Polymerization of Silicic Acid Adsorbed on Aluminium Hydroxide

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Factors controlling the absorption of silicic acid on aluminium hydroxide from aqueous solution and the polymerization of adsorbed silicic acid were studied. Measurements included the amount of silicic acid adsorbed on aluminium hydroxide, the amount and size distribution of the polysilicic acid formed, and the differential thermal analysis curve of aluminium hydroxide which had adsorbed silicic acid. The adsorption and the polymerization of silicic acid are affected by pH, the relative amounts of silicic acid and aluminium hydroxide, the reaction time between monosilicic acid and aluminium hydroxide, and the formation of amorphous aluminosilicate. The amount of adsorbed silicic acid and the rate of its polymerization are maximum at pH 9.0—9.5. A part of adsorbed monosilicic acid reacts with aluminium hydroxide to form an aluminosilicate. In an early stage of the polymerization of the adsorbed silicic acid, the polymerization mainly proceeds by the reactions between monosilicic acids and between monosilicic and polysilicic acids; the particle sizes of polysilicic acids gradually increase with time. When the polymer particles grow large enough to touch neighboring polymers, the growth rate of polymer particles becomes faster due to the polymer-polymer reactions.

Siliceous deposits from hot springs generally contain Al_2O_3 and Fe_2O_3; some deposits contain several percent of Al_2O_3.[1-3] Aluminium thus plays an important role in the formation of siliceous deposits. Adsorption characteristics of monosilicic acid on aluminium hydroxide have been studied,[4-6] but only a few reports were published with respect to the polymerization of silicic acid adsorbed on or coprecipitated with aluminium hydroxide.

Hingston and Raupach[7] suggested that a multilayer of silicic acid was formed by polymerization of silicic acid on an aluminium hydroxide surface. Jepson *et al.*[8] reported that, under given conditions, the adsorption of monosilicic acid on gibbsite exceeded the monolayer coverage. Yokoyama and Tarutani[9] reported that, when aluminium hydroxide was placed in a flask and then monosilicic acid solution (150 ppm SiO_2, pH 8) was made to flow continuously through the flask, the monosilicic acid adsorbed on aluminium hydroxide gradually polymerized to form silica particles of larger sizes than 0.1 μm after about 20 d.

In this work, factors controlling the amount of silicic acid adsorbed on aluminium hydroxide and the polymerization of adsorbed silicic acid were studied. The mechanism for the growth of particles of polysilicic acid is proposed.

Experimental

Samples and Reagents. All the reagents used were of analytical reagent grade. A stock solution of monosilicic acid was prepared by dissolving silica gel (Mallinckrodt Chemical Works) in sodium hydroxide solution. A monosilicic acid solution of the desired concentration was prepared by diluting a stock solution before use. Aluminium hydroxide was precipitated by adding sodium hydroxide solution to aluminium chloride solution; the hydroxide was then washed with distilled water. This was prepared immediately before each experiment.

Procedure. The pH of monosilicic acid solution (500 cm^3) of an appropriate concentration was adjusted to a desired pH value with hydrochloric acid or sodium hydroxide solution. A known amount of aluminium hydroxide was then introduced to the solution and the pH of the solution was readjusted. The suspension was stirred vigorously with a magnetic stirrer. The variation of pH of the suspension was maintained within ±0.1 pH by adding hydrochloric acid or sodium hydroxide solution. Adsorption experiments were carried out in a thermostated bath at 25 °C. After 5 h or at appropriate intervals, an aliquot of suspension was pipetted and filtered through a membrane filter having pore size of 0.1 μm. The concentration of monosilicic acid in the filtrate was determined by colorimetry. The aluminium hydroxide on the membrane filter was dissolved with 1 mol dm^{-3} hydrochloric acid. The resulting solution was filtered and diluted to 100 cm^3 with distilled water (solution A). The amount of monosilicic acid in the solution A was determined by colorimetry and the total silicic acid was determined after decomposing polysilicic acid with alkali. Silica particles larger than 0.1 μm remaining on the filter were determined by colorimetry after the filter had been ashed and the silica was fused with sodium carbonate. Aluminium ion concentration in the solution A was determined by EDTA titration .

The following symbols will be used: Si(M): the amount of monosilicic acid in the solution A; Si($<$0.1): the total amount of silicic acid (particles smaller than 0.1 μm) in the solution A; Si($>$0.1): the amount of silica (particles larger than 0.1 μm) remaining on the filter; Si(T): the sum of Si($<$0.1) and Si($>$0.1); Al(A): the amount of aluminium ion in the solution A; Si/Al(MR): the mole ratio of monosilicic acid to aluminium hydroxide in the initial solution; Si(T)/Al(A): the mole ratio of total silicic acid adsorbed to aluminium hydroxide; Si(M)/Si(T): the mole ratio of monosilicic acid to total silicic acid adsorbed on aluminium hydroxide. Since the difference between Si(M) and Si(T) can be regarded as the amount of polysilicic acid formed on the aluminium hydroxide, this ratio is an indicator of the amount of polysilicic acid formed.

Gel Chromatography. The size distribution of polysilicic acids formed on aluminium hydroxide was measured by gel chromatography. The pH of the solution A was adjusted to 2 and silicic acid was chromatographed on 1 cm × 60 cm column of Sephadex G-75 (Pharmacia Fine Chemicals) according to the procedure of Shimada and Tarutani.[10] After the effluent had been collected with a fraction collector, the amounts of silicic acid in the fractions were measured by colorimetry after decomposition of the polysilicic acid with alkali.

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Differential Thermal Analysis. Aluminium hydroxide which had adsorbed silicic acid was filtered, and then was dried at 25 °C for 10 d. Differential thermal analysis (DTA) was performed using a Rigaku Denki Thermaflex 8002 H/D thermoanalyzer.

Results

Effect of pH. The kinetic data for adsorption of silicic acid on aluminium hydroxide in 300 ppm (SiO_2) monosilicic acid solution of pH 9 showed that a rapid decrease in monosilicic acid concentration occurred in 1 h and then the rate of adsorption of silicic acid became relatively slow. Since, in 300 ppm monosilicic acid solution, monosilicic acid did not polymerize within 5 h, only monosilicic acid was adsorbed by aluminium hydroxide.

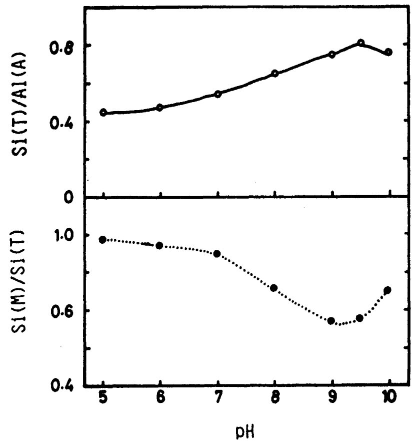

Fig. 1. The effect of pH on Si(T)/Al(A) and Si(M)/Si(T) ratios after 5 h.
Initial monosilicic acid concentration : 300 ppm. Si/Al-(MR)=2.1.

Adsorption of silicic acid by aluminium hydroxide and polymerization of adsorbed silicic acid were examined in the pH range 5—10. The results are shown in Fig. 1. The Si(T)/Al(A) ratio increased with increase in pH range 5.0—9.5, showing a maximum adsorption at pH 9.5. The Si(M)/Si(T) ratio decreased with increasing pH up to 9.0—9.5, increasing with further increase in pH. This indicates that the formation rate of polysilicic acid from silicic acid adsorbed on aluminium hydroxide is most rapid at pH 9.0—9.5. Silicic acid adsorbed on aluminium hydroxide at various pH's was chromatographed on a Sephadex G-75 column. Elution curves obtained are shown in Fig. 2. The dotted line is the elution curve for monosilicic acid, the position V_0 being the elution volume of Blue Dextran 2000, which is not diffusible in the gel phase. Polysilicic acid is eluted between the position V_0 and the elution position of monosilicic acid; the elution volume of monosilicic acid; the elution volume of polymer decreases with increasing particle size. The tailing from the peak for monosilicic acid indicates the presence of polysilicic acid in various sizes. Polymers larger in size than those in the particles separation range available with the gel are eluted together at V_0. As seen from the elution curves shown in Fig. 2, polysilicic acids formed at pH 9.0 and 9.5 have larger particle sizes than those formed at other pH's. This indicates that the rate of growth of polymer particles formed on aluminium hydroxide is most rapid at pH 9.0—9.5.

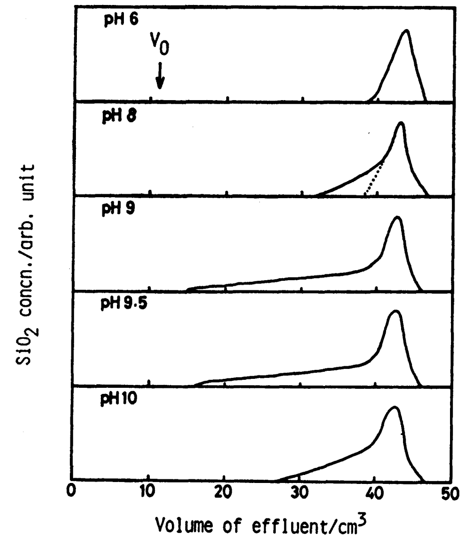

Fig. 2. Gel chromatograms for silicic acid adsorbed on aluminium hydroxide at various pH's after 5 h.
Initial monosilicic acid concentration : 300 ppm. Si/Al-(MR)=2.1. Gel : Sephadex G-75. Column: 1 cm × 60 cm.

Effect of Initial Concentration of Monosilicic Acid. The variations of Si(T)/Al(A) and of Si(M)/Si(T) ratios with the initial concentration of monosilicic acid are shown in Fig. 3. The Si(T)/Al(A) ratio increased with increasing initial concentration of monosilicic acid, whereas the Si(M)/Si(T) ratio decreased. The amount of adsorbed silicic acid and the degree of polymerization are strongly affected by the initial monosilicic acid concentration.

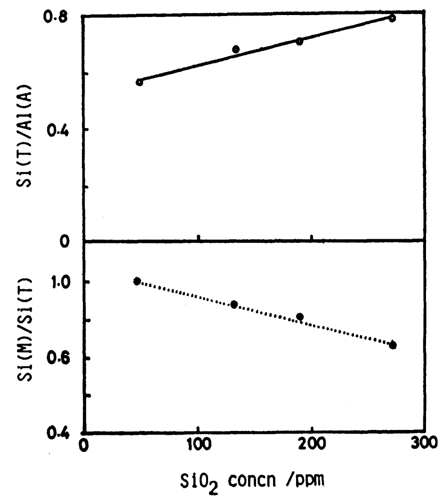

Fig. 3. Variation of Si(T)/Al(A) and Si(M)/Si(T) ratios as a function of initial monosilicic acid concentration.
Si/Al(MR)=0.96. pH : 9. Reaction time : 5 h.

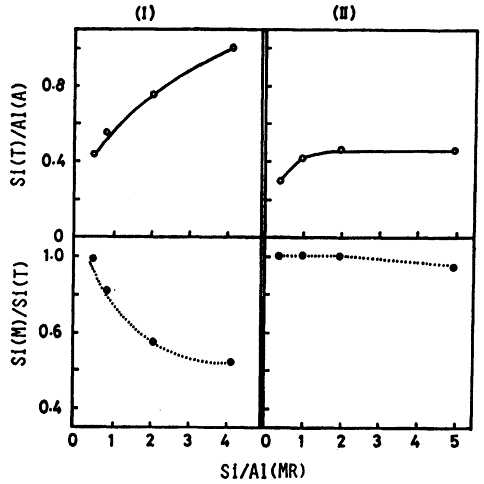

Fig. 4. Variation of Si(T)/Al(A) and Si(M)/Si(T) ratios as a function of Si/Al(MR) ratio.
Initial monosilicic acid concentration : (I) 300 ppm, (II) 100 ppm. pH : 9. Reaction time : 5 h.

Effect of the Relative Amount of Silicic Acid to Aluminium Hydroxide. Figure 4 shows the variations of Si(T)/Al(A) and of Si(M)/Si(T) ratios as a function of Si/Al(MR) ratio. The Si(T)/Al(A) ratio increased with an increase in the Si/Al(MR) ratio in 300 ppm monosilicic acid solution and the Si(M)/Si(T) ratio decreased. In 100 ppm monosilicic acid solution, above the Si/Al(MR) ratio of 2, the Si(T)/Al(A) ratio reached a limiting plateau region. The Si(M)/Si(T) ratio was unity in the Si/Al(MR) range of 0.3—2.0 and was slightly less than unity at the Si/Al(MR) ratio of 5.

Effect of Standing Time. The variations of Si(T)/Al(A), Si(M)/Si(T), and Si(>0.1)/Al(A) ratios with time in 300 ppm monosilicic acid solution are shown in Fig. 5. The Si(T)/Al(A) ratio increased with time, whereas the Si(M)/Si(T) ratio decreased. After 25 h, both ratios became almost constant. On the other hand, silica of particle size above 0.1 μm formed after 35 h; its amount (Si(>0.1)/Al(A)) increased with time.

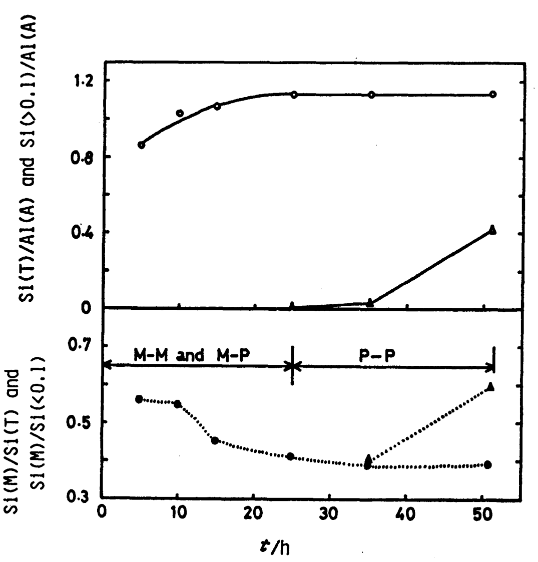

Fig. 5. Polymerization of silicic acid adsorbed on aluminium hydroxide.
Initial monosilicic acid concentration: : 300 ppm. Si/Al(MR) = 2.1. pH : 9.3.
—○—: Si(T)/Al(A), —△—: Si(>0.1)/Al(A), —●—: Si(M)/Si(T), —▲—: Si(M)/Si(<0.1).

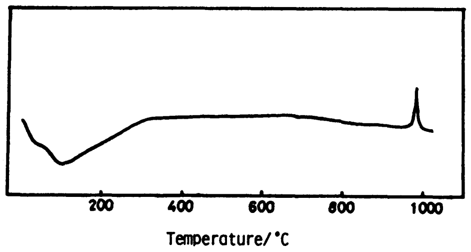

Fig. 6. DTA pattern of sample prepared at pH 8.

Differential Thermal Analysis. Figure 6 shows the DTA curve of aluminium hydroxide which had adsorbed silicic acid, prepared at pH 8. This curve has an endothermic peak at *ca.* 100—300 °C and an exothermic peak at around 1000 °C; it is very similar in basic features to the thermal curve of allophane, that is, amorphous aluminosilicate.[11] Appearance of the exothermic peak at around 1000 °C indicates that aluminosilicate is formed by the reaction of the adsorbed monosilicic acid and aluminium hydroxide. The exothermic peak was observed in all aluminium hydroxide which had adsorbed silicic acid.

Discussion

In 300 ppm (SiO_2) monosilicic acid solution, monosilicic acid did not polymerize within 5 h, whereas the monosilicic acid adsorbed on aluminium hydroxide did polymerize.

The amount of silicic acid adsorbed on aluminium hydroxide, the rate of polymerization of adsorbed silicic acid, and the formation of silica were affected by many factors, such as pH (Figs. 1 and 2), initial monosilicic acid concentration (Fig. 3), Si/Al(MR) ratio (Fig. 4), and standing time (Fig. 5). Amorphous aluminosilicate is formed by the reaction of adsorbed monosilicic acid and aluminium hydroxide (Fig. 6). The process of polymerization of adsorbed silicic acid is discussed on the basis of the data obtained at pH 9.3 (Fig. 5).

According to the preceding report,[12] the polymerization reaction of silicic acid in an aqueous solution is divided into three steps: (1) the reaction between monosilicic acids (M-M reaction), (2) the reaction between monosilicic and polysilicic acids (M-P reaction), and (3) the reaction between polysilicic acids (P-P reaction). Silicic acid adsorbed on aluminium hydroxide may also polymerize through similar reactions. An M-M reaction consists of two reactions, the reaction of the monosilicic acid adsorbed, and the reaction between the adsorbed monosilicic acid and that in the solution. The M-P reaction consists of the reaction between the adsorbed monosilicic acid and the polysilicic acid formed on the surface of solid, and the reaction between monosilicic acid in the solution and the polysilicic acid formed. The P-P reaction occurs between polysilicic acids formed on the surface of the solid, because polysilicic acid does not exist in the solution.

In Fig. 5, the Si(T)/Al(A) ratio reached nearly a constant value after 25 h. Similarly, the Si(M)/Si(T) ratio showed a constant value after 25 h. However, the Si($>$0.1)/Al(A) and Si(M)/Si($<$0.1) ratios increased even after 35 h. Since the Si(T)/Al(A) and Si(M)/Al(A) ratios were nearly constant after 25 h, the increase in the Si(M)/Si($<$0.1) ratio after 35 h suggests a decrease in the amounts of polymers smaller than 0.1 μm in size (Si($<$0.1)) according to P-P reactions.

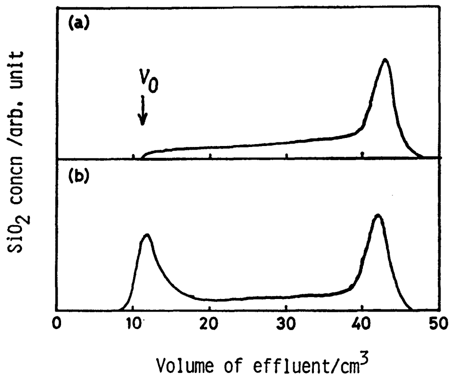

Fig. 7. Gel chromatograms for silicic acid adsorbed on aluminium hydroxide after (a) 20 h and (b) 30 h. Initial monosilicic acid concentration: 300 ppm. Si/Al(MR)=2.1. pH: 9.3. Gel: Sephadex G-75. Column: 1 cm×60 cm.

In order to confirm that a P-P reaction occurred, silicic acid absorbed on aluminium hydroxide after 20 and 30 h was chromatographed on a Sephadex G-75 column. Elution curves for silicic acid are shown in Fig. 7. Figure 7(a) shows no peak at the position V_0, while Fig. 7(b) shows a large peak. Polysilicic acids having larger sizes than the possible separation range of the gel are eluted together at the position V_0. These results suggest that the gradual increase in particle size of polymers occurred for the first 20 h (Fig. 7(a)) and then the further increase between 20 and 30 h occurred by P-P reaction (Fig. 7(b)). If a P-P reaction occurs from the beginning of the polymerization along with M-M and M-P reactions, the elution curve shown in Fig. 7(a) should show a peak at the position V_0, though the peak may be small. As shown in Fig. 5, the Si(T)/Al(A) ratio increased with time until 25 h and the Si(M)/Si($<$0.1) (=Si(M)/Si(T)) ratio decreased. From the evidence of gel chromatography, it is concluded that the polymerization of silicic acid mainly proceeds by M-M and M-P reactions in the reaction time up to 25 h.

The process of polymerization of silicic acid adsorbed on aluminium hydroxide can be explained as follows. Monosilicic acid is at first adsorbed on aluminium hydroxide and a part of monosilicic acid adsorbed forms amorphous aluminosilicate (Fig. 6). In an early stage of polymerization of adsorbed silicic acid, the polymerization mainly proceeds by M-M and M-P reactions and the particle sizes of polymers gradually increase with time. When the particles of the polymers grow large enough to touch neighboring polymers, the growth rate of polymers becomes faster due to P-P reaction.

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