Polymerization of Silicic Acid A Review

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Useful information on the polymerization of silicic acid is obtained from a combined use of (1) spectrophotometry based on the formation of yellow molybdosilicic acid, (2) trimethylsilylation of silicic acid and determination of trimethylsilyl derivatives by gas-liquid chromatography and (3) gel permeation chromatography of silicic acid. The polymerization of silicic acid is divided into three processes: (1) the formation of polysilicic acid by the reaction between molybdate reactive silicic acids (MRS acid), (2) the particle growth of polysilicic acid by the reaction between MRS acid and polysilicic acid, and (3) the particle growth of polysilicic acid by the reaction between polysilicic acids. The pH value giving maximum rate of polymerization of silicic acid is different among these three processes. Fluoride promotes processes (1) and (2); the effect of fluoride on the process (3) is relatively small.

Keywords Polymerization, silicic acid, spectrophotometry, trimethylsilylation-gas-liquid chromatography, gel permeation chromatography, catalytic effect, fluoride

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1 Introduction

Monosilicic acid in aqueous solution reacts with molybdate reagent under acidic conditions to form yellow molybdosilicic acid. This is a basic reaction for the spectrophotometric determination of monosilicic acid. Studies of silicic acid concentrations in natural water have revealed that concentrations are well below the solubility of amorphous silica. Since silicic acid in most natural water is of the monomeric form, its concentration can be determined by the spectrophotometric method. However, an analytically important fact is that at the appropriate pH monosilicic acid in supersaturated solutions, such as geothermal or hot spring water, will in time polymerize, thus the exact value of the total silicic acid concentration in aged solutions can not be obtained by the spectrophotometric method.

The polymerization of silicic acid in aqueous solution has been studied for a long time. Much of the work focused on reactions in which the initial monosilicic acid concentrations were relatively high and on the

production of silica sols or gels. More dilute systems have been employed for studying the conditions governing the polymerization of silicic acid. The factors that control the rates of polymerization of silicic acid are the pH, temperature, degree of supersaturation and presence of other substances. This review will present some information concerning the polymerization of silicic acid and related problems.

2 Solubility of Silica

The solubility of silica in water is a basic factor in the behavior of silicic acid. When solid phases of silica are in contact with water, small amounts of silica dissolve and enter the aqueous phase. The dissolution and deposition of silica in water involve both hydration and dehydration reactions:

Here, $(\text{SiO}_2)_n$ means solid silica or polysilicic acid in water. At equilibrium, the concentration of monosilicic

Fig. 1 Solubility of amorphous silica.

acid in the aqueous phase, determined by the molybdate method, is the solubility of silica.

The solubility of silica is dependent on many factors such as the state of the silica, whether it is in crystalline or amorphous form, pH of the solution, temperature and presence of other ions. The solubility of the crystalline forms of silica is low and need not be considered in analytical chemistry since the behavior of silicic acid in aqueous solution is dependent on the solubility of amorphous silica at temperatures lower than 100°C. The solubility of amorphous silica in water up to 100°C was reported by Kitahara (Fig. 1).¹ The solubility of amorphous silica is determined in two ways. When amorphous silica powder is suspended in water the concentration of monosilicic acid increases to an equilibrium solubility value. As polymerization proceeds in a supersaturated system, the monosilicic acid concentrations decrease, approaching the solubility of amorphous silica. However, different values for the solubility have been reported in the literature.² The variations in the solubility values are due to differences in the solubility characteristics of various form of silica. The solubility increases with decreasing particle size of amorphous silica.³

The solubility of amorphous silica in aqueous solutions at different pH values at 25°C is shown in Fig. 2.⁴ The solubility of amorphous silica barely changes in the pH range 1–9, but increases rapidly above pH 9, because of the formation of silicate ions.

The solubility decreases with increasing salt concentration.⁵

3 Polymerization of Silicic Acid

Investigations on the polymerization of silicic acid have been made by various methods. Among the methods, spectrophotometry, trimethylsilylation–gas-liquid chromatography and gel permeation chromatography are useful for studying the polymerization of silicic acid. Information concerning the polymerization

Fig. 2 Solubility of amorphous silica vs. pH (25°C).

Fig. 3 Variation of the concentration of MRS acid with pH. Initial monosilicic acid concentration: 500 ppm (SiO_2).

obtained by these methods is briefly reviewed.

3-1 Spectrophotometry

The kinetics of polymerization of monosilicic acid have usually been studied by spectrophotometry, based on the decrease in the concentration of monosilicic acid with time. This could be done because monosilicic acid reacts with molybdate reagent to give a yellow color, whereas polysilicic acid does not react with this reagent. During the polymerization of monosilicic acid, low-molecular-weight silicic acids, such as dimer and trimer, form. They then depolymerize and react with molybdate reagent. Hereafter, silicic acids which can be measured by molybdate method are called molybdate reactive silicic acid (henceforth abbreviated MRS acid), and silicic acids which do not react with molybdate reagent are called polysilicic acid.

The polymerization of silicic acid is strongly pH dependent. In Fig. 3, the concentration of MRS acid after 24 and 75 h is plotted against pH.⁶ In a strongly alkaline solution monosilicic acid does not polymerize.

Fig. 4 Variation of the concentration of MRS acid with time at pH 8.5. Initial monosilicic acid concentration: 600 ppm (SiO_2).

The MRS acid concentration decreases rapidly in slightly alkaline solutions, but does not decrease within 24 h within the pH range 1–3. Below this range the rate of polymerization increases with greater acidity.⁷

Figure 4 shows the effect of temperature on the polymerization of silicic acid at pH 8.5. At 20°C the MRS acid concentration abruptly decreased in 1 h. After 2 h its concentration only decreased very slowly. On the other hand, at 90°C the MRS acid concentration was identical with the initial monosilicic acid concentration until 4 h and then suddenly began to decrease. There exists an "induction period" during which there is no change in the concentration of MRS acid. Induction periods for the polymerization of MRS acid from geothermal waters have been reported.⁸ The induction period is greater at higher temperatures and decreases with increasing degree of supersaturation of monosilicic acid⁹ and salt concentration.¹⁰

The rate of decrease in the MRS acid concentration increases with increasing salt concentration.¹¹

One disadvantage of the spectrophotometric method is that it yields no information on the change in particle size of polysilicic acid with time.

3.2 Trimethylsilylation-gas-liquid chromatography

Lentz¹² described a chemical technique for studying mineral silicate structures based on the trimethylsilylation of silicic acids liberated from minerals by acid leaching. Trimethylsilylation studies provide valuable information about silicate solutions.

Low-molecular-weight silicic acid species are converted into relatively unreactive trimethylsilyl (TMS) derivatives, e.g. as in Eqs. (1) and (2), where $\text{X}=\text{Si}(\text{CH}_3)_3$.

TMS derivatives have been prepared by treating a silicate solution with a mixture of water, hydrochloric acid, isopropyl¹² or propyl¹³ alcohol and hexamethyldisiloxane. The TMS derivatives of low-molecular-weight silicic acids can be identified¹⁴ and quantified¹⁵ by gas-liquid chromatography (GLC). The distribution of derivative species reflects that which exists in the parent silicate solution.

Figures 5, 6 and 7 show the variation of concentrations of silicic acid species with time.¹⁶ Each silicic acid species is expressed in its anionic form. The Si(C) value is the concentration of silicic acid determined by spectrophotometry, and the Si(T) value is the sum of the concentrations of each silicic acid species whose TMS derivatives can be determined by GLC. The difference between the initial concentration of monosilicic acid and the Si(T) value indicates the amount of GLC-undeterminable silicic acid species.

At pH 1.8 (Fig. 5), $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_{10}^{8-}$ formed. During the first hour the amounts of $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_{10}^{8-}$ increased with rapid decrease in the amount of SiO_4^{4-} , but after this period did not change. This shows that after 1 h an equilibrium is established among these silicic acid species. The Si(T) and Si(C) values did not change with time and were equal to the initial concentration of monosilicic acid. This indicates that no GLC-undeterminable silicic acid species other than MRS acids formed.

In the 2500-ppm solution at pH 1.8 (Fig. 6), silicic acid species other than $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_{10}^{8-}$, such as $\text{Si}_3\text{O}_9^{6-}$, $\text{Si}_4\text{O}_{13}^{10-}$, $\text{Si}_5\text{O}_{15}^{10-}$ and $\text{Si}_6\text{O}_{17}^{10-}$ formed progressively. The values for $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_4\text{O}_{13}^{10-}$ were

Fig. 5 Changes in the concentration of silicic acid species in the solution of pH 1.8 with time. Initial monosilicic acid concentration: 600 ppm (SiO_2).

Fig. 6 Changes in the concentration of silicic acid species in the solution of pH 1.8 with time. Initial monosilicic acid concentration: 2500 ppm (SiO_2).

Fig. 7 Changes in the concentration of silicic acid species in the solution of pH 8.5 with time. Initial monosilicic acid concentration: 600 ppm (SiO_2).

not plotted in the figure because they were insignificant. Although the Si(T) value gradually decreased with time, the Si(C) value was equal to the initial concentration of monosilicic acid and did not change with time, indicating that all of the GLC-determinable and the GLC-undeterminable silicic acid species formed were determined by spectrophotometry. The results shown in Figs. 5 and 6 indicate the formation of oligomeric silicic acid species during the induction period.

At pH 8.5 (Fig. 7), the amounts of SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_{10}^{8-}$, and Si(T) and Si(C) values abruptly decreased in 1 h. This indicates a rapid formation of polysilicic acids.

The variation of the particle sizes of polysilicic acids

with time can be studied by gel permeation chromatography.

3.3 Gel permeation chromatography

One method for separating solute molecules according to their size is gel permeation chromatography (GPC), the basic principles of which have been explained in terms of a sieving effect or steric exclusion. The separation of the components of a sample in a solution is usually carried out on a column packed with a gel or other porous material. The elution volumes of molecules are correlated with their molecular size, larger molecules being eluted faster than smaller molecules.

Polysilicic acid can be separated from MRS acid by GPC.¹⁷ Solutions of silicic acid for GPC are usually adjusted to pH 2 at which polymerization does not occur for several hours or days.⁶

The distribution coefficient, K_{av} , for a given gel in GPC is defined¹⁸ as

$$K_{av} = (V_e - V_o) / (V_t - V_o)$$

where V_o is the void volume of the gel bed, V_t the total bed volume and V_e the elution volume of the solute. V_o , V_t and V_e are easily measured. Since K_{av} is correlated to V_e , it is a measure of the molecular size, decreasing with increasing particle size. All polymers that have larger sizes than the possible separation range of the gel are eluted at V_o .

Figure 8 shows typical elution curves for silicic acid, obtained at pH 9, 8 and 6 on a Sephadex G-100.⁶ The peaks on the right are due to MRS acid and those on the left to polysilicic acid. The concentration of MRS acid at a given time is shown in parentheses.

At pH 9.5 the elution curves for polysilicic acids indicate a symmetrical distribution of particle sizes; the curve for polysilicic acids obtained after 250 h was almost the same as that obtained after 100 h. This means that when the concentration of MRS acid is similar to the solubility of amorphous silica, the growth rate of the particles of polysilicic acids becomes very slow. Results indicate that the growth of polysilicic acids is due mainly to polymerization between MRS acid and polysilicic acid, and that polymerization between polysilicic acids hardly proceeds. Similar results were obtained at pH 9 and 2.

At pH 6 the elution curve for polysilicic acids obtained after 24 h indicates a broad and random distribution of particle sizes. After 75 h the peak of polysilicic acids appeared at V_o . This indicates that particles of polysilicic acids grow rapidly. The broad and random distribution of particle sizes arises from a random condensation of polysilicic acid species. Similar results were obtained at pH 7 and 4.

At pH 8 the elution curve for polysilicic acids obtained after 2 h was symmetrical. The MRS acid concentration after 75 h was not much different from that after 24 h and was near the solubility of amor-

Fig. 8 Variation with time of the elution curves for silicic acid in solutions of pH 9.5, 8 and 6. Initial monosilicic acid concentration: 500 ppm (SiO_2). Gel: Sephadex G-100. Column: 45×1.0 cm i.d. (1), pH 9.5: —, 6 h (M: 219 ppm); —, 100 h (M: 192 ppm); ···, 250 h (M: 174 ppm). (2), pH 8: —, 2 h (M: 230 ppm); —, 24 h (M: 147 ppm); ···, 75 h (M: 136 ppm). (3), pH 6: —, 24 h (M: 298 ppm); —, 75 h (M: 186 ppm).

phous silica, though particle growth still continued and the elution curves became asymmetrical. These results indicate that in the early stage of polymerization the growth of particles is due mainly to polymerization between MRS acid and polysilicic acid, though the polymerization between polysilicic acids is subsequently predominant.

The rate of particle growth of polysilicic acids increases with increasing sodium chloride concentration.¹¹ Crerar *et al.*¹⁹ reported that divalent metal salts (MgCl_2 , CaCl_2 , SrCl_2) promote the particle growth of polysilicic acids more than does NaCl.

The rate of particle growth of polysilicic acid by the polymerization between polysilicic acids is affected with temperature. Figure 9 shows the relationship between K_{av} values of polysilicic acids, calculated from the elution volumes, in solutions of pH 7 after 1 h and temperature.²⁰ The K_{av} value of polysilicic acid in initial solutions was 0.52. The concentration of MRS acid in each solution was nearly equal to the solubility of amorphous silica at given temperature. The K_{av} value of polysilicic acid decreases with temperature. This result shows that the rate of particle growth of polysilicic acid increases with increasing temperature.

4 pH Value Giving Maximum Rate of Polymerization of Silicic Acid

The polymerization of silicic acid is divided into three processes.

Fig. 9 Plot of K_{av} values of polysilicic acid against temperature.

- (1) Formation of polysilicic acid by a reaction between MRS acids (M-M reaction).
- (2) Particle growth of polysilicic acid by a reaction between MRS acid and polysilicic acid (M-P reaction).
- (3) Particle growth of polysilicic acid by a reaction between polysilicic acids (P-P reaction).

If it can be assumed that in the early stage of MRS acid polymerization the decrease in the concentration of MRS acid in solutions at various pH values is due mainly to an M-M reaction, it may be possible to obtain a relationship between the rate of the M-M reaction and the pH. The pH of the maximum of the decrease in the concentration of MRS acid after short period of time is the pH at which the rate of the M-M reaction is maximum. The kinetics of polysilicic acid formation obtained by monitoring the concentration of MRS acid as functions of the time and the pH are shown in Fig. 10. It is considered that the pH of the maximum of the decrease in the concentration of MRS acid after a few minutes may be close to the pH at which the rate of the M-M reaction is maximum. The pH giving the maximum rate of decrease in the concentration of MRS acid shifts slightly to a lower pH with the lapse of time. This may be due to the influence on polysilicic acid formation by the M-P reaction. The results indicate that at 20°C the M-M reaction is most rapid at around pH 9.3.

When MRS acid solution in which the M-M reaction does not occur within a certain period of time is mixed with a polysilicic acid solution and the concentration of MRS acid decreases with time from the moment of mixing of the solutions, the decrease in the concentration of MRS acid is due mainly to the M-P reaction. The pH of the maximum of the decrease in the concentration of MRS acid is the pH at which the rate of the M-P reaction is maximum. The procedure for the determination of the M-P reaction has been carried out under these conditions. Results are shown in Fig. 11. The decrease in the concentration of MRS acid was maximum at around pH 8.6 at 20°C.

When the concentration of MRS acid is close to the solubility of amorphous silica at a given pH, the M-M

Fig. 10 Variation of the concentration of MRS acid as functions of pH and time at 20°C. The horizontal line shows initial monosilicic acid concentration. Time after adjusting pH: 5 min (●); 10 min (●); 15 min (○).

Fig. 11 Change in the concentration of MRS acid with pH after 30 min at 20°C when polysilicic acid was added to a monosilicic acid solution. Initial concentrations: monosilicic acid, 314 ppm (SiO_2); polysilicic acid, 187 ppm (SiO_2).

and M-P reactions virtually do not occur. Since the P-P reaction proceeds regardless of the presence of MRS acid, the effect of pH on the P-P reaction can be measured by GPC from the change in the elution curves of silicic acid in solutions of various pH. The pH of the maximum of the decrease in K_{av} of polysilicic acid is the pH at which the P-P reaction is maximum. An aliquot of a solution containing polysilicic acid, of which the particle size distribution was known, was added to monosilicic acid solution. The monosilicic acid concentration in each sample solution was adjusted to be near the solubility of amorphous silica at the given pH.²¹ Figure 12 shows typical elution curves for silicic acid obtained after 48 h in solutions of various pH. The elution curve at pH 2 did not change within 48 h, and represents the particle size distribution of silicic

Fig. 12 Variation of the elution curves for polysilicic acid after 48 h in solutions of various pH at 20°C. Gel, Sephadex G-100; column, 45×1.5 cm i.d.; initial polysilicic acid concentration, 350 ppm (SiO_2). (1), pH 2 (—); pH 7 (---); pH 8 (····); pH 9.5 (— · —); pH 10 (— · — · —). (2), pH 1 (---); pH 2, 3 (—); pH 4 (— · —); pH 5 (····); pH 6 (— · — · —).

Fig. 13 Plot of K_{av} values of polysilicic acid against pH.

acid in initial solutions of various pH. At $\text{pH} > 4$ the elution curves obtained after 48 h were shifted to the left compared with that at pH 2. This means that the particle sizes of polysilicic acids were larger than under the initial solutions. Figure 13 shows the relationship between the K_{av} values of the polysilicic acids and the pH. The K_{av} value is minimum at around pH 6.8 at 20°C. This means that the P-P reaction is most rapid at this pH.

The pH values at which the M-M, M-P and P-P reactions at different temperatures are most rapid are listed in Table 1.²⁰ Polymerization due to three reactions mainly proceeds by a reaction between ionized and un-ionized silanol groups. The pH values

Table 1 The pH values for which M-M, M-P and P-P reactions are most rapid

Temperature/ °C	pH		
	M-M reaction	M-P reaction	P-P reaction
2	9.5	8.9	7.0
20	9.3	8.6	6.8
50	8.5	8.0	6.7
90	8.1	7.5	6.1

Fig. 14 Plot of K_{av} values of polysilicic acid after 5 h against the R value. Initial monosilicic acid concentration: 500 ppm (SiO_2). pH: 0.55 ($\square$); 1 (Δ); 2.5 ($\circ$).

giving the maximum rates of the M-M, M-P and P-P reactions shifted to lower pH values with increasing temperature. This may have been due to a change in the ionization constants of silicic acid species.

5 Catalytic Effect of Fluoride on the Polymerization of Silicic Acid

The gelling of silicic acid sols at low pH is markedly catalyzed by traces of fluoride.²² The rate of decrease with time of the concentration of MRS acid in an acidic solution in the presence of fluoride is faster than that in the absence of fluoride.²³ The rate of decrease in the concentration of MRS acid increases with decreasing pH. The rate of the M-M reaction in solutions in the pH range 2.5–0 is most rapid at a F/Si atomic ratio, R , of about 0.5, regardless of the difference in acidity.²⁴

In Fig. 14 the K_{av} values of polysilicic acids in solutions of various pH after 5 d are plotted against the R value. In silicic acid solutions containing fluoride (up to $R=2.0$) the rate of growth of polysilicic acid particles increased with increasing fluoride concentration and

Fig. 15 Elution curves for silicic acid and fluoride in solution of pH 1 after 4 d ($R=0.5$): ($\circ$) Si; ($\bullet$) F.

Fig. 16 Variation with time of the elution curves for silicic acid in a solution of pH 1 ($R=0.1$). Initial monosilicic acid concentration, 500 ppm (SiO_2); gel, Sephadex G-100; column, 45×1.0 cm i.d. Time: $\cdots$ 3 d (M: 343 ppm); $---$ 5 d (M: 262 ppm); $- \cdot -$ 10 d (M: 198 ppm); $—$ 17 d (M: 177 ppm).

was most rapid at about pH 1.

Elution curves for silicic acid and fluoride in solution ($R=0.5$) at pH 1 after 4 d are shown in Fig. 15. The elution volume of fluoride is equal to that of MRS acid, and polysilicic acid is not accompanied by fluoride.

The variation with time of the elution curves for silicic acid in solution ($R=1$) at pH 1 is shown in Fig. 16. The concentration of MRS acid is shown in parentheses. The elution curve for polysilicic acids after 5 d indicates a nearly symmetrical distribution of particle sizes. The elution curve obtained after 17 d was almost the same as that obtained after 10 d. These results indicate that when the MRS acid concentration is close to the solubility of amorphous silica the growth rate of polysilicic acid particles is very slow in spite of the presence of fluoride. It is concluded that the growth of polysilicic acid particles is due mainly to the M-P reaction, and that the catalytic effect of fluoride on the P-P reaction is relatively small.

Fluoride prevents the color development of molybdo-silicic acid in spectrophotometry. Aluminum, borate and beryllium ions which combine with fluoride to form fluoride complexes have a masking effect for fluoride and aluminum ion most effectively masks fluoride.²⁵ Similarly, the influence of fluoride on the polymerization of silicic acid can be overcome by the

addition of aluminum ion to give the desired atomic ratio of aluminum and fluoride (Al/F=10).²⁶

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