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ION-EXCHANGE PROPERTIES OF COPRECIPITATED SILICA-TITANIA GEL FOR ALKALI METAL IONS

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Silica-titania gel of mole ratio 3:1 prepared by a coprecipitation method was found to exhibit excellent cation-exchange abilities, which were enhanced by the pretreatment with HCl and the heat treatment at 200 °C, as compared with silica or titania gel. Separation of cesium from sodium in aqueous solution with the silica-titania gel was complete.

We revealed previously that a coprecipitated silica-titania binary gel, which was a good material for the adsorption of chromium (VI) ion from acidic solution[1)] and the recovery of uranium in sea water,[2)] possessed cation-exchange abilities for several alkali metal ions.[3)] The present investigation was undertaken to elucidate the effect of the pretreatment and the heat treatment of the gel, and to determine the optimum composition of the gel as an ion-exchanger. Further, we attempted the separation of cesium from sodium in aqueous solution by means of a column operation with the gel, which was related to the treatment of radioactive waste solutions by using inorganic substances.[4-8)]

The binary gel was precipitated from the mixtures of various ratios of 0.1 M sodium metasilicate acidified with hydrochloric acid (pH 1) and 0.1 M titanium (IV) chloride by adding 3 M sodium hydroxide until pH 7 at 20 °C. After aging for 10 h, the resultant precipitate was filtered by suction, thoroughly washed with deionized water, and then freeze-dried. Grinding the dried gel, followed by sieving to 100-200 mesh size, gave an ion-exchanger which included slightly sodium ion originated from one of the starting material (sodium metasilicate) and the precipitant. The pretreatment of as-prepared silica-titania gel was performed in order to convert to a proton-form ion-exchanger as follows: Hydrochloric acid (0.1 M) and deionized water were in turn passed through a glass tube (110 mm × 10 mmϕ) packed with 8 g of the gel under the conditions of a flow rate of 0.8 $cm^3 min^{-1}$ at a room temperature for 20 h. The ion-exchange capacity of the gel was increased from 0.86 mmol Na^+/ g to 1.78 mmol Na^+/ g by this pretreatment. The surface area measurement of the gel was carried out by applying the B.E.T. method to adsorption isotherm of nitrogen at -196 °C.

The distribution coefficients (K_d) of alkali metal ions, which were given by Eq. 1,

$$K_d = \frac{\text{Amount of metal ion in exchanger}}{\text{Amount of metal ion in solution}} \times \frac{\text{cm}^3 \text{ of solution}}{\text{g of exchanger}} , \qquad (1)$$

were determined in terms of a batchwise operation by shaking 0.2 g of the ion-exchanger with 20 cm^3 of aqueous solution containing 1×10^{-4} M alkali metal ion to be studied at 20 °C for 24 h. The pH of solution was adjusted by the addition of hydrochloric acid. Alkali metal ions in the solution were quantitatively analyzed by flame spectrophotometry.

Figure 1 shows the distribution coefficients of alkali metal ions as a function of the pH of the solution at equilibrium obtained with silica-titania gel of mole ratio 1:1. All the slopes of straight lines in the plots of $\log K_d$ vs. pH were closely equal to unity, implying that the ion-exchange reaction proceeded between alkali metal ions and protons located on the gel. The ion selectivity of this gel was shown in the order of $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, which accorded reversely with the order of the size of hydrated alkali metal ions. The difference in K_d values of cesium and sodium ions was remarkable; the separation factor (the ratio of K_d values) of the two ions was so large that the separation of cesium from sodium in aqueous solution with silica-titania gel seems to be possible.

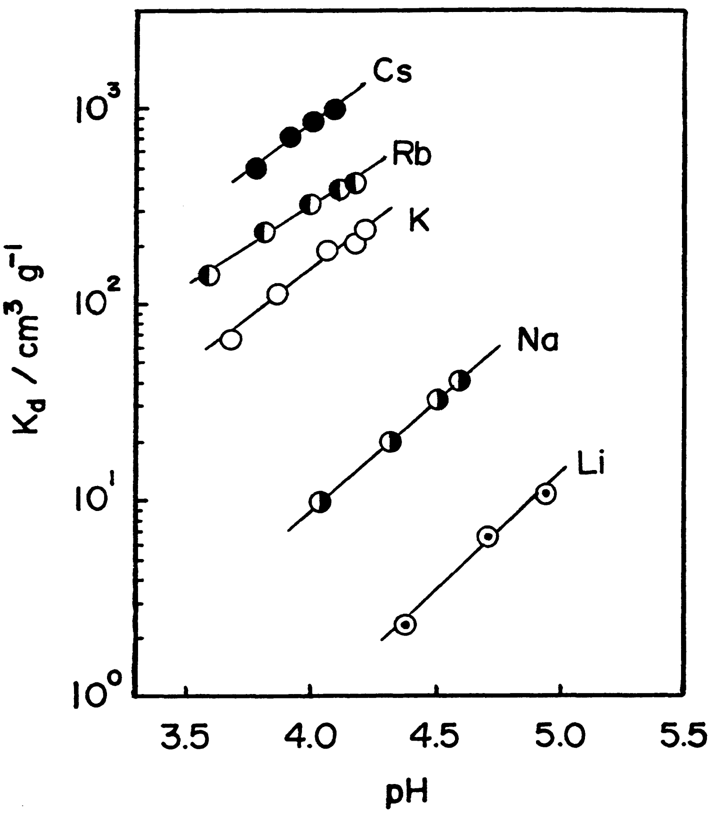

Fig. 1. Distribution coefficients of alkali metal ions on silica-titania gel.

The mixing of silica and titania gels was effective to the ion-exchange reaction of alkali metal ions (Fig. 2). Although both the silica and titania gels in the present study exhibited to some extent ion-exchange abilities for alkali metal ions as reported in the literature,[9,10] the K_d values of cesium and sodium ions with the silica-titania binary gels in the entire range of the composition were all larger than those with silica and titania gels. Also, the value of K_d of cesium ion was shown to be maximum at 25 mol% TiO_2 of the composition of the binary gel and decreased with increasing TiO_2 content in parallel with that of sodium ion, suggesting that the TiO_2 component of the gel effects on the ion selectivity and the SiO_2 component contributes to the efficient dispersion of TiO_2 as a matrix. Silica-titania gel may be regarded as the intimate mixture of silica and titania gels in which the framework of silica gel of large surface area (>400 m^2/g) is partly stuffed by widely dispersed titania gel.[3] It seems probable that the occurrence of the bond, Si-O-Ti, around the interface of silica and titania particles caused the binary gel to have a large number of acidic sites, participating in an ion-exchange reaction together with sodium ion sites.

Silica-titania gel containing 25 mol% TiO_2 was held in an electric furnace at 200-800 °C for 1 h before the pretreatment with hydrochloric acid. The K_d value of cesium ion with the gel heat-treated at 200 °C was largest and the separation factor against sodium ion was largely improved, as shown in Fig. 3. In addition, the distribution coefficients were correlated to the specific surface areas of the heat-treated gels except for as-prepared gel.

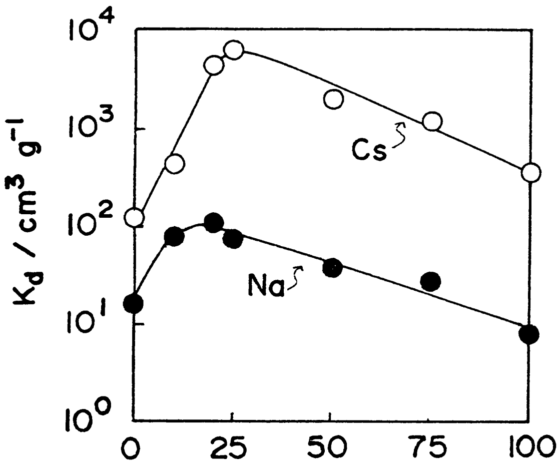

Fig. 2. Distribution coefficients of sodium and cesium ions as a function of TiO_2 content of silica-titania gel.

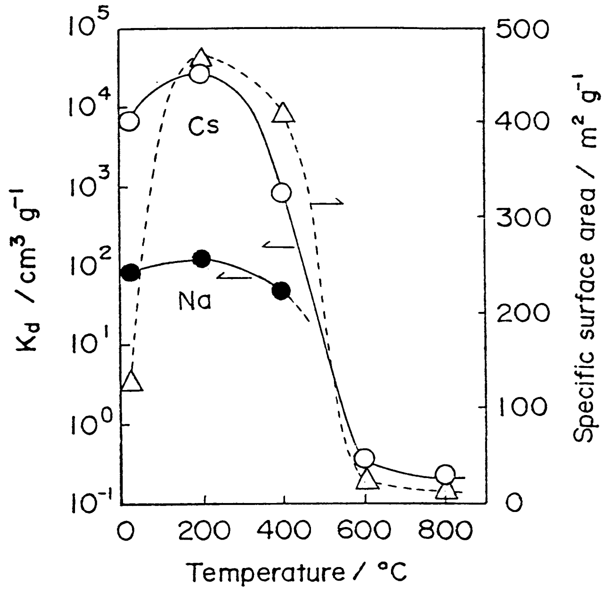

Fig. 3. Relationship between distribution coefficients of alkali metal ions and surface areas on silica-titania gels of mole ratio 3:1 heat-treated at various temperatures.

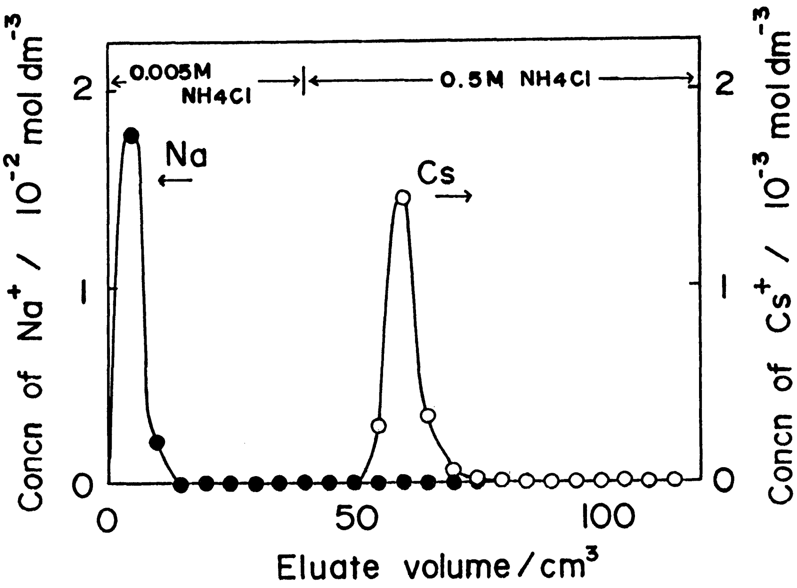

Fig. 4. Separation of cesium ion from sodium ion with the proton-form silica-titania gel of mole ratio 3:1 heat-treated at 200 °C. Column: 102 mm × 7 mmφ, flow rate: 0.12 $cm^3 min^{-1}$, and loadings of Na^+ and Ce^+: 100 μmol and 10 μmol, respectively.

The sodium and cesium ions loaded on the gel were sufficiently eluted with 0.005 M and 0.5 M ammonium chloride, respectively; both the profiles of sodium and cesium ions were sharp almost without tailing and overlapping, and then the recovery of cesium ion was quantitatively carried out (Fig. 4). Hence it has been proved that the proton-form silica-titania gel is a novel, useful inorganic ion-exchanger regarding to the separation of cesium ion from other alkali metal ions.

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