A Two-dimensional Silicon-29 Nuclear Magnetic Resonance Spectroscopic Study of the Structure of the Silicate Anions present in an Aqueous Potassium Silicate Solution

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The results of two-dimensional silicon-29 n.m.r. homonuclear correlation spectroscopy (COSY) experiments performed on a nominally 1.5 mol dm^{-3}, 1 : 1 potassium silicate solution prepared with isotropically enriched $^{29}SiO_2$ are consistent with the simultaneous presence of 22 silicate anions in solution. These include all of the species proposed in earlier double resonance studies. The results suggest that the additional species are silicate cages containing mixtures of both Q^2 and Q^3 groups in four-membered rings, and possible structures are discussed.

The structure of the silicate anions present in aqueous alkaline silicate solutions has long been the subject of debate.[1] Techniques of chemical analysis such as trimethylsilylation[2] and reactions with molybdic acid[3] have, until recently, provided the bulk of the information available, but it has long been appreciated that some structures thus identified may arise solely from unwanted side reactions occurring during the analytical processes.[2,4] More recently, ^{29}Si n.m.r. spectroscopy has been applied with some success to the elucidation of the structure of the silicate anions in solutions,[5–7] although the chemical likelihood of some of the species proposed has never been firmly established.[6] In addition, many resonances in the ^{29}Si n.m.r. spectra of more concentrated solutions remain unassigned.

In this work an attempt is made to confirm some of the more tentative assignments given earlier,[6] as well as to identify novel structures, using ^{29}Si n.m.r. homonuclear correlation spectroscopy (COSY) experiments performed on a ^{29}Si isotopically enriched potassium silicate solution.

Experimental

The solution used was prepared by dissolving $^{29}SiO_2$, enriched to 95.3% in ^{29}Si and obtained from Oak Ridge National Laboratories (Oak Ridge, TN, U.S.A.), in deuterium oxide, to which Ultrapure potassium hydroxide (Alfa Chemicals, Danvers, MA) has been added. The sample was heated to boiling in a Teflon container to facilitate dissolution of the $^{29}SiO_2$. This was, however, never completely achieved, and consequently the silicon concentration and K:Si ratio are estimates. The sample was stored in a polyethylene bottle under nitrogen when not in use.

All n.m.r. spectra were recorded on a 'home-built' 11.7-T spectrometer, operating at 99.32 MHz for ^{29}Si and using 10-mm sample tubes. Further details are given elsewhere.[8] Spectral parameters are given in the appropriate Figure captions.

Results and Discussion

Using a combination of high-field ^{29}Si n.m.r. spectroscopy, isotopic enrichment, and homonuclear ^{29}Si-$\{^{29}Si\}$ decoupling, Harris and Knight[6] determined, with varying degrees of certainty, the structures of eighteen silicate anions in an aqueous potassium silicate solution. In 1984, Harris *et al.*[7] confirmed the existence of some of these structures using ^{29}Si n.m.r. homonuclear correlation spectroscopy (COSY) but fell short of providing supporting evidence for the more esoteric (and questionable) anions originally proposed. This was largely a result of the poor signal-to-noise ratio of the COSY experiment, which was performed on a 9.4-T (400-MHz ^1H) instrument, resulting in difficulties in interpretation. Indeed, Harris *et al.*[7] concluded that: 'Further progress ... requires an improvement in S/N and reliability for the COSY experiment. We believe this might come about within a few years, but the results presented here are achieved at the limits of current technology.'

I felt that such signal-to-noise ratio problems might be partially alleviated by using a more concentrated sample and performing the experiment at an even higher field strength (11.7 T, 500-MHz ^1H). The resulting spectra are entirely consistent with the presence of all of the species originally proposed,[6] and indicate the presence of four additional anions in this solution. It should be noted, however, that in this sample much of the intensity arises from rather broad signals, often coincident with the sharper peaks, which show little or no multiplet structure, and which do not give rise to cross peaks in the COSY spectrum. This may be because of short T_1 and T_2 relaxation times, or because they contain interconnected silicon sites with similar chemical shift values, giving cross peaks very close to the diagonal, or that the rather severe filtering function required by the two-dimensional experiment effectively removes broad resonances and their cross peaks from the spectrum. The width of the resonance lines, however, indicates that the signals may arise from large, motionally hindered molecules, perhaps of colloidal dimensions, and reinforces the view that structural analysis by ^{29}Si n.m.r. spectroscopy is at present effectively limited to the smaller silicate anions present in solution.

Figure 1 shows the results of a ^{29}Si n.m.r. COSY experiment performed upon the nominally 1.5 mol dm^{-3}, 1:1 isotopically enriched potassium silicate solution, at 22 °C, together with the conventional ^{29}Si n.m.r. spectrum recorded under the same conditions.

Under conditions of full isotopic enrichment, the ^{29}Si n.m.r. signals of species containing only a single silicon site, such as the monomer, dimer, cyclic and regular cage structures, remain as single peaks. Signals from all other species will be split by scalar spin–spin coupling to give characteristic spin multiplets. It is clear from Figure 1 that at least five such singlets occur in the spectrum, in addition to the resonance of the monomer, which lies 8.59 p.p.m. to high frequency of the signal of the dimer, and is not illustrated. By comparison with previous work,[5,6] it is easy to identify the four high-frequency signals as those of the dimer (Q^1_2), the cyclic trimer (Q^2_3), the cyclic tetramer (Q^2_4) and the prismatic hexamer (Q^3_6), in order of decreasing resonance frequency (where Q represents a quadrifunctional silicate unit and the superscript indicates the number of directly attached siloxy linkages). The lowest-frequency singlet has recently been assigned by Kinrade and Swaddle[9] to the

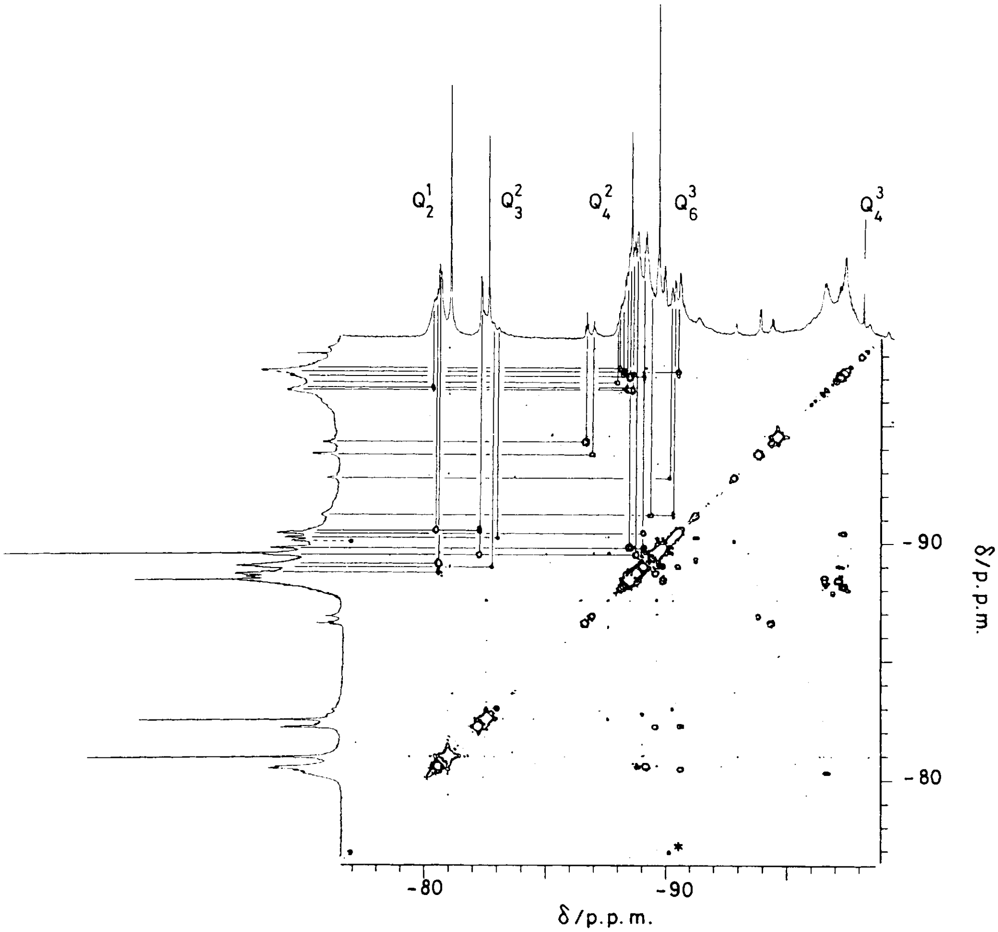

Figure 1. The 99.3-MHz ^{29}Si two-dimensional homonuclear correlation (COSY) n.m.r. spectrum of a nominally 1.5 mol dm^{-3}, 1:1 (K:Si) potassium silicate solution at 22 °C shown in the form of a contour plot. The sample was prepared in deuterium oxide to provide an internal field-lock signal. The experiment was performed using sixteen-step phase cycling and n-type peak selection. The spectral width in each dimension is 2 200 Hz, obtained from 1 024 t_1 points, using 16 transients for each point and a recycle delay of 7 s. A sine-bell filtering function was applied in both dimensions and the data set has been 'symmetrized'. The weak cross peaks coincident with the centre of the spectrum are considered to be artifacts. The signal assigned to site M of structure (**11**) (see Figure 2) is folded into the spectrum, and the cross peak arising from this is marked with an asterisk. The diagonal peak at $\delta = -94.5$ p.p.m. is due to the folded signal of the monomeric anion, Q^0. The conventional spectrum shown above and to the left of the contour plot required 479 40-μs (90°) pulses, with a recycle delay of 10 s. The spectrum was recorded using a sweep width of 3 kHz, although only the low-frequency portion is illustrated. An exponential line-broadening function of 0.9 Hz has been applied

tetrahedral tetramer (Q^3_4), on the basis of its chemical shift and T_1 relaxation dependence on temperature. Assignment of the remaining signals to specific silicate anions is greatly facilitated by the connectivity data shown in the COSY contour plot of Figure 1. Since ^4J coupling can be ignored in these systems,[6,7] the cross peaks apparently indicate silicate sites that are linked by a single Si–O–Si bond. Unfortunately, silicate solutions of this concentration and pH give somewhat broadened ^{29}Si n.m.r. resonances compared to more dilute solutions, and this, combined with the congested nature of the spectrum, renders in many cases the resolution of individual spin-multiplet patterns difficult or impossible. Consequently, structural assignments are based entirely upon the connectivity data obtained from the COSY experiments and the chemical shift of the silicate site, and therefore the structures proposed must be regarded as tentative solutions to these connectivity and chemical shift data. Nevertheless, I believe that the data shown in Figure 1 provide evidence for sixteen 'multisite' silicate anions, in addition to the six single-site species already mentioned. Their structures are shown in Figure 2, and the assigned ^{29}Si n.m.r. spectrum is shown in Figure 3. The Table lists the chemical shifts of the sixteen species shown in Figure 2, together with that of the six single-site structures.

The COSY spectrum provides connectivity data which are completely consistent with all of the species proposed by Harris and Knight[6] [species (**1**)—(**12**)], with the possible exception of the substituted cyclic tetramer [species (**12**)]. This structure requires a cross peak between its two chemically distinct Q^2 groups, in a position too close to the diagonal to resolve easily. The two other cross peaks required by the structure are, however, clearly visible, and I consequently include it in the assignments. The data provide particularly convincing evidence in favour of species (**11**), which has been regarded with some scepticism,[6] as well as revealing the chemical shift of site X of species (**10**), which had not been previously observed.

Species (**13**) has not been proposed elsewhere. It is included since it fulfils both chemical shift and connectivity requirements, and appears chemically reasonable. It is, moreover, consistent with results from earlier $^{29}Si\text{-}\{^{29}Si\}$ homonuclear decoupling experiments[6] (peaks 17, 24, 32, and 41 in ref. 6) once the

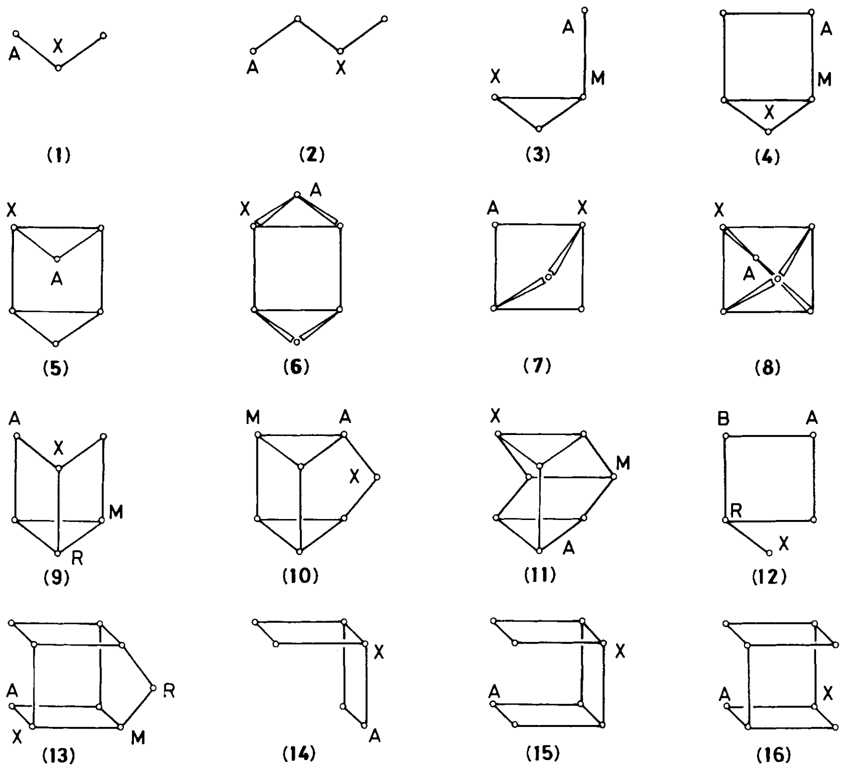

Figure 2. Representation of the sixteen silicate anion structures thought to be present in a nominally 1.5 mol dm^{-3}, 1 : 1 potassium silicate solution. The open circles represent silicon atoms and the solid lines represent a silicon–oxygen–silicon linkage. The diagrams are drawn so as to illustrate the connectivities within each anion, and are not intended to show the overall morphology of the molecule. A, X, M, R, and B are spin labels

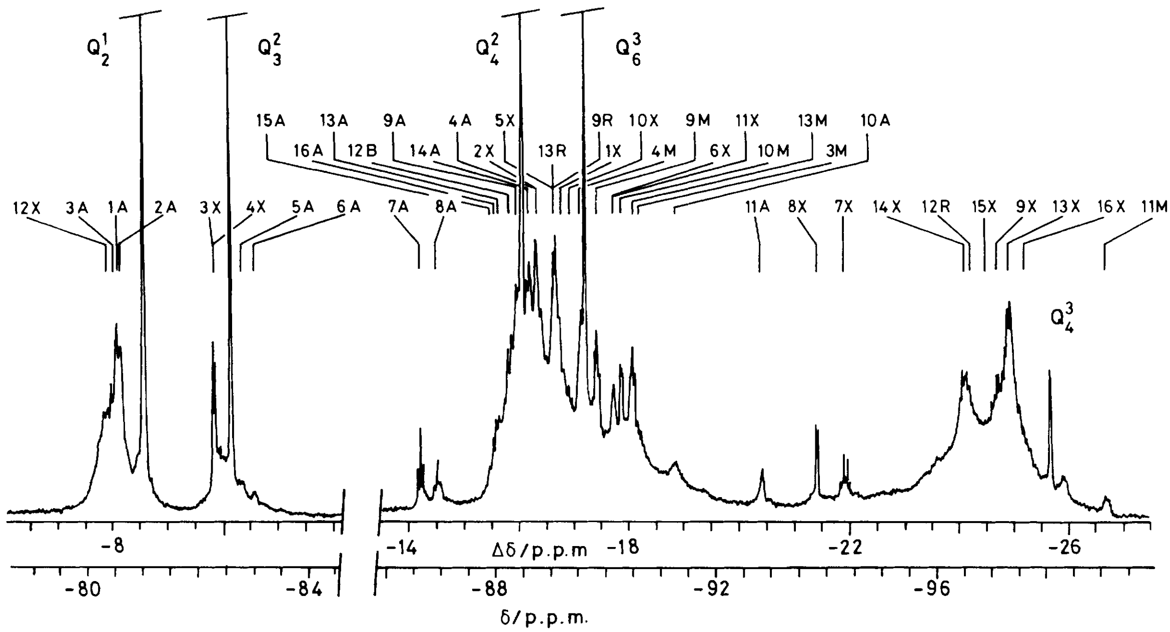

Figure 3. A portion of the 99.3-MHz ^{29}Si n.m.r. spectrum of a nominally 1.5 mol dm^{-3}, 1 : 1 (K:Si) potassium silicate, enriched to 95.3% in ^{29}Si, at 22 °C. The spectrum is that shown above and to the left of the COSY contour plot in Figure 1, and the assignments refer to the structures shown in Figure 2. The lower scale is relative to the ^{29}Si n.m.r. signal of an external solution of tetramethylsilane, 50% (v/v) in $(CD_3)_2CO$ (δ scale); the upper scale is relative to the signal of the monomeric, Q^0, anion (Δδ scale), which resonates at $\delta = -72.417$ p.p.m. in this solution, and is not shown in the Figure

Table. The chemical shift values of the silicate anions tentatively identified in a 1.5 mol dm^{-3}, 1:1 potassium silicate solution, at 22 °C, referenced to the monomer, which lies at $\delta = -72.417$ p.p.m. from the ^{29}Si n.m.r. signal of tetramethylsilane in a 50:50 (v/v) solution of $(CD_3)_2CO$

Species	Site	Δδ/p.p.m.
Monomer	Q^0	0.000
Dimer	Q^1_2	-8.59_3
Cyclic trimer	Q^2_3	-10.17_6
Cyclic tetramer	Q^2_4	-16.09_1
Prismatic hexamer	Q^3_6	-17.22_1
Tetrahedral tetramer[a]	Q^3_4	-25.69_4
(**1**) Linear trimer	Q^1(A)	-8.15_6
	Q^2(X)	-16.7[b]
(**2**) Linear tetramer	Q^1(A)	-8.3[b]
	Q^2(X)	-16.4[b]
(**3**) Substituted cyclic trimer	Q^1(A)	-8.06_4
	Q^2(X)	-9.86_5[c]
	Q^3(M)	-18.22_0
(**4**) Bicyclic pentamer	Q^2(X)	-9.86_5[c]
	Q^2(A)	-16.3[b]
	Q^3(M)	-17.16_1
(**5**) Tricyclic hexamer (cisoid)	Q^2(A)	-10.36_7
	Q^3(X)	-16.6[b,c]
(**6**) Tricyclic hexamer (transoid)	Q^2(A)	10.60_3
	Q^3(X)	-17.8[b]
(**7**) Bridged cyclic tetramer	Q^2(A)	-14.22_3
	Q^3(X)	-21.94_1
(**8**) Doubly bridged cyclic tetramer	Q^2(A)	-14.52_2
	Q^3(X)	-21.43_1
(**9**) Tricyclic hexamer	Q^2(A)	-16.0[b]
	Q^3(R)	-16.6[b,c]
	Q^3(M)	-17.46_0
	Q^3(X)	-24.72_3
(**10**) Pentacyclic heptamer	Q^2(X)	-16.92_9
	Q^3(M)	-17.89_9
	Q^3(A)	-18.88_8
(**11**) Hexacyclic octamer	Q^3(X)	-17.8[b]
	Q^3(A)	-20.42_4
	Q^3(M)	-26.72_4
(**12**) Substituted cyclic tetramer	Q^1(X)	-7.9[b]
	Q^2(B)	-15.84_4
	Q^2(A)	*d*
	Q^3(R)	-24.2[b]
(**13**) Pentacyclic nonamer	Q^2(A)	-15.7[b]
	Q^2(R)	-16.6[b,c]
	Q^3(M)	-18.10_6
	Q^3(X)	-24.9[b]
(**14**) Bicyclic hexamer	Q^2(A)	-16.2[b]
	Q^3(X)	-24.1[b]
(**15**) Tricyclic octamer	Q^2(A)	-15.5[b]
	Q^3(X)	-24.5[b]
(**16**) Tricyclic octamer	Q^2(A)	-15.6[b]
	Q^3(X)	-25.2[b]

[a] Assignment according to ref. 9. [b] Chemical shift value taken from the COSY experiment alone, the centre of the multiplet being difficult or impossible to locate in the conventional spectrum. The value is therefore less accurate. [c] Signal arising from coincident multiplets. [d] Unidentified.

concomitant effects of irradiating nearby signals are taken into account.

Finally, I believe that the results indicate the presence of three more silicate anions. Although it is impossible to be sure of their structure on the basis of the COSY experiment alone, it appears that each contains only two sites, one of which lies in the region ascribed to Q^2 groups in four-membered rings while the other falls in the spectral region attributed to Q^3 groups in four-membered rings. Species (**14**)—(**16**) are offered as (necessarily tentative) examples of this type of structure, whilst noting of course that any species containing an approximately equal number of interconnected Q^2 and Q^3 sites in four-membered rings would satisfy both requirements.

Acknowledgements

This work was supported in part by grants from the Solid-State Chemistry Program of the National Science Foundation (grant DMR 86-15206 to E. Oldfield) and by the Earth Sciences Program (grant EAR 84-08421 to R. J. Kirkpatrick).

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Received 13*th July* 1987; *Paper* 7/1246