Silicates

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Aqueous Alkali-Metal Silicate Anions Containing Fully Condensed Four-Coordinate Sites**

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The chemistry of aqueous silicates has long been investigated owing to its geochemical significance[1,2] and its numerous industrial applications in fields as diverse as cements and geopolymers,[3,4] pulp/textile bleaching,[5] sol–gel derived ceramics,[6] and waste/water treatment.[7] Many studies have been carried out recently to identify silicate molecules which participate directly in the pre-nucleation, nucleation and crystal growth of zeolites (microporous solids used for heterogeneous catalysis, separations and ion-exchange processes), based on the premise that a zeolite's unique properties are encoded at its earliest stages of formation in hydrothermal solution.[8–11] Additionally, research has been conducted to determine the mechanistic pathways employed by organisms such as diatoms, grasses and sponges to produce hierarchically ordered biosilica, with the goal of developing novel biomimetic ceramics.[6,12–15]

The first ^{29}Si NMR spectrum of a concentrated alkali-metal silicate solution (commercial "waterglass") was reported in 1973,[16,17] and revealed broad resonance bands which were assigned to end ($\underline{Q}^1$), middle ($\underline{Q}^2$) and branching ($\underline{Q}^3$) silicate centers by analogy to the ^{29}Si NMR spectra of polyalkylsiloxanes.[18] A broad peak at the low-frequency end of the spectrum, centered at -35 ppm with respect to the orthosilicate ($\underline{Q}^0$) signal, was assigned to tetrafunctional ($\underline{Q}^4$) units in colloidal silica. Improvements in spectrometer technology, combined with attention to factors such as solution composition and ^{29}Si NMR relaxation phenomena, have resulted in the ability to resolve signals from the individual spin sites of silicate anions. By employing materials that are highly ^{29}Si enriched together with structure elucidation techniques such as COSY, it thus becomes possible to characterize the parent anions.[19–24] To date, the structures of 48 different silicate anions have been determined in this manner.[25] They are all compact, containing no more than nine Si sites, and are largely based on three-, four- and five-membered silicate rings.[26] They exist in dynamic equilibrium with one another[27,28] and their relative abundances are highly dependent on solution pH, concentration and temperature.[24] Conspicuous by their absence, however, are 1) specialized building units that appear in zeolite frameworks ("secondary building units")[8,11,29] and 2) pre-nucleation or protomineral species which contain fully condensed $\underline{Q}^4$ sites. Indeed, only two $\underline{Q}^4$-containing structures have ever been found in solution and then only in the presence of tetraalkylammonium (TAA) cations, both being derivatives of the TAA-stabilized cubic octamer species.[30]

We report herein the existence of aqueous silicate ions containing fully condensed $\underline{Q}^4$ sites in alkali-metal hydroxide solution, thereby providing the first definitive evidence of the chemical nature of protomineral species in such systems.

Surprisingly, little direct mechanistic information has so far been obtained regarding early-stage polymerization from alkali-metal silicate solutions, although it is generally accepted that condensation occurs through simple stepwise associative addition of $Si(OH)_4$ units.[27,28] ^{29}Si NMR spectroscopy is uniquely suited to determining the structures of aqueous silicate anions since, being non-invasive, the equilibrium anion distribution remains undisturbed and structural information can be obtained directly from the spectrum. Using the experimental protocol described previously,[25] we undertook NMR analysis of potassium silicate solutions under conditions which favor a high degree of condensation (high Si concentration, $[KOH]:[SiO_2] \approx 1:1$). The silicate anion distribution in sodium and potassium silicate solutions is virtually the same,[31] but potassium silicates tend to yield slightly sharper resonances.[25,32]

We show in Figure 1 the ^{29}Si NMR spectrum of a solution containing 2.000 mol kg^{-1} $^{29}SiO_2$ and 2.001 mol kg^{-1} KOH. Together with the well attested ^{29}Si NMR resonances from the $\underline{Q}^0$, $\underline{Q}^1$, $\underline{Q}^2$ and $\underline{Q}^3$ sites of silicate anions, it exhibits a large number of weak overlapping signals between -28.8 and -36.1 ppm. This is the region assigned to fully condensed $\underline{Q}^4$ sites.[30] At least twenty sharp spin-multiplets can be resolved, as shown in Figure 2, indicating that these sites are present within rapidly tumbling silicate molecules in true solution rather than within colloidal or particulate silica which would yield signals too broad to resolve. Also shown in Figure 2 is the ^{29}Si–^{29}Si COSY NMR spectrum for this region, which contains many cross-peaks indicative of $\underline{Q}^4$ spin sites coupled to $\underline{Q}^1$, $\underline{Q}^2$ and $\underline{Q}^3$ centers. No $\underline{Q}^4$–$\underline{Q}^4$ or $\underline{Q}^4$–$\underline{Q}^2_A$ cross-peaks are apparent to within the detection limits (ca. 10^{-4}–10^{-3} mol kg^{-1}), indicating that the major species do not contain either linked inequivalent $\underline{Q}^4$ sites or $\underline{Q}^4$ centers coordinated to $\underline{Q}^2$ sites in three-membered rings. The $\underline{Q}^4$–$\underline{Q}^1$ cross-peaks are closely grouped at the high frequency extreme of the $\underline{Q}^1$ spectral range (above -7.9 ppm; see Figure S1 in the Supporting Information) and at the very low frequency end of

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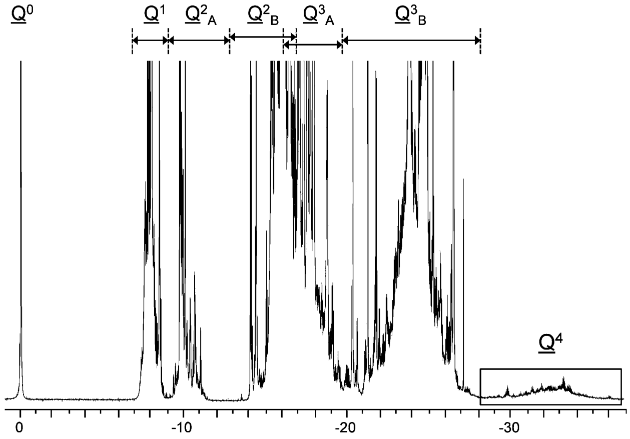


Figure 1. ^{29}Si NMR spectrum (149 MHz) at 277 K of a solution containing 2.000 mol kg^{-1} $^{29}SiO_2$ and 2.001 mol kg^{-1} KOH, vertically expanded to reveal a large number of weak, yet highly coupled, resonances in the low-frequency $\underline{Q}^4$ region.

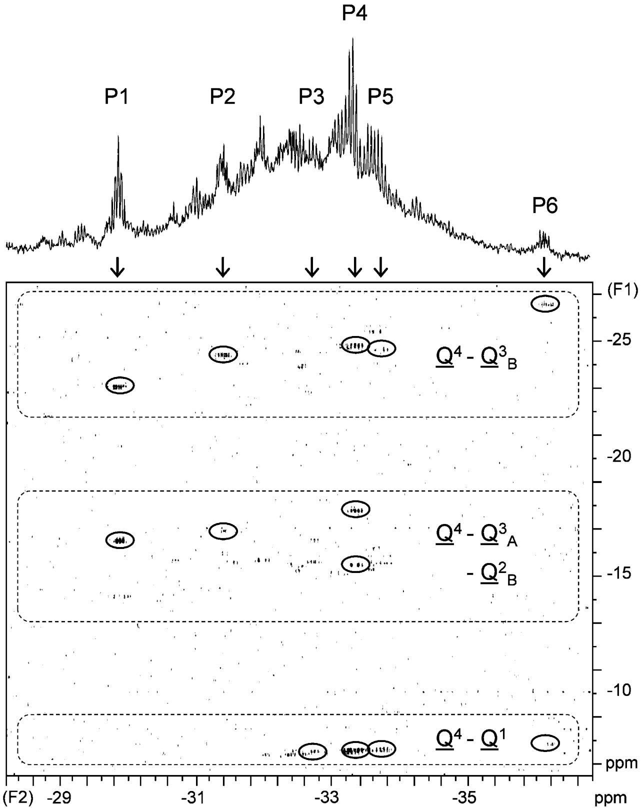


Figure 2. Expansion of the $\underline{Q}^4$ spectral region in Figure 1, and the corresponding F2 expansion in the ^{29}Si–^{29}Si COSY NMR spectrum. The six most prominent sets of $\underline{Q}^4$ cross-peaks (P1 to P6) are highlighted. (One of the P3 cross peaks is unobservable at the contour level shown in the figure.)

the $\underline{Q}^4$ region (below −32.0 ppm; see Figure 2). The corresponding $\underline{Q}^4$ signals are therefore the lowest frequency ^{29}Si NMR resonances noted for a ligand-free silicate solution.

We identify in Figure 2 the six most prominent sets of $\underline{Q}^4$ cross-peaks (P1 to P6, in order of decreasing frequency), from which we have derived five tentative structures (Table 1). The first step in doing so was to use the COSY data to identify self-consistent sets of interconnected signals. The chemical environment corresponding to each signal was then inferred by comparing its chemical shift to known peak assignments.[25] Taking the relative signal areas into account, a list of plausible structures was created and then, where possible, $^2J(^{29}\text{Si-O-}^{29}\text{Si})$ coupling constants were measured directly from the spectrum and used to generate a simulated spectrum. Finally, rudimentary molecular modelling was carried out for each proposed structure to ensure that it was physically viable. We stress that our assignments are necessarily tentative, both because weak COSY cross peaks may have gone undetected and because in each case at least one of the spin-multiplets was obscured by one or more overlapping signals. Nonetheless, as explained in detail below, we propose, with varying degrees of confidence, five $\underline{Q}^4$-containing silicate anions. Their chemical shifts, $^2J(^{29}\text{Si-O-}^{29}\text{Si})$ scalar coupling constants and systematic names are listed in Table 1. (Table S1 in the Supporting Information provides a complete list of all 54 aqueous silicate species we have identified to date in concentrated alkali-metal silicate solution.)

The molecule corresponding to the P1 set of resonances contains a $\underline{Q}^4$ site that is linked to both an unstrained $\underline{Q}^3_B$ center and either a $\underline{Q}^3_A$ or $\underline{Q}^2_B$ site (their spectral regions overlap). The latter sites are not linked with one another. The simplest structure we can deduce that fulfills these criteria is a cubic octameric cage with two four-rings fused on opposing edges (species **12A**). It is one of the two most abundant $\underline{Q}^4$-containing anions in solution.

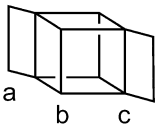
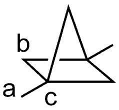
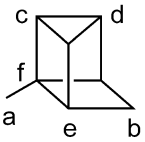
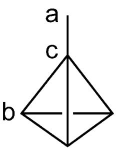
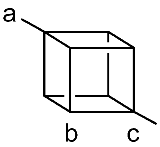
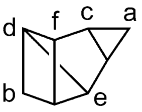
Peak set P2 again represents a molecule containing a $\underline{Q}^4$ site that is simultaneously linked to $\underline{Q}^3_B$ and $\underline{Q}^3_A$ (or $\underline{Q}^2_B$) sites. The cross-peak to $\underline{Q}^3_B$ is more intense than the other, indicating that the $\underline{Q}^3_A$ (or $\underline{Q}^2_B$) sites are outnumbered by $\underline{Q}^3_B$ sites. We are unable to propose a reasonable structure based solely on these data, and suspect that one or more additional cross-peaks have escaped detection.

P3 is the weakest self-consistent set of cross-peaks and indicates a structure that contains a $\underline{Q}^4$ center connected to $\underline{Q}^1$ and $\underline{Q}^2_B$ groups. The $\underline{Q}^2_B$ and $\underline{Q}^4$ spin-multiplets are well resolved, the former lying in an uncluttered spectral region corresponding to $\underline{Q}^2$ sites in singly bridged four-ring species (such as species **5D** and **6E**[25]). Overall, the data are consistent with **7L**, a doubly $\underline{Q}^1$-substituted analog of **5D**.[25]

The P4 peaks correspond to another relatively abundant $\underline{Q}^4$ containing molecule. The chemical shifts, spin–spin connectivities and resulting coupling patterns clearly point to species **8F**, a singly $\underline{Q}^1$ substituted version of tetracyclo[7.5.1.1^{3,7}.1^{5,11}] heptasilicic acid (**7J**),[25] which itself is the single most abundant silicate species in the solution.

The only structure we can suggest for peak set P5 is **5F**, the singly $\underline{Q}^1$ substituted version of the tetrahedral tetramer (species **4D**[16]). This assignment is important, since it provides the first corroborating evidence for this totally symmetric structure, which has long been suspected but for which unambiguous evidence has always been lacking.[33]

Table 1: Newly identified silicate species occurring at 277 K in an aqueous solution containing 2.000 mol kg^{-1} $^{29}SiO_2$ and 2.001 mol kg^{-1} KOH.[a]

Peak set	$-\Delta\delta(^{29}Si)$[b] [ppm]		$^2J(^{29}Si\text{-}O\text{-}^{29}Si)$ [Hz][c]		Probable structure type	
P1	a	16.493	a–c	11.5		heptacyclo[13.9.1.1^{1,19}.1^{3,13}.1^{5,19}.1^{7,13}.1^{7,17}]dodecasilicic acid (**12 A**)
	b	23.120	b–c	8.0		
	c	29.850				
P2	a	16.937	a–b			undetermined
	b	24.495	b–c	5.5		
	c	31.408				
P3	a	7.561	a–c	7.4		1,5-bis(trihydroxysilyl)-bicyclo[3.3.3]pentasilicic acid (**7 L**)
	b	13.539	b–c	6.2		
	c	32.719				
P4	a	7.613	a–f	7.7		11-trihydroxysilyl-tetracyclo[7.5.1.1^{3,13}.1^{5,11}]heptasilicic acid (**8 F**)
	b	15.693	b–e	6.1		
	c	17.827	c–d	3.7[d]		
	d	17.858	c–f	8.2		
	e	24.935	d–e	6.2[d]		
	f	33.308	e–f	7.8		
P5	a	7.623	a–c	8.1		trihydroxysilyl-tricyclo[3.3.1.1^{3,7}]tetrasilicic acid (**5 F**)
	b	24.791	b–c	7.7		
	c	33.734				
P6	a	7.852	a–c	11.3		1,7-bis(trihydroxysilyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1$^{7\text{-}13}$]octasilicic acid (**10 A**)
	b	26.272	b–c	7.6		
	c	36.130				
P7	a	10.713	a–c	4.2		tetracyclo[7.5.3^{5,7}.1.1^{3,11}]octasilicic acid (**8 E**)
	b	14.641	b–d	4.6		
	c	18.362	b–e	7.3		
	d	21.659	c–f	6.1[d]		
	e	22.403	d–f	5.5[d]		
	f	22.469	e–f	8.2[d]		

[a] Each line in the stick figures represents a Si-O-Si (siloxane) linkage. [b] Negative chemical shift with respect to the orthosilicic acid resonance. [c] Measured directly from the spectra unless otherwise stated. [d] Estimated from spectral simulation.

P6 is the second weakest set of $\underline{Q}^4$ cross-peaks detected, and, as with P3, a structural assignment is possible only because the signals occur in relatively uncluttered spectral regions. At −36.13 ppm, the $\underline{Q}^4$ resonance lies at the low-frequency extreme of the $\underline{Q}^4$ region, and appears to be a doublet of binomial quartets. The chemical shifts, coupling patterns and relative peak areas are consistent with the doubly $\underline{Q}^1$-substituted cubic octamer, **10 A**.

One additional set of cross-peaks, P7, corresponds to a previously uncharacterized species that does not contain a $\underline{Q}^4$ center (Table 1). The chemical shifts of the individual sites indicate that it must contain two inequivalent $\underline{Q}^2$ sites, one in a four-ring and one in a three-ring, together with four inequivalent $\underline{Q}^3$ sites. Spectral spin-system simulations performed for structure **8 E** yield spin-multiplet patterns that nicely match those observed experimentally.

Our experiments show, for the first time, that $\underline{Q}^4$ containing silicate anions are common in concentrated alkali-metal silicate solutions. No evidence, however, was found to support the existence of specialized zeolite building units. Our results add to the mounting evidence that silicate polymerization simply proceeds through stepwise condensation of monosilicate tetrahedra.

Experimental Section

A colloid-free solution containing 2.000 mol kg^{-1} $^{29}SiO_2$ and 2.001 mol kg^{-1} KOH was made by heating amorphous silica containing 99.35 atom % ^{29}Si (Isonics) with aqueous KOH, prepared from 99.99 % KOH (Sigma Aldrich) and type I deionized water (deuterated to 22 atom % to provide a field-frequency lock), in a PTFE-lined pressure vessel at 175 °C for 64 h. All ^{29}Si NMR spectra were recorded at 277 K on a Varian Inova 750 spectrometer operating at 149 MHz, using a 10 mm broadband probe and 9 mm inner diameter Kel-F NMR tube. A typical one-dimensional spectrum was acquired over 65 h, using 5164 $\pi/2$ pulses recycled every 45 s. The recycle period was shortened to 15 s for the ^{29}Si COSY experiment which ran for 163 h. Spectral simulations were conducted by using SpinWorks 3.1.8 (Kirk Marat, University of Manitoba).

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