally relatively weak. Thus, the complexes of Ce(III) and La(III) are likely to contain two counteranions. Although a 1:2 complex can be expected for the IDA resin **III** because the ligand group is sterically less restricted, the formation of such a complex must be rare due to its remarkably low ligand density (220 (mol g⁻¹)).

Selectivity for REEs for IDA Resins. The $\log k'$ values for the 14 REEs were plotted against $\log K_{\text{ML}}$ ($\text{M}:\text{L} = 1:1$) of the corresponding REE complexes⁹ in homogeneous systems. Panels a and b of Figure 4 show such a relationship for the IDA resin **I** and the REE complexes of IDA (Figure 4a) and Bz-IDA (Figure 4b). In both cases, only a poor correlation was obtained, and this trend is marked in the heavy REEs. Thus, the ligand selectivity is not fully reflected in the chelating resin when the spacer arm is short. Plots of $\log k'$ vs $\log K_{\text{ML}2}$ did not improve the deviation from linearity. Such an anomaly has been pointed out in the

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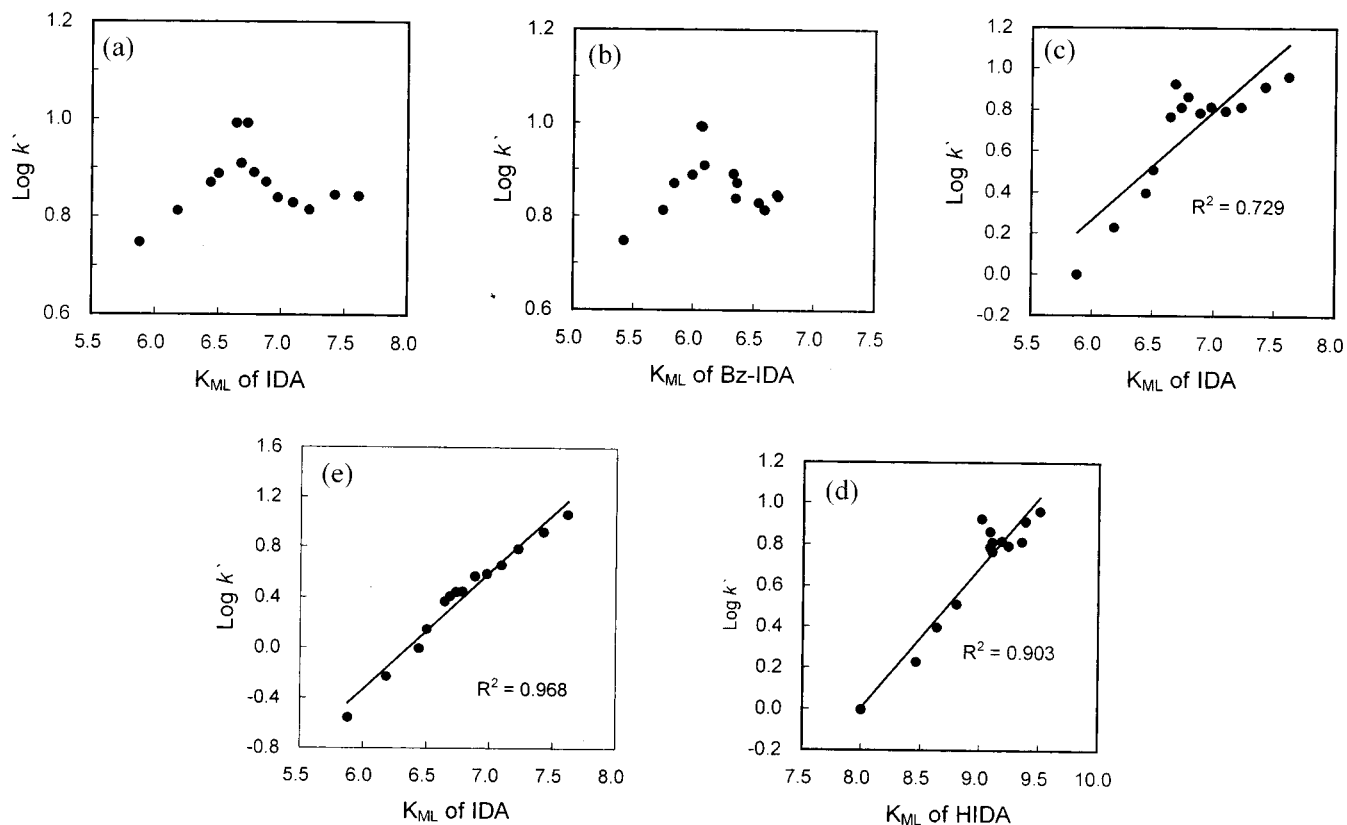


Figure 4. Plot of $\log K'$ of IDA resins **I**, **II**, and **III** vs K_{ML} of corresponding ligands. (a) IDA resin **I** vs IDA; (b) IDA resin **I** vs benzyl iminodiacetate; (c) IDA resin **II** vs IDA; (d) IDA resin **II** vs HIDA; (e) IDA resin **III** vs IDA. Column size: 4.6 mm i.d. \times 125 mm (IDA resins **I** and **III**), 4.6 mm i.d. \times 40 mm (IDA resin **II**). Column temperature, 40 °C. Mobile phase: 5 mM nitric acid (IDA resins **I** and **III**), 15 mM nitric acid (IDA resin **II**). Flow rate, 1.0 mL/min.

commercially available IDA resins especially for the adsorption of trivalent metal ions.^{8,10,11} Plots of $\log K'$ of the IDA resin **II** (Figure 4) against the $\log K_{ML}$ of IDA complexes gave rather poor correlation ($R^2 = 0.729$). However, a better correlation was obtained when $\log K'$ was plotted against the formation constants of HIDA complexes ($R^2 = 0.903$), presumably because the functional group of IDA resin **II** is structurally similar to that of HIDA rather than IDA (Figure 2). A very good correlation ($R^2 = 0.968$) was obtained in the case of IDA resin **III** as given in Figure 4d. The introduction of a longer spacer arm results in an increase in steric flexibility of the ligand, and hence it can behave in a manner similar to that in a monomeric system.

CONCLUSIONS

The retention selectivity of REEs on the IDA-type chelating resins was consistent with the stability trends in the monomeric ligand system when a longer spacer arm is present between the

ligand and the polymer matrix. This result can be attributed to an increase in the steric flexibility of the chelating group. The ligand density on the polymer surface affected the structure of the metal–IDA complex. Although a 1:2 (M:L) complex can be expected for IDA resin **III**, formation of such a complex appeared unfavorable due to the remarkably low ligand density, although 1:1 and 1:2 complexes are likely to be involved in the IDA resins **I** and **II** whose ligand densities are much higher. Freedom from steric restriction and the formation of a simple species caused the IDA resin **III** to show a good correlation in the retention behavior with that of the homogeneous system. In conclusion, the steric flexibility and the density of the chelating group play an important role in determining the retention selectivity and the metal complex species in the chelating resin.

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