The Unexpectedly Slow Approach to Thermodynamic Equilibrium of the Silicate Anions in Aqueous Tetramethylammonium Silicate Solutions

C. T. G. Knight,[a] R. James Kirkpatrick,[b] and Eric Oldfield[a]*

[a] *School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801, U.S.A.*

[b] *Department of Geology, University of Illinois at Urbana-Champaign, 1301 West Green Street, Urbana, IL 61801, U.S.A.*

Contrary to the widely accepted picture of the dynamics of alkaline silicate solutions, tetramethylammonium silicate solutions require many days to re-establish thermodynamic equilibrium following a perturbation, as monitored by ^{29}Si n.m.r. spectroscopy.

Aqueous alkaline silicate solutions are now known to contain a variety of low molecular weight silicate anions in dynamic equilibrium.[1,2] In early studies it was widely believed that concentrated solutions required many days for their constituents to reach thermodynamic equilibrium following a perturbation, such as dilution or a change of pH.[3] Lagerström[4] in 1959 demonstrated that this notion is only correct for solutions that were in, or had passed through, an 'instability range,' characterised by an alkali to silica ratio low enough to allow colloidal silica to exist. Equilibrium is attained 'very rapidly' for solutions whose composition places them outside this range. His findings have since been confirmed by several workers,[5] and recently Dent-Glasser and Lachowski,[6] using trimethylsilylation followed by chromatographic separation, showed that sodium silicate solutions had returned to equilibrium within five minutes of being diluted, or undergoing a change in pH. Furthermore, Harris *et al.*[7] have used ^{29}Si n.m.r. spectroscopy to demonstrate that a very concentrated (7 M) sodium silicate solution reaches equilibrium within the time (1 h) taken to record its spectrum and, moreover, that the effects of heating a silicate solution are entirely reversible, again within the time required to record the spectrum. However, once the solution has reached equilibrium, chemical exchange between its constituents appears to be slow, and magnetisation transfer ^{29}Si n.m.r. experiments[8] give rate constants of the order of 0.5 kg mol^{-1} s^{-1} and a free energy of activation of 93 kJ mol^{-1} for the dimerisation of the orthosilicate anion in a 2.8 mol kg^{-1}, 3.8 : 1 (K : Si) potassium silicate solution.

In recent years, considerable interest has been shown in alkaline silicate solutions prepared with an organic base, not least because of their role in zeolite synthesis.[9] Tetramethylammonium silicate solutions, in particular, have received much attention, since it is believed[10] that they may be, under some conditions, almost molecularly homogeneous, containing primarily the double four-membered (cubic octameric) silicate ring anion,[11,12] $[Si_8O_{20}]^{8-}$. Implicit in these investigations is the belief that, like their alkali-metal analogues, equilibrium between the anionic species in tetramethylammonium silicate solutions is rapidly established. We demonstrate

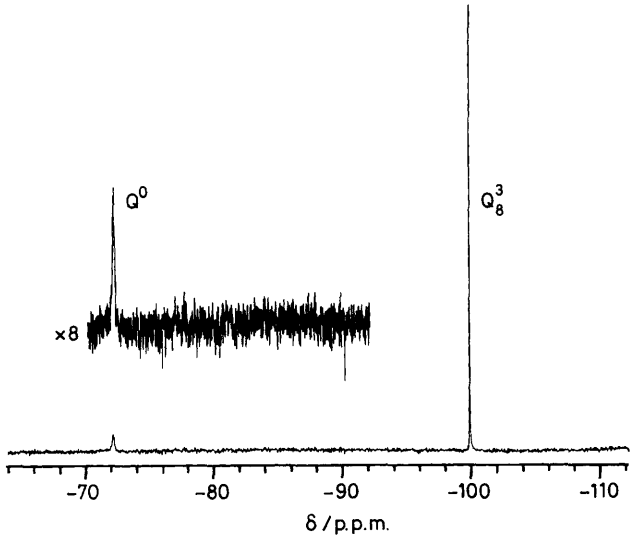

Figure 1. 99.32 MHz (11.7 Tesla) ^{29}Si n.m.r. spectra of a tetramethylammonium silicate solution that is 1 M in SiO_2, with a Si : N ratio of 1 : 2, at 20 °C, obtained 16 days after sample preparation. 20% v/v [$^2H_4$]methanol was added to provide a deuterium field/frequency lock signal. The spectrum was recorded using a sweep width of 5000 Hz and required 451 × 30° (14 μs) pulses. The acquisition time was 1.64 s and the interpulse delay was 20 s. Chemical shifts are given with reference to an external sample of tetramethylsilane, high frequency (paramagnetic, deshielded, low field) signals being denoted as positive (δ scale). Accuracies are ±0.005 p.p.m.

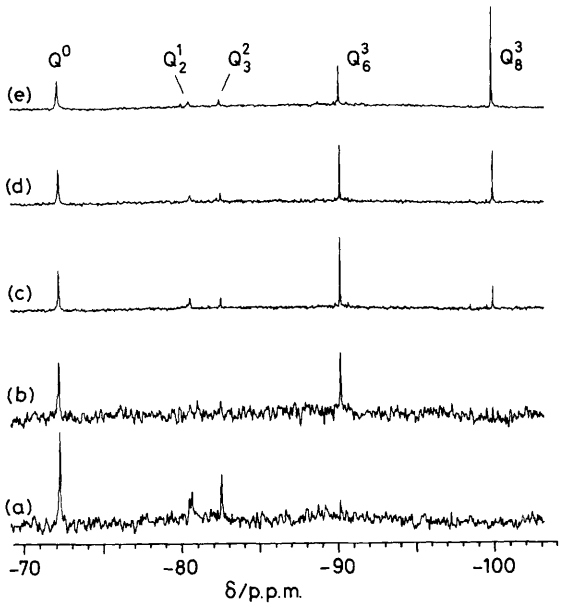

Figure 2. 99.32 MHz (11.7 Tesla) ^{29}Si n.m.r. spectra of the tetramethylammonium silicate described in the caption of Figure 1 as a function of time after heating to boiling, followed by quenching. All the spectra were recorded using the same spectral parameters as those given in Figure 1, with the exception that spectra (a) and (b) required 16 pulses, spectra (c) and (d) required 260 pulses and spectrum (e) required 555 pulses. The time referred to is that between re-equilibrating the sample to 20 °C and the end of spectral acquisition. For spectrum (a) this was 5 min, for spectrum (b) 2 h 7 min, for (c) 4 h 36 min, for (d) 16 h 48 min, and for (e) 45 h. The Q symbol refers to the tetrahedral SiO_4^{4-} unit, the superscript indicating the number of other Q units directly attached, and the subscript indicating the number of such Q sites in the molecule. The extent of protonation is ignored. Thus Q^0 is the monomeric unit, Q^1_2 is the dimer, Q^2_3 is the cyclic trimer, Q^3_6 is the prismatic hexamer, and Q^3_8 is the cubic octamer.

below that this is not necessarily the case, and that equilibrium may be approached very slowly, even for solutions well outside the 'instability range'.

We show in Figure 1 the 99.32 MHz (11.7 Tesla) ^{29}Si n.m.r. spectrum of a tetramethylammonium silicate solution, 1 M in SiO_2, with a Si : N ratio of 1 : 2, obtained 16 days after the sample was prepared. Sample preparation details are given elsewhere.[11] In agreement with previous work,[11,12] the intense low frequency signal is attributed to the cubic octameric cage silicate, and the weak high frequency signal is attributed to the monomeric SiO_4^{4-} unit. (Throughout the following discussion, the spectral assignments used are based on those given by Harris and Knight[13] for a potassium silicate solution.) After the spectrum was recorded, the sample was heated to boiling for *ca.* 30 s in a polyethylene tube, quenched in liquid nitrogen, then allowed to reach room temperature and returned to the n.m.r. tube. The sample always appeared monophasic on thawing, and silica precipitation was not observed. Successive n.m.r. experiments [Figure 2, (a)–(e)] reveal the following. (i) During the first few minutes after thawing, the solution contains primarily monomeric silicate anions [Figure 2(a)], together with a small amount of the dimeric and cyclic trimeric species. The cubic octameric cage is *not* observed. (ii) The prismatic hexameric cage is the next species formed, followed, after several hours, by the cubic octameric cage [Figure 2, (b)—(d)]. (iii) The concentration of the cubic cage gradually increases at the expense of the other anions present. However, after almost two days at 20 °C this structure still accounts for less than 50% of the silica in solution, as shown in Figure 2(e), and the equilibrium situation is only re-established after several weeks.

We believe that this slow anion rearrangement in tetramethylammonium silicate solutions has not been appreciated prior to this work, and indicates the necessity of considering solution history, as well as composition, when analysing the structure and stability of its components.

The work was supported in part by the U.S. National Science Foundation Solid-State Chemistry Program, by the Texaco Corporation, and by the Mobil Foundation.

Received, 15th July 1985; Com. 1017

References

1 R. K. Iler, 'The Chemistry of Silica,' Wiley, New York, 1979.
2 'Soluble Silicates,' ed. J. S. Falcone, American Chemical Society Symposium Series, 1982, vol. 194.
3 J. G. Vail, 'Soluble Silicates,' Reinhold, New York, 1952, vol. 1, p. 98.
4 G. Lagerström, *Acta Chem. Scand.*, 1959, **13**, 722.
5 N. Ingri, *Acta Chem. Scand.*, 1959, **13**, 758; T. L. O'Connor, *J. Phys. Chem.*, 1961, **65**, 1; J. F. Hazel, *J. Colloid. Sci.*, 1962, **17**, 162; A. J. Walker and N. Whitehead, *J. Appl. Chem.*, 1966, **16**, 230; W. Stumm, H. Huper, and R. L. Champlin, *Environ. Sci. Technol.*, 1967, **1**, 221.
6 L. S. Dent-Glasser and E. E. Lachowski, *J. Chem. Soc., Dalton Trans.*, 1980, 393.
7 R. K. Harris, J. Jones, C. T. G. Knight, and R. H. Newman, *J. Mol. Liq.*, 1984, **29**, 63.
8 C. J. Creswell, R. K. Harris, and P. T. Jageland, *J. Chem. Soc., Chem. Commun.*, 1984, 1261.
9 B. M. Lok, T. R. Canaan, and C. A. Messina, *Zeolites*, 1983, **3**, 282.
10 D. Hoebbel and W. Wieker, *Z, Anorg. Allg. Chem.*, 1971, **384**, 43.
11 R. K. Harris and C. T. G. Knight, *J. Mol. Struct.*, 1982, **78**, 273.
12 D. Hoebbel, G. Garzó, G. Engelhardt, and A. Vargha, *Z. Anorg. Allg. Chem.*, 1982, **494**, 31.
13 R. K. Harris and C. T. G. Knight, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1525; 1983, **79**, 1539.