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DISTRIBUTION COEFFICIENTS OF LANTHANIDE ELEMENTS AND SOME SEPARATIONS ON LAYERED HYDROUS TITANIUM DIOXIDE

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Distribution coefficients /K_d/ of lanthanide elements on layered hydrous titanium dioxide, $H_2Ti_4O_9 \cdot nH_2O$ /where n=1.2-1.3/, have been determined as a function of the pH of the aqueous phase. The plots of lg K_d vs. pH gave straight lines with slopes equal to +3 except for the data for heavier lanthanides, suggesting ideal ion-exchange equilibria between tervalent cations in the aqueous phase and hydrogen ions in the hydrous oxide. Mutual separations of La-Cs and La-Ba have been achieved on a column of this material on the basis of large differences in affinities between the metal ion pairs.

INTRODUCTION

Layered hydrous titanium dioxide, $H_2Ti_4O_9 \cdot nH_2O$, is a "clay-like" compound whose crystal structure is built up from titanate layers of $[Ti_4O_9{}^{2-}]_n$ with exchangeable protons between them[1-3]. Recently this material

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has attracted a lot of attention because it is expected to be employed for the safe treatment of fission products as ionic adsorbents or immobilizers[4].

We have studied, from the above mentioned point of view, the affinities of metal ion series onto layered hydrous titanium dioxide by measuring their distribution coefficients as a function of the pH value of the aqueous phase[5-7]. The obtained selectivity series were $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ for alkali metal ions[5], $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ for alkaline earth metal ions[6] and $Cu^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+}$ for divalent transition metal ions[7]. It is to be emphasized that considerably large separation factors were found between neighbouring ion pairs and these are some of the largest values reported for various inorganic ion-exchangers, suggesting a high capability of the material for separating metal ions.

It is important to study the soprtion behaviour of lanthanide elements, one of the principal components of fission products, and to compare affinities of these tervalent cations with those of the above mentioned metal ion series. This paper describes the sorption characteristics of lanthanide elements on layered hydrous titanium dioxide and its application to chromatographic separations.

EXPERIMENTAL

Reagents and materials

All the chemicals used were of 99.9% or higher purity. Layered hydrous titanium dioxide in a fibrous form was synthesized as in the procedure previously reported[3]. The stock solutions of lanthanide elements were prepared by dissolving corresponding nitrates in water. Their concentrations were standardized by EDTA titration. Distilled, deionized water was used.

Equilibrations

Ion-exchange experiments were conducted by treating a weighed amount of the exchanger, $H_2Ti_4O_9.nH_2O$, with an aqueous solution containing $1x10^{-4}M$ $M/NO_3/_3$ /where M: lanthanide elements/. The solution to solid ratio was 0.1 dm^3 g^{-1}. The pH value of the aqueous phase was controlled by adding an appropriate amount of nitric acid solution. The solution/solid mixtures were shaken occasionally at 25±0.5 °C until equilibrium was reached. An aliquot of the supernatant solution was pipetted and its metal ion content as well as its pH value was determined. The metal ion uptake by the exchanger was deduced from the difference between the initial and final concentrations of the aqueous phase.

Distribution coefficients $/K_d/$ were calculated as:

$$K_d = \frac{\text{moles of metal ion per 1 g of exchanger}}{\text{moles of metal ion per 1 cm}^3\text{ of solution}} \; /cm^3\ g^{-1}/.$$

Chromatographic separations

Mutual separations of lanthanum from cesium and barium were carried out on a column /0.5 cm i.d./ with 1.0 g of layered hydrous titanium dioxide. A mixed solution containing 2 μmol each of metal ions was loaded into the column and the metal ions were eluted with nitric acid solutions at a flow rate of 0.3 cm^3 min^{-1}. The effluent fractions were collected by an ATTO SJ-1410SR fraction collector and analyzed for their metal ion contents.

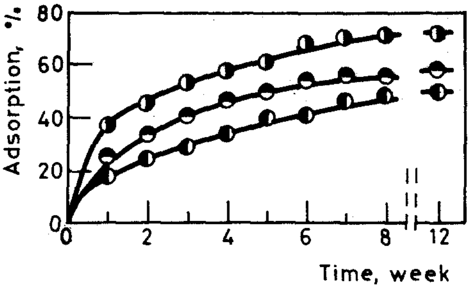

Fig. 1. Time dependence of sorption of some lanthanide elements.
/ ◑ / La, / ◒ / Gd, / ◐ / Lu; exchanger: 0.1 g of $H_2Ti_4O_9 \cdot nH_2O$; solution: 10 cm^3 of 1×10^{-4}M $M/NO_3/_3$. Equilibrium pH values were 3.33 for La, 3.48 for Gd and 3.50 for Lu

Instruments

Concentrations of metal ions in the aqueous phase were measured by a SEIKO SPS 1100 Inductively Coupled Plasma Atomic Emission or a Hitachi 180-80S Atomic Absorption Spectrophotometer. The pH measurements were performed by using a TOA HM 20E pH-meter.

RESULTS AND DISCUSSION

Equilibration time

Over 2-month shaking was required to attain equilibrium for lanthanide elements, as shown in Fig. 1. This equilibration time is extremely long compared with that for other metal ion series which had been studied previously[5-8]. The higher is the valency of the cation the longer the equilibration time: 1-3 days were required for univalent[5,8], 10-14 days for divalent[6,7] and over 60 days for tervalent ions. This tendency may be attributed to electrostatic interaction between metal ions and the host lattice of the exchanger: In an ion-exchange reaction on layered hydrous titanium dioxide, cations must reach exchange sites by diffusing through negative titanate layers, $[Ti_4O_9^{2-}]_n$. Thus the diffusion of higher-valent metal ions are more restricted owing to the larger coulombic attraction and this results in a slower attainment of the equilibrium.

pH dependence of distribution coefficients

The following equation describes the ion-exchange equilibrium existing between n-valent metal ions /M^{n+}/ in an aqueous phase and hydrogen ions on an exchanger /HR/.

$$nHR/s/ + M^{n+}/aq/ \rightleftharpoons MRn/s/ + nH^{+}/aq/ \qquad /1/$$

where subscripts "s" and "aq" represent solid and aqueous phases, respectively. Under a condition where a metal ion load is negligibly small compared to ion-exchange capacity, logarithms of distribution coefficients are proportional to the pH values of the aqueous phase[9,10]:

$$\lg K_d = npH + const. \qquad /2/$$

The slope coincides with the valency of the metal ion: +n. The relationship in Eq. /2/ was found to hold for alkali, alkaline earth and divalent transition metal ions on layered hydrous titanium dioxide[5-8].

In this study we measured distribution coefficients for 14 lanthanide elements as a function of pH. The results are shown in Fig. 2. The distribution coefficients were almost in the same order of magnitude for all the elements, which reflects the close similarity of chemical nature in the lanthanide series.

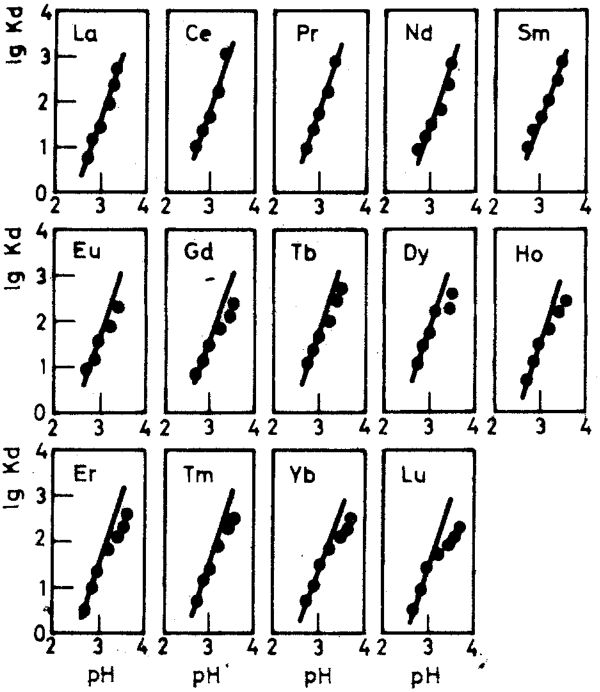

Fig. 2. pH dependence of distribution coefficients of lanthanide elements. Exchanger: 0.1 g of $H_2Ti_4O_9.nH_2O$; solution: 10 cm^3 of $1x10^{-4}M$ $M/NO_3/_3$. The solid lines have a slope of +3

Eq. /2/ is valid for this experiment since the metal ion load was negligible /0.54% of the ion-exchange capacity/ under the experimental conditions employed here. The solid lines in Fig. 2 have a slope of +3 for an ideal ion-exchange equilibrium between tervalent cations and hydrogen ions. The data for the lighter lanthanides, La-Sm, were mostly on the theoretical lines. This indicates that these elements were adsorbed via a 1:3 ion-exchange reaction.

For the heavier members, Eu-Lu, on the other hand, the lg K_d-pH plots deviated downwards from the straight

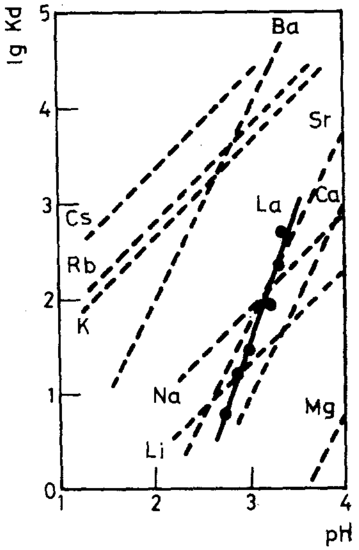

Fig. 3. Comparison of affinity of lanthanum towards layered hydrous titanium dioxide with those of alkali and alkaline earth metal ions

lines at pH values of 3.0 or above. This deviation becomes larger going from Eu to Lu. This tendency is parallel to the tendency to hydrolysis of lanthanide elements[11,12].

Chromatographic separations

Figure 3 shows the pH dependence of lg K_d for lanthanum together with the data for alkali and alkaline earth metal ions[5,6]. It is seen that layered hydrous titanium dioxide preferred strongly cesium, rubidium, potassium and barium to lanthanum. The separation factors between the elements amounted to over 150 at pH values of 3.0 or below suggesting feasible separations.

Almost quantitative separations of La-Ba and La-Cs were achieved by using nitric acid solutions at various

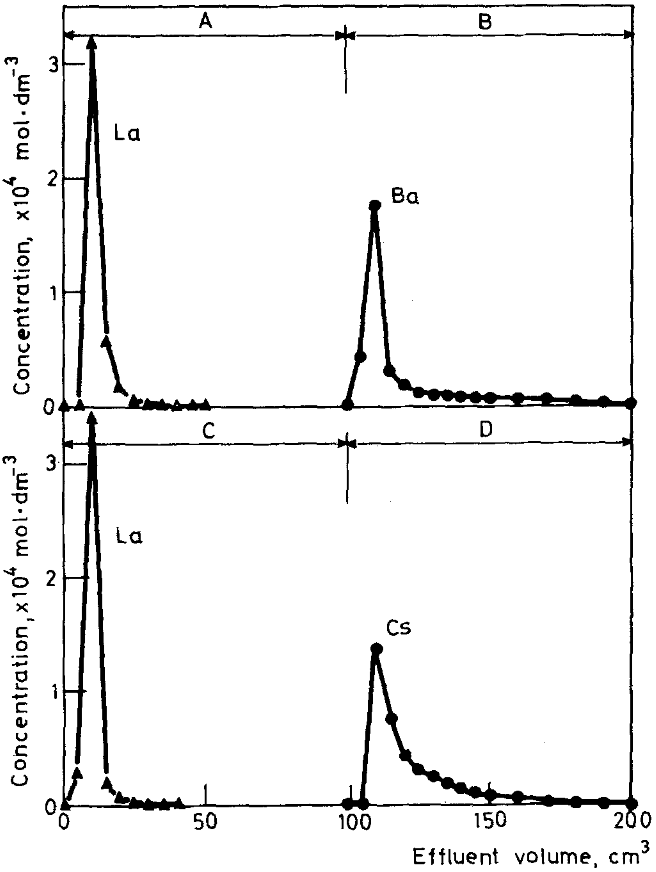

Fig. 4. Chromatographic separations of lanthanum from barium and cesium.
Eluents: A: 1.5x10^{-3}M HNO_3, B: 1M HNO_3, C: 3x10^{-3}M HNO_3; D: 3M HNO_3+1M NH_4NO_3

concentrations as eluents as shown in Fig. 4. There is no reason to doubt that separations of barium or cesium from the other lanthanides can be achieved by similar procedures. These separations suggest a potential use of this material for partitioning radioactive nuclides in high-level liquid wastes.

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