

Silicon-29 NMR Studies of Tetraalkylammonium Silicate Solutions. 1. Equilibria, ²⁹Si Chemical Shifts, and ²⁹Si Relaxation

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The addition of tetraalkylammonium cations to aqueous silicate solutions enhances the abundance of symmetric, cage-like, polysilicate anions including the cubic octamer, Si₈O₂₀⁸⁻. The equilibrium ratio of tetramethylammonium (TMA) cations to the octameric silicate anion is 8:1 for solutions with a concentration ratio [OH⁻]:[Si] ≥ 1:1. Evidence indicates that organocations directly associate with cage-like polyanions to form a protective shell of hydrophobic hydration that impedes hydrolysis of the central anion.

Introduction

Organic base silicate solutions have long been known to exhibit unique chemical and physical characteristics, including crystallization to distinctive clathrate hydrate structures.¹ As early as 40 years ago, organic base cations—specifically tetraalkylammonium (TAA) cations—were used as structure-directing agents in the synthesis of zeolite molecular sieves.² Today, tetraalkylammonium cations are employed in the production of most commercially important zeolites, and thus, their interaction with aqueous silicates has a direct and significant impact on a variety of industries ranging from petroleum refining to pollution control. Zeolite chemists envisage a day on which zeolites will be synthesized entirely “by design”—that is, to have predetermined pore geometry and catalytic activity—through rational choice of the organic structure-directing agent.³ For this goal to be realized, however, more needs to be learned about the interaction between silicate and organic molecules in the aqueous synthesis media. Additional interest in organocation–silicate interactions comes from the recent discovery of mesoporous molecular sieves,⁴ formed from aqueous mixtures of silicates and quaternary ammonium surfactants, along with related advances in biomimetic inorganic chemistry.⁵

As opposed to the multitude of small, often asymmetric, silicate anions found in alkali-metal silicate solutions,⁶ concentrated tetramethylammonium (TMA) silicates are dominated by two symmetric silicate cages, the cubic octamer (or “double four-ring”, Q³₈) and, to a lesser extent, the prismatic hexamer (or “double three-ring”, Q³₆).^{7–12} Similar control over speciation is exhibited by other quaternary ammonium ions; however, the extent decreases systematically with the number and size of alkyl (or aryl) substituents employed in place of the TMA methyl groups.^{8,9,11–13} The structure-directing tendency of all TAA cations is enhanced significantly by the addition of organic solutes such as alcohols and amines.^{12,14–16} Unfortunately, the overall picture provided of tetraalkylammonium silicate chemistry by these earlier investigations is somewhat confusing. Most

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(7) By convention, the Q^z symbol is used to denote a quadrafunctional Si center with *y*-coordinated SiO₄⁴⁻ tetrahedra and, when applicable, *z* indicates the number of equivalent centers in a totally symmetric anion. Thus, the monomer (H_{4-*y*}SiO₄^{*y-*}), dimer (H_{6-*y*}Si₂O₇^{*y-*}), cyclic trimer (H_{6-*y*}Si₃O₉^{*y-*}), prismatic hexamer (H_{6-*y*}Si₆O₁₅^{*y-*}), and cubic octamer (H_{8-*y*}Si₈O₂₀^{*y-*}) are respectively, and more conveniently, represented by Q⁰, Q¹₂, Q²₃, Q³₆, and Q³₈. See Figure 1 for a graphical depiction of these structures.

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investigators failed to appreciate that the favored Q³₈ and Q³₆ cages evolve very slowly in the absence of alkali-metal cations.¹⁷ Studies aimed at understanding the effects of sample pH on silicate speciation did not account for a concomitant change in the organic cation concentration, and vice versa. Comparisons made between the ²⁹Si NMR chemical shifts and relaxation rates of individual polysilicate structures, obtained under widely varying sample conditions, are meaningless since NMR data are well-known to be as sensitive to solution conditions as to molecular structure. Clearly, a more deliberate approach is required for an unambiguous picture to emerge of chemical speciation and dynamics in TAA silicate systems.

In this paper we present the results of a systematic ²⁹Si NMR investigation of tetraalkylammonium silicate equilibria. Taken together, the findings indicate that protective shells of solvated organocations form around individual cage-like polyanions such as Q³₈, a clathrate relationship previously alluded to by Hoebbel and co-workers.^{8c,d}

Experimental Section

All solutions were prepared with type-I deionized water and contacted only surfaces of low-density polyethylene and Teflon FEP/TFE, cleaned successively with dilute solutions of nitric acid, hydrochloric acid, and Na₂H₂EDTA. Stock hydroxide solutions were prepared from each of tetramethylammonium hydroxide (Johnson-Matthey, 99.999% in 25 wt % aqueous solution), tetraethylammonium hydroxide (Aldrich, 40 wt % aqueous solution), tetra(*n*-propyl)-ammonium hydroxide (Johnson-Matthey, 40 wt % aqueous solution), tetra(*n*-butyl)ammonium hydroxide (Aldrich, 40 wt % aqueous solution), (2-hydroxyethyl)trimethylammonium hydroxide (Aldrich, 20 wt % aqueous solution), NaOH (Aldrich, 99.99%), and CsOH (Aldrich, 99.9% in 50 wt % aqueous solution). Chloride sources were tetramethylammonium chloride (Aldrich, 97%), NaCl (Johnson-Matthey, 99.99%), and HCl (Caledon, ACS).

Amorphous silicon dioxide was obtained by hydrolysis of SiCl₄ (Aldrich, 99.999%)¹⁹ or was recovered using the method of DeFretas et al.²⁰ from spent samples that were 95 atom % enriched in ²⁹Si.^{18,19} Wide-spectrum ICP analysis of the isotopically enriched silica showed trace contamination (<0.01%) only by Fe, Mn, and Na. The dried silica (12 h at 180 °C) was dissolved in standardized hydroxide solutions at 50 °C. It dissolved quickly and completely in tetraalkylammonium hydroxide solutions with a concentration ratio [OH⁻]:[Si] ≥ 0.6:1 and in alkali-metal hydroxides with [OH⁻]:[Si] ≥ 1:1. Typically, the ²⁹Si-enriched silica was slower to dissolve. The solvent in each sample was ca. 20 atom % enriched in ²H to provide an NMR lock. All samples were left to equilibrate at room temperature for at least 2 weeks prior to NMR analysis.

pH measurements of representative solutions not containing ²H were conducted in a thermostated bath at 298.0 K using an Orion glass membrane electrode and a Ag/AgCl double-junction reference cell containing 1.0 mol kg⁻¹ TMAOH. The meter was calibrated with pH 10.01, 12.00, and 12.45 buffers.

Silicon-29 NMR spectra of approximately 380 different solutions were obtained using Bruker AC-E 200 (39.76 MHz; 15 mm probe head with 34 μs π/2 pulse) and AMX 500 (99.36 MHz; 10 mm probe head with 20 μs π/2 pulse) spectrometers, in conjunction with Si-free probe heads and sample tubes.²¹ NMR experiments were carefully designed to achieve quantitative results. Spectra, appropriately digitized, were

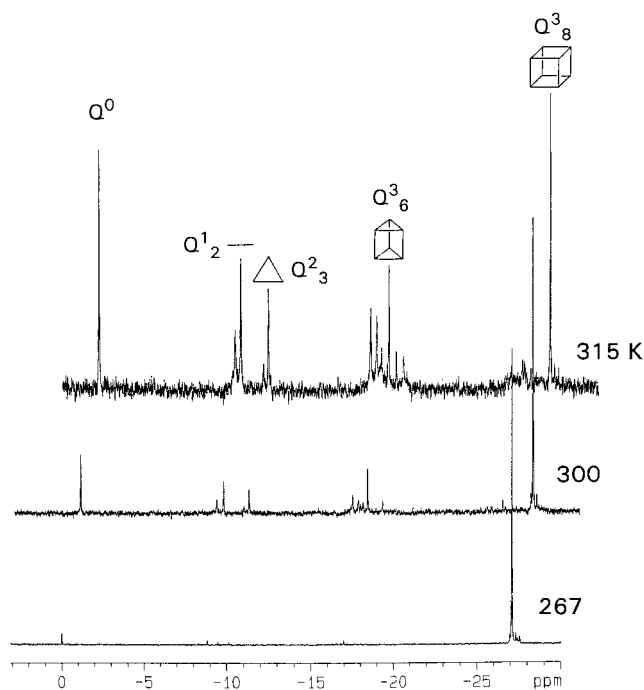


Figure 1. Variable-temperature ²⁹Si (99.36 MHz) spectra of a tetramethylammonium (TMA) silicate solution containing 1.0 mol kg⁻¹ SiO₂ and 2.0 mol kg⁻¹ TMAOH. Major peak assignments are depicted by stick figures in which each line represents a Si—O—Si bridge. Peak heights are normalized to that of the Q³₈ resonance.⁷ The Q³₈ and Q³₆ cage species are abnormally temperature sensitive and, for purely aqueous solutions, are undetectable above 350 K.

acquired using π/2 pulses cycled over periods (typically 60 s) greater than 3–5 times the maximum measured T₁ value. The solution temperature was calibrated using the ¹H spectrum of anhydrous ethylene glycol²² and varied by no more than 0.5 K during any run. Silicon-29 signals were referenced either internally to the monomer (Q⁰) resonance or externally to a coaxial sample of hexamethyldisiloxane (signal 79 ppm to high frequency of Q⁰). Longitudinal relaxation rates were measured by the inversion recovery method.

Results

Equilibria. Figures 1 and 2 show ²⁹Si NMR spectra of a representative series of tetramethylammonium silicate solutions at various temperatures and Si concentrations. The resonances were assigned to individual silicate anions in accordance with previous work using isotopically enriched materials.⁶ Although the distribution and nature of the smaller species are similar to those observed in alkali-metal silicate solutions, the concentrations of the cubic octamer, Q³₈, and prismatic hexamer, Q³₆, are typically higher. The enhanced abundance of these two species decreases significantly, however, as temperature is increased (Figure 1) or Si concentration is decreased (Figure 2). While other quaternary ammonium cations exhibit similar control over silicate speciation, the degree of control decreases as the TMA methyl groups are replaced with larger organic substituents and disappears completely when all four alkyl groups are C₄ or bigger.^{9,13} Consequently, the only discernible difference between alkali-metal and tetra(*n*-butyl)ammonium silicate solutions is the slightly higher stability afforded open-framework structures by the alkali-metal cations.²³ As noted elsewhere,^{12,14–16} the addition of miscible organic solvents to tetraalkylammonium silicate solutions shifts equilibria in favor

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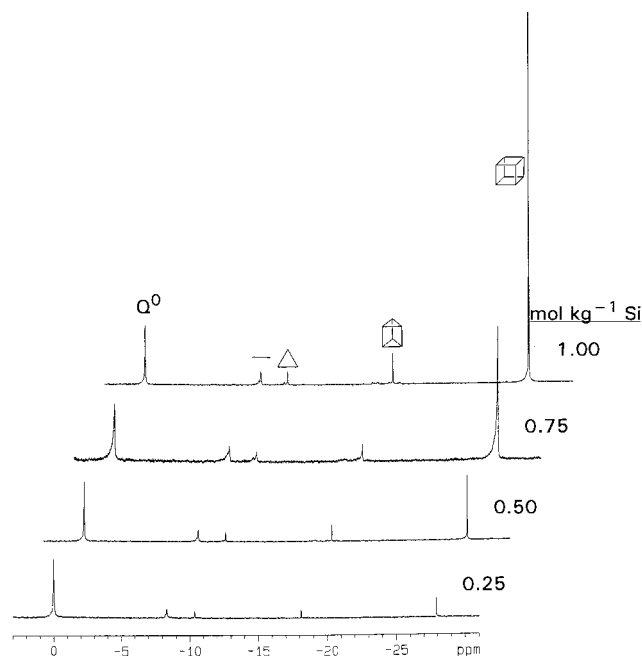


Figure 2. ^{29}Si (99.36 MHz) spectra at 299.6 K of solutions containing 2.00 mol kg^{-1} TMAOH and $0.25\text{--}1.00 \text{ mol kg}^{-1}$ SiO_2 . Peak heights are normalized to that of the monomer resonance.

of Q_6^3 and Q_8^3 . In the case of TMA silicates, equilibria are displaced entirely toward Q_8^3 .⁹ Moreover, organic cosolvents cause the symmetric Q_6^3 and Q_8^3 cages to be favored even in solutions containing very large quaternary ammonium ions (i.e., all substituents $\geq \text{C}_4$).^{12,24} (See Figure 3.) In the absence of organic cations, however, the addition of organic cosolvents simply increases the overall extent of oligomerization with no species being uniquely favored.

Although it has long been appreciated that the amount of Q_8^3 present in TMA silicate solutions is more or less proportional to the concentration of TMAOH,^{8–12} the independent effects of TMA^+ and OH^- on Q_8^3 abundance have not previously been studied. We therefore prepared three series of TMA silicate solutions of constant Si concentration in which we varied (a) the TMAOH concentration; (b) the TMAOH concentration while the concentration of TMA^+ was held constant by addition of TMACl; or (c) the TMACl concentration. (Details of sample compositions are given in the Supporting Information section of ref 25.) All solutions were allowed 3 weeks to equilibrate prior to the recording of ^{29}Si spectra. The results were found to depend on the $[\text{OH}^-]:[\text{Si}]$ ratio of the samples.

A. Solutions with $[\text{OH}^-]:[\text{Si}]$ Ratios of 1:1 or More. In such solutions, the concentration of Q_8^3 is independent of solution pH and Cl^- concentration as shown in Figure 4. All species other than Q_8^3 and Q_6^3 , however, depolymerize as pH is increased. The fact that Q_8^3 concentration is independent of pH is a significant departure from the well-characterized tendency in alkali-metal silicate solutions for silicate oligomers to depolymerize as alkalinity is increased.¹⁹ Figure 5 shows that the abundance of Q_8^3 depends entirely on the concentration of TMA^+ when $[\text{Si}]$ is held constant, demonstrating the unique equilibrium dependence of Q_8^3 and Q_6^3 on the TMA^+ cation. Indeed, while added TMA^+ favors these species, all other silicate anions depolymerize owing to the associated drop in residual Si concentration.

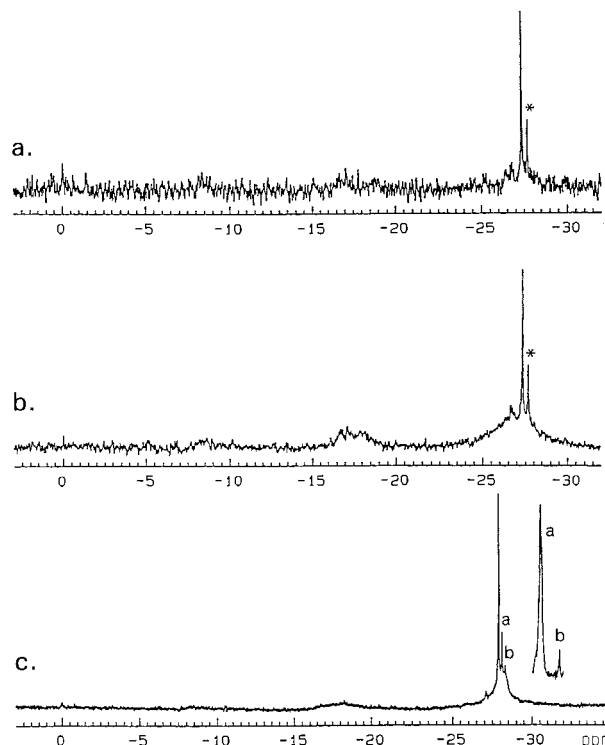
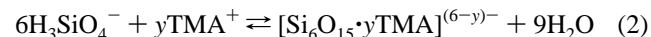
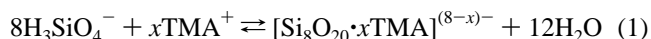


Figure 3. ^{29}Si (39.76 MHz) spectra of low-alkalinity solutions containing (a) 0.34 mol kg^{-1} SiO_2 , 0.17 mol kg^{-1} TPAOH, and 57 wt % (of solvent) DMSO at 296.1 K; (b) 1.4 mol kg^{-1} SiO_2 , 0.6 mol kg^{-1} TBAOH, and 40 wt % DMSO at 296.1 K; and (c) 1.9 mol kg^{-1} ^{29}Si -enriched (95 atom %) SiO_2 , 1.2 mol kg^{-1} TBAOH, and 35 wt % DMSO at 317.1 K. The peak that is about 0.25 ppm to low frequency of the dominant Q_8^3 signal, and marked with an asterisk in a and b, is a common feature of TAA silicate solutions with $[\text{OH}^-]:[\text{Si}] < 1:1$. Silicon-29 enrichment in spectrum c shows that this resonance (peak a) and possibly one other (peak b) are singlets (see expansion) and correspond, therefore, to completely symmetrical oligomers.

These observations lead us to propose the following reaction equilibria to account for the formation of Q_8^3 and Q_6^3 .



Here, H_3SiO_4^- is used to represent *any* of the pool of rapidly interchanging silicate centers, excluding those incorporated into the long-lived, TMA^+ -stabilized, Q_8^3 and Q_6^3 cages. The cages themselves are represented as ion-association complexes. Although the average charge per Si in solution increases from -1 as the $[\text{OH}^-]:[\text{Si}]$ ratio is raised above 1:1,¹⁷ we need only consider H_3SiO_4^- since multiply charged centers are comparatively unreactive in polymerization.^{19,26} Moreover, both the charge and concentration of Q_8^3 are independent of pH for $[\text{OH}^-]:[\text{Si}]$ ratios $\geq 1:1$. Applying the approximation of ideal solution behavior, we obtain the simplified equilibrium constant expressions,

$$K_{(1)} = [\text{Q}_8^3]/([\text{Si}']^8[\text{TMA}^+]^x) \quad (3)$$

$$K_{(2)} = [\text{Q}_6^3]/([\text{Si}']^6[\text{TMA}^+]^y) \quad (4)$$

where Q_8^3 and Q_6^3 are now used to represent the ion-association complexes and Si' represents free silicon, not incorporated in either cage. Data analysis shown in Figure 6 reveals that $x =$

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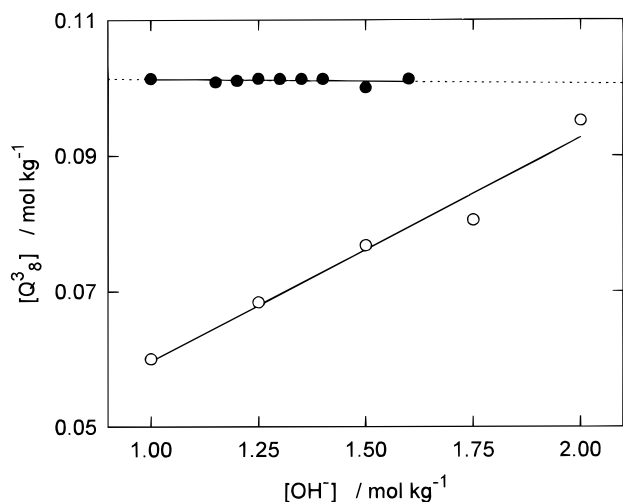


Figure 4. Equilibrium concentration of Q^3_8 at 296.1 K as a function of alkalinity in 1.0 mol kg^{-1} SiO_2 solutions that contain (O) variable TMAOH concentration or (●) variable TMAOH concentration with TMA^+ concentration fixed at 2.0 mol kg^{-1} by appropriate additions of TMACl.

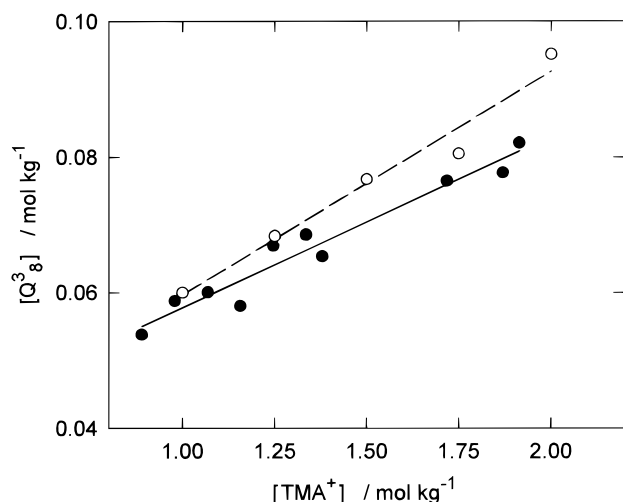


Figure 5. Equilibrium concentration of Q^3_8 at 296.1 K as a function of TMA^+ concentration for solutions that contain (O) 1.0 mol kg^{-1} SiO_2 , with variable TMAOH concentration; or (●) 0.90 mol kg^{-1} of SiO_2 and TMAOH, with variable TMACl concentration.

8 ± 1 , in accordance with charge balance considerations, and that $K_{(1)} = 30 \pm 6$ at 298 K. Thus, $\Delta G^\circ_{(1)} \approx -8.4 \pm 0.5$ kJ mol^{-1} at 298 K. The comparatively low concentration of Q^3_6 in TMA silicate solutions precludes determination of y and $K_{(2)}$.

B. Solutions with $[OH^-]:[Si]$ Ratios Less than 1:1. Whereas alkali-metal silicate solutions tend to be unstable and precipitate under these low-alkalinity conditions,¹⁹ tetraalkylammonium silicate solutions typically remain homogeneous down to ratios of about 0.7:1, at which point the onset of colloid formation is signaled by the appearance of broad Q^2 , Q^3 , and Q^4 resonances in the ²⁹Si NMR spectra (Figure 7). These bands obstruct spectral integration, precluding the quantitative equilibrium analysis performed above. Nonetheless, the Q^3_8 concentration clearly decreases as pH is raised (Figure 7), in marked contrast to the pH independence exhibited at $[OH^-]:[Si] \geq 1:1$. Moreover, new ²⁹Si peaks appear at approximately 0.23 and 0.35 ppm to low frequency of the Q^3_8 signal (marked with an asterisk in Figures 3 and 7). The concentration of the corresponding species, like that of Q^3_8 , increases with the addition of organic cosolvents (Figure 3). Others have tentatively assigned these peaks to double five-ring ($H_{10-q}Si_{10}O_{25}^{q-}$) and

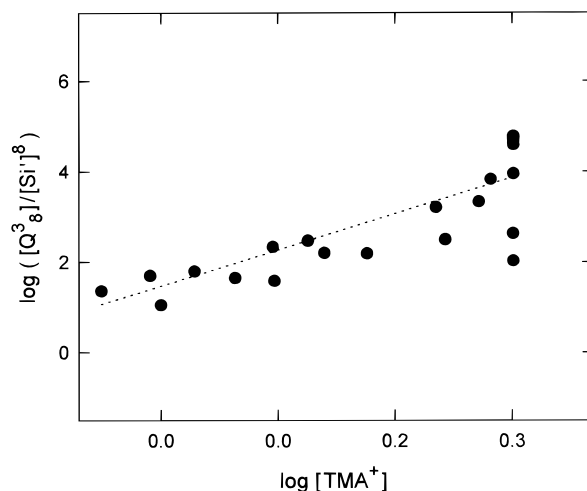


Figure 6. Least-squares fit of data obtained at 298 ± 2 K for the 27 solutions represented in Figures 2, 4, and 5 to the expression $K_{(1)} = [Q^3_8]/([Si']^8[TMA^+]^x)$ where $[Si']$ is the total Si concentration excluding that in the Q^3_8 and Q^3_6 cages. The analysis yields $x = 8 \pm 1$ and $K_{(1)} = 30 \pm 6$.

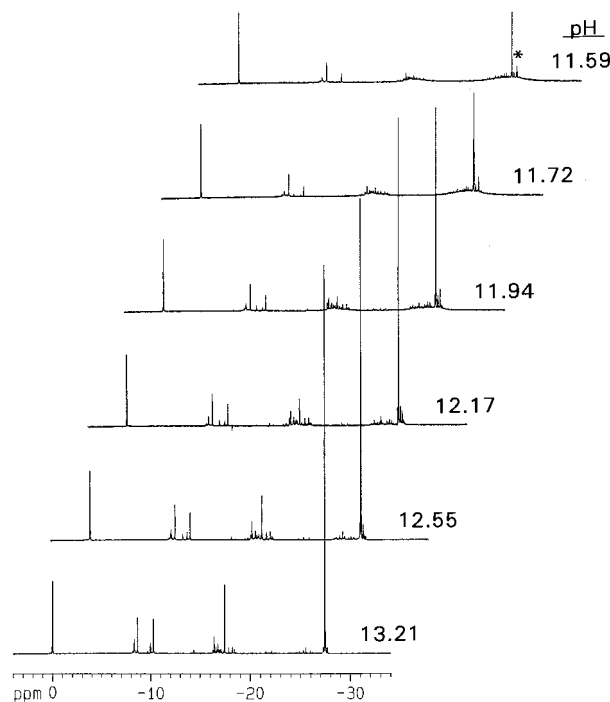


Figure 7. ²⁹Si (99.36 MHz) spectra at 299.6 K of solutions containing 1.0 mol kg^{-1} SiO_2 and TMAOH. The pH was decreased from 13.21 by addition of concentrated HCl. Peak heights are normalized to that of the monomer resonance. The broad Q^2 and Q^3 bands evident in the base line at pH < 12 arise from the formation of colloidal silicate particles. The peak marked with an asterisk is a common feature of low-pH solutions and corresponds to the peak similarly designated in Figure 3.

double six-ring ($H_{12-q}Si_{12}O_{30}^{q-}$) structures.^{12,27,28} They occur for all TAA silicate solutions in which Q^3_8 is stabilized and the $[OH^-]:[Si]$ ratio is <1:1. Both are singlets when solutions are enriched in ²⁹Si (Figure 3c), indicating that they indeed correspond to symmetric cage species. The assignment of these peaks is further discussed below.

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Table 1. Relative Ability of Cations Added to TMA Silicate Solutions To Produce Additional Q^3_8 Polyanions at 296.1 K^a

TMA ⁺	ETMA ⁺	TBA ⁺	TEA ⁺	Cs ⁺	Na ⁺
1.0	0.7	0.08	-0.2	-0.8	-1.0

^a Reference 24.

C. Mixed Cation Equilibria. Various TAA⁺ and alkali-metal cations were added to a previously characterized TMA silicate solution. The findings are summarized in Table 1. In accordance with previous studies, no other quaternary ammonium cation was observed to be as effective at stabilizing Q^3_8 as TMA⁺. The next most effective cation is (2-hydroxyethyl)trimethylammonium (ETMA), exerting about 70% of TMA's structure-directing influence. In purely aqueous solutions, the addition of tetra(*n*-butyl)ammonium (TBA) cations has almost no influence on TMA silicate equilibria. Smaller TAA cations such as tetraethylammonium (TEA) destabilize the TMA-favored Q^3_8 cages, as do the alkali-metal cations. Their destructive influence increases with charge-to-radius ratio, indicating that it may arise from an ability to overcome TMA's electrostatic association with Q^3_8 . Therefore, while the Q^3_8 -stabilizing influence decreases with the TAA⁺ ion's size, so does its destabilizing influence toward Q^3_8 anions that are already stabilized by TMA⁺. This apparent contradiction is discussed below.

Silicon-29 NMR Chemical Shifts. The Q^3_8 resonance is shifted to lower frequency by as much as 1 ppm (with respect to the monomer signal) for TAA silicates as compared to equivalent alkali-metal silicates, with the extent of line shift approximately coinciding with the enhancement in Q^3_8 concentration.^{8d,11} Increasing the pH of TAA silicate solutions while holding [TAA⁺] and [Si] constant causes all ²⁹Si peaks to shift up-frequency except (a) the Q^3_8 signal, which shifts down-frequency over the entire pH range; (b) two unassigned peaks that are +0.1 and -0.2 ppm from the Q^3_8 signal and move in unison with it, indicating that the corresponding structure(s) may be similar to Q^3_8 ; (c) the Q^3_6 signal, which moves down-frequency at pH > 13 only; and (d) two peaks from the cubelike, tricyclic octamer which shift similarly to the Q^3_6 peak. The Q^3_8 signal also moves slightly down-frequency as TAA⁺ concentration is raised, whereas other resonances remain roughly stationary. Complete details of the chemical shift measurements are presented in the Supporting Information.

Silicon-29 longitudinal relaxation rates, characterized by the first-order rate constant T_1^{-1} , were measured for a wide variety of silicate solutions. The detailed findings are provided as Supporting Information. For alkali-metal silicate solutions, large anions such as Q^3_8 tend to exhibit the lowest rates of ²⁹Si relaxation.¹⁸ This is true also for solutions that contain large quaternary ammonium cations such as TBA⁺. If the dominant cation is TMA⁺, however, Q^3_8 exhibits the *highest* rate of relaxation. Indeed, the relaxation rate for Q^3_8 closely correlates with TMA⁺ concentration and, thus, with the anion's increased stability.

Kinrade and Swaddle^{18b} have demonstrated that rapid Si-Si chemical exchange in alkali-metal silicate solutions causes gross averaging of individual relaxation rates measured by the inversion recovery method. This phenomenon is also observed for TMA silicate solutions, except that the Q^3_8 relaxation rate remains anomalously high even after the rates measured for other species have averaged to a common value (refer to Figure 4 in the Supporting Information). Hence, the cubic octamer undergoes slower intermolecular chemical exchange than other

Table 2. Half-Height ²⁹Si Peak Widths (±5%) at 296.1 K for a Solution Containing 0.90 mol kg⁻¹ SiO₂, TMAOH, and TMACl, before and after Being Saturated in MnCl₂

MnCl ₂ content	$\Delta\nu_{1/2}/\text{Hz}$				
	Q^0	Q^1_2	Q^2_3	Q^3_6	Q^3_8
nil	0.7	0.7	0.5	0.4	0.4
saturated	5.1	2.4	1.5	0.7	0.7

TMA silicate species, in agreement with the observations of Knight et al.¹⁷

What causes TMA to enhance the longitudinal relaxation rate of Q^3_8 nuclei? This is a difficult question to address experimentally given that the proposed [$Q^3_8 \cdot 8\text{TMA}$] complex would probably tumble too slowly for the extreme narrowing condition to hold.^{18,29} A major cause of longitudinal and transverse relaxation in alkali-metal silicate solutions is the presence of adventitious paramagnetic ions.^{18a} As documented in Table 2, the addition of paramagnetic Mn²⁺ ions to a TMA silicate solution causes all ²⁹Si peaks to broaden, some so much as to become undetectable. (Transverse relaxation is characterized by the rate constant T_2^{-1} which, nominally, is equal to $\pi\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the half-height peak width.²⁹) However, the Q^3_6 and Q^3_8 resonances are significantly less affected than all the other peaks. Therefore, paramagnetic impurities cannot account for the enhanced rate of relaxation for these species in TMA silicate solutions. On the contrary, the TMA-stabilized Q^3_6 and Q^3_8 cages must be protected from interaction with paramagnetic ions in some way.

Discussion

Why do the Q^3_6 and Q^3_8 species behave so differently from other silicate anions (including others having Q^3 sites) in solutions that contain TAA⁺ ions? Since silicates have negligible effects on the ¹H and ¹³C NMR spectra of aqueous TMAOH, any interaction that occurs between the organocation and silicate polyanions must be long range and indirect. We suggest that the answer may lie in the effect that TAA⁺ cations have on the motional characteristics of water molecules in the extended-hydration region of silicate anions. Electrolytes disrupt the normal hydrogen-bonded structure of water due to their ability to orient solvent dipoles, a phenomenon known as *hydrophilic hydration*. In addition, ions containing nonpolar alkyl groups are believed to induce *hydrophobic hydration*, whereby the hydrogen bonding (and thus mobility) of water molecules in the immediate hydration region is disrupted owing to the weak interaction between the alkyl groups and the solvent dipoles.^{31,32} It has been shown that water molecules in the vicinity of TAA⁺ alkyl groups form short-lived cage systems,^{32,33} believed to be comparable to the hydration structures of crystalline TAA⁺ clathrate hydrates.³⁴ As the concentration of the organocations is increased, long-range solute-solute interactions can occur. Hydration cages overlap and mutually enhance one another's stability, leading to regions of microheterogeneity in the solution medium and, ultimately, to the formation of solid clathrate hydrates.

We propose that, in the case of alkylammonium silicate solutions, encounters between TAA⁺ hydration spheres are

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expedited, even at low cation concentrations, by the existence of multiply charged silicate anions. Polysilicate species with open or irregular structures, however, are subject to considerable thermal motion such that any association formed between cations would exist only briefly. On the other hand, the Q³₆ and Q³₈ cages are fairly rigid and would yield longer lived TAA assemblies comprising greater numbers of cations. Moreover, the nearly spherical charge distribution on these cages would make it possible for TAA⁺ hydration spheres to join all around them, creating continuous (or near continuous) shells of hydrophobic hydration that isolate the oligomers from their aqueous environment. Indeed, the rate of hydrolysis is anomalously small for these species, as is apparently the distance to which paramagnetic ions are able to approach. In addition, raising the TAA⁺ concentration would be expected, as observed, to favor Q³₆ and Q³₈ at the expense of all other species. Hoebbel et al.^{8c,d} were first to suggest that the aqueous Q³₈ ion is stabilized by a water/TMA⁺ “clathrate structure”, proposing as a model the crystal structure of [TMA]₁₆[Si₈O₂₀][OH]₈·116H₂O.³⁵ We would expect the formation of TAA-clathrated polyanions to be entropy driven, primarily, owing to the release of water molecules hydrophobically bound to free TAA⁺.

If our model is correct, the formation of clathrated polyanions should be optimized by quaternary ammonium cations having (a) high surface charge density, as reflected in the charge-to-radius ratio, and (b) significant hydrophobic character, i.e., large alkyl groups. The observations bear out these competing influences. The compact tetramethylammonium cation has the largest surface charge density of all TAA⁺ cations and, thus, the strongest electrostatic attraction to silicate polyanions. Alkali-metal cations, being smaller, easily displace TMA⁺ from association with silicates, but have no hydrophobic character. Large cations such as tetra(*n*-butyl)ammonium, although far more hydrophobic than TMA⁺, have smaller charge-to-radius ratios, which prevent them from displacing TMA⁺ or from independently stabilizing silicate polyanions. Yet, large cations such as TBA⁺ do stabilize cages if employed along with organic cosolvents. Cosolvents decrease water activity and thus increase the extent of ion association, presumably enabling the larger TAA⁺ cations to participate in clathrate formation.

Perhaps the most convincing evidence for the role played by ion association is the observed 8:1 correlation between the concentrations of TMA⁺ and Q³₈ for solutions with [OH⁻]:[Si] ≥ 1:1. Under these conditions the polyanions are fully deprotonated,¹⁹ i.e., Q³₈ has a -8 charge, and their concentrations are pH independent. However, as [OH⁻]:[Si] is decreased from 1:1, protonation occurs and their abundance decreases owing to a weakening of the electrostatic attraction that holds the clathrate shell together. We tentatively assign the singlet resonance located 0.2 ppm down-frequency from the Q³₈ signal (Figure 3) to the singly protonated Q³₈ cage, HSi₈O₂₀⁷⁻. Unfortunately, the species' relatively short exchange lifetime prevents confirmation of the assignment (i.e., by Ge substitution^{6c}).

The anomalous influence that solution conditions—TAA⁺ concentration especially—have on the ²⁹Si chemical shifts and relaxation rates of Q³₈ and Q³₆ is indicative of the unusual association that these species have with TAA⁺ cations and, moreover, can be used to identify other clathrated polyanions. (Refer to Figure 1 in the Supporting Information.) For example, resonances corresponding to the tricyclic octamer, an immediate precursor of Q³₈, shift down-frequency as pH is increased, indicating that it too is clathrated by TAA⁺ cations (though less efficiently than Q³₈). Furthermore, the two unassigned peaks that, over a range in pH, remain at +0.1 and -0.2 ppm from the Q³₈ signal probably correspond to one or more clathrated molecules that are closely related to the Q³₈ structure.

In the following paper,²⁵ we explore the kinetics and mechanism of formation for the clathrated polysilicate anions.

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Supporting Information Available: Details of the ²⁹Si chemical shift and longitudinal relaxation measurements (3 pages). Ordering information is given on any current masthead page.

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