CHREV 181

CHROMATOGRAPHIC STUDIES IN THE FIELD OF SILICATE CHEMISTRY

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CONTENTS

1 INTRODUCTION

Much work on the polymerziation of silicic acid in aqueous solution has been reported[1], chiefly concerned with the production of silica sols or gels and using $\geqslant 1\%$ solutions More dilute systems have been employed for the study of the conditions governing the transformation of monosilicic acids into polysilicic acids The kinetics of polymerization of monosilicic acid have usually been studied by colorimetry[2–4], based on the decrease in the concentration of monosilicic acid with time, whereas monosilicic acid reacts with molybdate reagent in acidic solution to give a yellow colour, polysilicic acid does not react with this reagent The rate of polymerization is rapid in weakly alkaline solution, but very slow at pH 2 A disadvantage of this technique is that it yields no information on the change in particle size of the polysilicic acids with time

One method for separating solute molecules according to their size is gel chromatography, the basic principles of which have been explained in terms of a sieving effect or steric exclusion The separation of the components of a sample in a solution is usually carried out on a column packed with a gel or other porous material The elution volumes of molecules are correlated with their molecular size (weight), larger molecules being eluted faster than smaller molecules

Tarutani[5] first reported that polysilicic acid can be separated from monosilicic acid by gel chromatography Solutions of silicic acid for chromatography are usually adjusted to pH 2, at which polymerization does not occur for several hours or days[6] When the silicic acid solution is highly acidic, an anion-exchange resin (OH⁻) is used for adjustment of pH[7] In the presence of fluoride, aluminium ion, which is a masking agent for fluoride, is added to the sample solution[8,9] and the pH is adjusted to 2

Information with respect to the rate and mechanism of polymerization of silicic acid can be obtained from the changes in elution curves for silicic acid and in the

concentration of monosilicic acid This review deals with gel chromatographic studies of the polymerization of silicic acid

2 POLYMERIZATION OF SILICIC ACID IN AQUEOUS SOLUTION

Fig 1 shows typical elution curves for silicic acid, obtained at different pH values, on a Sephadex G-100 columns[6] 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 The term "monosilicic acid or monomer" here indicates the silicic acid species, which reacts with molybdate, while "polysilicic acid or polymer" indicates the unreactive silicic acid species
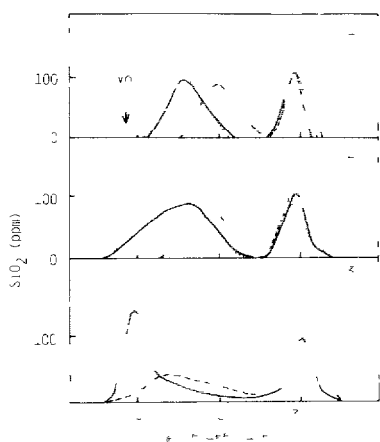

Fig 1 Variation with time of the elution curves for silicic acid in solutions of pH 9 5, 8 and 6 Initial monomer concentration 500 ppm (SiO₂) Gel Sephadex G-100 Column 45 × 1 0 cm I D (1), pH 9 5 ---, 6 h (monomer concentration 215 ppm), ——, 100 h (192 ppm), , 250 h (174 ppm) (2), pH 8 ---, 2 h (230 ppm), ——, 24 h (147 ppm), , 75 h (136 ppm) (3), pH 6 ---, 24 h (298 ppm), ——, 75 h (186 ppm)

The distribution coefficient, K_{av}, for a given gel in gel chromatography is defined[10] as

$$K_{av} = (V_e - V_o)/(V_t - V_o)$$

where V_o is the void volume of the gel bed, V_t the total bed volume and V_e the elution volume of the solute V_o, V_t and V_e are easily measured Since K_{av} is correlated to V_e, it is a measure of molecular size, decreasing with increasing particle size All polymers that have larger sizes than the possible separation range for the gel are eluted at V_o

At pH 9 5 the elution curves for the polymers indicate a symmetrical distribution of particle sizes, the curve for the polymers obtained after 250 h was almost the same as that obtained after 100 h This means that when the concentration of monomer is similar to the solubility of amorphous silica, the growth rate of the particles of the polymers becomes very slow The results suggest that the growth of

the polymers is due mainly to polymerization between monomer and polymer, and that polymerization between polymer species hardly proceeds Although the rates of polymerization at pH 9 and 2 were different from that at pH 9 5, similar results were obtained

The elution curve for the polymers obtained after 24 h at pH 6 is different from that at pH 9 5 and indicates a broad and random distribution of particle sizes After 75 h, the peak of the polymers was eluted at V_0 This suggests that the particles of the polymers grow rapidly The broad and random distribution of particle sizes arises from a random condensation 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

The elution curve for the polymers obtained after 2 h at pH 8 was symmetrical The monomer concentration after 75 h was not much different from that after 24 h and was near the solubility of amorphous silica, but particle growth still continued and the elution curves became asymmetrical These results indicate that in the early stage of polymerization the growth of the particles is due mainly to the polymerization between monomer and polymer, but that the polymerization between polymers subsequently becomes predominant

Crerar et al [11] reported that divalent metal salts ($MgCl_2$, $CaCl_2$, $SrCl_2$) promote the particle growth of polymers more than does NaCl

3 THE pH VALUE GIVING MAXIMUM RATE OF POLYMERIZATION OF SILICIC ACID

The polymerization of silicic acid occurs in three steps[12]
A reaction between monosilicic acids (reaction 1)
A reaction between monosilicic acid and polysilicic acid (reaction 2)
A reaction between polysilicic acids (reaction 3)
If it can be assumed that, in the early stages of polymerization of monosilicic acid, the decrease in the concentration of monosilicic acid in solutions at various pH values is due mainly to reaction 1, it may be possible to obtain the relationship between the rate of reaction 1 and the pH The concentration of monosilicic acid as functions of time and pH is shown in Fig 2 It is thought that the pH corresponding to the minima these curves may be close to the pH at which the rate of reaction 1 is maximal This pH is shifted to slightly lower values with increasing time, possibly due to the influence on polymer formation of reaction 2 The results indicate that at 20°C the reaction between monosilicic acids is most rapid at pH around 9 3

When monosilicic acid solution in which reaction 1 does not occur within a certain period of time is mixed with a polysilicic acid solution the concentration of monosilicic acid decreases with time from the moment of mixing the solutions, due mainly to reaction 2 Experiments carried out under these conditions are shown in Fig 3 The decrease in concentration of monosilicic acid is maximal at pH around 8 6 at 20°C It is concluded that reaction 2 is most rapid at this pH

When the concentration of monosilicic acid is close to the solubility of amorphous silica at a given pH, reactions 1 and 2 hardly occur Since reaction 3 proceeds regardless of the presence of monosilicic acid, the effect of pH can be measured by gel chromatography from the change in elution curves of silicic acid in solutions of various pH values An aliquot of a solution containing polysilicic acid, of which the
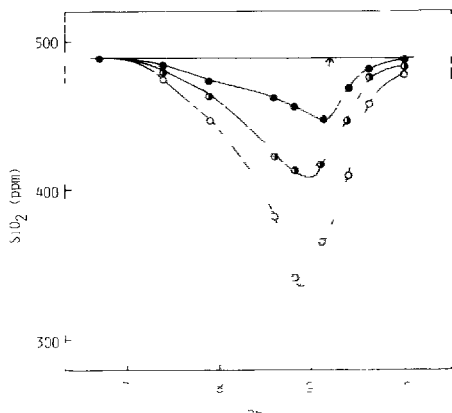
Fig 2 Variation of the concentration of monosilicic acid as functions of pH and time The horizontal line shows the initial monomer concentration Time after adjusting pH 5 min (●--●), 10 min (◑—◑), 15 min (○—○)

particle size distribution was known, was added to monosilicic acid solutions The monomer concentration in each sample solution was adjusted to be near the solubility of amorphous silica at the given pH[3,4,13] Fig 4 shows typical elution curves for silicic acid obtained after 48 h in solutions of various pH values The elution curve at pH 2 did not change within 48 h, and represents the particle size distribution of silicic acid in the initial solutions of various pH values At pH >4 the elution curves obtained after 48 h were shifted to the left compared with that at pH 2 This means that the particle sizes of the polymers were larger than in the initial solutions Fig 5 shows the relationship between the K_{av} values of the polymers, calculated from the elution volumes, and the pH The K_{av} values is minimal at a pH around 6 8 at 20°C This means that reaction 3 is most rapid at this pH

Ashley and Innes[14] suggested that the polymerization of silicic acid proceeds by a reaction between singly ionized and un-ionized silanol groups If the polymerization due to the reaction between monosilicic acids proceeds mainly by

$$(HO)_3Si-O^- + HO-Si(OH)_3 \rightarrow (HO)_3Si-O-Si(OH)_3 + OH^-$$
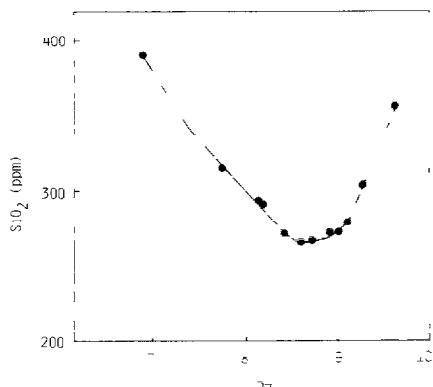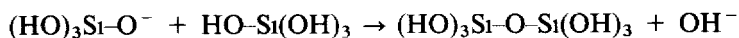

Fig 3 Change in the concentration of monosilicic acid with pH after 30 min when polysilicic acid was added to monosilicic acid Initial concentrations monomer, 314 ppm (SiO$_2$), polymer, 187 ppm (SiO$_2$)
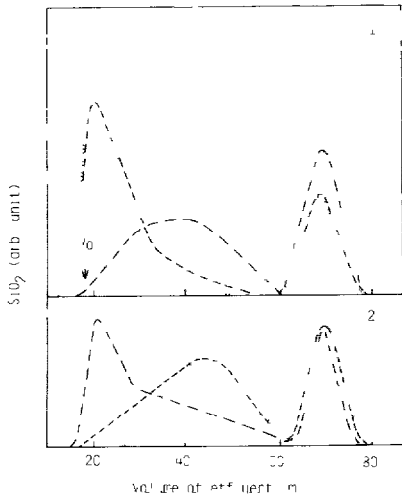
Fig 4 Variation of elution curves for silicic acid after 48 h in solutions of various pH Gel Sephadex G-100 Column 45 × 1 5 cm I D Initial polymer concentration 350 ppm (1) pH 7 (   ), pH 8 (---), pH 9 5 (- -) (2) pH 2 (   ), pH 4 (---), pH 5 (- -)

the rate of polymerization will be maximal at the pH at which the ratio $(H_3SiO_4^-)/(H_4SiO_4)$ is unity Greenberg and Sinclair[15] calculated the $(H_3SiO_4^-)/(H_4SiO_4)$ ratio by using the reported ionization constant of monosilicic acid and obtained a value of 1/1 at pH 9 5 Since the pH giving the maximum rate of reaction 1 is 9 3, it is concluded that reaction 1 reaches its maximum rate at the pH at which the ratio $(H_3SiO_4^-)/(H_4SiO_4)$ is unity

Since the $\equiv SiOH$ groups on the surface of colloidal silica have a pK_a of ca $7^{[16-18]}$, the ionization constant of such groups on the polymers will increase with molecular size, and a negative charge will develop on the polymer surface at a given pH If the reaction between monosilicic and polysilicic acids occurs between a negatively charged site on the polysilicic acid and un-ionized molecule of monosilicic acid, the rate of the polymerization by reaction 2 will be maximal at the pH at which the concentration of these species is sufficiently high It is expected that this value is lower
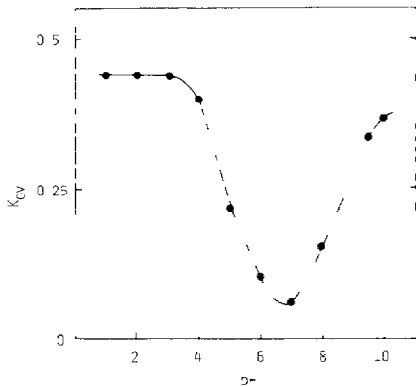

Fig 5 Plot of K_{av} values of polysilicic acid against pH

than that yielding the maximum rate of reaction 1 The results show that the polymer-ization due to reaction 2 is most rapid at a pH around 8 5

As the point of zero charge of colloidal silica is pH 3 5[17], negative ionic charges of silica particles increase with an increase in pH If it can be assumed that the formation of Si–O–Si bonds by the reaction of Si–O$^-$ and Si–OH is responsible for the growth of polymer particles due to reaction 3, and that Si–O$^-$ and Si–OH are present in suitable concentrations on the surface of the polymer particles, there may be an optimum pH at which the rate of growth of particles is at a maximum Since the pK_a value of silanol groups on the surface of colloidal silica is around 7, the ratio of the concentrations of Si–O$^-$ and Si–OH on the surface of the polymers may be unity at a pH of about 7 Moreover, as the rate of reaction 3 is at its maximum at a pH around 6 8, it is concluded that the rate of this reaction is controlled by the concentration of ionized and un-ionized silanol groups in the same manner as as reaction 1

The pH values giving the maximum rates of reactions 1, 2 and 3 at different temperatures are listed in Table 1[19] It is seen that they shift to lower pH values with increasing temperature This may be due to the effect of the decrease in pK_1[20,21] of monosilicic acid and in the pK_a of polysilicic acid

TABLE 1

THE pH VALUES GIVING THE MAXIMUM RATES OF THE REACTIONS BETWEEN MONO-SILICIC ACIDS, BETWEEN MONOSILICIC AND POLYSILICIC ACIDS AND BETWEEN POLYSILICIC ACIDS

Temperature (°C)	pH		
	Monomer and monomer	Monomer and polymer	Polymer and polymer
2	9 5	8 9	7 0
20	9 3	8 6	6 8
50	8 5	8 0	6 7
90	8 1	7 5	6 1

4 POLYMERIZATION OF SILICIC ACID IN ACIDIC SOLUTIONS

The rate of polymerization of silicic acid is lowest at a pH around 2 Below this pH the rate increases with increasing acidity[22] The polymerization of monosilicic acid in hydrochloric, nitric, perchloric and sulphuric acids has been studied[4] The rate of decrease in the concentration of monosilicic acid is in the order $HClO_4$ > HCl ≈ HNO_3 > H_2SO_4

The variation with time of the elution curves for silicic acid in 1 M hydrochloric acid is shown in Fig 6[7] The concentrations of monosilicic acid at the given times are shown in parentheses After 50 h the elution curve for the polymers indicates a symmetrical particle size distribution Fig 7 shows the variation with time of the K_{av} values of the polymers The K_{av} value obtained after 250 h was almost the same as that obtained after 100 h It is concluded that the increase in size of the polymer particles in 1 M hydrochloric acid is due mainly to the reaction between monomer
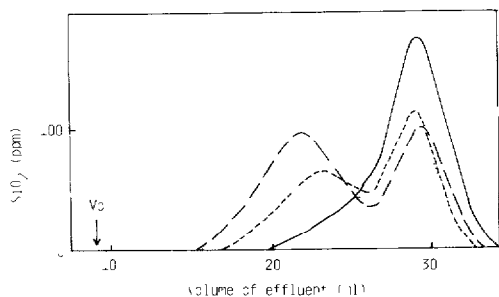
Fig 6 Variation with time of elution curves for silicic acid in 1 M hydrochloric acid Initial monomer concentration 500 ppm (SiO$_2$) Gel Sephadex G-100 Column 45 × 1 0 cm I D ———, 24 h (monomer concentration, 367 ppm), ---, 50 h (278 ppm), , 75 h (227 ppm), - - -, 100 h (204 ppm)
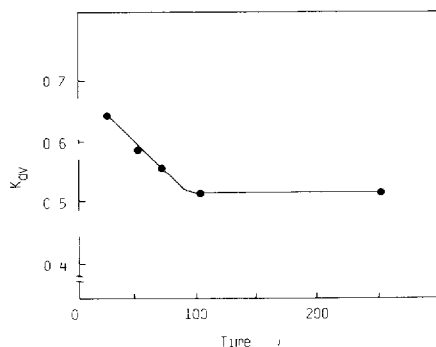

Fig 7 Plot of K_{av} values of polysilicic acid against time

and polymer, and that there is little polymerization between polymer species Similar results were obtained in other 1 M acid solutions

The variation with time of the elution curves for silicic acid in 3 M perchloric acid is shown in Fig 8 After 3 h only one peak was obtained because the peak for polymer was superposed on that for monomer Although the decrease in the concentration of monosilicic acid after 1 h was very slow, the elution curve for the polymers after 24 h indicates a broad particle size distribution and after 100 h the highest peak was obtained at V_0 The results indicate that the polymer particles grow by polymerization between polymer species The rate of polymerization of silicic acid in other acid solutions was slow compared with that in perchloric acid solution, but the results were similar

The rate of polymerization of silicic acid in 5 M acid solutions is faster than that in corresponding 3 M solutions but the mechanism of growth of the polymer particles is similar

5 POLYMERIZATION OF SILICIC ACID IN THE PRESENCE OF FLUORIDE

Iler[23] reported that the gelling of silicic acid sols at low pH is markedly catalyzed by traces of fluoride Tarutani[24] showed that the rate of decrease with time of
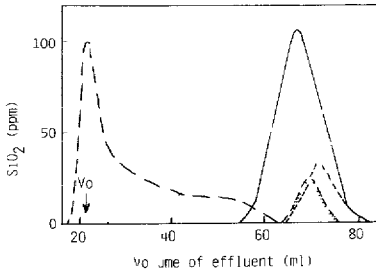
Fig 8 Variation with time of elution curves for silicic acid in 3 M perchloric acid Initial monomer concentration 500 ppm (SiO₂) Gel Sephadex G-100 Column 45 × 1 5 cm I D ——, 3 h (monomer concentration 92 ppm), ---, 3 h (monomer only 92 ppm), , 24 h (59 ppm), - - -, 100 h (39 ppm)

the concentration of monosilicic acid in the presence of fluoride is faster than that in the absence of fluoride

The effect of fluoride on the polymerization of silicic acid was studied in the range pH 2 5–0[9] The rate of disappearance of monosilicic acid was most rapid at a F/Si atomic ratio, R, of about 0 5 regardless of the acidity

Fig 9 shows elution curves for silicic acid and fluoride in solution (R = 0 5) at pH 1 obtained after 4 days The elution volume of fluoride is equal to that of monosilicic acid, and polysilicic acid is not accompanied by fluoride In silicic acid solutions containing fluoride up to R = 2 0, the rate of growth of polysilicic acid particles increased with increasing fluoride concentration
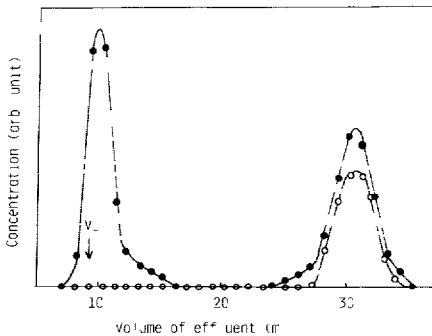

Fig 9 Elution curves for silicic acid (●—●) and fluoride (○—○) in solution at pH 1 (R = 0 5) after 4 days Initial monomer concentration 500 ppm (SiO₂) Gel Sephadex G-100 Column 45 × 1 0 cm I D

The variation with pH of the K_{av} values of polymers in solutions with R = 0 02 and 0 33 is shown in Fig 10 The K_{av} value is minimal at about pH 1 That is, the particle growth rate of the polymers is maximal at this pH

The variation with time of the elution curves for silicic acid in solution (R = 0 1) at pH 1 is shown in Fig 11 The concentration of monosilicic acid is shown in parentheses After 5 days the elution curve for the polymers indicates a nearly symmetrical distribution of particle sizes The elution curve obtained after 17 days was almost the same as that obtained after 10 days These results indicate that when the
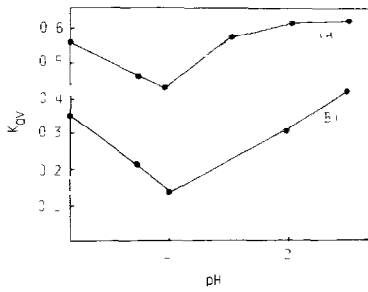
Fig 10 Plot of K_{av} values of polysilicic acid against pH (A), R = 0 02, 10 days (B), R = 0 33, 24 h
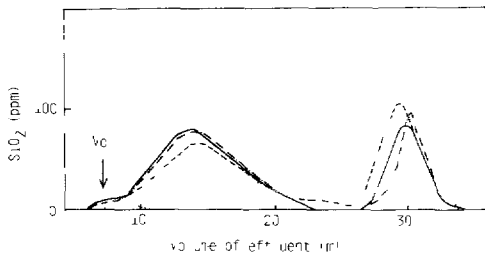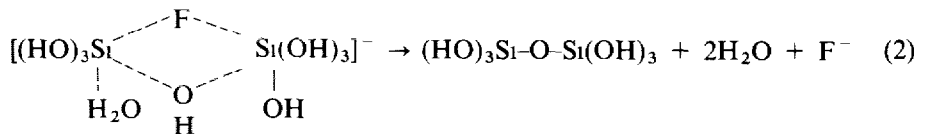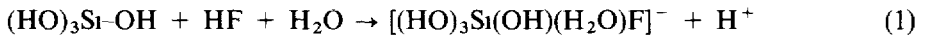

Fig 11 Variation with time of elution curves for silicic acid in solution at pH 1 (R = 0 1)   , 5 days (monomer concentration 343 ppm), ---, 5 days (262 ppm), - - -, 10 days (198 ppm), ——, 17 days (177 ppm)

monomer concentration is close to the solubility of amorphous silica the growth rate of polymer particles is very slow It is concluded that the growth of polymer particles is due mainly to polymerization between monomer and polymer, and that there is little polymerization between polymer species

Iler[22] 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 If this hypothesis is applied to the reaction between monosilicic acids in the presence of hydrogen fluoride as catalyst, the polymerization may proceed by the following mechanism

$$(HO)_3Si-OH + HF + H_2O \rightarrow [(HO)_3Si(OH)(H_2O)F]^- + H^+ \tag{1}$$

$$[(HO)_3Si(OH)(H_2O)F]^- + HO-Si(OH)_3 \rightarrow$$

$$[(HO)_3Si \underset{\underset{H}{\overset{|}{H_2O}} \quad \underset{H}{\overset{O}{}}}{\overset{\overset{F}{\diagup \diagdown}}{\diagdown \diagup}} \underset{\underset{OH}{|}}{Si(OH)_3}]^- \rightarrow (HO)_3Si-O-Si(OH)_3 + 2H_2O + F^- \tag{2}$$

As the rate of reaction between monosilicic acids is most rapid at R ≈ 0 5, it is suggested that this occurs when the ratio of the concentrations of the charged intermediate, $[(HO)_3Si(OH)(H_2O)F]^-$, and of the un-ionized species, $HO-Si(OH)_3$, is unity

Since polysilicic acid is not accompanied by fluoride and the growth of polymer particles is due mainly to the polymerization between monomer and polymer, the particle growth may be due to the reaction between ionized intermediates and un-ionized silanol groups of polymers

From the above results, it is concluded that fluoride promotes the reaction beween monosilicic acids and between monosilicic and polysilicic acids, but that its catalytic effects on the reaction between polysilicic acids is relatively small

6 POLYMERIZATION OF SILICIC ACID IN GEOTHERMAL WATERS

Discharge waters from geothermal power plants are generally supersaturated with respect to silica and silica deposition is an important practical problem It was therefore desirable to know the rate of particle growth of polysilicic acid in geothermal waters

Rothbaum and Wilson[25] estimated the molecular weights of the polymers in cooled and aged geothermal waters by gel chromatography

Yokoyama et al [26] sampled the geothermal water from Otake No 9 well and the sample was kept at 90°C At appropriate intervals, the monosilicic acid concentration and the size distribution of the polymers were measured An induction period of about 1 h, during which there is no change in the concentration of monosilicic acid as determined by colorimetry, was observed When the induction period was over the monomer concentration suddenly began to decrease Fig 12 shows the variation of the elution curves for silicic acid with time A small amount of polysilicic acid was initially present in the geothermal water After 1 h the particle size distribution of the polymers was almost the same as that immediately after sampling, but a small amount of larger polymers was formed After the induction period the growth of the polymer particles became very much faster, and after 3 h the polymers were eluted at V_o The induction period was shorter at higher monomer concentrations

Hachobaru geothermal water, in which the monomer concentration is higher than that of Otake No 9 well water, contained only monosilicic acid and no induction period was observed Fig 13 shows the variation with time of elution curves for silicic acid The rate of growth of the polymer particles was very much faster than that in Otake No 9 well water and after 15 min the polymers formed were eluted at V_o
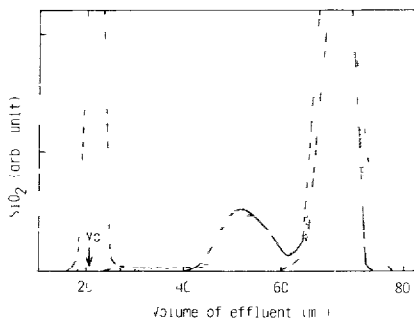

Fig 12 Variation with time of elution curves for silicic acid in Otake No 9 well water (pH 8 3, 90°C) Total silicic acid concentration 580 ppm (SiO₂) Gel Sephadex G-100 Column 45 × 1 5 cm 1 D ——, 0 h, ---, 1 h, , 3 h - - -, 5 h
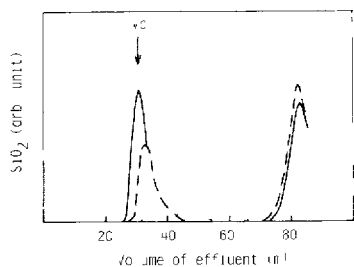
Fig 13 Variation with time of elution curves for silicic acid in Hachobaru geothermal water (pH 8 3, 90°C) Total silicic acid concentration 950 ppm (SiO₂)   , 5 min, - - -, 15 min, ——, 30 min

7 POLYMERIZATION OF SILICIC ACID ADSORBED ON METAL HYDROXIDES

Adsorption of silicic acid on iron(III) hydroxide has mainly been measured from the decrease in concentration of silicic acid However, the behaviour of adsorbed silicic acid has scarcely been studied Kojima and Tarutani[27] reported that monosilicic acid adsorbed on iron(III) hydroxide polymerizes in a short period of time The adsorption of silicic acid by iron(III) hydroxide and polymerization of silicic acid were studied in the range pH 4–12[28] The amount of silicic acid adsorbed increased in the range pH 4–9, but declined above pH 9 The maximum adsorption occurred at pH 9 The amount of silicic acid adsorbed increased with increasing initial monomer concentration Iron(III) hydroxide, which had adsorbed silicic acid, was dissolved with hydrochloric acid, and the silicic acid was chromatographed on Sephadex G-25 Fig 14 shows the resulting elution curves, the dotted line is the elution curve for monosilicic acid The mole ratio (MR) of monosilicic acid and iron(III) hydroxide in the initial solution is expressed as Si/Fe It is seen that the rate of growth of polymers is most rapid at pH 9

It was concluded that polymerization of silicic acid on the surface of iron(III) hydroxide occurred in two steps (1) the polymerization of adsorbed monosilicic acid

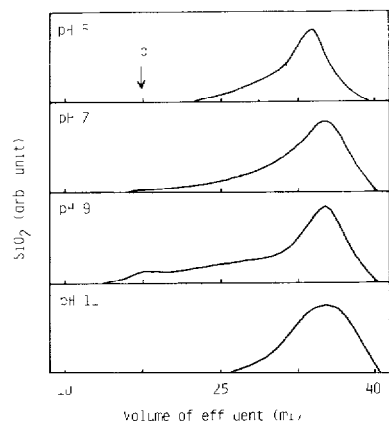Fig 14 Gel chromatograms for silicic acid adsorbed on iron(III) hydroxide at various pH obtained after 5 h Initial monomer concentration 300 ppm (SiO₂) Si/Fe(MR) 0 63 Gel Sephadex G-25 Column 60 × 1 cm I D
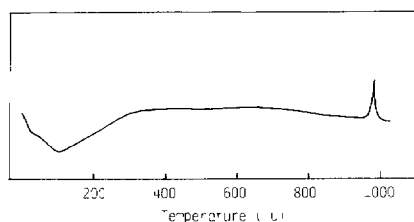
Fig 15 DTA curve of aluminium hydroxide which had adsorbed silicic acid at pH 8

and (2) the polymerization between monosilicic acid in solution and silicic acid species already present on the surface of iron(III) hydroxide, giving rise to a three-dimensional gel structure

Yokoyama *et al* [29] studied the behaviour of silicic acid adsorbed on aluminium hydroxide at various pH values Maximum adsorption occurred at pH 9 5 The gel chromatograms for adsorbed silicic acid obtained by the same manner as with iron(III) hydroxide indicated that the rate of growth of polymer particles is most rapid at pH 9 0–9 5

The behaviour of silicic acid adsorbed on aluminium hydroxide is different from that on iron(III) hydroxide Fig 15 shows the differential thermal analysis (DTA) curve of aluminium hydroxide which had adsorbed silicic acid at pH 8 This curve has an endothermic peak at *ca* 100–300°C and an exothermic peak at around 1000°C, it is very similar in nature to that of allophane, that is, amorphous aluminosilicate The exothermic peak at around 1000°C indicates that amorphous aluminosilicate is formed by the reaction of the adsorbed monosilicic acid and aluminium hydroxide It was found that, in the early stages of adsorption, monosilicic acid adsorbed on aluminium hydroxide is consumed by the formation of amorphous aluminosilicate until the mole ratio of the adsorbed silicic acid to aluminium hydroxide reaches 0 33–0 39, above this ratio, silicic acid adsorbed on aluminosilicate polymerizes[30] In the early stages, polymerization of adsorbed silicic acid proceeded mainly by the reactions between monosilicic acids and between monosilicic and polysilicic acids, and the polymer particle sizes gradually increased with time When the particles were large enough to contact neighbouring polymers, their growth rate became faster due to the reaction between polysilicic acids

REFERENCES

1 R K Iler, *The Chemistry of Silica*, Wiley, New York, 1979
2 E Richerdson and J A Waddams, *Research*, 7 (1954) S42
3 G B Alexander, W M Heston and P K Iler, *J Phys Chem* , 58 (1954) 453
4 T Tarutani, *Nippon Kagaku Zasshi*, 77 (1956) 1721
5 T Tarutani, *J Chromatogr* , 50 (1970) 523
6 K Shimada and T Tarutani, *J Chromatogr* , 168 (1979) 401
7 H Iwasaki, K Shimada and T Tarutani, *J Chromatogr* , 198 (1980) 429
8 T Tarutani, *Nippon Kagaku Zasshi*, 77 (1956) 1292
9 K Shimada and T Tarutani, *J Chromatogr* , 249 (1982) 111
10 T C Laurent and J Killander, *J Chromatogr* , 14 (1964) 317
11 D A Crerar, E V Axtmann and R C Axtmann, *Geochim Cosmochim Acta*, 45 (1981) 1259
12 K Shimada and T Tarutani, *Bull Chem Soc Jap* , 53 (1980) 3488
13 G Goto, T Okura and K Goto, *Geochim Cosmochim Acta*, 12 (1957) 123

14 K D Ashley and W B Innes, *Ind Eng Chem* , 44 (1952) 2857
15 S A Greenberg and D Sinclair, *J Phys Chem* , 59 (1955) 435
16 M Mushiake and N Masuko, *Seisankenkyu*, 29 (1977) 2
17 A Komura, K Hatsutori and H Imanaga, *Nippon Kagaku Kaishi*, (1978) 779
18 D N Strazhesko, V B Strelko, V N Belyakov and S C Rubanik, *J Chromatogr* , 102 (1974) 191
19 K Shimada and T Tarutani, *Mem Fac Sci , Kyushu Univ , Ser C*, 13 (1982) 311
20 T M Sewerd, *Geochim Cosmochim Acta*, 38 (1974) 1651
21 J A van Lier, P L de Bruyn and J T G Overbeek, *J Phys Chem* , 64 (1960) 1675
22 R K Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, New York, 1955
23 R K Iler, *J Phys Chem* , 56 (1952) 680
24 T Tarutani, *Nippon Kagaku Zasshi*, 77 (1956) 1811
25 H P Rothbaum and R D Wilson, *Bull -N Z Dept Sci Ind Res* , 218 (1977) 37
26 T Yokoyama, K Shimada, T Shimono and T Tarutani, *J Jap Geothermal Energy Assoc* , 20 (1983) 319
27 T Kojima and T Tarutani, *Mem Fac Sci , Kyushu Univ , Ser C*, 9 (1974) 1
28 T Yokoyama, T Nakazato and T Tarutani, *Bull Chem Soc Jap* , 53 (1980) 850
29 T Yokoyama, O Nakamura and T Tarutani, *Bull Chem Soc Jap* , 55 (1982) 975
30 T Yokoyama, *D Sc Thesis*, Kyushu University, 1980