

CHROM. 11,331

GEL CHROMATOGRAPHIC STUDY OF THE POLYMERIZATION OF SILICIC ACID

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(Received July 18th. 1978)

SUMMARY

The polymerization of silicic acid in the range from pH 9.5 to 1 *N* hydrochloric acid has been studied by gel chromatography. A mechanism for the growth of particles of polysilicic acids is proposed. It is concluded that the growth of particles of polymers in the pH range 9.5-9 and below 2 is due mainly to the polymerization between monosilicic and polysilicic acids, and in the pH range 7-4 mainly to the random condensation with each other of all of the polymer species. The growth rate of particles of polymers is maximal at pH 6.5-7.

INTRODUCTION

The kinetics of the polymerization of silicic acid have previously been studied by colorimetry¹⁻³, because monosilicic acid reacts with molybdate reagent in acidic solution to give a yellow colour, whereas polysilicic acid does not react with molybdate reagent.

Other methods for studying the polymerization of silicic acid have been used. Alexander⁴ studied the kinetics of the polymerization by freezing-point depression measurements. Audsley and Aveston⁵ used light scattering, ultracentrifugation, and viscosity measurements. However, the change in the molecular weight of silicic acids in solutions with a wide pH range has not been studied.

Gel chromatography is a method for separating solute molecules according to their size, larger molecules being eluted faster than smaller molecules. The elution volumes of molecules are correlated with their molecular weight (size). Tarutani⁶ suggested that gel chromatography is useful for the study of the polymerization of silicic acid. Kojima and Tarutani⁷ studied the formation of polysilicic acid from monosilicic acid adsorbed on iron(III) hydroxide by gel chromatography.

In this work, the effect of pH on the polymerization of silicic acid was studied by gel chromatography and the mechanism of the growth of particles of polysilicic acids is discussed here.

EXPERIMENTAL

Sample solutions and reagents

All reagents used were of analytical-reagent grade.

Monosilicic acid 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 to 1000 ml.

Blue Dextran 2000 solution of concentration 0.4% was used.

The eluent was 0.1 M sodium chloride solution of pH 2.

Preparation of Sephadex column

Sephadex G-100 (Pharmacia, Uppsala, Sweden) was suspended in the solution to be used as the eluent and allowed to swell for 3 days. The column was a 45 × 1.0 cm glass tube with a porous polystyrene disc at the bottom. The Sephadex G-100 column was prepared as described in the literature⁸. The total volume of the gel bed was about 30 ml.

Procedure

Monosilicic acid solution (500 ppm of SiO₂) was adjusted to the desired pH with hydrochloric acid. At different times, the pH of an aliquot of the sample solution was adjusted to 2 with hydrochloric acid or sodium carbonate solution, because polymerization and depolymerization do not occur for a short period at pH 2 (ref. 6). Five millilitres of sample solution were used for the determination of monosilicic acid by colorimetry. Two millilitres of sample solution were placed on the gel bed just as the last layer of eluent soaked into the bed and, when the last portion of the sample solution had vanished into the bed, the eluent was applied. Using an automatic fraction collector, the effluent was collected in fractions of 1 ml, with a flow-rate of 4–6 ml/h. The amounts of silicic acid in the fractions were measured by colorimetry after decomposition of polysilicic acid with alkali or atomic-absorption spectrometry using a Nippon-Jarrell Ash Model AA 781 instrument.

Blue Dextran 2000 was eluted by using the same procedure.

All experiments were carried out at 20 ± 1°.

RESULTS AND DISCUSSION

The rate of polymerization of silicic acid differs with pH. In Fig. 1, the concentrations of monosilicic acid measured by colorimetry after 24 and 75 h are plotted against pH. The monosilicic acid concentration decreased rapidly in slightly alkaline solutions but did not decrease within 24 h in the pH range 1–3. The decrease in the concentration of monosilicic acid with time is due to polymerization between monomers and between monomer and polymer. However, no information is available on the change in particle (molecular) size of the polymers with time.

The elution curves for silicic acid in solutions of various pH are shown in Figs. 2–4. The position shown as BD 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 2000 is equal to the void volume of the bed. The peaks on the right are due to monosilicic acid and those on the left to polysilicic acid. The concentration of monosilicic acid at a given time is shown in parentheses.

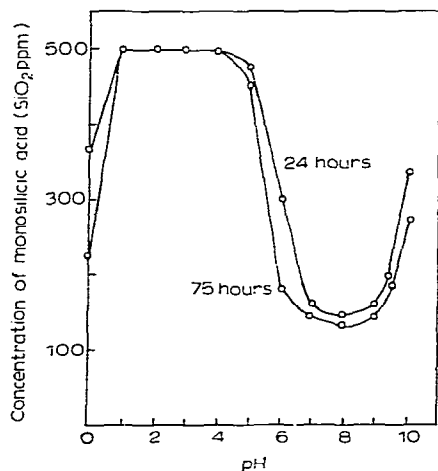


Fig. 1. Variation of the concentration of monosilicic acid with pH.

At pH 9.5 (Fig. 2), the elution curves for the polymers indicate a symmetrical distribution of particle sizes. The distribution of particle sizes of the polymers obtained after 250 h was almost the same as that obtained after 100 h. This suggests that when the concentration of monosilicic acid is close to the solubility of amorphous silica, the growth rate of the particles of the polymers becomes very slow. It is reasonable to assume that the growth of the particles of the polymers is due mainly to the polymerization between monomer and polymer, and the polymerization between polymer species hardly proceeds. Although the rate of polymerization at pH 9 was rapid compared with that at pH 9.5, similar results were obtained.

At pH 6 (Fig. 3), the elution curve for the polymers after 24 h is different from that at pH 9.5 and indicates a broad and random distribution of particle sizes. The

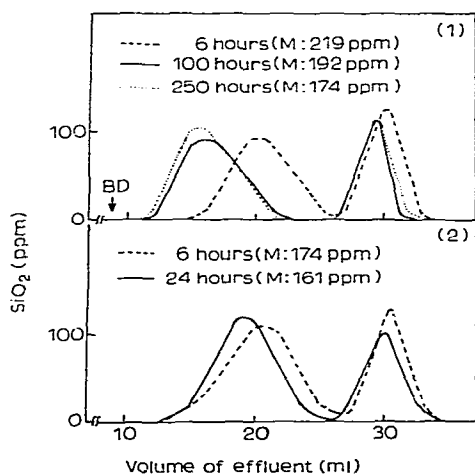


Fig. 2. Variation of the elution curves for silicic acid in alkaline solutions with time. 1, pH 9.5; 2, pH 9.

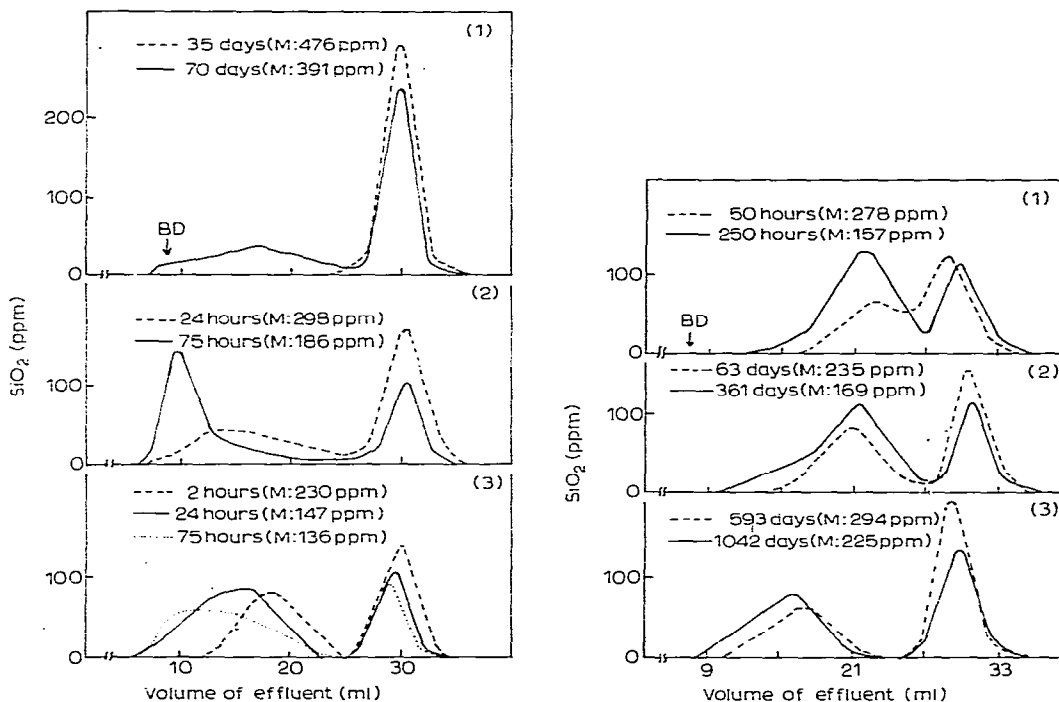


Fig. 3. Variation of the elution curves for silicic acid in solutions of pH 4, 6 and 8 with time. 1, pH 4; 2, pH 6; 3, pH 8.

Fig. 4. Variation of the elution curves for silicic acid in acidic solutions with time. 1, 1 *N* HCl; 2, pH 1; 3, pH 2.

highest peak was obtained at the elution position of BD after 75 h. This suggests that the particles of the polymers rapidly grew with time, because polymers that have larger sizes than the possible separation range for Sephadex G-100 are eluted together at the elution position of BD. Therefore, it is reasonable to conclude that a broad and random distribution of particle sizes of the polymers arises from a random condensation with each other of all of the polymer species. Although the rates of polymerization at pH 4 and 7 were different from that at pH 6, similar results were obtained.

At pH 8, the elution curve for the polymers after 2 h was symmetrical. Although the concentration of monosilicic acid after 75 h was not very different from that after 24 h, the growth of the particles of the polymers still continued and the elution curves became asymmetrical with time. However, the rate of random condensation with each other of all of the polymer species was slower than that at pH 6.

Variations in the elution curves for silicic acid in acidic solutions with time are shown in Fig. 4. The size distribution of the polymers is symmetrical. Therefore, although the rate of polymerization is very slow, it is suggested that the mechanism of the growth of the particles of the polymers is polymerization between monomer and polymer.

If the change in the particle size of polysilicic acids with pH and time is measured, the pH at which the growth rate of the particles of the polymers is maximal

can be obtained. The pH of monosilicic acid sample solutions was adjusted to 5–9.5 with hydrochloric acid and, after standing for 24 and 75 h, silicic acid in the sample solutions was chromatographed. As an example, elution curves for silicic acid after 24 h are shown in Fig. 5. The particle sizes of polysilicic acids formed in each pH solutions are randomly distributed.

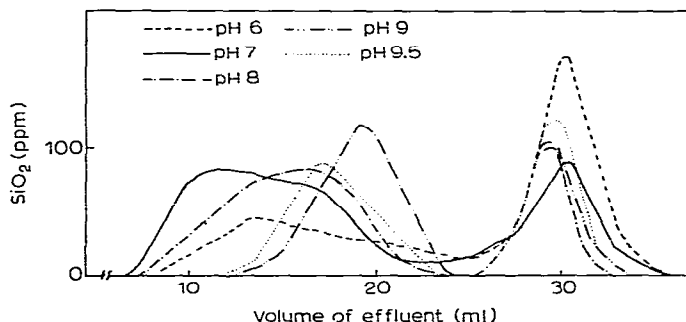


Fig. 5. Variation of the elution curves for silicic acid with pH.

Laurent and Killander⁹ defined a constant, K_{av} , for a given gel in gel chromatography:

$$K_{av} = \frac{V_e - V_0}{V_t - V_0} \tag{1}$$

where V_0 is the void volume, V_t the total bed volume and V_e elution volume. Here V_0 , V_t and V_e are easily measured. As the K_{av} value is correlated to V_e , it is a measure of molecular size and decreases with increasing particle size. As the elution volumes of polymers cannot be obtained directly from the elution curves shown in Fig. 5, mean elution volumes must be calculated. The mean elution volume, V_e , is given by

$$V_e = \frac{\sum C_i V_i}{\sum C_i} \tag{2}$$

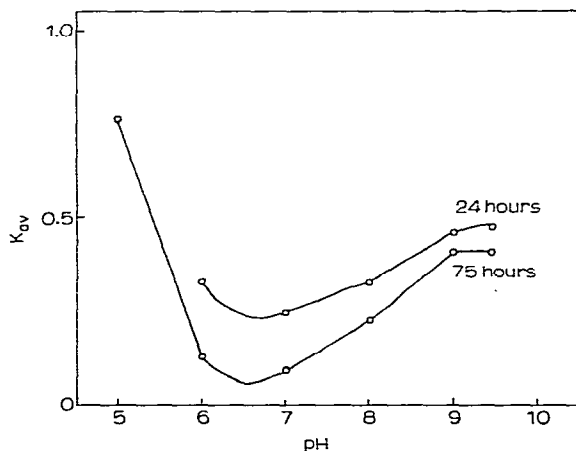


Fig. 6. Plot of K_{av} against pH.

where C_i is the concentration in the i th fraction and V_i is the volume of the i th fraction. In Fig. 6, K_{av} values, which were calculated from eqns. 2 and 1, are plotted against pH. K_{av} is minimal at pH 6.5–7, which means that the growth rate of the particles of the polymers is maximal at this pH.

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