

Note

Retarding effect of aluminium on the polymerization of silicic acid particles

CHIHO YAMANAKA, TAKUSHI YOKOYAMA* and TOSHIKAZU TARUTANI

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812 (Japan)

(Received June 17th, 1986)

The rate of polymerization of silicic acid is influenced by many factors, such as pH, the degree of supersaturation, temperature and ionic strength. However, little has been published on the effect of foreign elements on the polymerization of silicic acid. Iler¹, Tarutani² and Shimada and Tarutani³ reported an accelerating effect of fluoride on the polymerization of silicic acid. Crerar *et al.*⁴ pointed out that magnesium, calcium and strontium chlorides are more effective at promoting the growth of polysilicic acids than is sodium chloride. It was observed that the growth of particles of polysilicic acids in geothermal water is often slower than that in silicic acid solution under the same pH, temperature and silicic acid concentration. From the preliminary experiment, it was found that this phenomenon is attributed to the effect of a small amount of aluminium.

In this work, the retarding effect of aluminium on the growth of particles of polysilicic acids was studied by gel chromatography.

EXPERIMENTAL

Sample solutions and reagents

All reagents used were of analytical-reagent grade. Sodium silicate solution (800 ppm of SiO₂) was prepared by dissolving silica gel in 0.1 mol dm⁻³ sodium hydroxide solution. A 0.1 mol dm⁻³ sodium aluminate stock solution was prepared by dissolving AlCl₃ · 6H₂O in sodium hydroxide solution (NaOH/Al molar ratio = 5). The concentration of aluminium was standardized by EDTA titration. A sodium aluminate solution of the desired concentration was prepared by diluting a stock solution before use. A 0.4% Blue Dextran 2000 (Pharmacia, Uppsala, Sweden) solution was used for measurement of the void volume of the gel bed in gel chromatography.

Preparation of Sephadex column

Sephadex G-100 gel (Pharmacia) was suspended in hot water and allowed to swell fully. The column was a 45 × 1.6 cm I.D. or 45 × 1.0 cm I.D. glass tube with a porous polystyrene disk at bottom. The column was packed as described in the literature⁵.

Procedure

Sodium aluminate solution (5 cm^3) of appropriate concentration was added to 500 cm^3 of sodium silicate solution (800 ppm of SiO_2) to give the desired concentration of aluminium. The solution was heated to 70°C and then adjusted to pH 8 with hydrochloric acid and sodium hydroxide solution. The temperature and pH of the solution were maintained within $\pm 1^\circ\text{C}$ and ± 0.1 pH unit, respectively. The solution was stirred vigorously by a magnetic stirrer during the experiment. Periodically, an aliquot of the solution was adjusted to pH 2 with hydrochloric acid, because polymerization and depolymerization do not occur within short periods at pH 2. Silicic acid was chromatographed on a Sephadex G-100 column ($45 \times 1.6 \text{ cm I.D.}$). The volume of sample solution delivered to the column was 2 cm^3 . The eluent was 0.1 mol dm^{-3} sodium chloride solution of pH 2. Using an automatic fraction collector, the effluent was collected in fractions of 2 cm^3 with a flow-rate of about $12 \text{ cm}^3 \text{ h}^{-1}$. The amounts of silicic acid in the fractions were measured by atomic-absorption spectrometry using a Nippon-Jarrel Ash Model AA 781 instrument.

Blue Dextran 2000 was eluted by using the same procedure.

Sodium aluminate solution (5 ppm of Al) was heated to 50°C and then adjusted to pH 8. After 3 h, aluminium was chromatographed on a Sephadex G-100 column ($45 \times 1.0 \text{ cm I.D.}$). The eluent used was 0.1 mol dm^{-3} NaCl solution of pH 8. The amount of aluminium in each fraction was determined by spectrophotometric method with ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid) after alkali had been added to the fraction and the solution was heated.

Sodium silicate solution (800 ppm of SiO_2) containing aluminium (5 ppm of Al) was heated to 50°C and then adjusted to pH 8. After 3 h, silicic acid and aluminium were chromatographed on a Sephadex G-100 column ($45 \times 1.0 \text{ cm I.D.}$). The eluent used was 0.1 mol dm^{-3} NaCl solution of pH 8 containing monosilicic acid (100 ppm of SiO_2) to prevent a change of the state of silicic acid and aluminium. The amount of aluminium in each fraction was determined spectrophotometrically with ferron after alkali had been added to the fraction and the solution was heated. The amount of silicic acid was determined by atomic-absorption spectrometry.

RESULTS AND DISCUSSION

Elution curves for silicic acid in solutions in the absence and presence of aluminium at 70°C after 15 min are shown in Fig. 1. The peaks on the right are due to monosilicic acid and those on the left to polysilicic acid. 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. It can be assumed that the elution volume of Blue Dextran 2000 is equal to the void volume of the bed. Polysilicic acids larger in size than the possible separation range of the gel eluted together at V_0 . Polysilicic acid in the absence of aluminium eluted at V_0 , showing that the growth of polysilicic acid is very rapid. In the presence of aluminium, polysilicic acid eluted on the right of V_0 . It can be seen that the size of polysilicic acids decreases with increasing concentration of aluminium.

The variation of K_{av} values of polysilicic acids in solutions at 70°C as a function of time and aluminium concentration is shown in Fig. 2. The distribution coefficient, K_{av} , was calculated as described previously⁶. It is a measure of particle size and decreases with increasing particle size. The K_{av} values decreased more slowly with in-

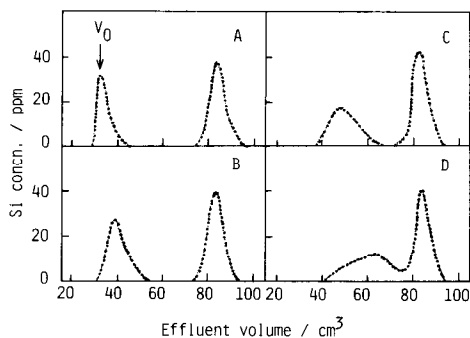


Fig. 1. Gel chromatograms after 15 min for silicic acid in solutions with different concentrations of aluminium. Aluminium concentration: (A) 0 ppm; (B) 0.5 ppm; (C) 5 ppm; (D) 26 ppm.

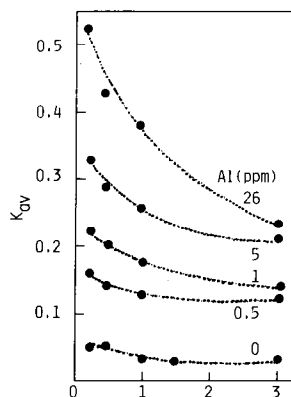


Fig. 2. Variation of K_{av} values of polysilicic acid with time.

creasing concentration of aluminium, indicating that the growth of particles of polysilicic acids is increasingly retarded with increasing concentration of aluminium up to 26 ppm.

The elution curve for aluminium in aluminate solution at 50°C after 3 h is shown in Fig. 3. One peak was obtained at the elution position of monosilicic acid.

The elution curves for silicic acid and aluminium in silicic acid solution containing aluminium at 50°C after 3 h are shown in Fig. 4. It can be seen that the elution volume of aluminium is equal to that of polysilicic acid and no aluminium is found at the elution position of monosilicic acid. The results shows that aluminium is bonded to polysilicic acid.

Iler⁷ presumed that at pH 8 an aluminium atom adsorbed on the surface of amorphous silica is coordinated with four oxygen atoms, forming negatively charged aluminosilicate sites. Although the growth of particles of polysilicic acids by the reaction between polymers proceeds rapidly at high temperature⁸, aluminium retards the reaction between polymers. It may be reasonable to assume that the growth of

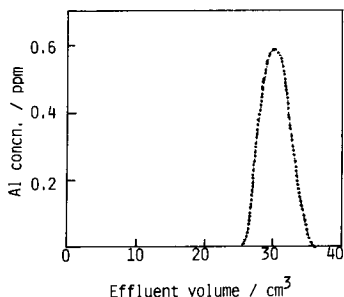


Fig. 3. Gel chromatogram for aluminium.

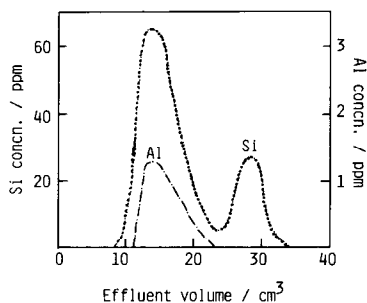


Fig. 4. Gel chromatograms for silicic acid and aluminium.

particles of polysilicic acids is retarded by repulsion between the polymer particles due to the formation of negative aluminosilicate sites.

REFERENCES

- 1 R. K. Iler, *J. Phys. Chem.*, 56 (1952) 680.
- 2 T. Tarutani, *Nippon Kagaku Zasshi*, 77 (1956) 1811.
- 3 K. Shimada and T. Tarutani, *J. Chromatogr.*, 249 (1982) 111.
- 4 D. A. Crerar, E. V. Axtmann and R. C. Axtmann, *Geochim. Cosmochim. Acta*, 45 (1981) 1259.
- 5 L. Fisher, *An Introduction to Gel Chromatography*, North-Holland, Amsterdam, 1969.
- 6 K. Shimada and T. Tarutani, *J. Chromatogr.*, 168 (1979) 401.
- 7 R. K. Iler, *J. Colloid Interface Sci.*, 43 (1973) 399.
- 8 K. Shimada and T. Tarutani, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, 13 (1982) 311.