CHEMISTRY LETTERS, pp. 1839-1842, 1991.

Enhancement of Separation Efficiency in a Dysprosium(III) and Erbium(III) Pair by the Combination of a Chelating Resin with a Selective Complexing Agent

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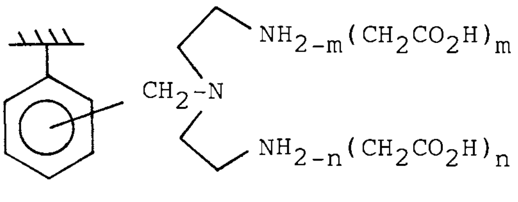
The enhancement of separation efficiency in Dy(III) and Er(III) pair has been observed by the combination of a chelating resin having amine-N-acetates group with a solution of α-hydroxyisobutyric acid (HIBA). A favorable separation of Dy/Er was attained by use of the chelating resin as a column stationary phase and HIBA as an eluent.

Although there is a growing demand of highly purified rare earth elements (REE) in various industries, their mutual separation requires tedious procedures due to the remarkable similarities in their physical and chemical properties.1) Ion-exchange chromatography has significantly contributed to the separation of REE and has successfully applied to the industrial separation process to obtain highly purified REE.2,3) In general, a cation exchanger is used as the column stationary phase and an aqueous solution of a complexing agent as a mobile phase.2) Since the selectivity of conventional cation exchangers is very small,4) the separation efficiency for REE pair depends on the selectivity of the eluent.

Recently a number of workers used metal-selective polymer resins as the stationary phase for the chromatographic separation of REE.5-7) We have measured the distribution coefficients (K_d) of the chelating resin (CMA resin) functionalized with diethylenetriamine-N,N,N',N'-acetates for a series of REE.7) The chelating resin showed the selectivity which can be attributed to the nature of the functional group immobilized on the matrix. A chromatographic separation of some REE pairs has been demonstrated by use of the chelating resin as column stationary phase and a simple buffer solution as



CMA resin (m,n = 0,1,2)

the eluent.

The combination of a selective chelating resin with a solution of selective complexing agent is an interesting approach to obtain better separation efficiency due to a combined selectivity between resin phase and aqueous phase.[8)] The experimental evidence for such cases has not been available. In the present study, we have measured the distribution coefficients of Dy and Er for the chelating resin in the presence of HIBA. Application to the column separation system has also been carried out.

The preparation of the chelating resin (CMA resin) was described elsewhere.[7,9)] The resin matrix is a macroreticular type styrene-10%-divinylbenzene copolymer with the surface area and mean pore diameter, 7.3 $m^2\ g^{-1}$ and 720 Å, respectively. The maximum capacity of the resin for the adsorption of Dy and Er is approximately 1.4 mmol g^{-1}. The adsorption selectivity of REE toward the CMA resin has been evaluated by measuring the distribution coefficient (K_d) as the function of pH; a linear plots of log K_d vs. pH was obtained. The log K_d values at pH 1.6 for fifteen REE are given in Fig. 1.[7)] The selectivity sequence is in good accordance with that of the

$$K_d = \frac{\text{amount of metal adsorbed on one gram of the resin}}{\text{amount of metal remaining in 1 cm}^3\text{ of the solution}} \qquad (1)$$

stability constant of diethylenetriamine-N,N,N',N",N"-pentaacetic acid complexes where the gradual decrease in stability constant takes place. Whereas the stability constants of HIBA complexes increase with increasing atomic number of REE (Fig. 1).[10)] Thus the selectivity trend of the CMA resin and HIBA for REE are reversed in the heavier REE. As has been predicted before,[8)] the separation factor increases in the presence of complexing agent only in those cases where the stability trend is antiparallel between resin phase and aqueous phase. When the stability constants have parallel tendency, the presence of complaxing agent will give a negative effect. We chose Dy(III) and Er(III) pair from heavier REE in order to

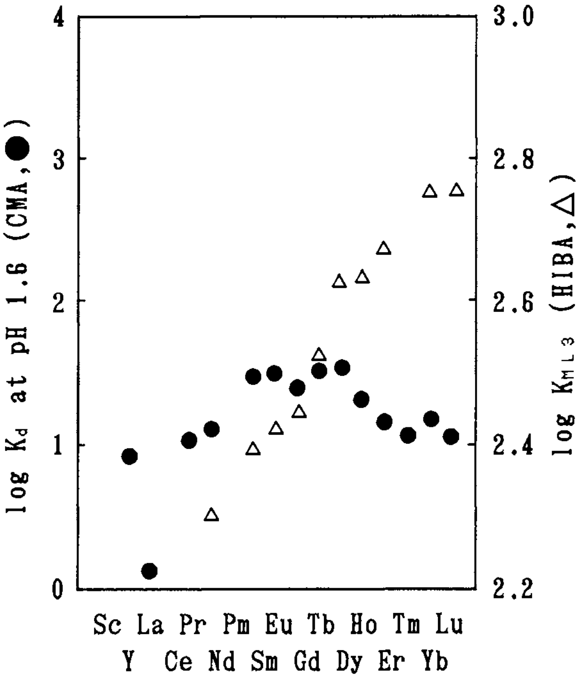


Fig.1. The log K_d values at pH1.6 of the CMA resin(●) and the stability constants of HIBA complexes(△) for REE.

clarify the above prediction experimentally; The CMA resin has higher affinity to Dy(III) than Er(III), while HIBA forms much stable complex with Er(III). The K_d values for the adsorption of Dy(III) and Er(III) were determined with the CMA resin in the presence of HIBA (pH 3.0). The K_d values decreased as the concentration of complexing agent increased. While the separation factors expressed by the ratio of K_d values of Dy(III) and

$$S = K_d(Dy) / K_d(Er) \qquad (2)$$

Er(III) increased with the increase of HIBA concentration (Fig. 2). The separation factor is 2.2 in the absence of complexing agent whereas the value reached to 6.2 in the presence of 0.8 M HIBA (M=mol dm^{-3}). When the solid phase has no selectivity for Dy(III) and Er(III), the separation factor of Dy(III) and Er(III) can be approximately given by the ratio of two stability constants i.e., K_{ErL3}/K_{DyL3} = 1.7.[3,10] The observed separation factor was far better than this value. Thus, remarkable enhancement of separation factor was realized by the combination of the selective resin with the selective complexing agent. This result suggests the possibility of efficient separation of Dy-Er by the column chromatography with HIBA as an eluent.

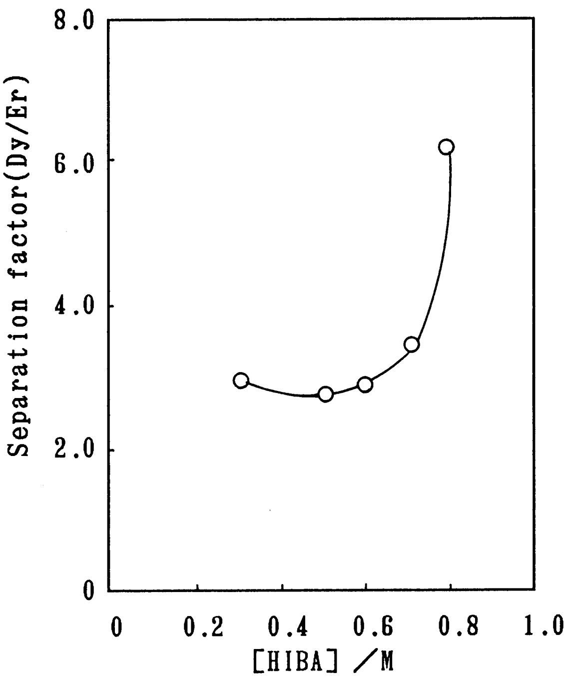


Fig.2. The separation factor(Dy/Er) of the CMA resin in the presence of HIBA. 25 ℃

The CMA resin (8 g) was swollen with water and packed into a jacketed glass column (ϕ1.0 X 26 cm). An aqueous solution containing Dy(III) and Er(III) (0.4 mmol each, pH 3.0-4.0) was supplied to the column, and the adsorbed metal ions were then eluted with a buffered solution (pH 3.0) of 0.8 M HIBA at a rate of 0.4 cm^3 min^{-1}. While elution, the column temperature was kept 45 °C by circulating the thermostated water inside the jacket. By this condition it is noteworthy that Dy(III) was quantitatively retained on the CMA resin column while a pure Er(III) was found in the eluate. The retained Dy(III) was recovered as 96-97% purity by elution with 2 M HCl after rinsing the column with 100 cm^3 of water.

It has been demonstrated that the separation efficiency in a heavier REE pair (Dy/Er) was amplified by the combination of the selective chelating resin and the selective complexing agent. The present system has realized the complete separation of Dy(III) and Er(III) which usually requires tedious procedures.

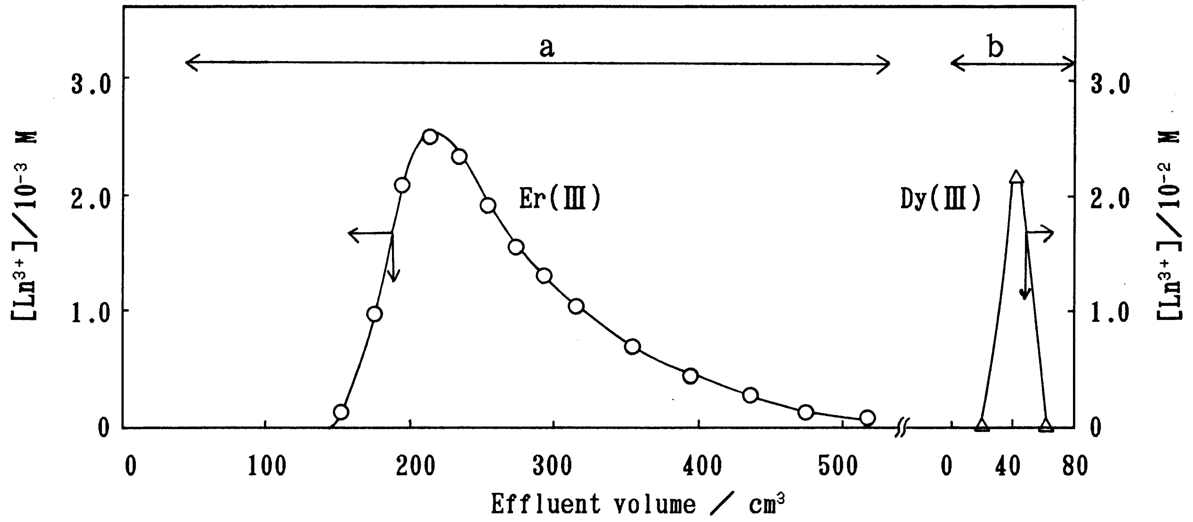


Fig.3. Separation of Dy/Er with the CMA resin. Column size: ϕ1.0×26 cm(resin 8 g), Amount of each metal ion:0.4 mmol, Flow rate:0.4 cm^3min^{-1}(a), 1.0 cm^3min^{-1}(b), Column temperature:45 ℃(a), r.t.(b), Eluent:0.8 M HIBA(a), 2 M HCl(b).

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(Received July 29, 1991)