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Separation of Rare Earth Metals by the Chelating Resin Functionalized with Lysine-N^{α},N^{α}-diacetic Acid

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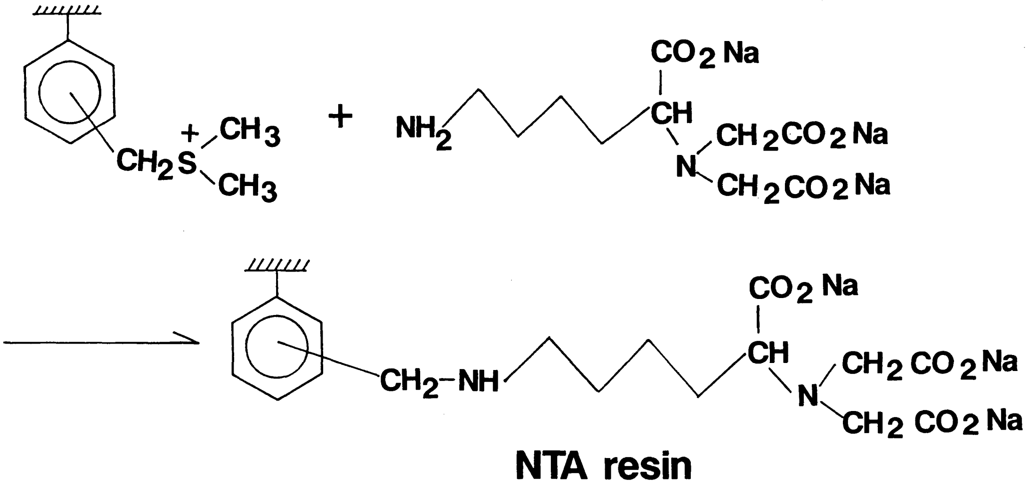
Adsorption properties of rare earth elements toward a cross-linked polystyrene resin having functional groups structurally similar to nitrilotriacetic acid (NTA) have been studied. The selectivity sequence of the resin for a series of rare earth metals was in good accordance with that of the corresponding stability constants of NTA complexes. The chromatographic separation of Pr(III) and Nd(III) has been achieved merely by elution with 0.1 mol dm^{-3} hydrochloric acid.

Highly purified rare earth elements (REE) have become of great importance recently in industrial applications. Due to their remarkable similarity, the mutual separation of REE requires tedious procedures. Ion exchange chromatography is one of the important procedures used to obtain highly purified REE in industry as well as in the analysis of individual REE.1,2) Recently selective polymer resins including chelating resins and reagent-impregnated resins have been applied to the column stationary phase for the chromatographic separation of REE.3-8) When the stationary phase is sufficiently selective, mineral acids may be used as eluents in place of chelating reagents.

The selectivity of a chelating resin is mainly attributed to the nature of the ligand immobilized on the polymer matrix. Since the ligand is chemically fixed to the rigid polymer, the complex formation of the chelating resin tends to be different from that observed in homogeneous reaction. In order to attain a high selectivity, the chelating groups should be uniform in structure and be free from the steric restrictions. We have incorporated a lysine-N^{α},N^{α}-diacetate derivative into a polystyrene matrix and the resulting resin involves the chelating group in an uniform structure.9) In addition, the metal binding site which is structurally similar to nitrilotriacetic acid (NTA) is located spacially remote from the bulky polymer matrix. In the present study, we have measured the distribution coefficient for a series of REE with the present resin and examined the correlation between the observed distribution data and the formation constants of NTA complexes. Chromatographic separation of Pr(III) and Nd(III) has also been carried out.



Scheme 1.

Lysine-N$^{\alpha}$,N$^{\alpha}$-diacetic acid was immobilized onto cross-linked polystyrene beads (32-60 mesh) by a one-step reaction as given in scheme 1. Nitrogen analysis indicated that the chelating resin thus obtained (NTA resin) contains 1.1 mmol of the ligand per gram resin. The resin matrix is a macroreticular type styrene-10%-divinylbenzene copolymer with a surface area and mean pore diameter of 7.3 m^2 g^{-1} and 720 Å, respectively. The concentration of REE was determined by a SEIKO ICP-atomic emission spectrometer, model SPS-1200A.

The reaction of the NTA resin with metal ions can be expressed as follows;

$$M^{n+} + RHm \overset{K}{\rightleftharpoons} RHm\text{-}nM + n\,H^{+} \qquad (1)$$

where R denotes the resin group.

The equilibrium constant of the above reaction can be given by

$$K = \frac{[RHm\text{-}nM][H^{+}]^{n}}{[M^{n+}][RHm]} \qquad (2)$$

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

$$K_d = \frac{[RHm\text{-}n\ M]}{[M^{n+}]} \qquad (3)$$

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

$$\log K_d = \log K + \log [RHm] + npH \qquad (4)$$

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 K_d value was measured as a function of pH under the resin being excess over metal ion. A linear plot of log K_d vs. pH was obtained with a slope approximately 3 (Fig. 1). This observation indicates that the adsorption of a REE ion is accompanied by the release of three protons. The K_d value at the given pH increases in general with the increase in ionic radii of the REE. This trend in selectivity is in good accordance with the stability sequence of the NTA complexes of REE in solution. In fact, a linear relatinship holds for log K_d at the given pH and log K_{ML} of the corresponding NTA complexes (Fig. 2).[10] In the present resin, the ligand is remote from the polymer matrix so that it can behave in a similar manner to that of the ligand in a monomeric system.

The NTA resin was applied to the chromatographic separation of Pr(III) and Nd(III). The resin (15 g) was swollen with water and packed into a jacketed glass column (ø 1.0 cm x 46.5 cm). A buffered solution containing

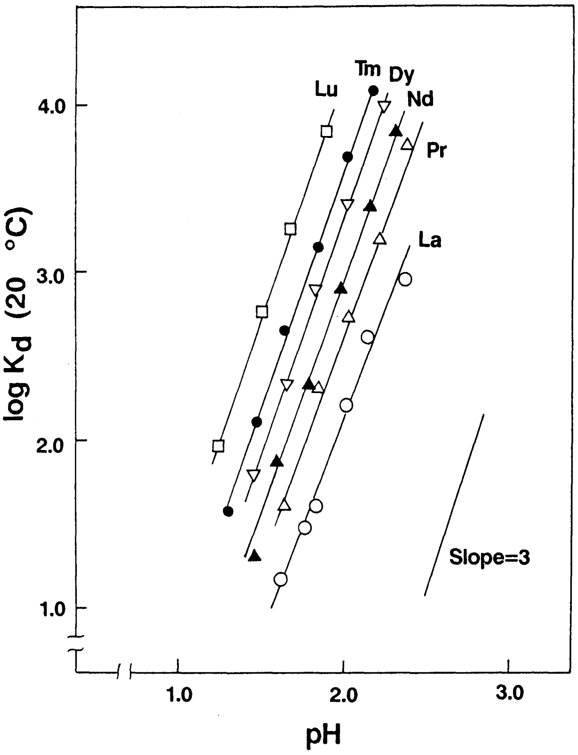


Fig. 1. The log K_d of the NTA resin for several rare earth metals as a function of pH.

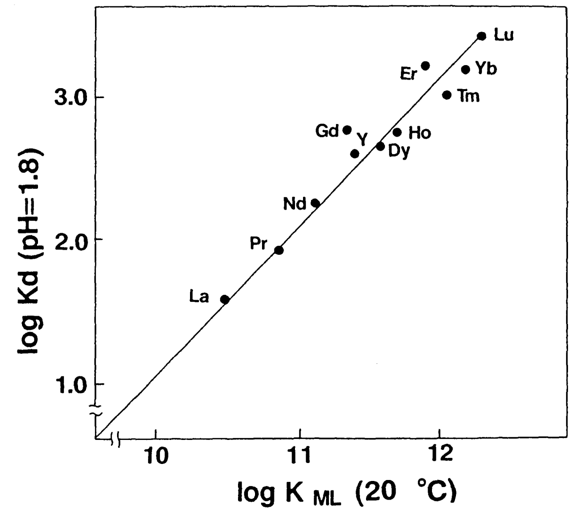


Fig. 2. Plots of log K_d values of the NTA resin (at pH 1.8) against the formation constants (K_{ML}) of rare earth metal complexes of nitrilotriacetic acid.[10]

Pr(III) and Nd(III) (1 mmol each, pH 4.5) was supplied to the column, and the adsorbed metal ions were then eluted with 0.1 mol dm^{-3} hydrochloric acid at a rate of 1 cm^3 min^{-1}. During elution, the column was kept at 65 °C by circulating thermostated water inside the jacket. The effluent was fractionated into 11 cm^3 portions and the amount of metal ions was determined. Figure 3 shows a typical chromatogram for the separation of Pr(III) and Nd(III).

The unique advantage of the present system is that the mutual separation can be achieved merely by elution with mineral acid which may simplify the followed treatment for the isolation of individual metals.

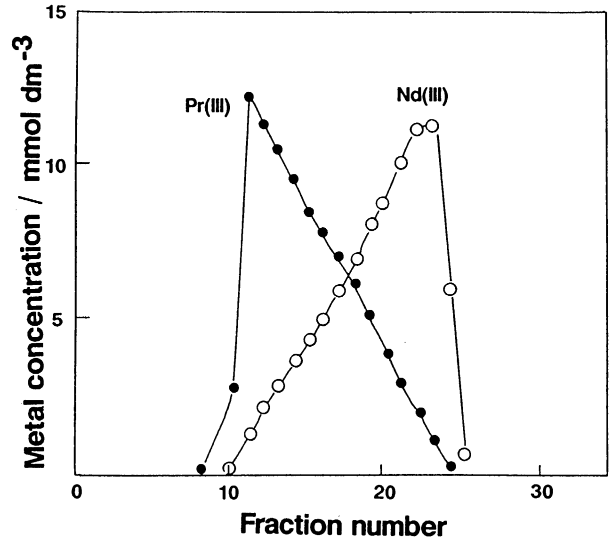


Fig. 3. Chromatogram for the separation of Pr(III) and Nd(III) with the NTA resin column. Metal ion: 1 mmol each, Eluent: 0.1 mol dm^{-3} HCl.

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