Silicate Species in Solution. Part 1. Experimental Observations

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Changes in the pH or concentration of sodium silicate solutions produce changes in the degree of polymerisation of the silicate species, and these have been followed by the technique of trimethylsilylation. Provided that the pH remains relatively high, above *ca.* 10 or 11 according to concentration, equilibrium is rapidly re-established after such changes. At lower pH, equilibrium is approached more slowly, and changes in distribution with time can be followed.

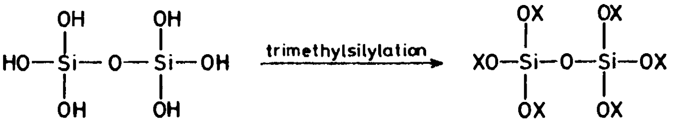
SODIUM SILICATE solutions can be prepared having a wide range of concentration and soda : silica ratio. The monomeric orthosilicate ions present in very dilute or very alkaline solutions polymerise as the concentration increases or the pH drops, and most solutions of practical importance appear to contain an equilibrium mixture of species.

Early measurements of the conductivities, viscosities, and pH [1,2] of such solutions suggested that they required quite long intervals (from a few hours to a few days) to reach equilibrium after dilution or a change in pH. For this reason, many workers (including the present authors) have allowed their solutions to stand for a few days after preparation before making any measurements. However, Lagerström [3] reported that solutions reached equilibrium quickly, unless they were in, or had passed through, an ' instability range ' in which the alkali : silica ratio was low enough to produce colloidal silica, which was slow to equilibrate. He showed that many of the solutions previously thought to require lengthy equilibration periods were in fact in this instability region. Stumm *et al.*[4] and Walker and Whitehead [5] have confirmed Lagerström's findings.

The classical methods listed above give at best only limited information about the distribution of silicate ions among the various polymeric species. More information about this can be obtained from ^{29}Si n.m.r. spectroscopy [6-9] or by using the technique of trimethylsilylation introduced by Lentz.[10-12] With present techniques, the former requires runs of many hours' duration and is thus unsuitable for studying reaction rates.

In the present work the trimethylsilylation method was used. In this, the labile silicate groups are converted into relatively unreactive trimethylsilyl derivatives, *e.g.* as in equations (1) and (2) where $X = Si(CH_3)_3$. The silicate groups are shown as fully protonated because the reaction takes place in acid solution. Provided that no rearrangement of the silicate groups takes place prior to reaction (a point discussed later) the distribution of derivative species reflects that in the parent silicate solution.

$$\mathrm{HO{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}{-}OH} \xrightarrow{\text{trimethylsilylation}} \mathrm{XO{-}\overset{\overset{OX}{|}}{\underset{\underset{OX}{|}}{Si}}{-}OX} \qquad (1)$$



$$\mathrm{HO{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}{-}O{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}{-}OH} \xrightarrow{\text{trimethylsilylation}} \mathrm{XO{-}\overset{\overset{OX}{|}}{\underset{\underset{OX}{|}}{Si}}{-}O{-}\overset{\overset{OX}{|}}{\underset{\underset{OX}{|}}{Si}}{-}OX} \qquad (2)$$

The derivatives are extracted into an organic solvent (hexamethyldisiloxane in the present study) and those of the smaller (up to eight Si) silicate ions can be identified and quantified by gas–liquid chromatography (g.l.c.). Derivatives of larger units, hereafter called ' polysilicate ', can be studied by gel-permeation chromatography (g.p.c.) to obtain information about molecular weights.[12] Carbon and hydrogen analyses enable the connectivity to be estimated: this will be expressed as $\bar{Q}$, the mean number of shared corners per tetrahedron as estimated from the carbon analysis. (In a ring, or an infinite chain, $\bar{Q} = 2$; in an infinite sheet, or a closed cage, $\bar{Q} = 3$.) Values estimated in this way are probably slightly too high; the ratio of H : C found is usually slightly more than the 3.0 : 1 required by CH_3 groups, the surplus H presumably being due to the presence of unchanged silanol groups. It is difficult to make a meaningful correction for these, in view of the probable errors of C and H analyses, but it seems unlikely that they exceed 10% of the total silanol groups originally present.

As the polysilicate increases in molecular weight, groups of colloidal dimensions are formed. Although these appear to react on the surface to give derivatives, the product is not soluble in hexamethyldisiloxane, and so is not directly detectable by the method. The term polysilicate will be reserved for that part of the highly polymerised silicate that can be extracted and characterised, and colloidal silicate for that part not detected; it is to be understood that these terms cover a range of sizes, and that the ranges probably overlap.

If conversion of each silicate species in the solution into its corresponding derivative were quantitative, the technique would provide a precise method of studying the distribution of species in solution. Unfortunately, this is almost certainly not the case. The critical step is probably the acidification of the solution, which must be accomplished as rapidly as possible to avoid polymerisation of the silicate groups.[11-13] The more concentrated the solution, the more difficult it is to do this, and solutions more concentrated than *ca.* 1 mol dm^{-3} with respect to silicon can be handled only with great difficulty. Comparison with ^{29}Si n.m.r. data [14] suggests that orthosilicate in particular may be lost during the reaction, although the ratio of this to more condensed species is in fair agreement with that obtained from n.m.r. spectroscopy. Results from trimethylsilylation studies are therefore only semi-quantitative. Despite this limitation, trimethylsilylation studies provide valuable information about silicate solutions that cannot be obtained by other chemical methods.

In the present work the technique was used to check previous reports on the rate of equilibration and to study the changes in the distribution of silicate species that occur when sodium silicate solutions are subjected to: (1) dilution; (2) change in pH by the addition of acid or alkali; and (3) removal of sodium ion by ion exchange. The dissolution of crystalline sodium metasilicate was also studied.

EXPERIMENTAL

Preparation of Sodium Silicate Solutions.—Solutions were prepared in CO$_2$-free deionised water from the following silicates: $Na_2H_2SiO_4\cdot 8H_2O$, prepared from 'sodium metasilicate pentahydrate' (B.D.H.) by recrystallisation as described previously; [12] Na_2SiO_3, prepared by drying $Na_2H_2SiO_4\cdot 8H_2O$ at 200 °C and then igniting at 900 °C for 2 h (solutions prepared from these two sources have mol ratio $Na_2O : SiO_2 = 1 : 1$); and Pyramid brand No. 1 sodium silicate solution (Joseph Crosfield and Sons, Ltd), which has a $Na_2O : SiO_2$ mol ratio 1 : 3.41 and is *ca.* 6.8 mol dm^{-3} in silica.

The solutions were stored in tightly stoppered glass bottles that were opened only briefly for sampling in order to avoid contamination by atmospheric CO$_2$. Solution concentrations are given in terms of their molarity in silica. They were analysed for sodium and silicon using a Perkin-Elmer model 305 atomic absorption spectrophotometer.

Preparation and Estimation of Trimethylsilyl Derivatives.—The trimethylsilylation procedure used was that described by Lentz [10] in which the reagent is a mixture of hexamethyldisiloxane, isopropyl alcohol, and hydrochloric acid. The silicate solutions were added dropwise to the vortex of a rapidly stirred reagent mixture. Turbulent mixing, using either baffled vessels or an ultrasonic mixer, did not give significantly different results. Low-molecular-weight species were studied by g.l.c. as described previously; [12,15] where these species only were to be studied, quantities used were only one tenth of those given by Lentz. The principal volatile species detected were the derivatives of: orthosilicate groups, or monomer, as in equation (1) (designated Si$_1$); pyrosilicate groups, or dimer, as in (2) (Si$_2$); linear trimer (Si$_3$); cyclic tetramer (Si$_4$); several hexameric species not readily separable by g.l.c.[16] (Si$_6$); and an octamer, Si_8O_{21}, with a cage-like structure [17] (Si$_8$).

Only insignificant amounts of derivatives of the cyclic trimer postulated from n.m.r. spectroscopy [8,9] were found. However, it is possible that in solution the ring form exists in equilibrium with the linear form of the trimer, and that the latter trimethylsilylates more readily and is thus the only form detected. The trimethylsilylated ring derivative is quite difficult to prepare even from crystalline solids known to contain Si_3O_9 rings: this might indicate that the derivative is sterically hindered, although it might also mean that the ring, which is thought to be strained,[18] readily opens to a chain when released from the confines of a crystal structure.

Where the higher-molecular-weight polysilicate fraction was to be studied by g.p.c., larger scale preparations were needed, and for reasons of economy only a few of these were made. After reaction, a portion of extract was retained for study by g.l.c., and the solvent distilled from the remainder; the residue was dried at 115 °C. All or some of the monomer and dimer derivatives were lost in the process (the amount could be estimated by g.l.c.), the loss decreasing as the molecular weight and degree of cross-linking of the polysilicate increases (presumably through physical trapping of the small species by the larger). The polysilicate fraction thus consists mainly of species from the trimer upwards.

In timed experiments, the reagents for trimethylsilylation were prepared in advance, and the sample withdrawn and immediately added to the stirring mixture.

Flow-time Measurements.—These were used to compare viscosities, as a check on the results from other methods. A Hewlett-Packard 5901B Auto Viscometer with a 5903A Programmer was used. All solutions, water, flasks, and viscometers were stored in the thermostatted bath used for the measurements; solutions were filtered three times through a No. 4 sintered glass filter to remove dust before being transferred to the viscometer. Nitrogen was used in the programmer pneumatic system, to avoid contamination of the solutions by CO$_2$.

Equilibration Studies.—The various treatments to which the solutions were subjected are shown in Figure 1, which is adapted from Stumm *et al.*,[4] as modified by Barby *et al.*[19] The treatments are described below, and figures in square brackets relate to positions on Figure 1.

Dilution. A 6.8 mol dm^{-3} sodium silicate solution of 3.41 : 1 mol ratio [1] was quickly weighed into a standard flask. About 90% of the required water was added and timing started. The flask was shaken vigorously to disperse the viscous silicate solution as quickly as possible, made up to the mark, and shaken again. For trimethylsilylation a sample was taken as soon as dilution was completed, further samples being taken at intervals. Solutions diluted to 1.0 [2] and 0.1 mol dm^{-3} [3] were studied in this way.

Dissolution of Na_2SiO_3. Anhydrous sodium metasilicate was dissolved in a manner similar to the above to give a 0.125 mol dm^{-3} solution [8]. Because dissolution took some time, samples withdrawn for trimethylsilylation were also analysed for sodium and silicon.

Change in pH. The soda to silica ratio of a 0.1 mol dm^{-3} (1 : 3.41 [3]) solution was changed to 1 : 1 [4] by the addition of AnalaR (B.D.H.) sodium hydroxide pellets. Vigorous stirring with a magnetic stirring bar ensured that the sodium hydroxide dissolved within 2 min. Timing began immediately the sodium hydroxide was added; samples for trimethylsilylation were withdrawn immediately before and at intervals afterwards.

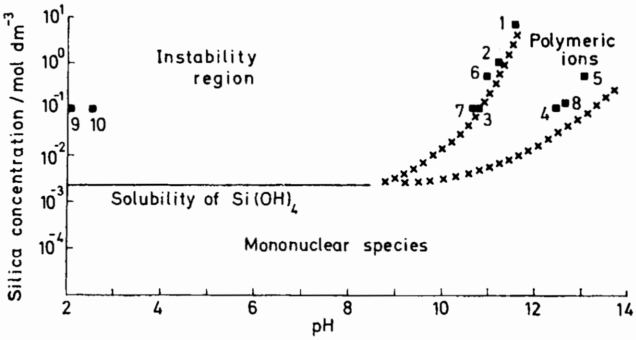


FIGURE 1 Diagram showing pH and concentration of the various solutions studied in relationship to the instability region; after Stumm *et al.*[4] and Barby *et al.*[19] The numbered squares represent solutions discussed in the text

Change of pH in the reverse direction was studied by adding AnalaR (B.D.H.) hydrochloric acid to 0.1 and 0.5 mol dm^{-3} (1 : 1) solutions, [4] and [5]. The change in concentration of silicon (1.1 and 5.4%) was minimised by using concentrated acid, which was added in a thin stream to the vigorously stirred solutions. The pH values dropped from *ca.* 12.5 and 13.0 to 10.7 and 11.1 respectively, [7] and [6]. Sampling followed the same pattern as for the addition of sodium hydroxide.

Titration with hydrochloric acid. Vigorously stirred 0.1 and 0.5 mol dm^{-3} (1 : 1) solutions, [4] and [5], protected from CO$_2$, were titrated with concentrated HCl until gelling became apparent. Samples were withdrawn for trimethylsilylation at intervals of *ca.* 0.5 pH units.

A Radiometer type G202B electrode, standardised frequently against sodium tetraborate buffer, was used for the pH measurements. It was found to be important to use the same magnetic stirrer during all measurements and standardisations. These relatively dilute silicate solutions appeared not to affect the electrode, but more concentrated ones (*e.g.* 1.0 mol dm^{-3}) caused its output to drift considerably.

Ageing of silicic acid prepared by ion exchange. Two samples of silicic acid were prepared by a method similar to that described by Alexander.[20] One (A) was prepared directly from solid $Na_2H_2SiO_4 \cdot 8H_2O$ by portionwise addition of the crystals to a vigorously stirred slurry of Zerolit 325 ion-exchange resin in 0.05 mol dm^{-3} sulphuric acid at 2 °C. Filtration gave a clear solution (or perhaps sol) 0.1 mol dm^{-3} in SiO$_2$, 5.6 × 10^{-4} mol dm^{-3} in Na$_2$O, and with a pH of 2.02 [9]. The other (B) was prepared in a similar manner from a 0.5 mol dm^{-3} (1 : 1) solution; this was 0.1 mol dm^{-3} in SiO$_2$, 3.7 × 10^{-4} mol dm^{-3} in Na$_2$O, and had a pH of 2.55 [10].

Both samples were aged at room temperature.

RESULTS AND DISCUSSION

Dilution Experiments.—Table 1(*a*) gives the results of a full-scale examination of the constitution of a 1 : 3.41 solution at various times up to 2 d after dilution from 6.8 to 1.0 mol dm^{-3} (from [1] to [2] on Figure 1): in addition to the volatile species (Si$_1$—Si$_8$) the total polysilicate as determined by weight is given. Table 1(*b*) gives the results of studies on the polysilicate fraction, and also the values of $\bar{N}_n$ and $\bar{N}_w$ for all species in solution, obtained by correcting the polysilicate values for the monomer and dimer lost in drying. Table 2 gives the results of a small-scale repeat determination, and Table 3 those of a small-scale determination after dilution of the same solution to 0.1 mol dm^{-3}.

TABLE 1

Trimethylsilylation of a 1 : 3.41 solution after dilution from 6.8 to 1.0 mol dm^{-3} SiO$_2$

(*a*) Yields

Time		Percentage SiO$_2$ recovered as:							Percentage lost in drying	Total (%)
t/min	h	Si$_1$	Si$_2$	Si$_3$	Si$_4$	Si$_6$	Si$_8$	Poly-silicate		
5		2	2	2	2	5	5	80	4	84
10		3	2	2	2	5	5	72	3	75
30		4	2	2	3	6	5	82	3	85
60		5	3	2	2	7	6	82	6	88
120	(2)	4	2	2	2	7	5	82	5	87
300	(5)	4	3	2	2	6	6	73	5	78
1 440	(24)	6	2	2	2	5	4	85	5	90
2 880	(48)	6	2	2	2	5	4	84	6	90

(*b*) Average degree of polymerisation

Time	Polysilicate					Corrected	
t/min	$\bar{N}_n$	$\bar{N}_w$	C (%)	H (%)	H/C	$\bar{N}_n$	$\bar{N}_w$
5	7.2	11.1	27.5	7.3	3.18	6.9	10.1
10	6.0	9.8	27.8	7.6	3.28	5.9	9.7
30	6.6	10.7	27.4	7.3	3.20	5.6	10.3
60	8.1	11.7	27.3	7.1	3.12	5.8	11.0
120	7.9	12.2	27.5	7.2	3.14	5.9	11.6
300	7.4	11.7	27.5	7.5	3.27	5.5	11.1
1 440	7.4	11.7	27.6	7.2	3.13	5.5	11.4
2 880	7.7	11.5	27.6	7.2	3.13	5.6	10.9

The symbols Si$_1$, Si$_2$, *etc.* represent various silicate polymers as discussed in the text. $\bar{N}_n$ and $\bar{N}_w$ are the numbers of Si in the original silicate species on a number and weight average basis respectively.

These results are given in full to indicate the precision (or lack of it) of the method: it will be seen that scatter is considerable, and that no significant changes occur over the time investigated. The flow-time experiments confirmed this; there was no significant variation in solution viscosity over the first 24 h after dilution. At 25 °C times were in the range 92.5—92.6 s for the 0.1 mol dm^{-3} and 116.0—116.2 s for the 1.0 mol dm^{-3} solution.

TABLE 2

Distribution of low-molecular-weight species in a 1 : 3.41 solution after dilution from 6.8 to 1.0 mol dm^{-3} SiO$_2$

Time	Percentage SiO$_2$ recovered as:						Total
t/min	Si$_1$	Si$_2$	Si$_3$	Si$_4$	Si$_6$	Si$_8$	(%)
5	6	2	2	2	5	4	21
10	5	2	2	2	4	4	19
30	5	2	2	1	4	4	18
60	6	2	2	2	4	4	20
120	6	2	2	2	5	5	22
300	5	2	2	2	5	5	21
1 440	5	2	2	1	4	3	17
2 880	5	2	1	2	4	4	18

Unfortunately, because of the time needed to ensure homogeneity of the solution, and for dropwise addition to the reagents in the case of trimethylsilylation and filtration in the case of flow-time measurements, neither technique could be used to examine the solution less than 5 min after dilution.

These results seem to show that changes in the solution happen rapidly, both to small and large species. On the other hand, we have noticed differences in the distribution of low-molecular-weight species found in solutions of apparently identical composition made by diluting different batches of commercial silicate solution;[21] indeed, the solution used in the present studies yields a significantly higher proportion of monomer than that used previously.[12] The two observations are not in fact irreconcilable. All the solutions lie close to the boundary of the instability region, and probably contain significant amounts of colloidal material. The size of such particles could depend on the exact conditions under which the glass had been dissolved in the course of their production, or perhaps on the amount of iron (always present in commercial solutions) or the extent of CO_2 contamination.

TABLE 3

Distribution of low-molecular-weight species in a 1 : 3.41 solution after dilution from 6.8 to 0.1 mol dm^{-3} SiO_2

Time	Percentage SiO_2 recovered as:						Total
t/min	Si_1	Si_2	Si_3	Si_4	Si_6	Si_8	(%)
5	34	6	3	3	6	3	55
10	35	8	3	2	6	3	57
30	32	7	4	3	6	3	55
60	36	8	3	2	6	3	58
120	33	7	4	3	6	3	56
300	30	8	4	3	6	3	54
1 440	35	7	3	3	5	3	56
2 880	36	7	4	3	4	3	57

If very large particles such as these participate in solution equilibria only through their surfaces, the effective contribution of (say) two 500-unit particles would be greater than that of one 1 000-unit particle by a factor of $2 \times 500^{\frac{2}{3}}/1\,000^{\frac{2}{3}} = 1.26$, assuming that the particles are roughly spherical with radii proportional to the cube root of the number of silicate units they contain. Such a situation represents only quasi-equilibrium, but it is apparent that true equilibrium would be approached extremely slowly, in accord with earlier conclusions about the instability region.

TABLE 4

Distribution of low-molecular-weight species on dissolving anhydrous Na_2SiO_3

Time	Percentage SiO_2 recovered as:						Total	Molarity	
t/min	Si_1	Si_2	Si_3	Si_4	Si_6	Si_8	(%)	Na_2O	SiO_2
5	42	24	11	7	10	0	94	0.117	0.122
10	48	22	10	8	8	0	96	0.121	0.122
60	42	20	9	8	7	0	86	0.121	0.125
2 880	40	22	13	9	7	1	92	0.121	0.125

Additional determinations made after 30, 120, and 420 min did not differ significantly.

Dissolution Experiment.—Table 4 gives the distribution of low-molecular-weight species at intervals after the addition of anhydrous sodium metasilicate to water. The constitution of the solution became essentially constant within 5 min, although complete dissolution took over 10 min. The break-up of the infinite chains in the Na_2SiO_3 crystals seems to be instantaneous.

Change of pH.—Table 5 gives the results of adding sodium hydroxide pellets to a 0.1 mol dm^{-3} (1 : 3.41) solution to give a solution of 1 : 1 ratio (from [3] to [4] on Figure 1). Table 6(*a*) and 6(*b*) gives the result of a pH change in the opposite direction, adding hydrochloric acid to 0.1 and 0.5 mol dm^{-3} (1 : 1) solutions ([4] and [5] to [7] and [6] respectively on Figure 1). In no case is any significant change observed after the first five minutes. Moreover, comparison of the first line in Table 5 with the second and subsequent lines of Table 6(*a*), and of the first line in Table 6(*a*) with the second and subsequent lines of Table 5, shows fair agreement: that is, the condition of a solution at the given points in Figure 1 is independent of the method of preparation, suggesting that equilibrium has been approached, if not actually attained.

TABLE 5

Distribution of low-molecular-weight species in 0.1 mol dm^{-3} SiO_2 (1 : 1) solution, produced by addition of Na[OH] to 1 : 3.41 solution

Time	Percentage SiO_2 recovered as:						Total
t/min	Si_1	Si_2	Si_3	Si_4	Si_6	Si_8	(%)
0 *	35	7	3	3	6	3	57
5	55	25	11	6	4	0	101
10	58	24	10	6	4	0	102
60	56	22	11	8	6	0	103
2 880	60	22	10	7	4	0	103

* Sample taken immediately before addition of Na[OH]. Determinations made after 30, 120, 360, and 1 440 min agreed with the above.

TABLE 6

Distribution of low-molecular-weight species after addition of hydrochloric acid to 1 : 1 solutions

Time	Percentage SiO_2 recovered as: [a]						Total
t/min	Si_1	Si_2	Si_3	Si_4	Si_6	Si_8	(%)
(*a*) 0.1 mol dm^{-3} SiO_2: pH changed from 12.50 to 10.70 on addition of acid							
0 [b]	63	20	9	5	5	0	102
5	26	6	3	2	6	3	46
10	30	7	3	2	7	5	54
60	27	6	4	3	4	4	48
2 880	25	5	2	2	3	4	41
(*b*) 0.5 mol dm^{-3} SiO_2: pH changed from 13.08 to 11.00 on addition of acid							
0 [b]	35	14	10	9	16	0	84
5	8	2	1	1	<1	0	12
30	7	2	1	1	3	2	16
60	7	2	2	1	2	2	16
120	7	2	2	1	2	2	16
1 440	7	2	1	1	3	2	17

[a] Intermediate determinations at 30, 120, 300, and 1 440 min did not differ significantly. [b] Samples taken immediately before addition of acid.

Titration Experiments.—The rapid response of solutions to the changes described above makes it possible to study the changes that occur during the titration of sodium silicate solutions with acid. Figure 2 shows how the abundances of monomer, dimer, trimer, and cyclic tetramer vary with pH as a 0.1 mol dm^{-3} (1 : 1) solution is titrated with hydrochloric acid. The curves for Si_6 and Si_8 are omitted for clarity: the curve for the former lies very close to that for Si_4, and the latter was found only between pH 11.5 and 10.5. The maximum amounts of Si_6 and Si_8 were quite high, 9 and 7% respectively. Both Si_1 and Si_2 diminish steadily with falling pH, but the other species all show a slight increase in abundance before finally falling off as the pH falls. Below pH *ca.* 9 the only detectable low-molecular-weight species was Si_1. Visible gelling was noticed by pH *ca.* 7.5, as shown by the broken line, but the formation of colloidal silica must have begun well before that point. Figure 1 shows that by pH 10 the system is well within the instability region, in which the condition of rapid equilibration no longer applies.

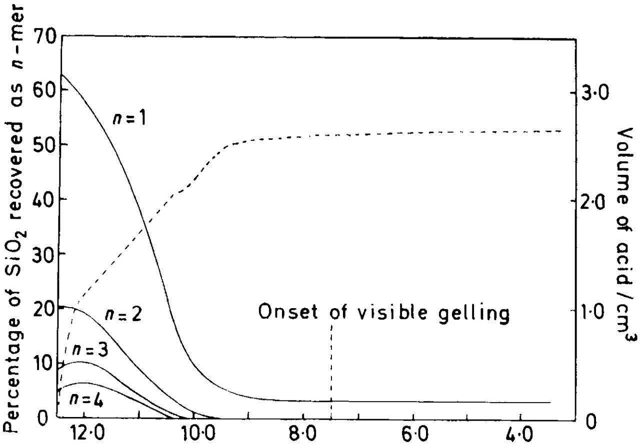


FIGURE 2 Effect of pH of 0.1 mol dm^{-3} sodium metasilicate. The titration curve is given by the broken line

Because the apparent maxima in Figure 2 exceed the initial values only by an amount comparable with the experimental error, the run was repeated using 0.5 mol dm^{-3} (1 : 1) solution; the results are shown in Figure 3. Here Si_1, Si_2, Si_3, and Si_4 all decrease with increasing pH; the Si_1 and Si_2 curves are concave, while the Si_3 and Si_4 curves are slightly convex, rather like those for Si_1 and Si_2 in Figure 2. The curves for Si_6 and Si_8 show distinct maxima around pH 12. The solution gelled at around pH 10.5, and at that point Si_1 was the only detectable low-molecular-weight species.

Thus the picture that emerges is that of an increase in degree of polymerisation with decreasing pH until gelling occurs. Monomer always remains *numerically* the most abundant species, but the main mass of silica is found progressively in more and more highly polymerised form as the pH falls, individual species rising to a maximum and then diminishing again as yet more highly condensed species form at their expense.

Ageing of Silicic Acid.—The two preparations, each 0.1 mol dm^{-3} in SiO_2, were sampled when freshly prepared and after ageing; the full-scale procedure was used, and the results are given in Table 7. The A series began from solid $Na_2H_2SiO_4{\cdot}8H_2O$ and the B series from 0.5 mol dm^{-3} (1 : 1) solution, this latter also being sampled (B0). Changes were relatively slow, in agreement with earlier work.[2-5,22,23]

The initial values obtained for the volatile species in the A series agree fairly well with those for 0.1 mol dm^{-3} (1 : 1) solutions both here (Table 6) and in earlier work,[12] although the silicic acid preparation seems rather higher in Si_6 and Si_8 content. The polysilicate seems to be rather more condensed than that derived from 0.1 mol dm^{-3} (1 : 1) solution,[12] values for which are given in parentheses: $\bar{N}_n$ 1.4 (1.2), $\bar{N}_w$ 2.2 (1.4), $N_{max.}$ 72 (13), and $\bar{Q}$ 2.2 (1.8). Alexander[20] reported $\bar{N}_n$ as 1.1 in a similarly prepared sample.

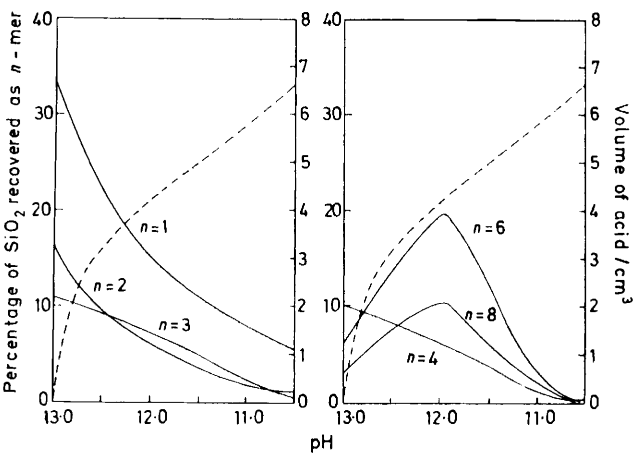


FIGURE 3 Effect of pH on 0.5 mol dm^{-3} sodium metasilicate. The titration curve is given by the broken line

TABLE 7

Species recovered from silicic acid preparation

(*a*) Yields

Solution no.	Ageing t/h	Percentage SiO_2 recovered as: Si_1	Si_2	Si_3	Si_4	Si_6	Si_8	Poly-silicate	Percentage lost in drying	Total (%)
A1	0	51	14	7	5	9	2	28	65	93
A2	72	15	1	0	0	0	0	56	14	70
B0		27	12	8	8	17	5	52	36	88
B1	0	28	8	4	4	14	2	62	35	97
B2	24	20	5	2	2	3	1	68	21	89
B3	48	17	4	2	1	2	1	38	14	52

(*b*) Average degree of polymerisation

	Polysilicate						Corrected	
Solution	$\bar{N}_n$	$\bar{N}_w$	$N_{max.}$	C (%)	H (%)	$\bar{Q}$	$\bar{N}_n$	$\bar{N}_w$
A1	4.6	5.6	72	31.2	7.9	2.2	1.4	2.2
A2	7.5	10.3	68	30.2	8.1	2.4	3.1	8.3
B0	3.8	4.2	26	31.8	8.2	2.1	2.1	3.0
B1	6.5	7.7	35	28.0	7.0	2.7	2.4	5.3
B2	6.1	8.7	125	27.9	7.3	2.7	2.8	6.7
B3	6.9	12.1	221	28.0	7.2	2.7	2.4	8.3

Solutions: A1, from $Na_2H_2SiO_4{\cdot}8H_2O$ when freshly prepared (0.1 mol SiO_2 per litre); A2, as A1 then aged for 72 h; B0, 0.5 mol dm^{-3} metasilicate solution; B1, 0.1 mol dm^{-3} SiO_2 from 0.5 mol dm^{-3} metasilicate when freshly prepared; B2, as B1 then aged for 24 h; B3 as B1 then aged for 48 h.

After ageing for 72 h at room temperature, the sample contained only monomer, a trace of dimer, and polysilicate. Some gel or colloidal material was also present, and since this is not extracted the total yield was reduced. About twice as much polysilicate was recovered as from the freshly prepared sample, and its molecular weight and $\bar{Q}$ value had both increased.

The results from the B series, in which 0.5 mol dm^{-3} (1 : 1) solution is simultaneously diluted and subjected to ion exchange, are harder to interpret. Comparison of the distribution of the volatile species from the original solution (B0) and the freshly prepared silicic acid (B1) suggest that the structure of the solution is preserved, but this is not borne out by the polysilicate results [Table 7(*b*)], which show a considerable change in the degree of polymerisation. With ageing, the amount of polysilicate increases slightly and then decreases, but its structure as shown by $\bar{N}_n$ and $\bar{Q}$ remains little changed. $\bar{N}_w$ and $\bar{N}_{max.}$ however increase steadily with age, while the total recovery drops, suggesting that colloidal silica is forming at the expense of the polysilicate. The amounts of volatile species also diminish steadily with ageing. Polysilicate thus behaves rather like the smaller intermediate species Si_6 and Si_8 in the titration experiment.

Differences in behaviour of the A and B series are most probably caused by the rather different distribution of species in the initial solutions. The results confirm that changes in solution at low pH are indeed comparatively slow.

Conclusions.—Despite the admitted limitations of the method of trimethylsilylation, it can be used to obtain significant information about the distribution of species in solution, and about changes in this. While recognising that the reaction itself may produce changes in the solution under test, rendering the results semi-quantitative rather than quantitative, we feel that the trends observed provide real information. For example it is difficult to believe that the maxima for certain species shown in Figures 2 and 3, or the trends observable in Table 7, can be due solely to an artefact introduced by the technique.

Bearing this in mind we can draw the following conclusions.

(1) In alkaline solutions above pH *ca.* 10, the attainment of equilibrium is rapid, unless the solutions contain particles of colloidal dimensions. Even in solutions that do contain such particles, the smaller species rearrange rapidly to produce quasi-equilibrium. These results are in accord with those of earlier workers.

(2) Solutions produced by dissolving anhydrous Na_2SiO_3 (which contains SiO_3 chains) are, within the shortest time that can be measured, identical with those produced by dissolving $Na_2H_2SiO_4\cdot8H_2O$ (which contains orthosilicate groups).

(3) In acid solutions at pH *ca.* 2 equilibrium is attained only very slowly. Again this is in accord with earlier work.

(4) As conditions in a solution are changed in the direction of increasing polymerisation, the amounts of a given polymerised species at first increase and subsequently decrease as successively more highly polymerised species form at its expense. Similar changes probably occur with time during the polymerisation of silicic acid at low pH.

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