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Mechanism of the Copolymerization of Silicic Acid and Metal Ions in Aqueous Media

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Synopsis. The mechanism of copolymerization of silicic acid and metal ions was found to depend on the magnitude of the hydrolysis constant of the aqua-metal cations. It was also demonstrated that the pH of the solution is the major factor governing the Si/metal ion ratios in the solid phases.

Silicic acid forms a variety of minerals upon crystallization with metal ions. Although the polymerization processes$^{1)}$ involving silicic acid and metal ions (M^{n+}) are important reactions as a preceding step to crystallization (or nucleation), little is known about the mechanism of the reaction. Low-temperature syntheses of silicate minerals have been widely studied,$^{2)}$ where an understanding of the initial process of polymerization is considered to be vital. In this paper we describe the mechanism of the reaction between silicic acid and metal ions with an emphasis on the acid-base equilibria of silicic acid and aqua-metal cations.

A typical procedure for the reaction of silicic acid with metal ions in this work is as follows. A solution of 1—70 mM$^{3)}$ of sodium orthosilicate, Na_4SiO_4,$^{4)}$ in 200 cm^3 of deionized water was acidified with 1 M hydrochloric acid and the pH was adjusted to 3.0. In the resultant solution was dissolved 0.2—50 mmol of metal chlorides. The polymerization was initiated by slowly adding 0.1 M sodium hydroxide to the mixture at room temperature. As aqueous sodium hydroxide was added the solution became turbid and precipitation occurred. The IR spectra of the precipitates showed a strong absorption centered at 940—1020 cm^{-1}, reflecting Si-O-M bonds. Table 1 summarizes the chemical compositions of the precipitates prepared from $MgCl_2$ (or $ZnCl_2$), $Si(OH)_4$, and NaOH. The concentrations of Si, Mg, and Zn were determined by use of atomic absorption spectroscopy. As shown in Table 1, an increase in the amounts of hydroxide ion resulted in an increase in the magnesium (or zinc) contents in the precipitates.

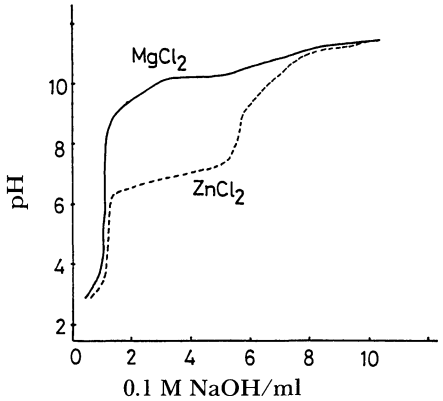

Fig. 1. Titration curves for addition of 0.1 M NaOH to 200 cm^3 of a solution containing 2 mM of $Si(OH)_4$ and 2 mM of either $MgCl_2$ (solid line) or $ZnCl_2$ (dashed line).

The titration curves for the silicic acid-magnesium (and zinc) chloride mixtures are shown in Fig. 1. In order to examine the mechanism of the initial step of the polymerization, the equilibrium pH of the suspensions containing 2 mmol of silicic acid, 2 mmol of metal chlorides, and 1 mmol of sodium hydroxide in 1 L of deionized water was measured after the suspensions were aged for 72 h. The observed pH values (pH_{gel}) are plotted against the hydrolysis constants$^{5)}$ of the metal ions (p^*K_1) in Fig. 2. Based on the plot, the metal ions can be divided into two groups; Group A consists of Al^{3+}, Cu^{2+}, Y^{3+}, Zn^{2+}, Ni^{2+}, and Co^{2+} whose pH_{gel} values linearly correlate with p^*K_1, and Group B consists of Mg^{2+}, Ca^{2+}, and Ba^{2+} whose pH_{gel} values are independent on p^*K_1 values.

Because the aqua-metal cations for Group A are more acidic than silicic acid (pK_a=9.8$^{6)}$), we can assume that the protonation-deprotonation equilibrium of aqua-metal cations (Eq. 1) is established first, followed by condensation with silicic acid (Eq. 2).

Table 1. Effects of Amounts of Hydroxide Ion on the Chemical Compositions of Silicate Gels$^{a)}$

Metal ions M^{n+}	OH^-/Si molar ratios	M^{n+}(mmol) in gels	Si^{4+}(mmol) in gels	M^{n+}/Si molar ratios in gels
Mg^{2+}	0.75	1.0	3.5	0.29
Mg^{2+}	1.50	2.2	3.7	0.59
Mg^{2+}	2.25	3.3	3.7	0.89
Zn^{2+}	0.75	1.3	3.0	0.43
Zn^{2+}	1.50	2.6	3.4	0.76
Zn^{2+}	2.25	3.3	3.6	0.92

a) The gels were allowed to precipitate from 200 cm^3 of aqueous solutions containing 19 mmol of $Si(OH)_4$ and 17 mmol of $MgCl_2$ (or $ZnCl_2$) by the addition of 1 M sodium hydroxide and aged for 24 h.

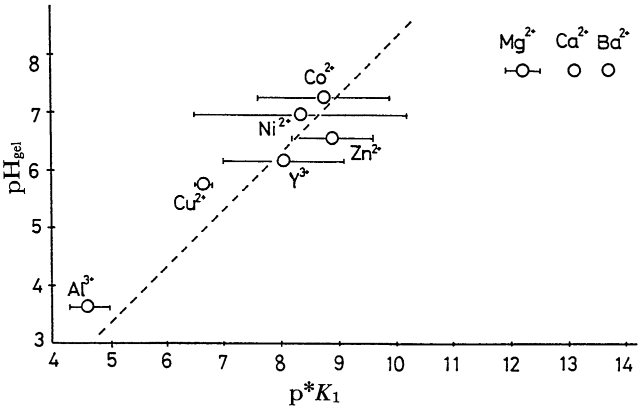

Fig. 2. Correlation between pH_{gel} and p^*K_1. Values of pH_{gel} were determined by measuring the pH of the solutions containing 2 mM of $Si(OH)_4$, 2 mM of metal chlorides and 1 mM of NaOH after the solution was aged for 72 h.

$$M(OH_2)^{n+} + OH^- \rightleftarrows M(OH)^{(n-1)+} + H_2O \tag{1}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}OH + M(OH)^{(n-1)+} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}O\text{-}M^{(n-1)+} + H_2O \tag{2}$$

When we assume that the pH of the suspension is determined solely from the acidity of aqua-metal cations, the pH_{gel} values can be calculated from p^*K_1 values as follows. The hydrolysis constant $^*K_1$ is defined[5] by

$$^*K_1 = \frac{[M(OH)^{(n-1)+}][H^+]}{[M^{n+}][H_2O]} \tag{3}$$

When $[NaOH]_0/[M^{n+}]_0=0.5$ and the values of the pH are in a neutral range,[7] then $[M(OH)^{(n-1)+}] \fallingdotseq [M^{n+}]$. Under these conditions, Eq. 3 reduces to

$$pH = p^*K_1 - 1.74, \tag{4}$$

which is plotted with a dashed line in Fig. 2.

As shown in Fig. 2, for the metal ions of Group A, the observed values of pH_{gel} agree well with those calculated from Eq. 4. This agreement indicates that the values of the pH of the reaction mixtures are determined by the protonation-deprotonation equilibria of aqua-metal cations (Eq. 1). In addition, it suggests that both coordination of silicate species to the metal ions (Eq. 2) and subsequent polymerization have minor effects on the acidity of the metal cations incorporated in the gels.

Because the aqua-metal cations of Group B are less acidic than silicic acid, we can assume that the equilibrium of silicic acid (Eq. 5) is established first, followed by bond formation of metal cations to silicate anion (Eq. 6).

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}OH + OH^- \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}O^- + H_2O \tag{5}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}O^- + M^{n+} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}O\text{-}M^{(n-1)+} \tag{6}$$

As shown in Fig. 2, the pH_{gel} values for Group B metal ions are constant, regardless of the p^*K_1 values. This indicates that the values of pH_{gel} are primarily determined from the equilibrium of silicic acid (Eq. 5). The discrepancy between pK_a of silicic acid and the values of pH_{gel} for Group B metal ions may be attributable to the effect of the polymerization on the acidity of silicic acid. We suggest that the coordination of the oxygen atoms of silicic acid to metal ions increases the acidity of silicic acid and, consequently, the pH_{gel} is smaller than that calculated from pK_a of silicic acid.

In conclusion, this work illustrates that the initiation reaction of silicate gel formation can be accounted for in terms of the acid-base equilibria of silicic acid and aqua-metal cations. We suggest that the polymerization proceeds in two different mechanisms according to the magnitude of p^*K_1 of the aqua-metal cations. It is also demonstrated that the amounts of hydroxide ion added (or pH of the aqueous phase) is the most important factor governing the Si/metal ion ratios in the solid phases.

References

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3) $M=mol \cdot dm^{-3}$.

4) The silicon content of the sodium orthosilicate sample was obtained by atomic absorption spectrophotometry.

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7) The relation between $^*K_1$ and the proton concentration is given by

$$^*K_1 = \frac{[NaOH]_0+[H^+]-[OH^-]}{[M^{n+}]_0-[NaOH]_0-[H^+]+[OH^-]} \cdot \frac{[H^+]}{[H_2O]}$$

Under the experimental conditions, i.e. $[NaOH]_0=1\times10^{-3}$ M, $[M^{n+}]_0=2\times10^{-3}$ M, the equation above reduces to Eq. 4 in the pH range from 3.5 to 10, where $[NaOH]_0 \gg [H^+]-[OH^-]$ and $[M^{n+}]_0-[NaOH]_0 \gg [OH^-]-[H^+]$.