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GEL CHROMATOGRAPHIC STUDY OF THE POLYMERIZATION OF SILICIC ACID IN ACID SOLUTIONS

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SUMMARY

The polymerization of silicic acid in hydrochloric, nitric, perchloric and sulphuric acid solutions has been studied by gel chromatography. The rate of polymerization of silicic acid is in the order of $HClO_4 > HCl \approx HNO_3 > H_2SO_4$. A mechanism for the growth of particles of polysilicic acids is proposed. The growth in 1 N acid solutions is due mainly to the reaction between monosilicic and polysilicic acids, whereas that in 3 N and 5 N acid solutions is due mainly to the reaction between polymer species.

INTRODUCTION

The rate of polymerization of silicic acid is lowest in aqueous solution of about pH 2. Below this pH, the rate increases with increasing acidity[1,2]. Tarutani[1] studied the polymerization of silicic acid in various acid solutions by colorimetry. Elmer and Nordberg[3] studied the solubility of porous vitreous silica in up to 9 N nitric acid solutions.

Gel chromatography has also been used to study the polymerization of silicic acid[4]. The mechanism of the growth of polymer particles was discussed[5] on the basis of changes in the elution curves for polysilicic acids.

In this work, the effect of the concentration of hydrochloric, nitric, perchloric and sulphuric acids on the polymerization of silicic acid was studied by gel chromatography, and a mechanism is proposed for the growth of particles of polysilicic acids.

EXPERIMENTAL

Sample solutions and reagents

All reagents used were of analytical reagent grade. A stock solution of monosilicic acid was prepared by fusing 2.000 g of anhydrous silica with 10.0 g sodium carbonate, dissolving the melt in distilled water and diluting to 1000 ml. A 0.4% Blue Dextran 2000 solution 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 eluent solution and allowed to swell for 3 days. The column (45 × 1.0 cm I.D. or 45 × 1.5 cm I.D.) was a glass tube with a porous polystyrene disc at the bottom. The Sephadex G-100 column was prepared as described in the literature[6].

Procedure

Monosilicic acid solution (500 ppm of SiO_2) of desired acidity was prepared by mixing aliquots of monosilicic acid stock solution and acid. At different times, an aliquot of sample solution was adjusted to pH 2 by adding anion-exchange resin, Dowex 1-X8 (OH^-). The concentration of monosilicic acid was measured by colorimetry and the silicic acid was then chromatographed on a Sephadex column. The volume of sample solution delivered to the column was 2 ml. Using an automatic fraction collector, the effluent was collected in fractions of 1 or 2 ml, with a flow-rate of 8–12 ml/h. The amounts of silicic acid in the fractions were measured by 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°C.

RESULTS AND DISCUSSION

Effect of concentration of hydrochloric acid on the polymerization of silicic acid

Polymerization and depolymerization of silicic acid in solutions of low concentrations of electrolytes do not occur over short periods at pH 2 (ref. 4). Therefore, silicic acid is usually chromatographed on a Sephadex column after the sample solution has been adjusted to pH 2. However, when monosilicic acid solution containing a high concentration of hydrochloric acid was allowed to stand for a desired period and then adjusted to pH 2 with sodium hydroxide, gel was formed rapidly. It is suggested that the concentration of sodium chloride is so high as to accelerate the polymerization reaction. Therefore, as it is necessary to minimize the concentration of electrolytes after adjustment of pH, an anion-exchange resin (OH^-) was used for adjustment of pH. Addition of the anion-exchange resin had no effect on the polymerization of silicic acid.

The rate of polymerization of silicic acid changes with changing acidity. In Fig. 1, the concentration of monosilicic acid in hydrochloric acid solutions, as measured by colorimetry after 3 h, is plotted against normality of hydrochloric acid. The concentration of monosilicic acid decreases in proportion to the acidity. The decrease in the concentration is due to polymerization of monosilicic acids and of monosilicic and polysilicic acids.

The variation with time of the elution curves for silicic acid in 1 N hydrochloric acid solution is shown in Fig. 2. The point V_0 is the elution volume of Blue Dextran 2000. 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 concentrations of monosilicic acid at the given times are shown in parentheses. The elution curves for the polymers after 50 h indicate a symmetrical particle-size distribution.
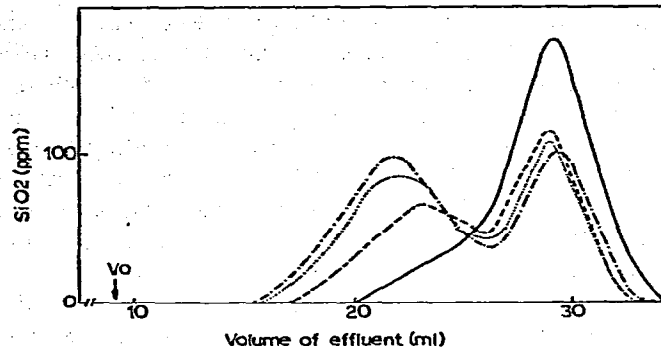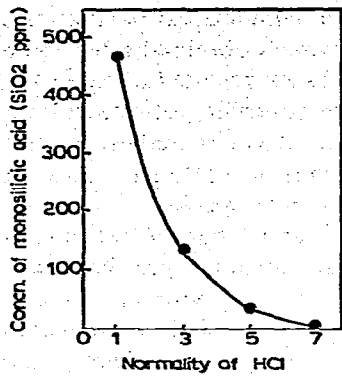
Fig. 1. Plot of the concentration of monosilicic acid after 3 h against normality of hydrochloric acid.

Fig. 2. Variation with time of the elution curves for silicic acid in 1 N hydrochloric acid solution. Column, 45 × 1.0 cm I.D. ————, 24 h [M(monosilicic acid concentration) = 367 ppm; — — —, 50 h (M = 278 ppm); ....., 75 h (M = 227 ppm); —.—.—, 100 h (M = 204 ppm).

The distribution coefficient, K_{av}, for a given gel in gel chromatography is defined[7] as

$$K_{av} = (V_e - V_0)/(V_t - V_0) \qquad (1)$$

where V_0 is the void volume, V_t the total bed volume and V_e the elution volume. K_{av} is a measure of molecular size and decreases with increasing particle size. When the elution curve for polysilicic acid indicates a broad particle-size distribution, the mean elution volume, V_e, must be calculated, using the relationship

$$V_e = \Sigma C_i V_i / \Sigma C_i \qquad (2)$$

where C_i is the concentration in the ith fraction and V_i is the volume of the ith fraction. In Fig. 3, K_{av} values, calculated from eqns. 1 and 2, are plotted against time.
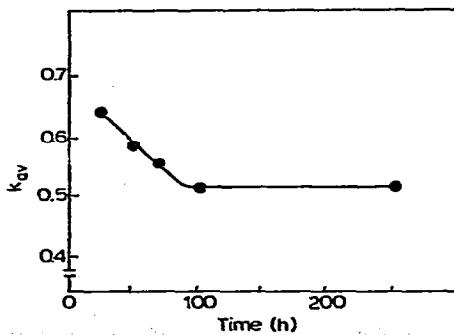

Fig. 3. Plot of K_{av} values against time.

The elution curves for the polysilicic acids indicate a symmetrical particle-size distribution after 50 h (Fig. 2), and the K_{av} value of the polymers obtained after 250 h was almost the same as that obtained after 100 h (Fig. 3). These results indicate that, when the concentration of monosilicic acid is close to the solubility of amorphous silica, the growth rate of the polymer particles is very slow. It is concluded that the growth of the polymer particles is due mainly to polymerization between monomer and polymer, and there is little polymerization between polymer species.

Solutions of 3 N hydrochloric acid containing different concentrations of monosilicic acid were allowed to stand for 3 h and then chromatographed. The results are shown in Fig. 4. The elution curves for the polymers are symmetrical, and the K_{av} values calculated are almost same in spite of differences in the initial concentration of monosilicic acid. This means that the growth of the polymer particles under these conditions is due mainly to polymerization between monomer and polymer.
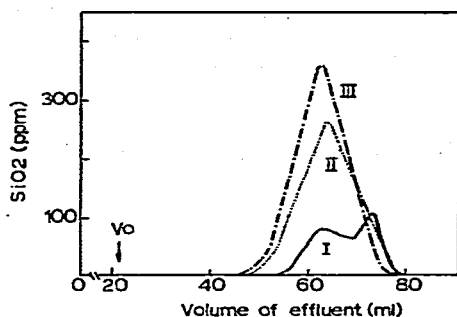

Fig. 4. Elution curves after 3 h for silicic acid in 3 N hydrochloric acid solutions with different initial concentrations of monosilicic acid. Initial monosilicic acid concentration: I, 500 ppm; II, 1000 ppm; III, 1500 ppm. Column, 45 × 1.5 cm I. D. ————, I (M = 136 ppm); ....., II (M = 136 ppm); —.—.—, III (M = 163 ppm).

Polymerization of silicic acid in various acid solutions

The variation with time of the concentration of monosilicic acid in 3 N solutions of hydrochloric, nitric, perchloric and sulphuric acids is shown in Fig. 5.
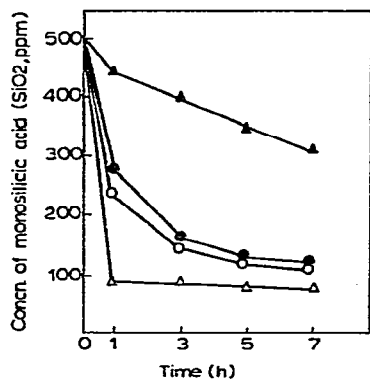

Fig. 5. Variation with time of the concentration of monosilicic acid in 3 N solutions of hydrochloric (O), nitric (●), perchloric (△) and sulphuric (▲) acids.

The rate of decrease in the concentration of monosilicic acid is in the order $HClO_4 >$ $HCl \approx HNO_3 > H_2SO_4$.

The elution curves for silicic acid in 1 N solutions of these acids after 250 h are shown in Fig. 6. A symmetrical particle-size distribution in all the solutions is indicated, and the K_{av} values are almost identical in spite of the differences in the concentration of monosilicic acid after 250 h. From the results shown in Figs. 2 and 6, it is concluded that the increase in size of the polymer particles is due mainly to the reaction between monomer and polymer in 1 N acid solutions, and that there is little polymerization between polymer species. The behaviour of silicic acid in nitric acid solution seems to be identical with that in hydrochloric acid solution (Figs. 5 and 6).
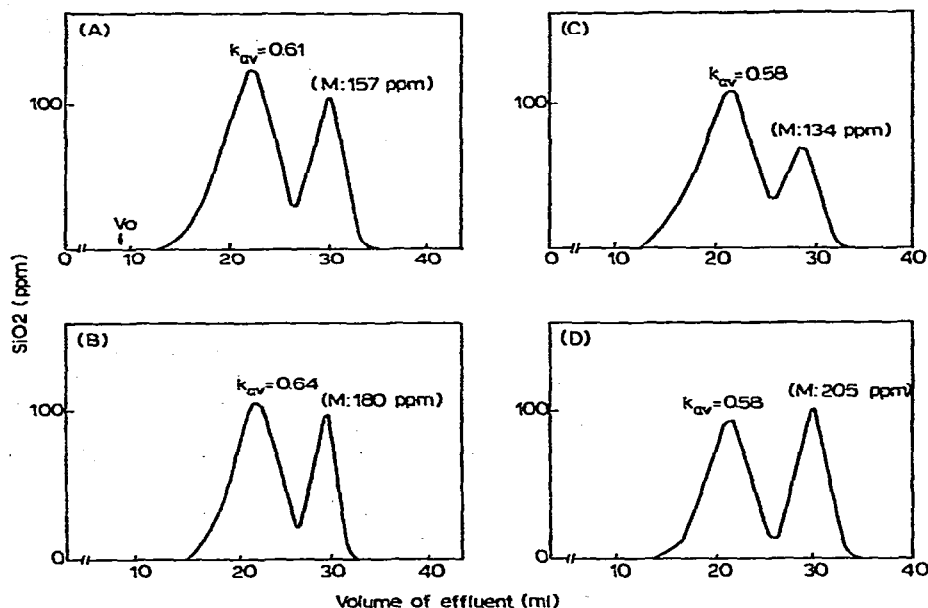

Fig. 6. Elution curves after 250 h for silicic acid in 1 N solutions of hydrochloric (A), nitric (B), perchloric (C) and sulphuric acids (D). Column, 45 × 1.0 cm I.D.

The variation with time of the elution curves for silicic acid in 3 N solutions of hydrochloric, perchloric and sulphuric acids is shown in Fig. 7. In 3 N perchloric acid solution only one peak was obtained for silicic acid after 3 h (Fig. 7C) because the peak for polymer was superposed on that for monomer. The elution curve for the polymers after 24 h indicates a broad particle-size distribution. The highest peak was obtained at the point V_0 after 100 h. All polymers that have larger sizes than the possible separation range for Sephadex G-100 are eluted at V_0. The results indicate that the growth of the polymer particles proceeds by the polymerization between polymer species, because the decrease in the concentration of monosilicic acid was very slow after 1 h (Fig. 5). The mechanism of the growth of the polymer particles in 3 N acid solutions is different from that in 1 N acid solutions (Figs. 2 and 6). Although the rate of polymerization of silicic acid in hydrochloric and sulphuric acid
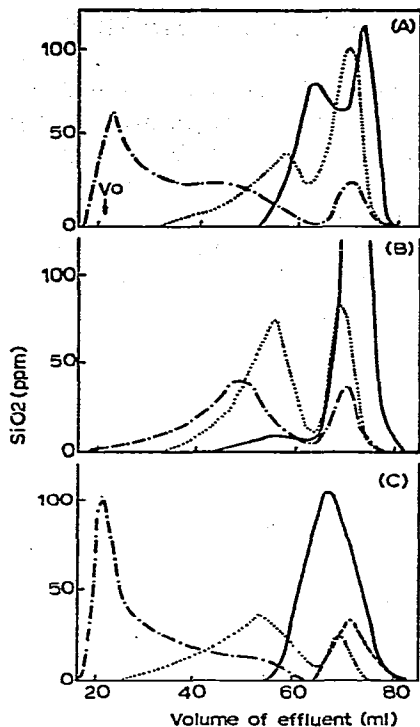
Fig. 7. Variation with time of the elution curves for silicic acid in 3 N solutions of hydrochloric, perchloric and sulphuric acids. Column, 45 × 1.5 cm I.D. A, HCl, ———, 3 h (M = 154 ppm); ....., 24 h (M = 115 ppm); ·—·—·, 100 h (M = 52 ppm). B, H_2SO_4, ———, 3 h (M = 403 ppm); ....., 24 h (M = 162 ppm); ·—·—·, 100 h (M = 134 ppm). C, $HClO_4$, ———, 3 h (M = 92 ppm); — — —, 3 h monomer; ....., 24 h (M = 59 ppm); ·—·—·, 100 h (M = 39 ppm).
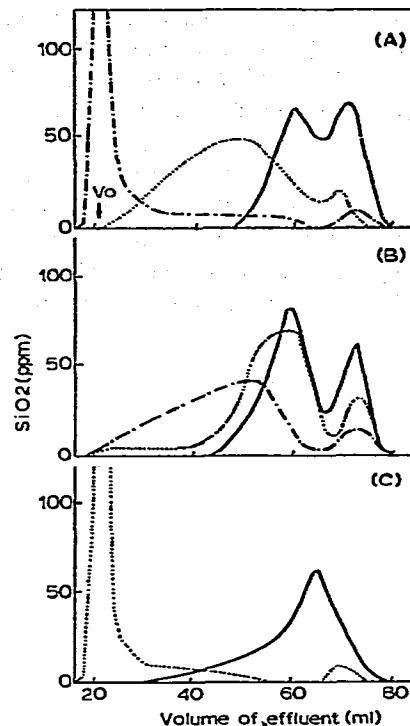
Fig. 8. Variation with time of the elution curves for silicic acid in 5 N solutions of hydrochloric, perchloric and sulphuric acids. Column, 45 × 1.5 cm I.D. A, HCl, ———, 3 h (M = 103 ppm); ....., 24 h (M = 14 ppm); ·—·—·, 100 h (M = 11 ppm). B, H_2SO_4, ———, 3 h (M = 47 ppm); ....., 24 h (M = 41 ppm); ·—·—·, 100 h (M = 39 ppm). C, $HClO_4$, ———, 3 h (M = 16 ppm); ....., 24 h (M = 9 ppm).

solutions was slow compared with that in perchloric acid solution, similar results were obtained.

The elution curves for silicic acid in 5 N solutions of hydrochloric, perchloric and sulphuric acids are shown in Fig. 8. The rate of polymerization of silicic acid in these solutions is faster than that in the corresponding 3 N solutions, and the mechanism of growth of the polymer particles is similar to that in the latter solutions.

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