

Polymerisation of the Silicate Anion in Acidic Solutions. Gelation and Trimethylsilylation Studies

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Summary Trimethylsilylation studies on silicic acid solutions, produced by hydrolysis of tetramethoxysilane, show that gel time is independent of the rate of disappearance of monomeric silicic acid.

THE results of ^{29}Si n.m.r. studies¹ showed a remarkable persistence of monosilicic acid at pH 3—4 despite the fact that gelation is known to be much more rapid here than at lower pH values. The accepted minimum in gel time occurs at pH 5—7 and the maximum at pH 1—3. Since the monosilicic acid used was prepared by hydrolysis of tetramethoxysilane, it seemed possible that the resulting high concentration of methanol might be a stabilising influence. This has stimulated further work employing trimethylsilylation techniques and gel-time investigations to determine what effect, if any, the presence of methanol has on the system.

The aim of the present series of experiments was to determine the effect of methanol on gel time under conditions similar to those used in the n.m.r. experiments and

to correlate both sets of results with the determination of low molecular weight species by the technique of trimethylsilylation.²

For gel-time investigations, tetramethoxysilane, $\text{Si}(\text{OMe})_4$, was mixed with HCl of various concentrations; after hydrolysis was complete (10 s—1 min) the pH was measured using a Radiometer Type B electrode with a calomel reference. The solutions, which were 1.5 M in SiO_2 , were stored at -13 , 4, and 20°C in screw-top jars. Gel time was taken to be when the meniscus did not remain horizontal on tilting the jar. The results are plotted in Figure 1, and show that the pattern produced is in accord with previous findings on different systems.³ At the time of writing the solutions between pH 1.5 and 2.5 at -13°C had not gelled, the maximum projected gel time being about 14 months.

Two solutions, prepared as above at pH 1.85 and 3.25, were stored at -13°C and sampled at intervals. Trimethylsilyl derivatives of low molecular weight species were prepared^{4,5} and examined by g.l.c. The results are plotted in Figure 2 and confirm the n.m.r. spectroscopy findings¹ that the low molecular weight species are more persistent at pH 3—4 than at pH 1—2.

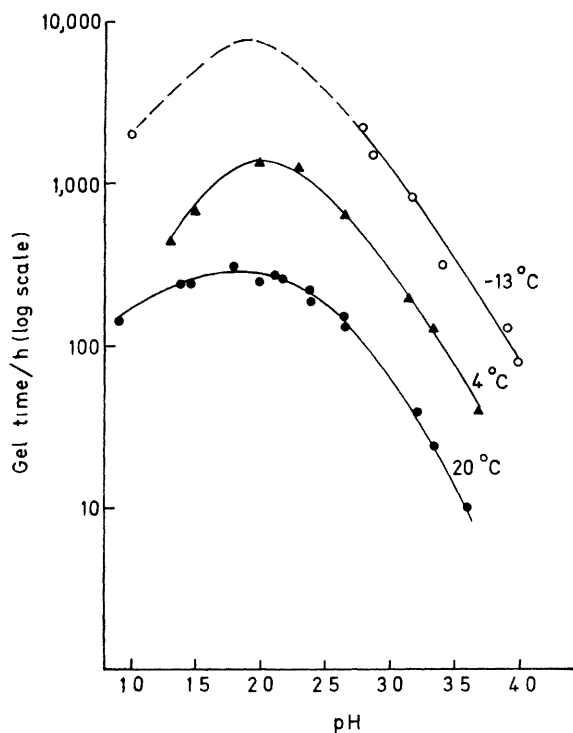


FIGURE 1 Gel time vs pH for 1.5 M SiO_2 solutions produced by acid hydrolysis of $\text{Si}(\text{OMe})_4$ at various temperatures. Dashed line represents probable extension of -13°C curve.

Since these solutions are directly comparable with those used for the gel-time studies, we conclude that there is no direct relationship between disappearance of monomeric silicic acid and production of silica gel. Although, at first sight, this conclusion seems startling, it is in accord with earlier theories of gelation such as that put forward by Carmen⁶ which suggested that gelation is not a simple, stepwise polymerisation process.

Solutions of silicic acid prepared from $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot 8\text{H}_2\text{O}$ by acid ion-exchange were also examined, both with and without the addition of 20% methanol. In the first few hours, the two solutions differed little in the concentration

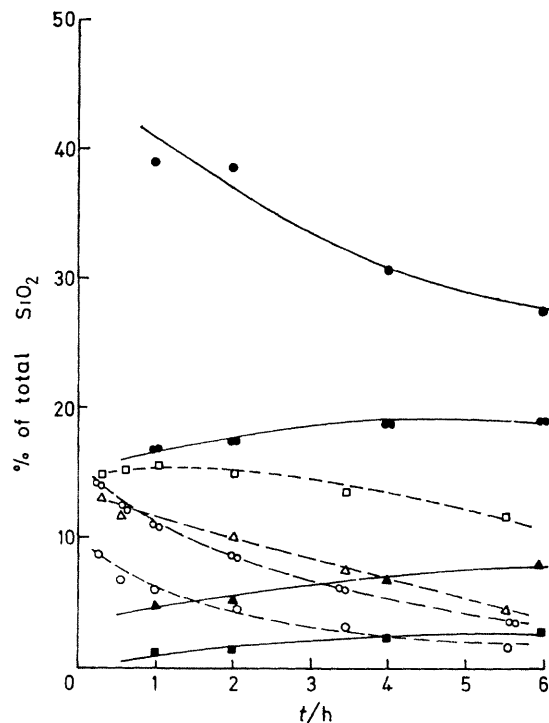


FIGURE 2 Change in low molecular weight species with time at -13°C for 1.5 M SiO_2 solutions produced as described in the caption to Figure 1 as determined by trimethylsilylation. --- pH 1.85 ——— pH 3.25 ○ monomer, ∞ dimer, Δ linear trimer, □ cyclic tetramer, at pH 1.85. Solid symbols for pH 3.25.

of low molecular weight species, but later stabilisation, especially of hexamer and larger species, was found in the methanolic solution, whose gel time was also prolonged compared with its aqueous equivalent. Despite these differences, the results do not conflict with the conclusion stated in the previous paragraph.

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