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ION-EXCHANGE PROPERTIES OF SILICA-TITANIA MIXED-OXIDE GEL FOR AMMONIA IN AQUEOUS SOLUTIONS

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Proton-form silica-titania gel of mole ratio 1:1 exhibited high ion-exchange abilities for ammonia in aqueous solutions. Its apparent capacity increased with increasing pH of solution tested, which attained above 4 mmol g^{-1} at pH 9. Separation of ammonia and sodium in aqueous solution loaded in advance on the silica-titania gel was complete when used hydrochloric acid as an eluent.

The separation or removal of ammonia in aqueous solutions is the subject which is concerned with environmental pollution, artificial kidney, analytical chemistry, etc. Zeolite,[1)] zirconium phosphate,[2-6)] titanium phosphate,[7)] layered hydrous titanium dioxide fiber,[8)] hydrous titanium dioxide,[9)] and activated carbon[10,11)] as inorganic adsorbents have hitherto been tested. However, none of them has been shown to be appropriate from the standspoints of preparation method, adsorption capacity, selectivity, chemical durability, and expense.

We first found out good adsorptive abilities of silica-titania mixed-oxide gel prepared by wet precipitation method.[12-14)] Furthermore, this binary gel possessed cation-exchange abilities for alkali metal ions.[15)] The separation of cesium and sodium in aqueous solution was possible by means of a column operation using this gel.[16)] In order to develop as a synthetic inorganic adsorbent or ion-exchanger, we studied here the ion-exchange properties of silica-titania gel for ammonia in aqueous solutions and attempted the separation of ammonia and sodium using the gel also.

The binary gel was precipitated from the mixture of 0.1 M sodium metasilicate acidified with hydrochloric acid (pH 1) and 0.1 M titanium chloride by adding 3 M sodium hydroxide solution until pH 8 at 20 °C. After aging for 10 h, the resultant precipitate was filtered by suction, thoroughly washed with deionized water, and then dried with an electronic range (SANYO Model EM-400). Grinding the dried gel once, followed by sieving to 100-200 mesh size, gave an ion-exchanger. The pretreatment of as-prepared ion-exchanger was performed in order to convert to a proton-form ion-exchanger as follows: Hydrochloric acid and deionized water were in turn passed through a glass tube (110 mm × 10 mmϕ) packed with as-prepared ion-exchanger. The specific surface area, average micropore diameter, and micropore volume less than 200 Å of the proton-form ion-exchanger were 374 m^2g^{-1}, 29 Å, and 0.27 cm^3g^{-1}, respectively.

The uptake of ammonia in aqueous solutions was examined in terms of a batchwise operation by shaking 0.25 g of ion-exchanger with 50 cm^3 of 1.0×10^{-3} M ammonium chloride solution for 24 h at 20 °C. Ammonium ion was determined spectrophotometrically with the Nessler's reagent[17] and sodium ion by flame spectrophotometry. For a pH titration, the equilibrium pH's of solutions were measured after 0.5 g of ion-exchanger was added to the mixed solutions of ammonium chloride and aqueous ammonia of various volume ratios (ionic strength 0.1). The solid acidity of ion-exchanger was measured by titration with n-butylamine using 4-benzeneazo-1-naphthylamine (pK_a=+4.0) as an indicator.

In order to learn the acidic and basic properties of a proton-form silica-titania gel, the pH titration curves were determined, as shown in Fig. 1; the pH of solution containing the silica-titania gel was almost the same with that of the blank test in the low range below pH 3, but was brought down in the higher range especially between pH 4-9. The fall in this range and the slight deviation in the higher range resulted probably from the dissociation of surface protons on the gel and the dissolution of silicic acid from the gel,[15] respectively. Also, this curve changed abruptly at about pH 7.9 just as in the previous paper,[15] suggesting that the gel possessed exchangeable proton sites of different acid strengths and then was regarded as a polybasic acid.

Figure 2 shows the relationship between the apparent ion-exchange capacity of silica-titania gel and the equilibrium pH. The ion-exchange capacity for ammonium

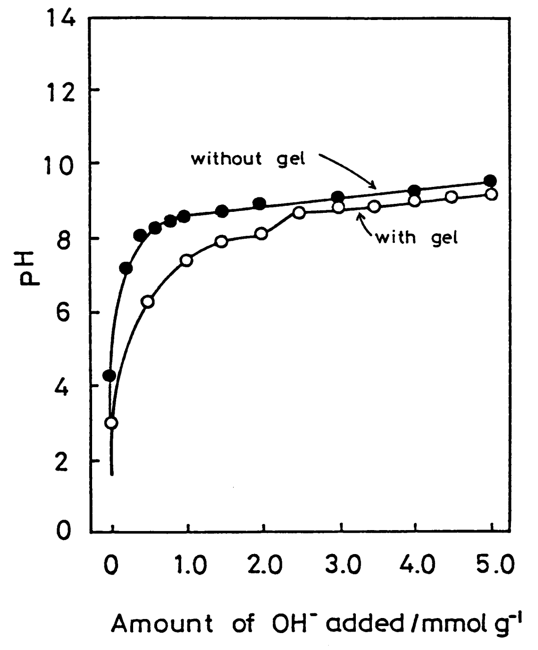

Fig. 1. Titration curve of silica-titania gel for ammoniun ion.

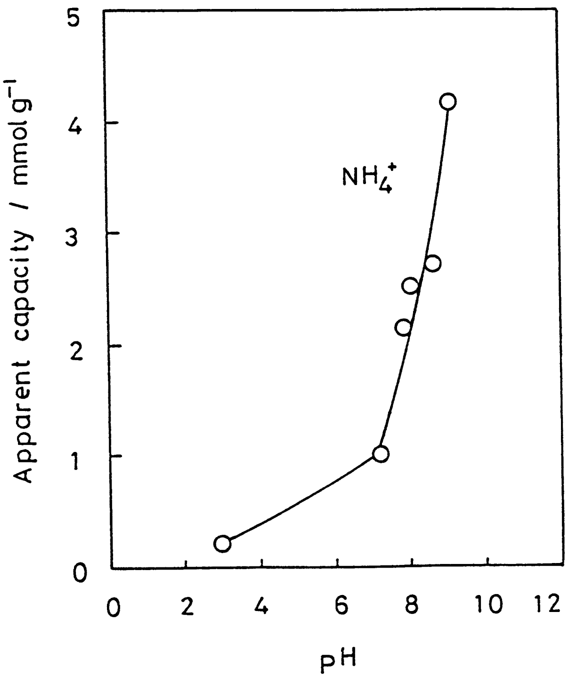

Fig. 2. Ion-exchange capacities of silica-titania gel as a function of pH.

ion of the gel showed an upward trend with increasing pH values, which went up to over 4.0 mmolg^{-1} at pH 9. It has, therefore, been proved that silica-titania gel was superior to layered hydrous titanium dioxide fiber[8)] and hydrous titanium dioxide,[9)] but inferior to zirconium phosphate[4,6)] with respect to the capacity for ammonium ion. Additionally, this ion-exchange capacity was taken in less than 2 h. The rate of ion-exchange also was relatively large compared with zirconium phosphate[18)] and layered hydrous titanium dioxide fiber.[8)]

The distribution coefficient, K_d (cm^{3}g^{-1}), was given by Eq. 1,

$$K_d = \frac{I - F}{F} \times \frac{V}{W} \qquad (1)$$

where I is the initial concentration of ion in solution, F the final concentration after uptake test for 24 h, V the volume of solution, W the weight of ion-exchanger. We further investigated the distribution coefficient of ammonium ion as a function of the pH of aqueous solution at equilibrium, as shown in Fig. 3. The slope of straight line in plots of logarithmic K_d versus pH was closely equal to unity, comfirming that the ion-exchange reaction here made progress just between ammonium ion and proton. We also obtained the same slope with regard to sodium ion (Fig. 3). The difference in K_d values of ammonium and sodium ions at the same pH seemed to be significant; the separation factor (the ratio of K_d values) of the two ions was to some extent large (about 6) so that the separation of ammonium and sodium ions using silica-titania gel must be possible. The ion selectivity of silica-titania gel for monovalent ion was shown in the order of $Cs^+ > Rb^+ > K^+ \approx NH_4^+ > Na^+ > Li^+$, which accorded reversely with the order of the size of hydrated ion, because the distribution coefficient of ammonium ion on the gel was comparable to that of potassium ion.[16)]

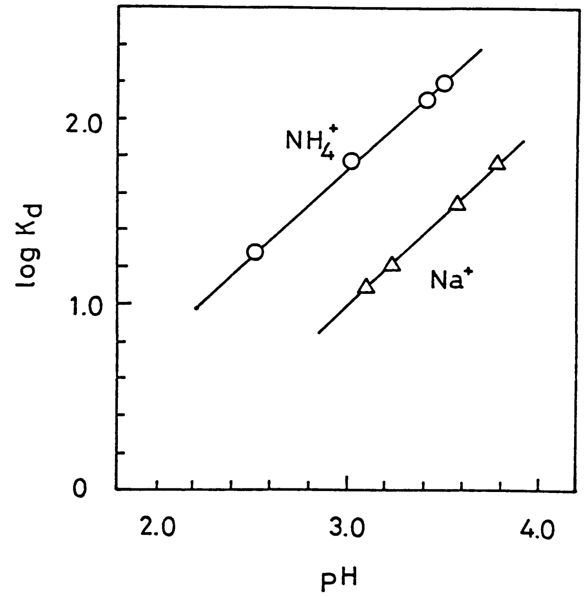

Fig. 3. Distribution coefficients of ammonium and sodium ions on silica-titania gel.

An attempt of separation of ammonia in aqueous solution and any other ion by means of a column operation using inorganic substance was scarecely known. Then, the column operation using a proton-form silica-titania gel was carried out under the following conditions: Column, 21 mm × 7 mmϕ; ion-exchanger, 0.5 g (apparent density 0.4 g cm^{-3}); loadings of NH_4^+ and Na^+, 7.5 μmol and 2.5 μmol, respectively; eluate, hydrochloric acid; flow rate, 0.12 cm^{3}min^{-1}. As a result, the sodium and ammonium ions loaded in advance on the gel were completely eluted with 1.6×10^{-4} M and 5×10^{-2} M hydrochloric acid, respectively, as can be seen in Fig. 4. Both profiles were clearly separated without tailing and overlapping, and then the recovery of both ions was quantitatively performed.

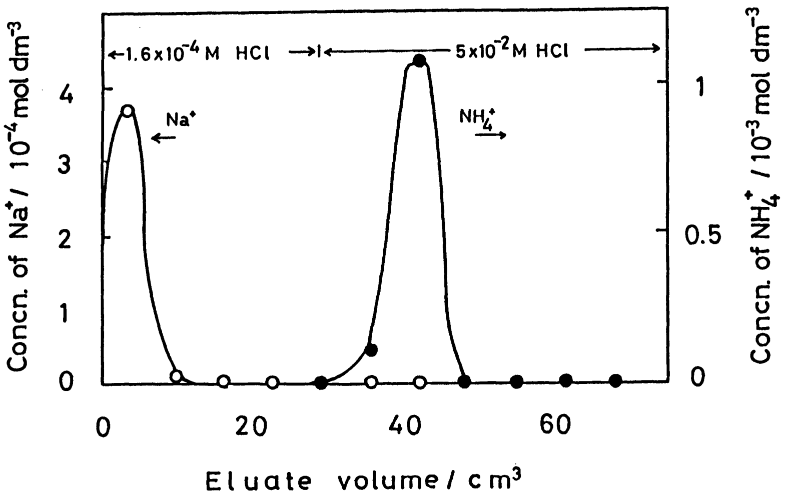

Fig. 4. Separation of ammonium and sodium ions with silica-titania gel.

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