Silicon-29 NMR Studies of Tetraalkylammonium Silicate Solutions. 2. Polymerization Kinetics

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The kinetics of formation of the silicate cubic octamer, Q^3_8, in aqueous tetramethylammonium (TMA) silicate solutions was investigated by ^{29}Si NMR. The rate equation for solutions at pH 13.2−13.6 is $d[Q^3_8]/dt = k_f$ $[H^+]^{1.6\pm0.1}[TMA^+]^{0.36\pm0.08}[Si]^{0.8\pm0.3}$ where $k_f = (2.2 \pm 0.8) \times 10^{16}$ $mol^{-1.8}$ $kg^{1.8}$ s^{-1} at 296 K. The findings prove unequivocally that alkylammonium cations participate directly in the formation and subsequent stabilization of cagelike polysilicate anions. This implies a radically different mechanistic role than "templating" for alkylammonium cations in the synthesis of molecular sieves.

Introduction

A principal characteristic of aqueous tetraalkylammonium (TAA) silicate solutions is the prevalence of symmetrical, cagelike, silicate anions, most notably the cubic octamer, Q^3_8, and the prismatic hexamer, Q^3_6.[1] In freshly prepared solutions, however, it can take up to a month at 298 K to establish equilibrium levels for these particular species.[2] Indeed, Keijsper and Post[3] have demonstrated that the rates of Si−Si chemical exchange between these and other silicate anions are abnormally low. By comparison, other silicate species (including Q^3_6 and Q^3_8 in solutions that do not contain organic cations) have intermolecular Si−Si exchange lifetimes on the order of 10^{-1}−10^1 s at 298 K, depending on pH.[4,5]

In the preceding paper,[1] we demonstrated that the equilibrium concentrations of Q^3_6 and Q^3_8 depend primarily on the abundance of TAA$^+$ cations. The stoichiometric ratio of tetramethylammonium (TMA) ions to the deprotonated Q^3_8 polyanion, for example, is approximately 8:1. This relationship together with observations of anomalous ^{29}Si chemical shifts and relaxation rates indicates that organic cations participate in the formation and subsequent stabilization of these cagelike species. In this paper, we examine polymerization kinetics in tetraalkylammonium silicate solutions and determine whether TAA$^+$ cations indeed figure directly in the formation of silicate polyanions.

Experimental Section

Full details of sample preparation, pH measurements, and NMR operation are given in the preceding paper.[1] Germanate solutions were additionally prepared by dissolving amorphous germanium dioxide, made by hydrolysis of GeCl$_4$ (Johnson-Matthey, 99.9999%), in standardized hydroxide solutions at 50 °C.

Results

Polymerization Kinetics. Several dynamic NMR techniques were evaluated to determine how best to monitor Si−Si exchange in TAA silicate solutions. Classical band-shape analysis of ^{29}Si spectra acquired between 0 and 100 °C revealed that the rate of exchange between species other than Q^3_6 and Q^3_8 closely matches that observed for alkali-metal silicate solutions,[4,5] with most species having an average lifetime of 0.4 s at 298 K in solutions with [OH$^-$]:[Si] = 1:1. However, the Q^3_6 and Q^3_8 resonances show no sign of kinetic broadening at temperatures up to 80 °C (beyond which they are undetectable). Employing the method of selective saturation transfer, Keisper and Post[3] have demonstrated already that the intermolecular exchange rate for these two species is anomalously slow. A number of 1- and 2-D saturation transfer techniques are available for characterizing exchange rates that are of the same order of magnitude as the longitudinal relaxation rates. However, we found that the required criteria—high spin site concentrations along with comparable rates of exchange and relaxation—limit their application to an extremely narrow range of silicate sample conditions. The best method for characterizing the formation of Q^3_6 and Q^3_8 turned out to be the simple boil−freeze−thaw technique of Knight et al.[2] In this procedure, the sample, contained in a Teflon-FEP NMR tube liner, is heated to boiling to break down all TAA-stabilized species, frozen in liquid nitrogen to halt chemical exchange, and then placed in the spectrometer at the preset temperature. Spectra are acquired at regular intervals to monitor evolution of the silicate equilibria. Representative boil−freeze−thaw experiments are shown in Figure 1. Immediately after thawing, TMA silicate solutions contain a wide distribution of oligomers—similar to that

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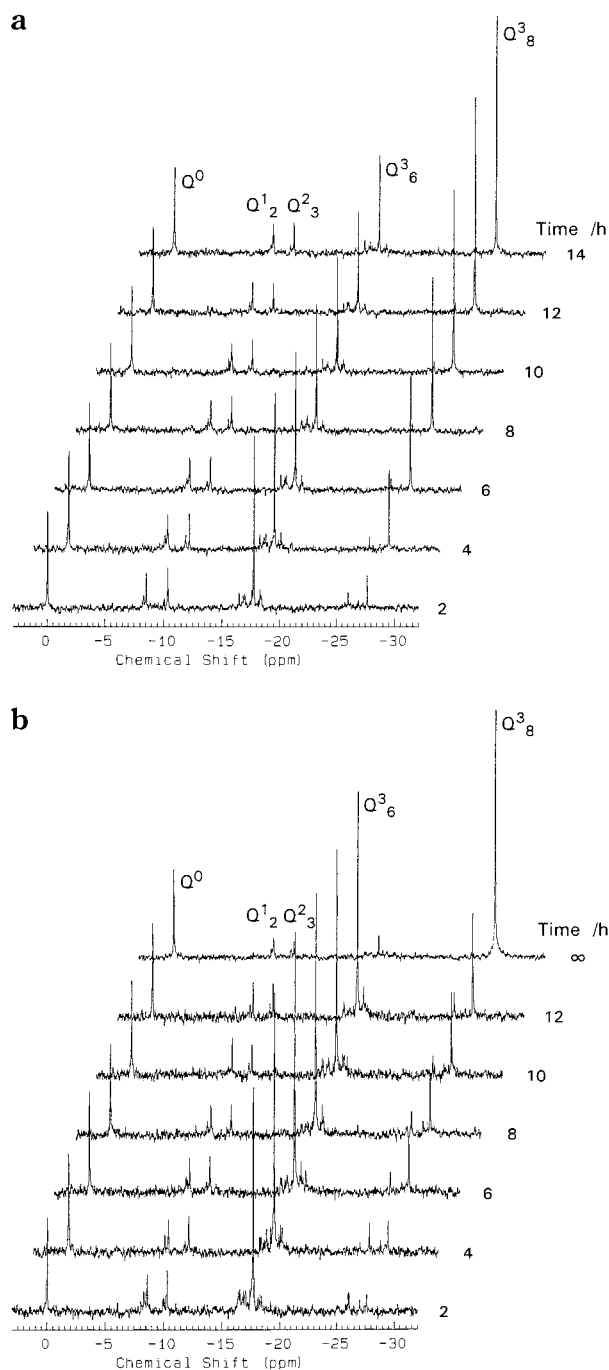 (5) Kinrade, S. D. *J. Phys. Chem.* **1996,** *100,* 4760.

a

b

Figure 1. Time dependence of [29]Si (39.76 MHz) spectra, acquired over 2 h intervals, for a solution containing 1.0 mol kg^{-1} SiO$_2$, 1.4 mol kg^{-1} TMAOH, and 0.6 mol kg^{-1} TMACl following the boil−freeze−thaw procedure. The solution temperatures represented are (a) 287.0 K and (b) 296.1 K.

observed in equivalent alkali-metal silicate solutions—except, in most cases, for an elevated amount of Q$^3_6$. The Q$^3_8$ signal is undetectable at first, but appears after a short while (15−30 min) and grows at the expense of all others. In contrast, alkali-metal silicate solutions contain an equilibrium distribution of oligomers well within 15 min of being thawed.[2]

Kinetic measurements were made at 296.1 K for three series of TMA silicate samples having (a) varying OH$^-$, but constant Si and TMA$^+$ concentrations; (b) varying TMA$^+$, but constant Si and OH$^-$ concentrations; and (c) varying Si, but constant TMA$^+$ and OH$^-$ concentrations. Details of the individual sample compositions are given in the Supporting Information. The time dependence of Q$^3_8$ concentration is depicted in Figure

2 for two representative samples from each series. Figure 2a indicates that the rate of Q$^3_8$ formation decreases as the nominal OH$^-$ concentration is increased. Figure 2b shows a small increase in the rate of Q$^3_8$ formation as TMA$^+$ concentration is increased by the addition of TMACl. (We note here that the *initial* sample pH—that is, the pH immediately following the boil−freeze−thaw procedure—was unaffected by TMA$^+$ concentration.) Figure 2c shows that raising the SiO$_2$ content of a solution, and concomitantly decreasing pH, accelerates formation of Q$^3_8$.

In all cases, Q$^3_8$ was undetectable within the first 15 min after thawing of the sample. This observation was critical since it legitimized use of the method of initial rates for determining the rate equation for Q$^3_8$ formation. Each silicate oligomer is involved in numerous inter- and intramolecular exchange reactions such that, for a given species S, the net reaction rate is given by

$$\frac{d[S]}{dt} = \sum_i R_{f,i(S)} + \sum_j R_{d,j(S)}$$

where $R_{f,i(S)}$ and $R_{d,j(S)}$ are the reaction rates corresponding to the formation (i.e., condensation) and dissociation (i.e., hydrolysis) pathways of S, respectively. At equilibrium, of course, d[S]/dt = 0. Following a perturbation such as the boil−freeze−thaw procedure, however, it takes time for the various equilibria to become reestablished. At $t = 0$, immediately after thawing, Q$^3_8$ is absent to within the short-term detection limits of the spectrometer, estimated here to be about 3% of the total Si concentration. Therefore, the initial rate (or rates) of Q$^3_8$ dissociation is set to 0, and the overall reaction rate for Q$^3_8$ at $t = 0$ becomes

$$\left(\frac{d[Q^3_8]}{dt}\right)_0 = \sum_i R_{f,i(Q^3_8)}$$

The initial Q$^3_8$ reaction rate for each solution was determined by fitting the first four points of the curves represented in Figure 2 to the second-order polynomial [Q$^3_8$] = $x + yt + zt^2$. Since Q$^3_8$ is undetectable at $t = 0$, the constraint $x = 0$ can be used. The initial reaction rate, y, was extracted by taking the derivative of the fitted curve and setting t equal to 0. A complete listing of the results is provided in the Supporting Information. In developing a general rate equation for Q$^3_8$ formation, we assumed that the active reagents consisted of (a) a small concentration of H$^+$, as determined from pH measurements; (b) TMA$^+$ cations; and (c) a pool of dissolved Si existing in the form of rapidly interconverting silicate anions, but excluding the Si within TMA-stabilized Q$^3_6$ and Q$^3_8$ cages. At $t = 0$ the rate equation is thus

$$\left(\frac{d[Q^3_8]}{dt}\right)_0 = k_f[H^+]_0{}^a[TMA^+]_0{}^b[Si]_0{}^c \qquad (1)$$

where k_f is the overall forward rate constant, and a, b, and c are reaction orders. The term [Si]$_0$ represents the *total* dissolved silica concentration since, at $t = 0$, the concentration of both Q$^3_6$ and Q$^3_8$ is effectively 0.

The log−log correlation between the initial Q$^3_8$ reaction rate and [H$^+$]$_0$, shown in Figure 3a, is relatively linear over the pH range 13.23−13.57 and yields $a = 1.64 \pm 0.14$. The marked change in slope at pH 13.6 is probably caused by an abrupt rise in the average charge per Si center and, if so, coincides with the third acid dissociation constant p$K_{a,3}$ averaged over
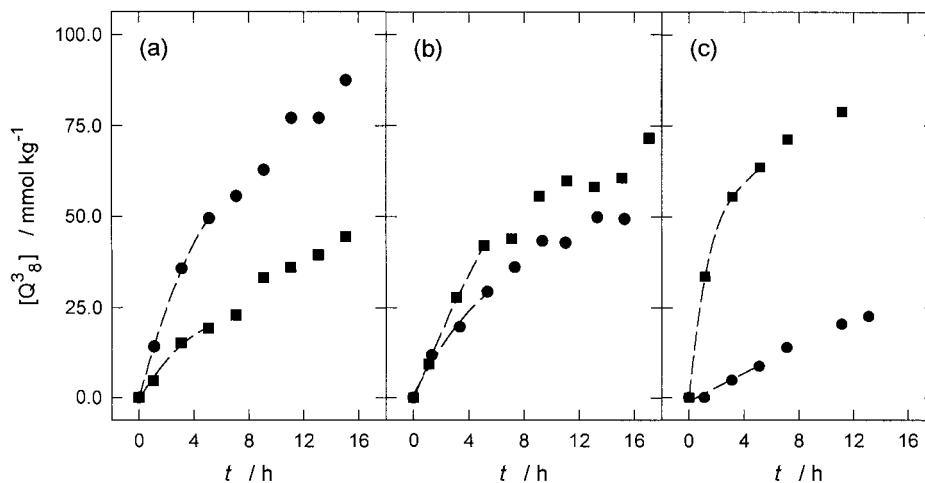
Figure 2. Evolution of Q^3_8 at 296.1 K in a number of representative solutions following the boil−freeze−thaw procedure: (a) varied OH⁻ concentration = 1.15 (●) or 1.7 mol kg⁻¹ (■); (b) varied TMA⁺ concentration = 1.4 (●) or 3.1 mol kg⁻¹ (■); (c) varied SiO₂ concentration (with 1.25 mol kg⁻¹ TMAOH) = 0.6 (●) or 1.2 mol kg⁻¹ (■). The first 4 data points of each experiment were fitted to a second-order polynomial curve to determine the initial rate of Q^3_8 formation. A complete listing of reaction rates is given in the Supporting Information.

all of the smaller silicate oligomers. The linear log−log correlation of rate with $[TMA^+]_0$, shown in Figure 3b, yields $b = 0.362 \pm 0.076$. Finally, the rate dependence on $[SiO_2]_0$ shown in Figure 3c yields $c = 0.82 \pm 0.25$ for the pH range 13.23−13.57. The overall rate equation for formation of Q^3_8 over this pH range can now be written as

$$\left(\frac{d[Q^3_8]}{dt}\right) = k_f[H^+]^{1.6\pm0.1}[TMA^+]^{0.36\pm0.08}[Si]^{0.8\pm0.3} \quad (2)$$

where, at 296 K, $k_f = (2.2 \pm 0.8) \times 10^{16}$ mol⁻¹·⁸ kg¹ s⁻¹ as determined from the average y-axis intercept of Figure 3c. Although general application of eq 2 may at first seem quite limited due to the narrow pH range over which it applies, a surprisingly wide variety of solutions have pH values in that range owing to the inherent buffering ability of silicates.

Transient Species. Knight et al. observed that Q^3_6 forms much sooner than Q^3_8 in TMA silicate solutions following the boil−freeze−thaw procedure, and yet it is eventually sacrificed in favor of the octamer. Hasegawa et al.[7] suggested that this relationship, seen plainly in Figure 1, demonstrates that Q^3_6 is a major intermediate in the formation of Q^3_8 in TMA silicate solutions. It is an unusually stable anion, certainly, and requires addition only of two SiO_4^{4-} units to yield Q^3_8. If Q^3_6 is indeed an intermediate, the highest rate of Q^3_8 formation would occur at or soon after the moment of maximum Q^3_6 concentration. However, this was never observed. The highest rate of Q^3_8 formation was always at $t = 0$, while Q^3_6 concentration typically peaked 2−6 h later. More probably, Q^3_6 is a *transient* species which results from a condensation pathway parallel to the one yielding Q^3_8 and is sacrificed in favor of the more stable octamer when the reactant pool is depleted. Indeed, peaks corresponding to at least five additional, albeit minor, transient species were also observed. None of these peaks were apparent under equilibrium conditions, however. Two of the transient species could be assigned with reasonable certainty on the basis of homonuclear correlation spectra of solutions enriched in ²⁹Si. They are the TAA-associated, doubly bridged four-ring and

tricyclic octamer. (See Figure 4.) The corresponding peaks are shifted about 3 ppm up-frequency from the positions normally observed for these species, e.g., in the case of alkali-metal silicate solutions. If the assignments are correct, these TMA-induced shifts are substantially greater than anything exhibited by the Q^3_8 signal,[1] which is probably due to their higher average charge per Si center and, thus, greater extent of TAA⁺ association. Transient species assigned far more tentatively include the tetrahedral tetramer (Q^3_4) and the pentacyclic nonamer.[8]

Alkali-Metal Addition. It has been noted elsewhere that the addition of alkali-metal cations to tetramethylammonium silicate solutions causes an irreversible drop in the concentration of both Q^3_8 and Q^3_6.[1,9,10] Figure 5 shows that Q^3_8 depolymerizes slowly, but at several times the rate at which it is first formed. In the course of our experiments we noticed that Na⁺ ions also cause a unique but reproducible shift of the Q^3_8 and Q^3_6 signals. Immediately following addition of Na⁺, all NMR signals move approximately 1 ppm to lower frequency. This shift is irreversible for all signals except the Q^3_8 and Q^3_6 peaks, which, as shown in Figure 5, return to higher frequencies at precisely the same rate as that at which the corresponding species depolymerizes.

Heteroatom Substitution. Next, we consider the influence of tetraalkylammonium ions on the kinetics of heteroatom substitution in aqueous silicates. The solubilities of alumino-, boro-, gallo-, germano-, and stannosilicates are all markedly higher in TAA hydroxide solutions than in equivalent alkali-metal hydroxide solutions.[11−13] However, the TAA-stabilized Q^3_8 and Q^3_6 cages are extremely resistant to substitution. For example, there are no reports of B-, Ga-, or Sn-substitution into Q^3_8 or Q^3_6, whereas all of these metals readily incorporate into smaller oligomers. Germanium-substituted Q^3_6 and Q^3_8 cages form after equilibria are perturbed by heating the solution to

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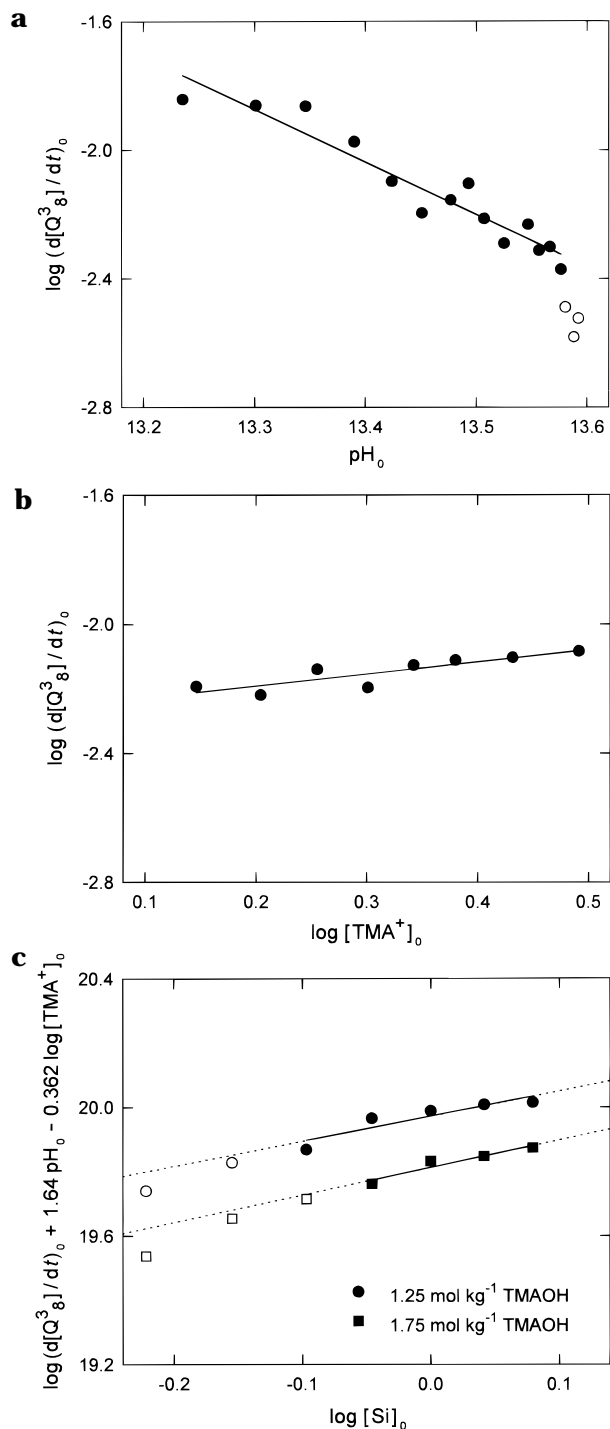
Figure 3. (a) Dependence of the initial rate of Q^3_8 formation on initial pH at 296.1 K for solutions containing 1.0 mol kg^{-1} SiO$_2$ and 2.0 mol kg^{-1}, in total, TMAOH and TMACl. (Refer to Table 1 in the Supporting Information.) The nominal OH$^-$ concentration was varied by adjusting the relative concentrations of TMAOH and TMACl. The slope of the linear correlation at pH $\leq$ 13.57 (solid symbols) is 1.64 $\pm$ 0.14. (b) Dependence of the initial rate of Q^3_8 formation on TMA$^+$ concentration at 296.1 K for samples containing 1.0 mol kg^{-1} SiO$_2$, 1.4 mol kg^{-1} TMAOH, and varied TMACl concentration. (Refer to Table 2 in the Supporting Information.) The initial pH of all solutions was 13.451 $\pm$ 0.010. The slope of the fitted line is 0.362 $\pm$ 0.076. (c) Dependence of $\{(d[Q^3_8]/dt)_0[H^+]^{1.64}[TMA^+]^{0.36}\}$ on dissolved Si concentration at 296.1 K for samples containing 1.25 ($\bullet$) or 1.75 ($\blacksquare$) mol kg^{-1} TMAOH and varied SiO$_2$ concentration. (Refer to Table 3 in the Supporting Information.) The average slope for the linear correlations at pH $\leq$ 13.57 (solid symbols and lines) is 0.82 $\pm$ 0.25, and the average *y*-intercept is 19.89 $\pm$ 0.22.
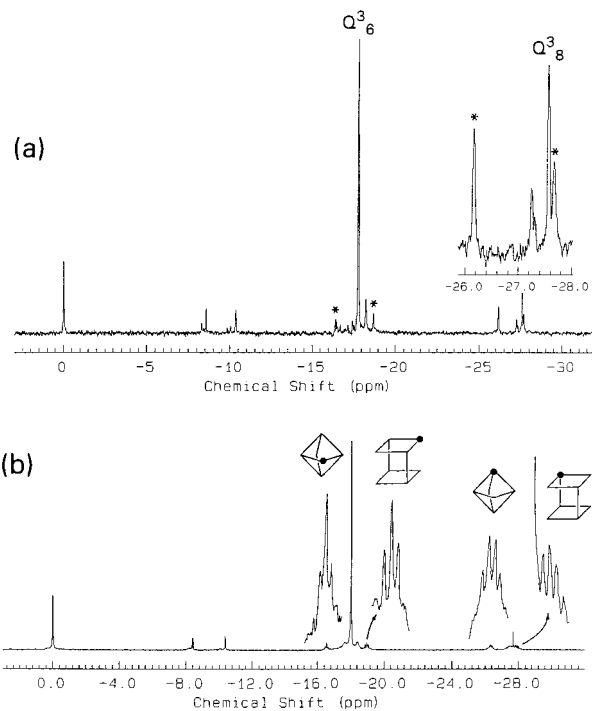

Figure 4. (a) [29]Si (99.36 MHz) spectrum at 280.0 K of a solution containing 1.0 mol kg^{-1} SiO$_2$, 1.4 mol kg^{-1} TMAOH, and 1.7 mol kg^{-1} TMACl. The spectrum was acquired over the 10 h immediately following application of the boil$-$freeze$-$thaw procedure. Transient resonances are indicated with asterisks. (b) Spectrum acquired at 273.8 K of an equivalent solution, 95 atom % enriched in [29]Si, during the 10 h following boil$-$freeze$-$thaw. The multiplets and corresponding assignments are shown for four of the transient peaks. The ^2J ([29]Si$-$O$-$[29]Si) coupling constant of the peaks at -16.4 and -26.2 ppm is 3.2 Hz (doubly bridged tetramer), and that of the peaks at -18.7 and -27.7 ppm is 4.0 Hz (tricyclic octamer).
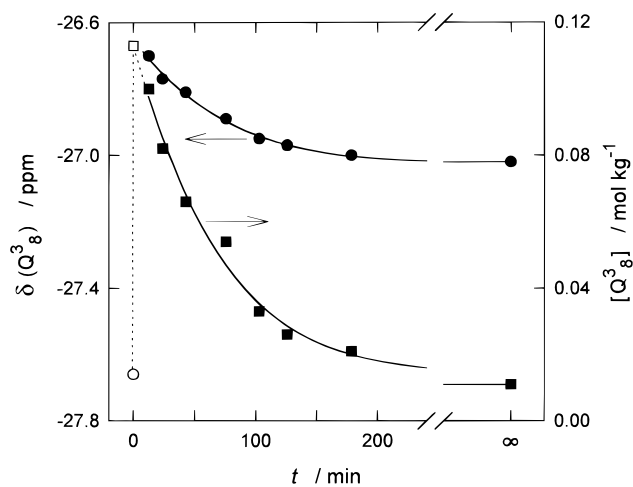

Figure 5. The time dependence at 296.1 K for the concentration ($\blacksquare$) and [29]Si peak position ($\bullet$) of Q^3_8 after 1.7 mol kg^{-1} NaCl is added to a solution containing 1.0 mol kg^{-1} SiO$_2$, 1.4 mol kg^{-1} TMAOH, and 0.6 mol kg^{-1} TMACl. Open symbols denote conditions prior to NaCl addition. The equilibrium values for the concentration and resonance frequency of Q^3_8 were reached after 5 h. The concentration and peak position of Q^3_6 also shifted in unison, reaching their limiting values after about 20 min.

boiling, yet they are metastable and never exist for more than a few weeks.[8,11] The ^{29}Si NMR resonances corresponding to Q^3_6, Q^3_8, and Ge-substituted Q^3_8 are all quite sharp, whereas all the signals corresponding to silicate oligomers that are not stabilized by TAA$^+$ cations are extremely broad. (See Figure

1 in the Supporting Information.) Variable temperature experiments indicate that the Ge-induced broadening is kinetic in origin, presumably due to rapid Si–Si chemical exchange between silicate and short-lived germanosilicate centers. The large quadrupolar moment of ^{77}Ge has so far precluded detection of any of the corresponding ^{77}Ge resonances. The incorporation of aluminum into TAA-stabilized Q^3_6 and Q^3_8 cages similarly requires that the equilibria first be perturbed either by warming or by acidification. Aluminum-substituted Q^3_8 is also metastable, although less so than the Ge-substituted analogue.

Discussion

As for any complicated solution phase reaction, it would be quixotic to formulate a detailed mechanism for Q^3_8 formation based solely on the observed rate law. This is true especially when the solvent plays such a key, yet enigmatic, role. Nonetheless, the near first-order rate dependence on Si concentration and roughly second-order dependence on H$^+$ are entirely consistent with earlier work which revealed that the rate-determining step in silicate polymerization is the formation of a neutral silicate center, primarily in highly mobile, monomeric and dimeric species.[4] The second pK_a for H_4SiO_4 and $H_6Si_2O_7$ would be expected to range from about 12.7 to 13.5 in the solutions analyzed,[14] which, being at pH 13.4 ± 0.2, must contain a significant concentration of doubly deprotonated Si centers. Therefore, it is reasonable to expect that up to two protons are required to neutralize the Si centers of low-molecular-mass species. Of far greater importance, however, is the presence of the TMA$^+$ term in eq 2. This proves unequivocally that tetraalkylammonium ions play a fundamental role in the growth of symmetrical, cagelike polyanions. As discussed already,[1] a subsequent role of TAA$^+$ cations is to shield the resulting cage structures from interaction with the bulk solution, thereby impeding hydrolysis. This is further evidenced by the resistance that Q^3_6 and Q^3_8 exhibit toward heteroatom substitution. In the previous paper,[1] we showed that added alkali-metal cations (M$^+$), having comparatively high surface charge densities, displace TAA$^+$ from association with silicate polyanions and, hence, decrease the equilibrium concentrations of the TAA-stabilized Q^3_6 and Q^3_8 cages. Here we report that the addition of M$^+$ causes the NMR resonances corresponding to these two species to undergo an immediate down-frequency shift, followed by a gradual return back up-frequency (Figure 5). These peaks undergo a similar, slow, up-frequency shift when TAA$^+$ salts are added to solution, indicating that the up-frequency shift arises from the (re)-association of free TAA$^+$ ions with the Q^3_6 and Q^3_8 cages.

Altogether, the equilibrium, kinetic, and NMR data presented in this and the preceding paper[1] lead us to propose a general mechanism for polymerization in silicate solutions containing organic cations. Silicate-cation ion pairing serves to weaken the electrostatic repulsion between silicate anions and in this way helps to promote condensation.[15] In addition, the attraction of organic cations to adjacent ≡SiO$^-$ sites will induce the hydrophobic hydration spheres on the cations to merge, freeing some of the hydrophobically bound waters and, moreover, decreasing solvent mobility near the silicate anion. Cagelike species, with anionic sites projecting in several directions, thus become surrounded by a continuous, or nearly continuous, shell

of hydrophobic hydration that impedes hydrolysis. The transient species observed in the boil–freeze–thaw experiments (e.g., the doubly bridged four-ring and the tricyclic octamer) are favored in this way. However, nonrigid and/or irregular species such as these are only loosely clathrated and, eventually, give way to cages with the greatest rigidity and optimum charge distributions, i.e., Q^3_6 and Q^3_8. It is important to note that none of the silicate structures identified in this study are exclusive to TAA silicate solutions; therefore, the menu of viable structures is only marginally affected by the nature of the cations present in solution.

Davis and co-workers[16,17] have suggested a different mechanism for silicate polymerization in organic base solutions that is based on the template model of zeolite synthesis. They speculated that silicate ions replace the hydration spheres around alkylammonium cations to form composite species that, in effect, are the inverse of the TAA-enclathrated silicate cages. They were able to demonstrate that TAA$^+$ and silicate ions exist in close proximity in a tetrapropylammonium silicate solution—supporting either polymerization model—by detecting cross-polarization between the corresponding ^{1}H and ^{29}Si nuclei. The present findings, however, clearly do not support their proposed mechanism.

What can be inferred about zeolite synthesis from the existence of clathrated polyanions and from the bulk solution chemistry in general? It is widely believed that the structure of synthetic zeolites is sensitive to the nature of the silicate species that are present in the growth medium (see, e.g., ref 18). This idea, in our opinion, is extremely misleading, being rooted in the discredited secondary-building-unit hypothesis.[19] Silicate species in the gel and bulk solution have no *direct* influence on zeolite growth. However, the chemical mechanisms that control the nature of these species obviously also influence zeolite evolution. We propose that, at the crystal surface, partially formed TAA-clathrate shells serve to stabilize open silicate structures that would be energetically unfavorable otherwise. Thus, they act as a form of external scaffolding. Ultimately (depending on charge-balancing requirements), some of the solvated TAA$^+$ cations will become trapped in the emerging zeolite structure and subsequently serve a space-filling role arising from van der Waals interactions with the silicate framework atoms, thereby acting as internal scaffolding. The well-documented importance of using small amounts of alkali-metal cations to accelerate zeolite nucleation and growth[20] is probably a consequence of their ability to displace organic cations from silicate surfaces, thereby weakening and periodically releasing the external scaffolding which would then expedite further polymerization. Similarly, the use of relatively large organic cations having low surface charge densities would be expected to yield faster nucleation and crystal growth (because of more facile scaffolding release), but at the same time, they may necessitate the addition of organic solvents to enhance the extent of hydrophobic hydration (better scaffolding integrity).

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Supporting Information Available: Complete listings of sample compositions and rate determinations, along with a [29]Si germanosilicate spectrum (4 pages). Ordering information is given on any current masthead page.

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