

Silicate Anions Formed in Tetramethylammonium Silicate Methanolic Solutions as Studied by ^{29}Si Nuclear Magnetic Resonance

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The $\text{Si}_8\text{O}_{20}^{8-}$ silicate anion is selectively formed in tetramethylammonium silicate methanolic solution from the SiO_4^{4-} silicate anion or at the expense of $\text{Si}_6\text{O}_{15}^{6-}$ and highly cross-linked polymeric silicate anions which are once formed.

Tetramethylammonium ions (N^+Me_4) are effective in forming selectively a silicate anion with the double four-membered ring structure ($\text{Si}_8\text{O}_{20}^{8-}$, cubic octamer) in methanolic silicate solution containing a small amount of water¹ as well as in aqueous silicate solution.²⁻⁶ In the methanolic system, the distribution of silicate species is simpler than that in the aqueous solutions. In our previous study on the system by the trimethylsilylation technique combined with g.l.c.,¹ only the monomer (SiO_4^{4-}) and the cubic octamer were detected, and other low-molecular weight species, such as the dimer and linear trimer, were not detected.

Since the high-molecular weight species cannot be detected by g.l.c., the structures of such species could not be ascertained in the previous study. Also, some side reactions which may occur during the trimethylsilylation have to be taken into account.^{7,8} In this study, ^{29}Si n.m.r. spectroscopy was employed for studying tetramethylammonium silicate methanolic solutions. Tetra-alkoxysilane has been used as a silica source, for its methanolic solutions consist of a single phase from the beginning of the preparation, which would make the discussion on the process of the singular formation of the cubic octamer simple and clear.

Figure 1 shows ^{29}Si n.m.r. spectra of the tetramethylammonium silicate methanolic solutions at an N/Si ratio (the molar ratio of tetramethylammonium ions to silica) of 1.0, a $\text{H}_2\text{O}/\text{Si}$ ratio (the molar ratio of water to silica) of 10.0 and SiO_2 concentrations of (a) 0.2, (b) 0.5, and (c) 1.0 mol dm^{-3} . The solutions were prepared by mixing 20% methanolic tetramethylammonium hydroxide solution, methanol, water, and tetramethoxysilane [$\text{Si}(\text{OMe})_4$], and stirring for 2 days at room temperature in closed vessels. Dried nitrogen gas was

passed in the vessel to avoid the influence of moisture. There are three kinds of peaks on the spectra. On the basis of the previous studies,^{3,5,6} a sharp peak at -99.2 p.p.m. [Figure 1 (b) and (c)] is assigned to the cubic octamer. In Figure 1 (a) a broad peak appears around -115 p.p.m. with a shoulder around -99 p.p.m. Since the sample holder was made of Teflon, the peak around -115 p.p.m. obviously may be attributed to the silica component in the sample. The broad peak around -115 p.p.m. is assigned to the Q^4 unit, that is, tetra-branching unit in the silicate structure, $\text{Si}(\text{OSi})_4$.⁹⁻¹¹ The shoulder around -99 p.p.m. is assigned to the Q^3 unit, tri-branching unit, $\text{Si}(\text{OSi})_3(\text{O}^-)$. As the cubic octamer consists of Q^3 units, the peak due to the cubic octamer may also be involved in the shoulder. However, the broadness of the shoulder would indicate that a number of types of Q^3 units are involved there. These facts are evidence for the presence of highly cross-linked polymeric species with uncontrolled structures in the solution at 0.2 mol dm^{-3} . No peaks due to low-molecular weight species are observed at all, indicating that silicate species are present as the cubic octamer and more polymeric species.

The intensity of the peak due to the cubic octamer increases and those due to the polymeric species decrease with increasing SiO_2 concentration. In the solution at 1.0 mol dm^{-3} , the peak due to the cubic octamer is dominant and those due to the polymeric species are hardly seen. It is assumed that the structure of the soluble silicate species is controlled by tetramethylammonium ions at higher SiO_2 concentrations, so that only the cubic octamer might be formed.

The peak around -115 p.p.m. is very strong in the solution

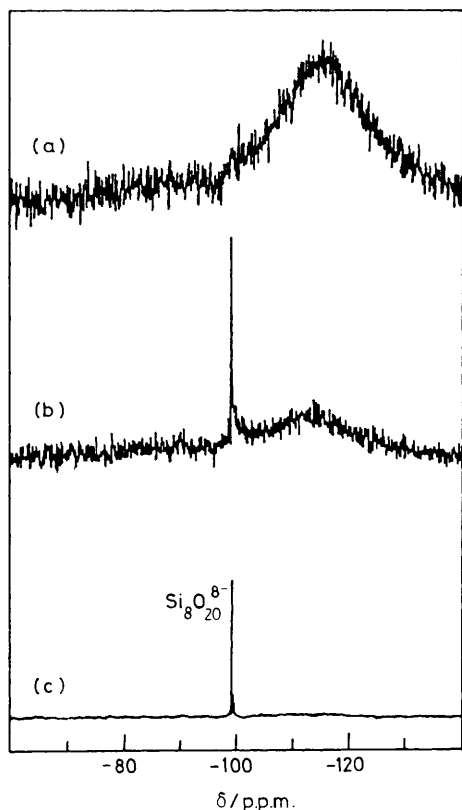


Figure 1. 79.42 MHz ^{29}Si n.m.r. spectra of the tetramethylammonium silicate methanolic solutions at an N/Si ratio of 1.0, a $\text{H}_2\text{O}/\text{Si}$ ratio of 10.0, and SiO_2 concentrations of (a) 0.2, (b) 0.5, and (c) 1.0 mol dm^{-3} , containing 5% v/v $[\text{}^2\text{H}_4]$ methanol to provide a deuterium field/frequency lock signal. The spectra were recorded on a JEOL GSX-400 spectrometer, using a pulse angle of 45° , a delay time of 5 s, and an acquisition time of 0.084 s. Chemical shifts are given with reference to an external sample of tetramethylsilane.

at 0.2 mol dm^{-3} . It should be noted that highly cross-linked polymeric species are formed in this solution, although the N/Si ratio is the same as that of the solution at 1.0 mol dm^{-3} , where no such species are formed. The change of the yield of the cubic octamer with the SiO_2 concentration may be attributed to the difference of the amount of OH^- ions. It is known that the polymerization behaviour of silicate species depends on the pH of the solution.¹² As the tetramethylammonium ion is added as a hydroxide and the N/Si ratio is fixed at 1.0, the amount of OH^- ions is less at lower SiO_2 concentrations. This suggests that the equilibrium of this system is mainly governed by tetramethylammonium ions and OH^- ions. It appears that, in the tetramethylammonium silicate methanolic solution at low SiO_2 concentrations, the effect of OH^- ions on the polymerization of silicate species is more dominant than that of the tetramethylammonium ion, resulting in the presence of highly cross-linked polymeric silicate species.

In the tetramethylammonium silicate aqueous solution at an N/Si ratio of 1.0 and a SiO_2 concentration of 0.2 mol dm^{-3} , low-molecular weight species are predominant.^{2,4} In the methanolic solution at the same N/Si ratio and SiO_2 concentration, however, highly cross-linked polymeric species are mainly present. The difference in the distribution of silicate species would suggest that methanol has an effect of increasing the degree of polymerization of silicate species and stabilizing the higher molecular weight species. Such an effect of methanol is also confirmed in acidic silicate solutions.¹³

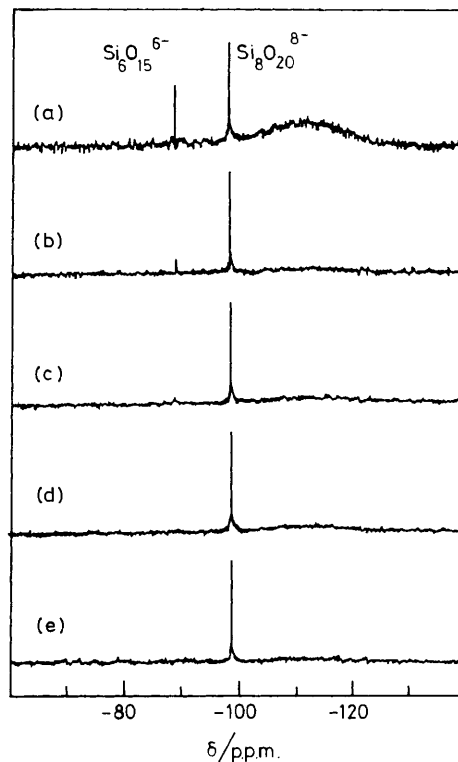


Figure 2. 79.42 MHz ^{29}Si n.m.r. spectra of the tetramethylammonium silicate methanolic solution at an N/Si ratio of 1.0, a $\text{H}_2\text{O}/\text{Si}$ ratio of 10.0, and a SiO_2 concentration of 1.0 mol dm^{-3} at (a) 15 min, (b) 1.5 h, (c) 3 h, (d) 4.5 h, and (e) 4 days from the preparation of the solution.

Figure 2 shows the change of ^{29}Si n.m.r. spectra with time for the tetramethylammonium silicate methanolic solution at an N/Si ratio of 1.0, a $\text{H}_2\text{O}/\text{Si}$ ratio of 10.0, and a SiO_2 concentration of 1.0 mol dm^{-3} . After mixing, the solution was stirred for 5 min and put into a Teflon sample tube. Figure 2 (a) shows the spectrum of the solution kept at 27°C for 10 min after the mixing. A new peak appears at -89.6 p.p.m. which may be assigned to a silicate anion with the double three-membered ring structure ($\text{Si}_6\text{O}_{15}^{6-}$, prismatic hexamer).^{3,5,6,14} The intensity of this peak is *ca.* 60% of that of the peak due to the cubic octamer. The peaks due to low-molecular weight species are not seen in this figure, suggesting that the hydrolysis and polycondensation of tetramethoxysilane proceed abruptly.

After 1.5 h in the sample tube, the intensity of the peak due to the prismatic hexamer obviously decreases as is seen in Figure 2 (b), and the peak almost disappears after 3 h [Figure 2 (c)]. The intensities of the peaks due to the polymeric species also decrease, while that due to the cubic octamer increases, meaning that the selective formation of the cubic octamer proceeds with time. Briefly, the prismatic hexamer and highly cross-linked polymeric species which are initially formed are consumed to form the cubic octamer.

It was reported¹⁵ that the prismatic hexamer was present together with some oligomeric silicate species in the course of the formation of the cubic octamer during the re-establishment of the equilibrium in the tetramethylammonium silicate aqueous solution at an N/Si ratio of 2.0 and a SiO_2 concentration of 1.0 mol dm^{-3} kept at 20°C after being heated to boiling and then cooled. In the methanolic solution, the presence of the prismatic hexamer is also confirmed. This

suggests that the prismatic hexamer may be an intermediate in the selective formation of the cubic octamer. In our previous study on the methanolic solutions by the trimethylsilylation technique,¹ the presence of prismatic hexamer could not be confirmed clearly, probably because side reactions during the trimethylsilylation in the method of Lentz⁷ destroyed the prismatic hexamer.

The formation of the cubic octamer starts very abruptly, as seen in Figure 2 (a) and described previously.¹ This means that the cubic octamer is also formed directly in the course of the hydrolysis and polycondensation of tetramethoxysilane. The intensities of the peaks due to highly cross-linked polymeric species decrease and that due to the cubic octamer increases with time. No peaks due to low-molecular weight species are observed during the changes. These findings indicate that the polymeric species once formed are degraded and reformed only into the cubic octamer but not into low-molecular weight species.

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