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The Kinetics of the Polymerization of Silicic Acid

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The process of the polymerization of silicic acid can be divided into three steps: (1) a reaction between monosilicic acids, (2) a reaction between monosilicic and polysilicic acids, and (3) a reaction between polysilicic acids. The rates of the reactions between monomer-monomer, monomer-polymer and polymer-polymer are most rapid at pH values around 9.3, 8.5, and 6.8 respectively. It is concluded that, above about pH 4, the polymerization due to Reactions 1, 2, and 3 proceeds mainly by a reaction between ionized and un-ionized silanol groups.

The rate of the polymerization of silicic acid differs with the pH values of the solution.[1—4] The polymerization of silicic acid is rapid in weakly alkaline and strongly acidic solutions, but very slow in the pH range of 1—3. The kinetics of polymerization of silicic acid have been studied by colorimetry,[1,4] because monosilicic acid reacts with a molybdate reagent in an acidic solution to give a yellow color, whereas polysilicic acid does not react with a molybdate reagent. However, no information is available on the change in particle size of the polymers with time. From a gel chromatographic study of the polymerization of silicic acid, it has been suggested that the mechanism of the growth of particles of polysilicic acid differs with the pH.[5]

The process of the polymerization of silicic acid may be divided into three steps.

(1): A reaction between monosilicic acids.
(2): A reaction between monosilicic and polysilicic acids.
(3): A reaction between polysilicic acids.

The first step of the polymerization of monosilicic acid is to form disilicic acid by the Reaction 1. If it can be assumed that, in the early stage of polymerization, the decrease in the concentration of monosilicic acid in solutions of various pH values is due mainly to Reaction 1, it may be possible to obtain the relationship between the rate of Reaction 1 and the pH.

When the concentration of monosilicic acid is higher than the solubility of amorphous silica at a given pH, monosilicic acid generally polymerizes, but the rate of polymerization depends on the concentration of monosilicic acid. In a solution with an adequate concentration of monosilicic acid, Reaction 1 does not occur within a certain period of time. Therefore, when monosilicic acid solution in which Reaction 1 does not occur within a certain period of time is mixed with a polysilicic acid solution and the concentration of monosilicic acid decreases with time from the moment of mixing the solutions, it is concluded that the decrease in the concentration of monosilicic acid is due mainly to Reaction 2.

When the concentration of monosilicic acid is close to the solubility of amorphous silica at a given pH, Reactions 1 and 2 virtually do not occur. As Reaction 3 proceeds regardless of the presence of monosilicic acid, the effect of the pH on the reaction between polysilicic acids can be measured by gel chromatography from the change in elution curves for silicic acid in the solutions of various pH values.

The present paper describes the effect of the pH on the rate of Reactions 1, 2, and 3. The term "monosilicic acid" here indicates the total sum of monosilicic acid (H_4SiO_4) and its conjugate base ($H_3SiO_4^-$), unless otherwise specified, while the term "polysilicic acid" indicates the dimer and larger polymer species.

Experimental

Sample Solution and Reagents. All the reagents used were of an analytical reagent grade. The monosilicic acid stock solution was prepared by fusing 0.500 g of anhydrous silica with 2.5 g of sodium carbonate, dissolving the melt in distilled water, and diluting the solution to 500 cm^3. A solution of Blue Dextran 2000 (Pharmacia Fine Chemicals, 0.4%) was used for the measurement of the void volume of gel bed in gel chromatography. The eluent for elution of silicic acid and Blue Dextran 2000 was a 0.1 mol/dm^3 sodium chloride solution of pH 2.

Preparation of Sephadex Column. Sephadex G-100 (Pharmacia Fine Chemicals) was suspended in the solution to be used as an eluent and was allowed to swell for three days. The column was a 1.0×45 cm or 1.5×45 cm glass tube with a porous polystyrene disc at the bottom. The Sephadex G-100 column was prepared as has been described in the literature.[6]

Procedure for Determination of Reaction 1. The monosilicic acid solution (500 ppm SiO_2) was adjusted to the desired pH with hydrochloric acid. After 5, 10, and 15 min, the concentration of monosilicic acid was measured by colorimetry.

Procedure for Determination of Reaction 2. The pH of the monosilicic acid solution (500 ppm) was adjusted to 8.3 with hydrochloric acid. After the solution had stood for 5 h, the pH of this solution was adjusted to 2 with hydrochloric acid, because polymerization and depolymerization do not occur for a short period at pH 2.[4] The concentration of monosilicic acid in this solution (Solution A) was 205 ppm, with the remainder being polysilicic acid. Several sample solutions containing 314 ppm of monosilicic acid and 187 ppm of polysilicic acid were prepared by mixing aliquots of Solution A and a 1000 ppm monosilicic acid solution. At the same time, the sample solutions were adjusted to the pH range of 6.9—9.6. After the solution had stood for 30 min, the concentration of monosilicic acid was measured by colorimetry and the silicic acid was chromatographed on Sephadex G-100 column. Elution was performed with a procedure similar to one previously reported.[5]

Procedure for Determination of Reaction 3. The pH of the monosilicic acid solution (500 ppm) was adjusted to 8 with hydrochloric acid. After the solution had stood for 5 h, the pH of this solution was adjusted to 2 with hydrochloric acid. The polysilicic acid was concentrated by the addition of dried Sephadex G-25 gel to the solution. After this treatment, the concentrations of monosilicic acid and polysilicic acid in

Table 1. The concentrations of monosilicic acid in initial sample solutions of various pH values

pH	SiO_2(ppm)	pH	SiO_2(ppm)
1	150	6	115
2	190	7	110
3	190	8	120
4	140	9.5	210
5	120	10	320

the solution (Solution B) were 179 and 536 ppm respectively. Ten sample solutions of various pH values containing 350 ppm polysilicic acid and monosilicic acid, in concentrations of various pH values shown in Table 1, were prepared by mixing solution B, a 1000 ppm monosilicic acid solution, distilled water, and a sodium hydroxide solution or hydrochloric acid. After the solutions had stood for 48 h, the pHs of these sample solutions were adjusted to 2 and the silicic acid was chromatographed.

All the experiments were carried out at 20±1 °C.

Results

Effect of pH *on the Reaction between Monosilicic Acids.* The kinetics of polymer formation obtained by monitoring the concentration of monosilicic acid as functions of time and the pH is shown in Fig. 1. As it can be assumed that the decrease in the concentration of monosilicic acid is due mainly to the formation of disilicic acid by a Reaction 1 in an early stage of the polymerization, it is considered that the pH of the maximum of the decrease in the concentration of monosilicic acid after a few minutes may close to the pH at which the rate of the formation of disilicic acid is maximal. The pH giving the maximum rate of decrease in the concentration of monosilicic acid slightly shifted to a lower pH with lapse of time. This may be due to the effect of polymer formation by Reaction 2 as will be discussed later. The results indicate that the reaction between monosilicic acids is most rapid at a pH value around 9.3.

Effect of pH *on the Reaction between Monosilicic and Polysilicic Acids.* When the pHs of 330 ppm monosilicic acid solutions were adjusted to 8.6 and 9.0, the concentration of monosilicic acid in these solutions did not decrease within 30 min. That is, the monosilicic acid does not polymerize within this short period of time under these conditions. If the concentration of monosilicic acid decreases from the moment of mixing after polysilicic acid is introduced into the monosilicic acid solution of about 300 ppm, it may be concluded that the decrease in monosilicic acid is caused by the reaction between monosilicic and polysilicic acids. The procedure for the determination of Reaction 2 has been done under these conditions. The results are shown in Fig. 2. The decrease in the concentration of monosilicic acid was maximal at a pH value around 8.5.

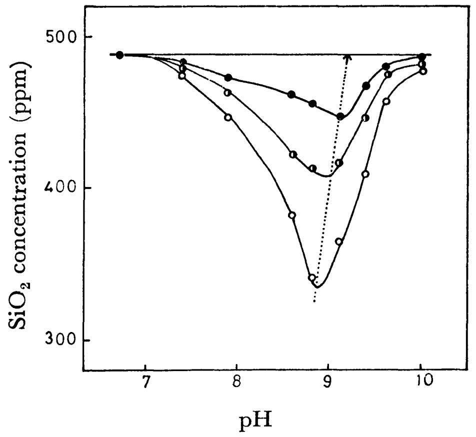


Fig. 1. Variation of the concentration of monosilicic acid as a function of pH. Time after ajusting pH: 5 min (—●—), 10 min (—◐—), 15 min (—○—).

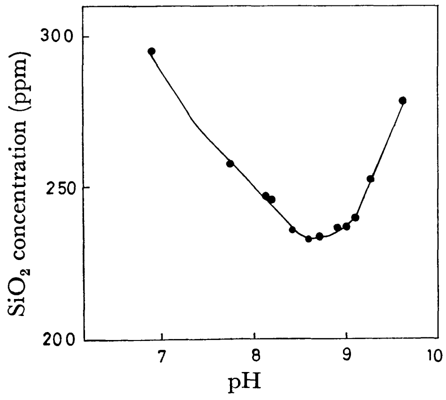


Fig. 2. Change in the concentration of monosilicic acid with pH after 30 min when polysilicic acid was added in monosilicic acid solutions.

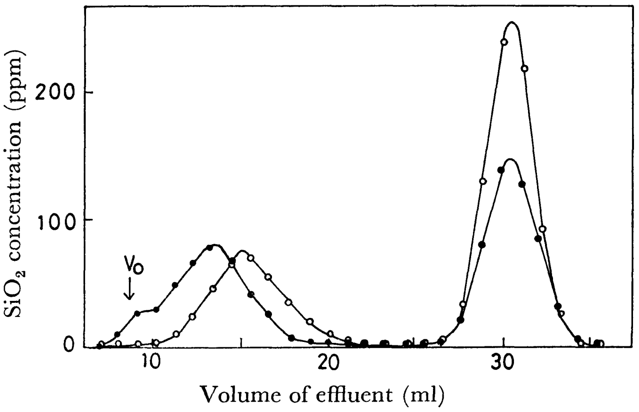


Fig. 3. Variation of elution curves for silicic acid in the solution of pH 8.9 with time. (Column, 1×45 cm). Initial solution: (—○—), solution after 30 min: (—●—).

The variation in elution curves for silicic acid with time is shown in Fig. 3. The position shown as V_0 is the elution volume of Blue Dextran 2000, which is considered not to be able to diffuse in the gel phase. It can be assumed that the elution volume of Blue Dextran is equal to the void volume of the bed. The peaks on the right are due to monosilicic acid, while the peaks on the left are due to polysilicic acid. The elution curve for silicic acid in the initial solution is symmetrical. The elution curve for the polysilicic acid in the solution shifts to the left after 30 min, but the shape of the elution curve, except shoulder at the V_0 position, is almost the same as that obtained from the initial solution. The shoulder of the elution curve at the V_0

position means that polysilicic acids larger in size than the possible separation range of the gel are eluted together at the V_0 position. If the growth of particles of polymers is due mainly to polymerization between monomer and polymer, the elution curves for polysilicic acid are symmetrical, and this symmetry is maintained in spite of the lapse of time.[5] The results shown in Fig. 3 reveal that the growth of the particles of the polymers is due mainly to the polymerization between monomer and polymer. From the results shown in Figs. 2 and 3, it is concluded that the polymerization between monomer and polymer is most rapid at a pH value around 8.5.

Effect of pH *on the Reaction between Polysilicic Acids.* The concentrations of monosilicic acid shown in Table 1 are close to the solubility of amorphous silica at a given pH.[1,7,18] Reactions 1 and 2 did not occur in 1.0—10.0 pH range within 48 h. As the reaction between polymers proceeds regardless of the presence of monosilicic acid, the results obtained by the procedure used for the determination of Reaction 3 give the relationship between Reaction 3 and the pH. The elution curves for silicic acid in solutions of various pH values after they have stood for 48 h are shown in Fig. 4. The elution curve for silicic acid in the solution of pH 2 did not change within 48 h. This elution curve represents the distribution of particle sizes of silicic acids in initial solutions of various pH values. In the solutions above pH 4, the elution curves due to polymers shifted to the left after 48 h compared with that at pH 2. This means that the particle sizes of polymers became larger than in the initial solutions. The elution curve for silicic acid in the solution of pH 3 after 48 h was identical with that in the initial solution.

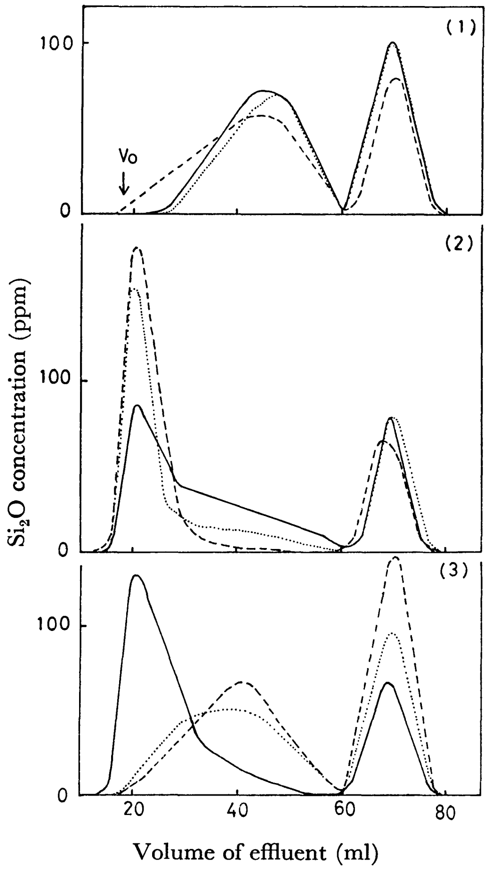


Fig. 4. Variation of elution curves for silicic acid in the solutions of various pH. (Column, 1.5×45 cm). (1): pH 1 (——), pH 2 (······), pH 4 (– – –), (2): pH 5 (——), pH 6 (······), pH 7 (– – –), (3): pH 8 (——), pH 9.5 (······), pH 10 (– – –).

Laurent and Killander[8] defined a constant, K_{av}, for a given gel in gel chromatography:

$$K_{av} = \frac{V_e - V_o}{V_t - V_o}$$

where V_o is the void volume; V_t, the total bed volume, and V_e, the elution volume. Here, V_o, V_t, and V_e are easily measured. As the K_{av} value is correlated to V_e, it is a measure of the particle size and decreases with an increase in the particle size. As the elution volumes of polymers can not be obtained directly from the elution curves shown in Fig. 4, the mean elution volumes must be calculated using the following relationship;

$$V_e = \sum C_i V_i / \sum C_i$$

where V_e is the mean elution volume, C_i is the concentration in the i-th fraction, and V_i is the volume of the i-th fraction. The relationship between the pH and the K_{av} values of polysilicic acids in the solutions of various pHs after 48 h is shown in Fig. 5. It appears that the K_{av} value of polysilicic acid is at its minimum at a pH around 6.8. The results show that the rate of reaction between polysilicic acids is most rapid at a pH around 6.8.

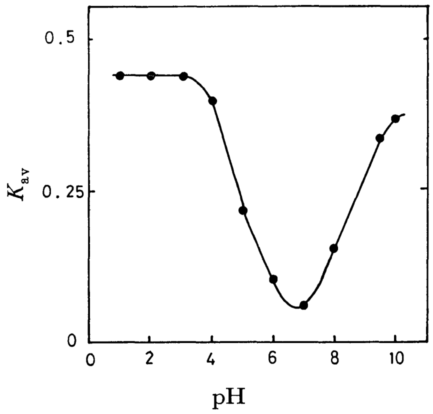
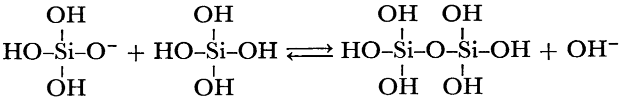


Fig. 5. Plot of K_{av} against pH.

Discussion

The rates of the reactions between monomer-monomer, monomer-polymer, and polymer-polymer are most rapid at pH values around 9.3, 8.5, and 6.8 respectively. From the variation in ammonium molybdate reactive monosilicic acid, Richardson and Waddams[9] found that the polymerization is most rapid between pH 8—9. Merrill and Spencer[10] reported that the pH at the minimum gel time is about 7; Ray and Gangly[11] obtained similar results for gelation reactions. This discrepancy in the pH at which the maximum polymerization takes place can be explained by the facts that Richardson and Waddams measured the rate of polymerization caused by Reactions 1 and 2, while, on the other hand, Merrill and Spencer measured the rate of Reaction 3.

As singly ionized monosilicic acid forms in a basic solution, the concentration of the singly ionized form becomes higher with an increase in the pH. Ashley and Innes[12] proposed that the polymerization of silicic acid proceeds by a reaction between singly ionized and un-ionized silicic acids. Reaction 1 does have its maximum rate at a pH around 9.3 (Fig. 1). At this pH the concentration of un-ionized silicic acid and the singly ionized form is reasonably high; Greenberg and Sinclair[13] calculated the $(H_3SiO_4^-)/(H_4SiO_4)$ ratio based on the reported ionization constant of silicic acid and obtained the ratio of 1/1 at pH 9.5. As the pH giving the maximum rate of Reaction 1 is almost the same as that giving the $(H_3SiO_4^-)/(H_4SiO_4)$ ratio of 1/1, it is concluded that Reaction 1 mainly proceeds by the reaction of singly ionized silicic acid and un-ionized silicic acid, and that the rate of the formation of disilicic acid reaches its maximum at the pH at which the $(H_3SiO_4^-)/(H_4SiO_4)$ ratio is unity.



$$\mathrm{HO{-}\underset{OH}{\overset{OH}{Si}}{-}O^-} + \mathrm{HO{-}\underset{OH}{\overset{OH}{Si}}{-}OH} \rightleftarrows \mathrm{HO{-}\underset{OH}{\overset{OH}{Si}}{-}O{-}\underset{OH}{\overset{OH}{Si}}{-}OH} + \mathrm{OH^-}$$

Komura *et al.*[15] have reported that the point of the zero charge of colloidal silica is pH 3.5 and that the negative charge of colloidal silica increases with an increase in the pH. If it can be assumed that the reaction between monosilicic acid and polysilicic acid is a reaction between a negatively charged site on the surface of polysilicic acid and un-ionized monosilicic acid, the rate of the polymerization due to Reaction 2 will reach its maximum at the pH at which the concentration of the negative ionic charge of polysilicic acids and un-ionized monosilicic acid is reasonably high. It is expected that the pH giving the maximum rate of polymerization by Reaction 2 is lower than that giving that by Reaction 1 because of the high concentration of un-ionized monosilicic acid at low pHs. The results show that the rate of polymerization due to Reaction 2 is most rapid at a pH around 8.5 (Fig. 2). At pH 8.5, the concentration of the negative charge of polysilicic acids is high and monosilicic acid mainly exists as an un-ionized form. Above pH 8.5, the concentration of the negative charge of polysilicic acids increases, and the concentration of un-ionized monosilicic acid decreases, with an increase in the pH. Below pH 8.5, the concentration of the negative charge of polysilicic acids decreases, and the concentration of un-ionized monosilicic acid increases, with a decrease in the pH. As is shown in Fig. 2, the rate of Reaction 2 becomes slow below and above pH 8.5. This means that Reaction 2 mainly proceeds by the reaction between an ionized silanol group of polysilicic acids and un-ionized monosilicic acid.

The isoelectric point of colloidal silica is between pH 1 and 2,[14] while the point of the zero charge of colloidal silica is pH 3.5.[15] However, below pH 3.5, the stability of polysilicic acid is very high in spite of these being no charge of polysilicic acids (Fig. 5). The DLVO theory can not be applied to this system. As negative ionic charges of silica particles increase with an increase in the pH, and as, above pH 9, a sufficient concentration of the negative charge is developed on the surface of the particles, causing mutual repulsion, the rate of Reaction 3 becomes very slow.[5] When it can be assumed that the growth of polymer particles due to Reaction 3 is mainly caused by the formation of Si–O–Si bonds by the reaction of $Si–O^-$ and Si–OH, and that the concentrations of Si–OH and $Si–O^-$ on the surface of polymer particles are suitable, there may be an optimum pH at which the rate of growth of particles is at its maximum. The rate of Reaction 3 is maximal at a pH around 6.8 (Fig. 5), for at this pH polysilicic acids have a negative charge and there may be a repulsive force between polymers. However, as Reaction 3 is most rapid at pH 6.8, it is suggested that repulsive force between polymers is weak at this pH and that polymers can collide. As the value of the acidity constant of the silanol group, Si–OH, on the surface of colloidal silica is around $pK_a = 7$,[14–16] the ratio of Si–OH and $Si–O^-$ on the surface of polymers may be unity at a pH of about 7. As the rate of Reaction 3 is at its maximum at pH 6.8, it is concluded that the rate of Reaction 3 is controlled by the concentrations of ionized and un-ionized silanol groups in the same manner as in Reaction 1. From the experimental evidence of this study, it is concluded that, above about pH 4, the polymerization due to Reactions 1, 2, and 3 mainly proceeds by a reaction between ionized and un-ionized silanol groups.

References

1) T. Tarutani, *Nippon Kagaku Zasshi*, **77**, 1721 (1956).

2) T. Kojima and T. Tarutani, *Mem. Fac. Sci., Kyushu Univ., Ser. C, Chem.*, **9**, 1 (1974).

3) R. K. Iler, "The Colloid Chemistry of Silica and Silicate," Cornell Univ. Press, Ithaca, N. Y. (1955).

4) T. Tarutani, *J. Chromatogr.*, **50**, 523 (1970).

5) K. Shimada and T. Tarutani, *J. Chromatogr.*, **168**, 401 (1979).

6) L. Fisher, "An Introduction to Gel Chromatography," North-Holland, Amsterdam (1969).

7) G. B. Alexander, W. M. Heston, and R. K. Iler, *J. Phys. Chem.*, **58**, 453 (1954).

8) T. C. Laurent and J. Killander, *J. Chromatogr.*, **14**, 317 (1964).

9) E. Richardson and J. A. Waddams, *Research*, **7**, S42 (1954).

10) R. C. Merrill and R. W. Spencer, *J. Phys. Chem.*, **54**, 806 (1950).

11) R. C. Ray and P. B. Gangly, *J. Phys. Chem.*, **34**, 352 (1930).

12) K. D. Ashley and W. B. Innes, *Ind. Eng. Chem.*, **44**, 2857 (1952).

13) S. A. Greenberg and D. Sinclair, *J. Phys. Chem.*, **59**, 435 (1955).

14) K. Mushiake and N. Masuko, *Seisankenkyu*, **29**, 2 (1977).

15) A. Komura, K. Hatsutori, and H. Imanaga, *Nippon Kagaku Zasshi*, **1978**, 779.

16) D. N. Strazhesko, V. B. Strelko, V. N. Belyakov, and S. C. Rubanik, *J. Chromatogr.*, **102**, 191 (1974).

17) M. L. Hair and W. Hertle, *J. Phys. Chem.*, **74**, 91 (1970).

18) W. F. Linke, "Seidell's Solubilities," 4th ed, Am. Chem. Soc., Washington, D. C. (1965), Vol. 2, p. 1452.