Investigation of Aqueous Sodium Metasilicate Solutions by ^{29}Si N.m.r. Spectroscopy

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Summary The presence of a variety of polysilicates, including branched chain species, in aqueous sodium metasilicate solutions has been shown by ^{29}Si n.m.r.

Most of the early work on aqueous sodium metasilicate ($SiO_2/Na_2O = r = 1$) solutions[1] leads to the conclusion[2] that the silicate species is entirely monomeric. However their Raman spectra show a band which has been attributed to a polymeric species,[3] and trimethylsilation experiments[4] indicate that besides the monomer there are substantial amounts of the dimer, linear trimer, cyclic tetramer, and other unidentified polymers. We now report ^{29}Si n.m.r. spectra which provide new information about the nature of the polymeric species in metasilicate solutions.

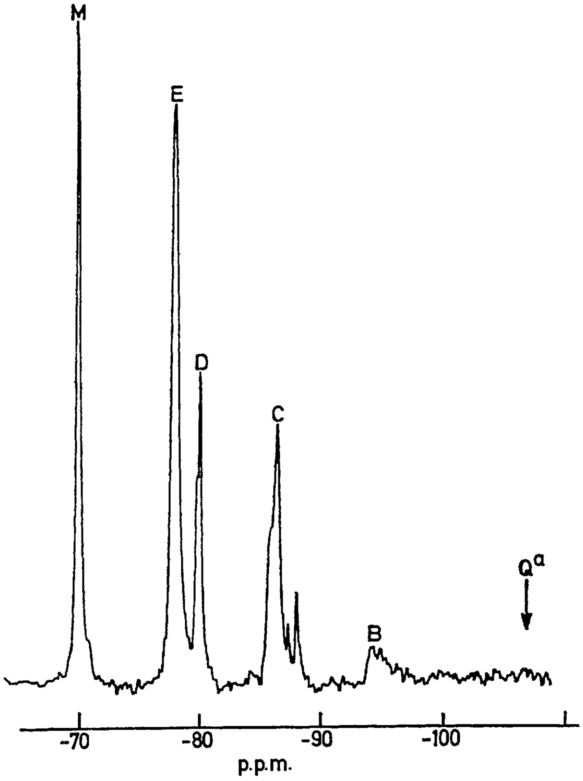

FIGURE. ^{29}Si F.T. n.m.r. spectrum at 19·9 MHz of 1·35 mol dm^{-3} Na_2SiO_3 ($r = 1$) at 26° (66430 transients, $\pi/2$ pulse, repetition rate 0·8 s). For identification of resonances see text. The relative peak areas are not proportional to Si concentrations. [a] Position of resonance observed for solutions with high SiO_2/Na_2O ratios, e.g. $r = 3{\cdot}8$ (see text), but not for metasilicate ($r = 1$) solutions.

Measurements were made at 26° using 10 mm outside diameter n.m.r. tubes and a Varian XL-100 spectrometer operating in the Fourier Transform mode at 19·9 MHz. Sodium metasilicate solutions ($r = 1$) were prepared from carefully recrystallised $Na_2SiO_39H_2O$ and those with $r \neq 1$ from the appropriate amounts of Analar NaOH and pure SiO_2 powder In all cases the solutions were made up with distilled water to which was added $D_2O(15\%)$ for use as an internal lock and were filtered through a 0·2 μm filter. Care was taken to prevent the ingress of impurities such as CO_2 which would disturb the pH and possibly cause formation of colloidal silica.

A typical sodium metasilicate solution spectrum is shown in the Figure. The relative magnitudes of the peaks show a small variation with concentration and it follows that these solutions contain a variety of silicate species. The spectra are consistent with previous work[4] which suggests that these species are polysilicates in which each Si atom is bound tetrahedrally to four oxygen atoms each of which can form a bond with another Si atom. The narrow low field peak (M) is the only one which remains when the SiO_2/Na_2O ratio r is reduced to 0·16 but it is almost completely absent from solutions with $r > 3$ and it is therefore considered to arise from monomeric species. Similar observations of the variation of relative peak areas with r show that peaks (E) and (D) belong to end group Si atoms (*i.e.* those linked *via* oxygen to one other silicon) and that peak (D) is most probably that of the dimer; that the cluster of peaks (C) is due to chain silicons (*i.e.* those linked by oxygens to two other silicon atoms) and that the small group (B) is due to branching silicons (*i.e.* those linked by oxygens to three other Si atoms). The resonances all lie upfield of that for Me_4Si and the shifts of (M), (E), and (D) relative to Me_4Si are $-70{\cdot}4$, $-78{\cdot}4$, and $-80{\cdot}4$ p.p.m. respectively. The shifts of the three resonances in cluster (C) are $-86{\cdot}7$, $-87{\cdot}6$, and $-88{\cdot}4$ p.p.m. and that of the main peak in cluster (B) is $-94{\cdot}4$ p.p.m. The general pattern is similar to that observed in the ^{31}P n.m.r. spectra of polyphosphates[5] in which the resonance of the chain group phosphorus lies 10 p.p.m. upfield of that of the end groups.

These observations show that ^{29}Si n.m.r. provides a powerful new method for the investigation of soluble silicate solutions and suggest that its use to elucidate the structures present in water glasses should prove worthwhile. Preliminary measurements on a solution with $r = 3{\cdot}8$ suggest that the polymeric species in water glasses have fewer end groups and more branching and chain silicons than those found in solutions with lower SiO_2/Na_2O ratios. Especially important is the detection of a broad peak (Q) with a chemical shift of -107 p.p.m., which is believed to be due to Si atoms linked to four others since its shift lies between those[6] for silica (-113 p.p.m.) and the central atom of $(Me_3SiO)_4Si$ (-101 p.p.m.).

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