Polymerization of Silicic Acid Adsorbed on Iron(III) Hydroxide

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Adsorption of silicic acid on iron(III) hydroxide from aqueous solution and polymerization of adsorbed silicic acid were affected by pH, concentration of silicic acid before and after adsorption, or the relative amount of silicic acid and iron(III) hydroxide. The amount of adsorbed silicic acid and the rate of its polymerization were maximum at pH 9. The polymerization reaction of silicic acid on the surface of iron(III) hydroxide was found to consist of two steps: (1) polymerization of adsorbed monosilicic acid and (2) polymerization between monosilicic acid in the solution and silicic acid species already present on the surface of iron(III) hydroxide, giving a three-dimensional gel structure.

Iron(III) hydroxide removes silicic acid from a solution in a high amount by adsorption or coprecipitation reaction. Kato[1] reported that dissolved silica is controlled by the oxidation-reduction cycle of iron and manganese in lake water. Ferruginous sinters deposited from hot spring waters contain a large amount of silica. However, few reports have been published with respect to the behavior of silicic acid adsorbed on or coprecipitated with iron(III) hydroxide.

Harder and Flehmig[2] found the formation of quartz in iron(III) hydroxide-silica-precipitates. Kojima and Tarutani[3] reported that monosilicic acid adsorbed on iron(III) hydroxide polymerizes in a short period of time. Herbillon and Vinh An[4] studied precipitates formed by the addition of iron(III) and iron(II) chloride solutions to sodium silicate solutions. Their results indicate that Si is incorporated into the precipitate by two distinct processes. When SiO_2/Fe_2O_3 mole ratio (MR) was less than 0.1, Si was chemisorbed. In the range MR>0.1, silica polymerized as a separate phase.

In this work, factors controlling the amount of silicic acid adsorbed on iron(III) hydroxide and the polymerization of adsorbed silicic acid were studied. The term "monosilicic acid" refers to the total sum of monosilicic acid, H_4SiO_4, and its conjugate base, $H_3SiO_4^-$, the term "polysilicic acid" refers to dimer and larger polymer species.

Experimental

Samples and Reagents. All the reagents were of analytical reagent grade. A stock solution of monosilicic acid was prepared by dissolving silica gel (Mallinckrodt Chemical Works) in sodium hydroxide solution. Monosilicic acid solution of desired concentration was prepared by diluting stock solution.

Iron(III) hydroxide was precipitated by adding sodium hydroxide solution to iron(III) chloride solution and then washed with distilled water. Iron(III) hydroxide was prepared immediately before each experiment.

Procedure. Monosilicic acid solution (500 ml) of an appropriate concentration was adjusted to the desired pH with hydrochloric acid or sodium hydroxide solution. A known amount of iron(III) hydroxide was then introduced into 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 in the range of ±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, an aliquot of suspension was pipetted and filtered through a membrane filter having pores of 0.1 μm. The concentration of monosilicic acid in the filtrate was determined by colorimetry. The iron(III) hydroxide on the membrane filter was dissolved with 1 mol dm^{-3} hydrochloric acid, the resulting solution being filtered and diluted to 50 ml with distilled water (solution A). After iron(III) ion in an aliquot of the solution A had been removed by treating with cation exchange resin, the amount of monosilicic acid was determined by colorimetry and the total silicic acid was determined after decomposition of polysilicic acid with alkali. Silica larger than 0.1 μm remaining on the filter was determined by colorimetry after the filter had been ashed and the silica was fused with sodium carbonate. Iron(III) ion concentration in solution A was determined by colorimetry.

The size distribution of polysilicic acids formed on the surface of iron(III) hydroxide was determined by gel chromatography. After iron(III) ion in solution A had been eliminated by treating with cation exchange resin, the pH of the solution was adjusted to 2 and silicic acid was chromatographed on an 1×60 cm column of Sephadex G-25 according to the procedure of Shimada and Tarutani.[5] 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 polysilicic acid with alkali.

The following symbols are used. Si/Fe(MR): the mole ratio of monosilicic acid and iron(III) hydroxide in the initial solution, Si(M): the amount of monosilicic acid in solution A, Si(<0.1): the total amount of silicic acid (smaller than 0.1 μm) in solution A, Si(>0.1): the amount of silica larger than 0.1 μm remaining on the filter, Si(T): the sum of Si(<0.1) and Si(>0.1), Fe(A): the amount of iron(III) ion in solution A, Si(T)/Fe(A): the mole ratio of silicic acid adsorbed and iron(III) hydroxide, Si(M)/Si(T): the mole ratio of monosilicic acid and total silicic acid adsorbed on iron(III) hydroxide. This ratio indicates the degree of polymerization of adsorbed silicic acid.

Results

The Kinetics of Adsorption. The kinetic data for adsorption of silicic acid on iron(III) hydroxide at three Si/Fe(MR) ratios and at pH 9 are shown in Fig. 1. The initial concentration of monosilicic acid was 300 ppm (SiO_2). A rapid decrease in monosilicic acid concentration occurred in one hour, the rate of adsorption of silicic acid then becoming relatively slow with

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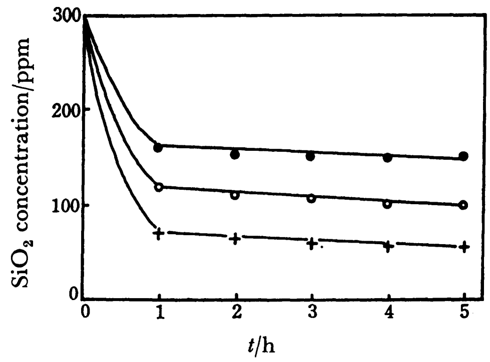

Fig. 1. The rate of adsorption of monosilicic acid by iron(III) hydroxide at pH 9.
Initial monosilicic acid concentration: 300 ppm.
Si/Fe(MR): —●— 1.31, —○— 0.65, —+— 0.44.

time. Since monosilicic acid did not polymerize in the solution of 300 ppm within 5 h, only monosilicic acid was adsorbed by iron(III) hydroxide.

Effect of pH. Adsorption of silicic acid by iron(III) hydroxide and polymerization of adsorbed silicic acid were examined in the pH range 4—12. The results are shown in Figs. 2 and 3. Si(T)/Fe(A) ratio increased in the pH range 4—9, declining above pH 9. The maximum adsorption with respect to pH occurred at pH 9 (Fig. 2). Si(M)/Si(T) ratio decreased with increasing pH up to 9, increasing with further increase in pH. This indicates that the polymerization of silicic acid adsorbed on iron(III) hydroxide is most rapid at pH 9. In 300 ppm monosilicic acid solution, monosilicic acid adsorbed polymerized in the pH range 4—12. In 100 ppm monosilicic acid solution, the concentration being lower than the solubility of amorphous silica, monosilicic acid adsorbed polymerized in weakly alkaline solutions.

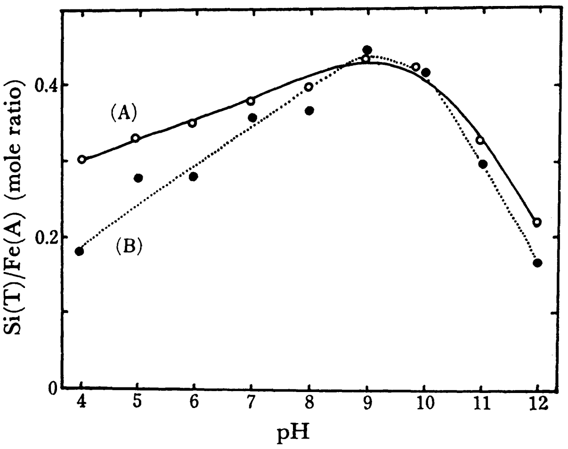

Fig. 2. The effect of pH on the amount of silicic acid adsorbed on iron(III) hydroxide after 5 h.
Initial monosilicic acid concentration: (A) 300 ppm, (B) 100 ppm.
Si/Fe(MR): (A) 0.63, (B) 1.31.

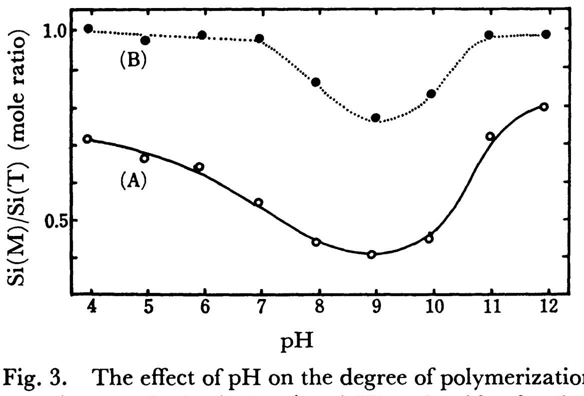

Fig. 3. The effect of pH on the degree of polymerization of silicic acid adsorbed on iron(III) hydroxide after 5 h. The experimental conditions are the same as those of Fig. 2.

Distribution of Particle Size of Polysilicic Acids. As shown in Fig. 3, the amount of polysilicic acid formed on the surface of iron(III) hydroxide differs with pH. No information is available on the change in particle size of the polymers.

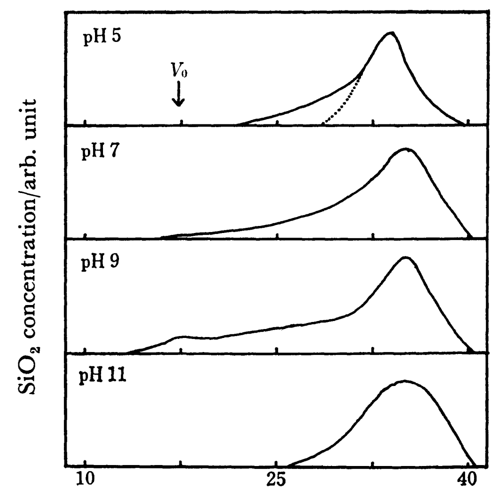

Fig. 4. Gel chromatograms for silicic acid adsorbed on iron(III) hydroxide at various pH after 5 h.
Initial monosilicic acid concentration: 300 ppm.
Si/Fe(MR): 0.63.

Silicic acid adsorbed on iron(III) hydroxide at various pH was chromatographed on Sephadex G-25 column. Elution curves for silicic acid are shown in Fig. 4. The dotted line is the elution curve for monosilicic acid, the position V_0 being the elution volume of Blue Dextran 2000, which does not seem 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 polymer decreasing with increasing particle size. Polymers larger in size than those in the possible separation range for the gel are eluted together at V_0. From the elution curves we see that the growth of polymers is most rapid at pH 9.

Effect of Initial Concentration of Monosilicic Acid. Figure 5 shows the variation of Si(T)/Fe(A) and Si(M)/Si(T) ratios with initial concentration of monosilicic acid, the former increasing with an increase in the initial concentration of monosilicic acid and the latter decreasing. The amount of adsorbed silicic acid

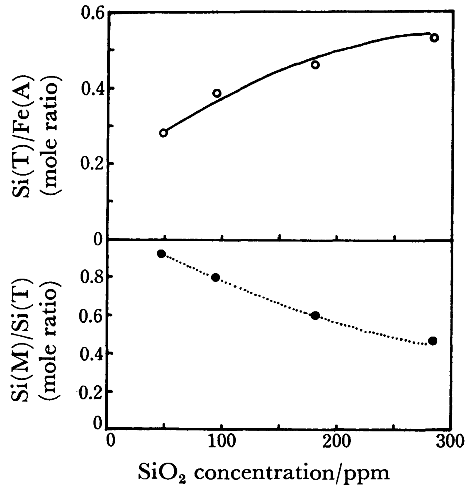

Fig. 5. The variation of Si(T)/Fe(A) and Si(M)/Si(T) ratios as a function of initial silicic acid concentration. pH: 9. Reaction time: 5 h. Si/Fe(MR): 0.87.

and the degree of polymerization are greatly influenced by initial monosilicic acid concentration.

Effect of the Relative Amount of Silicic Acid and Iron(III) Hydroxide. Figure 6 shows the variation of Si(T)/Fe(A) and Si(M)/Si(T) ratios as a function of the Si/Fe(MR) ratio. Increase in the Si(T)/Fe(A) ratio and decrease in the Si(M)/Si(T) ratio were rapid with an increase in Si/Fe(MR) ratio in 300 ppm monosilicic acid solution. On the other hand, in 100 ppm monosilicic acid solution, at above Si/Fe(MR) ratio of unity, the Si(T)/Fe(A) ratio reached a limiting plateau region, indicating a *ca.* 0.38 Si(T)/Fe(A) ratio. The decrease in the Si(M)/Si(T) ratio became very slow at above a 2 Si/Fe(MR) ratio.

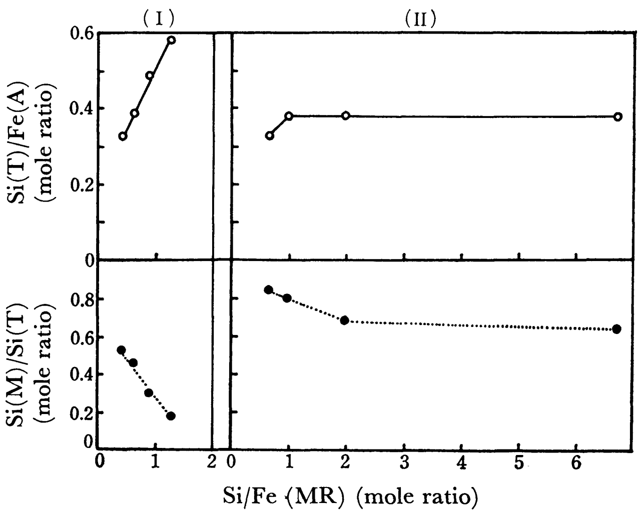

Fig. 6. The variation of Si(T)/Fe(A) and Si(M)/Si(T) ratios as a function of Si/Fe(MR) ratio.
Initial monosilicic acid concentration: (I) 300 ppm, (II) 100 ppm.
pH: 9. Reaction time: 5 h.

Effect of Standing Time. The variation of Si(T)/Fe(A) and Si(M)/Si(T) ratios with time in 300 ppm monosilicic acid solution is shown in Fig. 7. At a 0.65 Si/Fe(MR) ratio, both Si(T)/Fe(A) and Si(M)/Si(T) ratios reached limiting values after 10 h, indicating that adsorption and polymerization of silicic acid apparently do not proceed after 10 h.

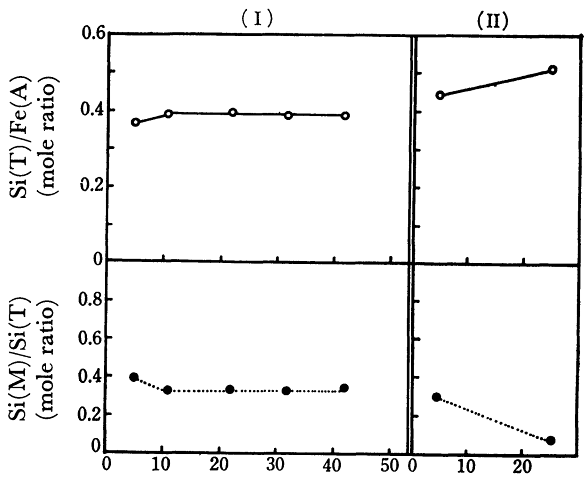

Fig. 7. The variation of Si(T)/Fe(A) and Si/(M)Si(T) ratios with time.
Initial monosilicic acid concentration: 300 ppm.
Si/Fe(MR): (I) 0.65, (II) 2.1. pH: 9.

At a 2.1 Si/Fe(MR) ratio, the Si(T)/Fe(A) ratio increased with time, the Si(M)/Si(T) ratio decreasing. Silica of size larger than 0.1 μm was obtained after 5 h, its amount increasing with time.

Discussion

Since the amount of silicic acid adsorbed on iron(III) hydroxide and the degree of polymerization of adsorbed

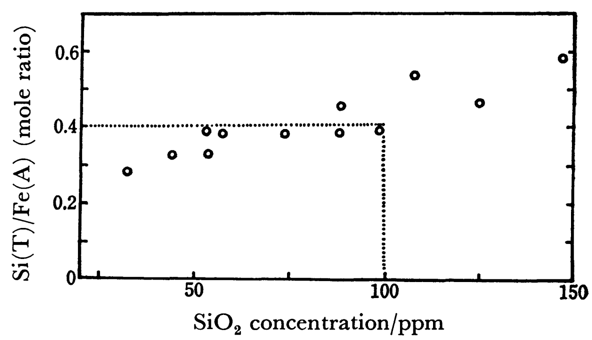

Fig. 8. Relationship between Si(T)/Fe(A) ratio and the concentration of monosilicic acid after 5 h at pH 9.

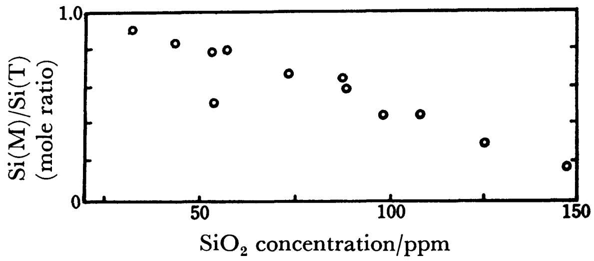

Fig. 9. Relationship between Si(M)/Si(T) ratio and the concentration of monosilicic acid after 5 h at pH 9.

silicic acid were largest at pH 9 (Figs. 2 and 3), the behavior of silicic acid was studied at pH 9.

The Si(T)/Fe(A) ratio increased with increasing initial concentration of silicic acid, the Si(M)/Si(T) ratio decreasing (Fig. 5). However, these ratios are expected to be affected also by silicic acid concentration after adsorption. On the basis of the experimental data (Figs. 5 and 6), Si(T)/Fe(A) and Si(M)/Si(T) ratios measured after 5 h were plotted against the concentration of silicic acid in the solutions. The results are shown in Figs. 8 and 9. The Si(T)/Fe(A) ratio is *ca.* 0.39 in the silicic acid solutions in the concentration range 50—100 ppm. Tarutani and Kato[6] reported that when 50 ppm monosilicic acid solution of pH 8 is continuously flowed through a flask containing iron(III) hydroxide, the Si(T)/Fe(A) ratio reaches the limiting value 0.39 after 10 d. It may be concluded that this value is the adsorption capacity of iron(III) hydroxide for silicic acid. When silicic acid concentration is higher than 100 ppm, the Si(T)/Fe(A) ratio increases with increasing silicic acid concentration. The Si(M)/Si(T) ratio decreased with increasing concentration of silicic acid (Fig. 9), suggesting that polymerization is affected by the concentration of silicic acid after adsorption as well as the initial silicic acid concentration.

The following conclusion was made. The polymerization reaction of silicic acid on the surface of iron(III) hydroxide consists of two steps: (1) the polymerization of adsorbed monosilicic acid and (2) the polymerization between monosilicic acid in the solution and silicic acid species already present on the surface of iron(III) hydroxide, giving rise to a three-dimensional gel structure.

In the solution of initial silicic acid concentration of 100 ppm, the amount of adsorbed silicic acid is nearly constant at above Si/Fe(MR) of unity, but the amount of polysilicic acid gradually increases with increasing Si/Fe(MR) ratio (Fig. 6). This suggests that polysilicic acid is mainly formed by Reaction 1. In silicic acid solutions in the concentration range 50—100 ppm, the Si(T)/Fe(A) ratio is almost constant (Fig. 8). When silicic acid concentration is higher than 100 ppm, the Si(T)/Fe(A) ratio increases with increasing silicic acid concentration. This seems to be caused by Reaction 2.

Amorphous silica of size larger than 0.1 μm is formed after 5 h on the surface of iron(III) hydroxide in the solution of initial silicic acid concentration of 300 ppm at a 2.1 Si/Fe(MR) ratio (Fig. 7). This suggests that polysilicic acid rapidly grows on the surface of iron(III) hydroxide in silicic acid solution which has a concentration higher than the solubility of amorphous silica.

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