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GEL CHROMATOGRAPHIC STUDY OF THE POLYMERIZATION OF SILICIC ACID IN THE PRESENCE OF FLUORIDE

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SUMMARY

The effect of fluoride on the polymerization of silicic acid was studied in the pH range 2.5-0. The polymerization of silicic acid was accelerated by fluoride. The rate of reaction between monosilicic acids was most rapid at an F/Si atomic ratio of about 0.5. In silicic acid solutions containing fluoride up to an F/Si atomic ratio of 2.0 the growth rate of polysilicic acid particles increased with increasing fluoride concentration and was most rapid at about pH 1. It is suggested that the growth of polysilicic acid particles is due mainly to the reaction between monosilicic and polysilicic acids, because the reaction between polysilicic acids is relatively slow.

INTRODUCTION

The rate of polymerization of silicic acid is least rapid in aqueous solution of about pH 2. Below this pH, the rate increases with increasing acidity. The rate is also accelerated by fluoride in acidic solution.

Iler¹ reported that, below about pH 1.5, gelling of silicic acid is catalyzed by trace amounts of fluoride present as an impurity. He also suggested that the catalyst for the polymerization of silicic acid is probably hydrogen fluoride and the polymerization mechanism may involve a temporary expansion of the coordination number of silicon from four to six. Tarutani² showed that when the concentration of fluoride is relatively low compared with that of silicic acid, the rate of polymerization of silicic acid increases with an increase in fluoride concentration at constant acidity. However, the particle growth of polysilicic acids in the presence of fluoride has not yet been studied.

Tarutani³ suggested that gel chromatography is useful for studying the polymerization of silicic acid, because a change in the elution curves for polysilicic acids with time reflects the mechanism of the particle growth of polysilicic acids^{4,5}.

In this work, the effect of fluoride on the polymerization of silicic acid was studied by gel chromatography and colorimetry, and a mechanism is proposed for the growth of particles of polysilicic acids.

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Fluoride prevents the colour development of molybdosilicic acid in colorimetry. Aluminium, borate and beryllium ions which combine with fluoride to form fluoride complexes have a masking effect for fluoride, and aluminium ion most effectively masks fluoride⁶. Similarly, the influence of fluoride on the polymerization of silicic acid can be overcome by the addition of aluminium ion. Therefore, aluminium chloride was used as a masking agent in this work.

EXPERIMENTAL

Sample solutions and reagents

All reagents used were of analytical reagent grade. A stock solution of monosilicic acid was prepared by fusing 2.00 g of anhydrous silica with 10.0 g of sodium carbonate, dissolving the melt in distilled water and diluting to 1000 ml. 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. The eluent was 0.1 M sodium chloride solution of pH 2.

Preparation of Sephadex column

Sephadex G-100 (Pharmacia) was suspended in the eluent solution and allowed to swell for 3 days. The column (45 × 1.0 cm I.D.) was a glass (or polyethylene) tube with a porous polyethylene disc at the bottom. The column was packed as described⁷.

Procedure A

Monosilicic acid solution (500 ppm as SiO_2) of desired pH was prepared by mixing aliquots of monosilicic acid stock solution and hydrochloric acid. The appropriate amount of sodium fluoride was added to the sample solution to give the desired F/Si atomic ratio, R . Periodically, an aliquot of sample solution was adjusted to pH 2 and aluminium chloride was added to give the desired atomic ratio of aluminium and fluoride ($\text{Al/F} = 10$). The concentration of monosilicic acid was determined by colorimetry, and silicic acid was chromatographed on a Sephadex G-100 column according to the procedure of Shimada and Tarutani⁴.

Procedure B

The apparent solubility of amorphous silica in the presence of fluoride at pH 1 was determined by colorimetry (Table I).

Monosilicic acid solution (500 ppm) was adjusted to pH 8.3 with hydrochloric acid. After standing for 4 h, the pH of this solution was adjusted to 2 with hydro-

TABLE I

APPARENT SOLUBILITY OF AMORPHOUS SILICA IN THE PRESENCE OF FLUORIDE AT pH 1 (20°C)

$R (= F/Si)$	SiO_2 (ppm)
2.0	350
1.0	200
0.2	177
0.1	177

chloric acid. The concentration of monosilicic acid in the solution was 195 ppm and the remaining silicic acid was polysilicic acid (solution A). Several silicic acid solutions of pH 1 containing 250 ppm polysilicic acid and monosilicic acid, at various R values (Table I), were prepared by mixing solution A, 2000 ppm monosilicic acid stock solution, hydrochloric acid, sodium fluoride and distilled water. After standing for 5 and 8 d, the sample solutions were adjusted to pH 2 and aluminium chloride ($Al/F = 10$) was added; the silicic acid was chromatographed.

All experiments were carried out at 20°C

RESULTS

Procedure A

The variation of the concentration of monosilicic acid in solutions of various pH as a function of time and R value is shown in Fig 1. As it can be assumed that the decrease in the concentration of monosilicic acid is due mainly to the formation of disilicic acid by a reaction between monosilicic acids in an early stage of the polymerization, it is considered that the R value giving the maximum decrease in concentration of monosilicic acid is close to that at which the rate of formation of disilicic acid is maximal. The results indicate that the rate of reaction between monosilicic acids is most rapid at about $R = 0.5$ regardless of the difference in acidity.

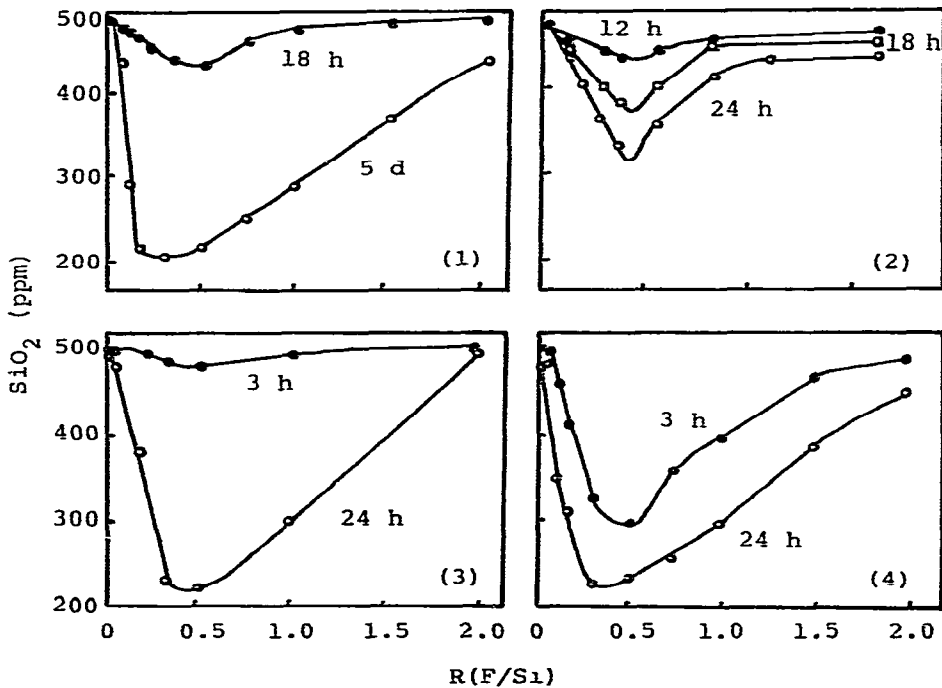


Fig 1 Plot of the concentration of monosilicic acid against R value pH 2.5 (1) 1 (2) 0.55 (3) and 0 (4)

Fig. 2 shows the variation of the concentration of monosilicic acid with pH at different R values after 24 h. The rate of decrease in the concentration of monosilicic acid increases with decreasing pH.

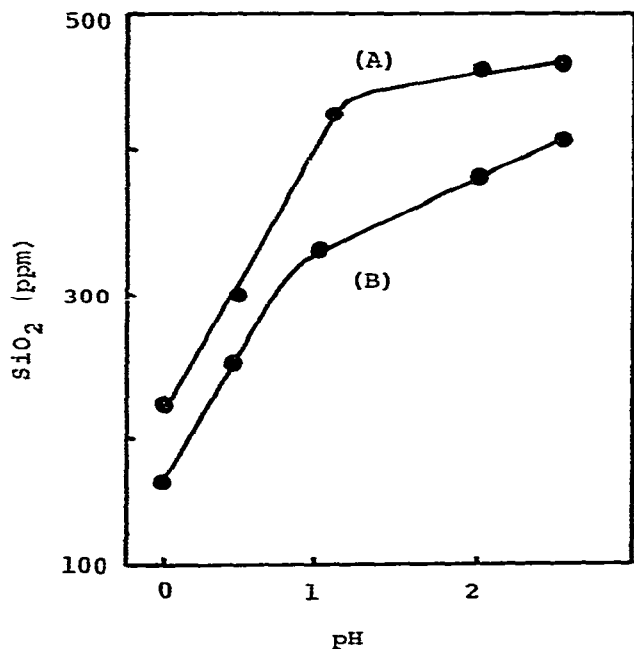


Fig. 2. Plot of the concentration of monosilicic acid after 24 h against pH $R = 1.0$ (A) and 0.33 (B)

Elution curves for silicic acid and fluoride in solution ($R = 0.5$) at pH 1 after 4 d are shown in Fig. 3. A polyethylene column was used. In this case, aluminium chloride was not added to the solution and fluoride was determined spectrophotometrically by the lanthanum-complexone method. Two peaks were obtained from silicic

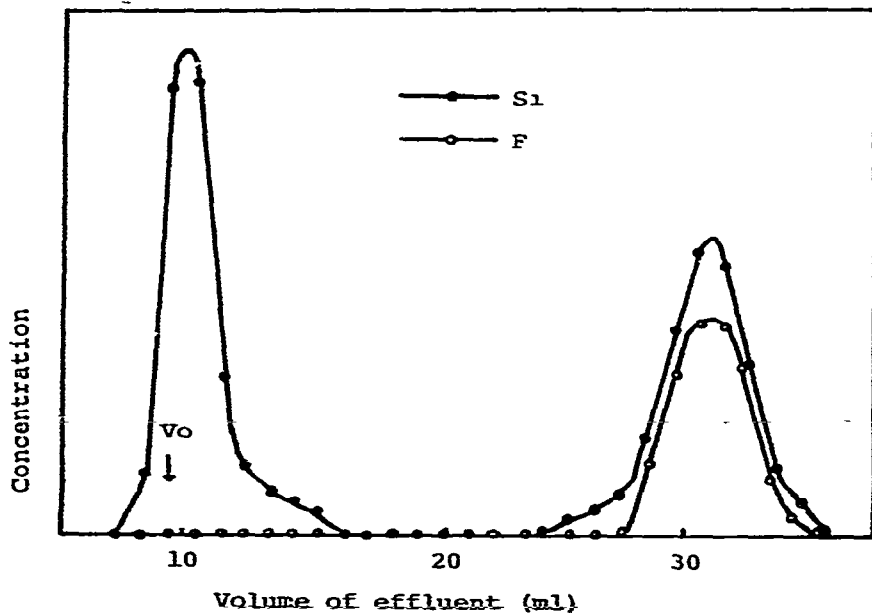


Fig. 3. Elution curves after 4 d for silicic acid (●—●) and fluoride (○—○) in solution of pH 1 ($R = 0.5$)

acid The peak on the right is due to monosilicic acid and the peak 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 phase 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 are eluted together at V_0 . It is seen that the elution volume of fluoride is equal to that of monosilicic acid, and polysilicic acid is not accompanied by fluoride

The variation of the elution curves for silicic acid in solution ($R = 0.1$) at pH 1 with time is shown in Fig 4 The concentration of monosilicic 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 for these acids after 17 d was almost the same as that obtained after 10 d These results indicate that when the concentration of monosilicic acid is close to the solubility of amorphous silica (*cf.*, Table I) the growth rate of particles of polysilicic acids is very slow in spite of the presence of fluoride It is concluded that the growth of polymer particles is due mainly to polymerization between monosilicic and polysilicic acids, and that there is little polymerization between polymer species

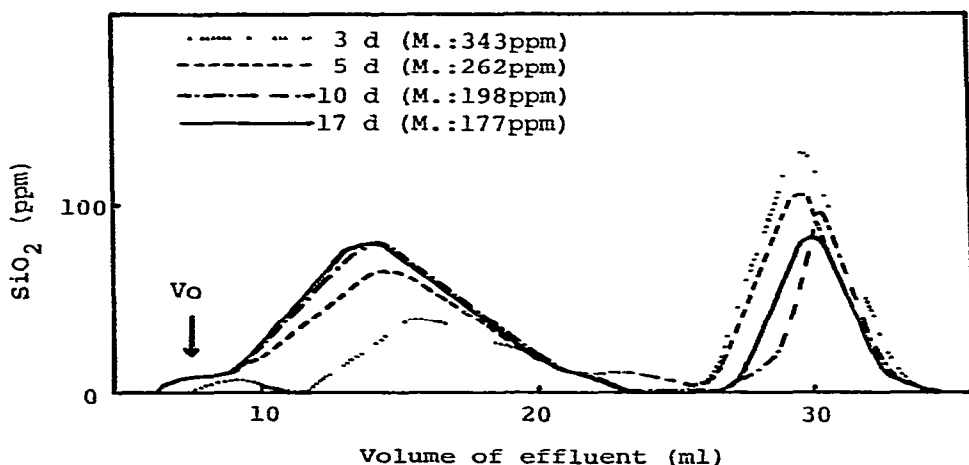


Fig. 4 Variation with time of the elution curves for silicic acid in solution of pH 1 ($R = 0.1$)

The variation of the elution curves for silicic acid in solution of pH 2.5 with R value after 5 d is shown in Fig 5 In Fig 6, the K_{av} values of polysilicic acids in solutions of various pH after 5 d are plotted against R value. The distribution coefficient, K_{av} , was calculated as described previously⁴. It is a measure of particle size and decreases with increasing particle size The K_{av} values decreased with increasing R value showing that the rate of particle growth of polysilicic acids increases with increasing amount of fluoride.

In Fig. 7 the K_{av} values of polysilicic acids in solutions with R values of 0.02 and 0.33 are plotted against pH The K_{av} value is minimal at about pH 1. Therefore, the growth rate of particles of polysilicic acids is maximal at this pH. In Fig. 8, the proportion of polysilicic acid formed after a given time is plotted against pH. The amount of polysilicic acids increased with decreasing pH

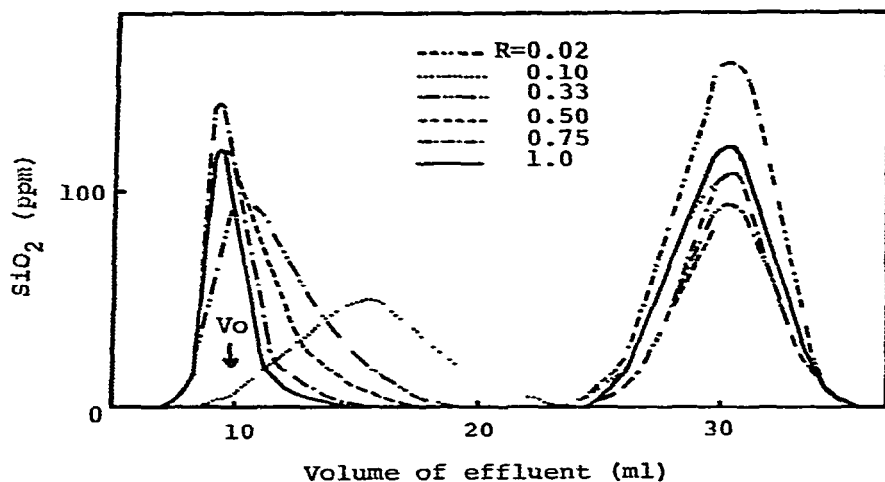


Fig. 5 Elution curves after 5 d for silicic acid in solutions of various R values at pH 2.5

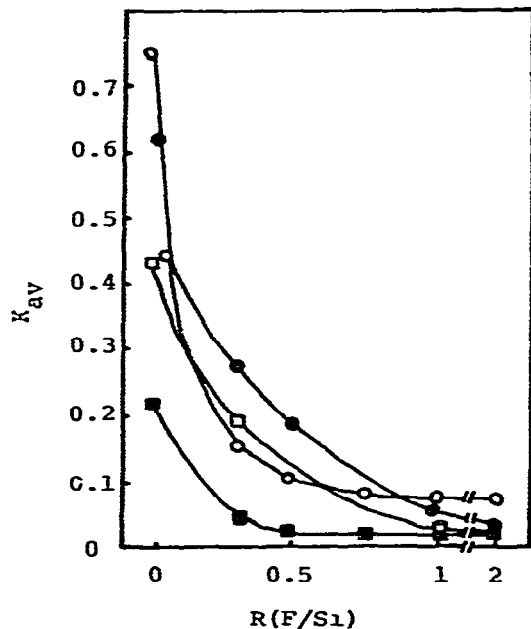


Fig. 6 Plot of K_{av} values of polysilicic acid after 5 d against R value. pH 0 (●), 0.55 (□), 1 (■) and 2.5 (○).

Procedure B

When the concentration of monosilicic acid is close to the solubility of amorphous silica at a given R value, there is little reaction between monosilicic acids or between monosilicic and polysilicic acids. As the reaction between polysilicic acids proceeds regardless of the presence of monosilicic acid, the procedure B was used for the determination of this reaction. The elution curves after 5 d for polysilicic acid in solutions of various R values at pH 1 are shown in Fig. 9, together with that for

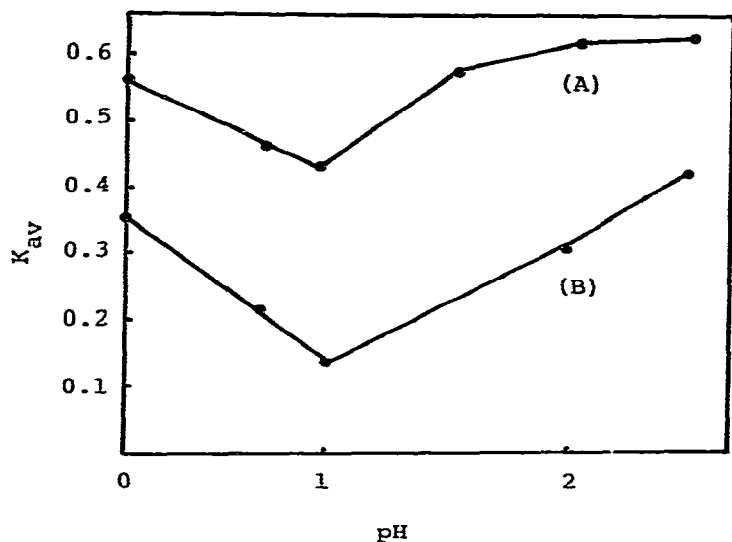


Fig. 7 Plot of K_{av} values of polysilicic acid against pH (A), $R = 0.02, 10\text{ d}$, (B) $R = 0.33, 24\text{ h}$

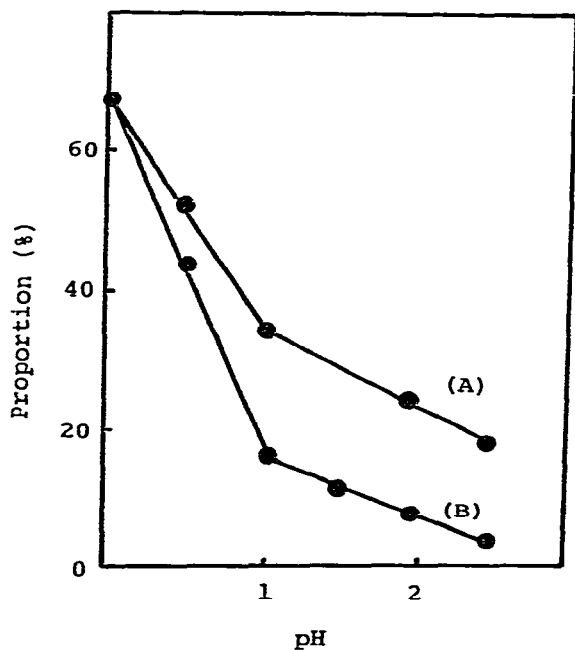


Fig. 8 Plot of the proportions of polysilicic acid formed after a given time against pH (A), $R = 0.02, 10\text{ d}$ (B) $R = 0.33, 24\text{ h}$

polysilicic acid in the initial solutions. The K_{av} values of polysilicic acids after 5 and 8 d are listed in Table II. It appears that the K_{av} values of polysilicic acids decrease with increasing R value, showing that the rate of polymerization between polysilicic acids increases with increasing concentration of fluoride.

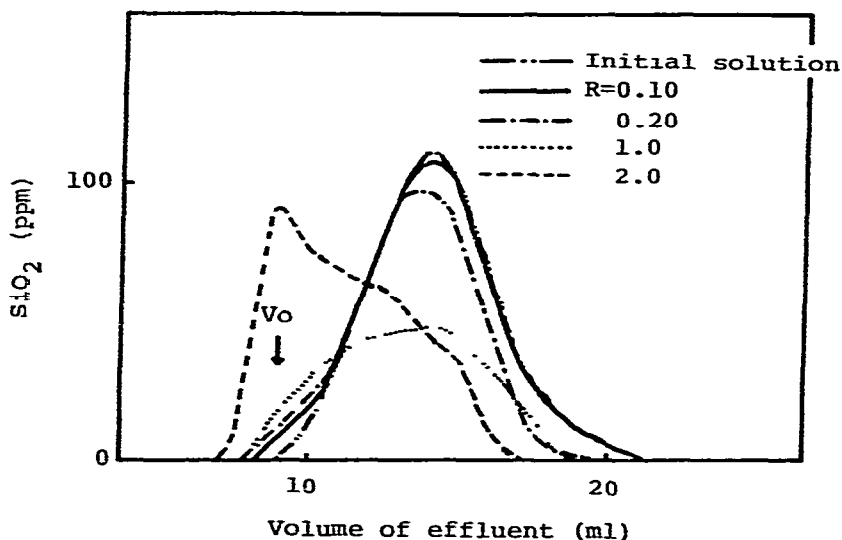


Fig. 9 Elution curves after 5 d for polysilicic acid in solutions of various R values at pH 1.

TABLE II

CHANGE WITH TIME OF K_{av} VALUES OF POLYSILICIC ACIDS AT pH 1

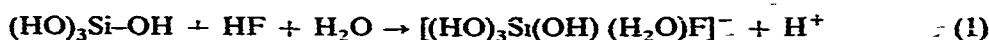
K_{av} of polysilicic acids in initial solutions is 0.25

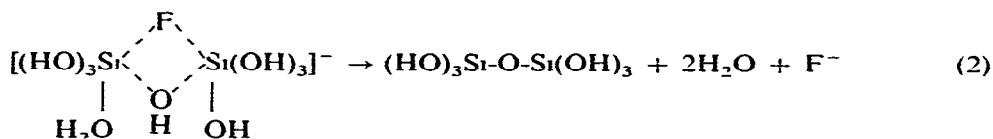
Time (day)	$R (= F/St)$			
	2.0	1.0	0.2	0.1
5	0.13	0.21	0.23	0.24
8	0.10	0.18	0.21	0.23

DISCUSSION

The concentration of monosilicic acid in acidic solution in the presence of fluoride decreases more rapidly than in the absence of fluoride², and the rate of decrease at constant fluoride concentration increases with increasing acidity (Fig. 2). It is reasonable to assume that the effective catalyst is probably hydrogen fluoride, because the dissociation constant of hydrogen fluoride is about 10^{-3} mol/l. The rate of reaction between monosilicic acids is most rapid at about $R = 0.5$ regardless of the difference in acidity (Fig. 1). This suggests that one molecule of hydrogen fluoride participates in a reaction between two molecules of monosilicic acid.

From the above results, if the hypothesis⁸ of a temporary expansion of the coordination number of silicon from four to six is applied to the reaction between monosilicic acids in the presence of hydrogen fluoride as catalyst, the polymerization may proceed by the following mechanism:





As the rate of reaction between monosilicic acids is most rapid at about $R 0.5$, it is suggested that this occurs when the ratio of charged species, $(\text{HO})_3\text{Si}(\text{OH})(\text{H}_2\text{O})\text{F}^-$, and un-ionized species, $\text{HO}-\text{Si}(\text{OH})_3$, is unity

The growth of polysilicic acid particles is due to the reactions between monosilicic and polysilicic acids and between polysilicic acids. Hydrogen fluoride also promotes the rate of growth of polysilicic acid particles. The rate of growth increases with increasing fluoride concentration (Figs 5 and 6) and is most rapid at about pH 1 (Fig. 1). As the rate of growth of polysilicic acid particles by the reaction between polysilicic acids is relatively slow (Table II), it is supposed that the growth of polysilicic acid particles is due mainly to the reaction between monosilicic and polysilicic acids.

In the pH range 2.5–1, the amounts of polysilicic acids gradually increased with increasing acidity (Fig. 8) and the K_{av} values decreased (Fig. 7). These results indicate that the rate of particle growth of polysilicic acids due to the reaction between monosilicic and polysilicic acids increases with increasing acidity.

Below pH 1, the amount of polysilicic acids increased rapidly with increasing acidity (Fig. 8) and the K_{av} values also increased (Fig. 7). These results indicate that, with increasing acidity, the amount of polysilicic acids with smaller sizes rapidly increases, and as the concentration of monosilicic acid rapidly decreases (Fig. 2) the growth of particles of polysilicic acids by the reaction between monosilicic and polysilicic acids becomes slow.

It is concluded that hydrogen fluoride promotes the reactions between monosilicic acids and between monosilicic and polysilicic acids, and that the catalytic effect of hydrogen fluoride on the reaction between polysilicic acids is relatively small.

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