Monitoring Solvent Dynamics and Ion Associations in the Formation of Cage-like Polyanions in Tetraalkylammonium Silicate Solutions

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Monitoring Solvent Dynamics and Ion Associations in the Formation of Cubic Octamer Polyanion in Tetramethylammonium Silicate Solutions

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NMR methods were utilized to monitor the in-situ structural and dynamic changes of various species in highly alkaline tetramethylammonium (TMA) silicate solutions. Quantitative ^{29}Si NMR, ^{1}H, ^{2}H, and ^{17}O relaxation NMR, and ^{1}H and ^{29}Si diffusion NMR of silicates, TMA, H_2O and D_2O demonstrate that the growth of the cubic octamer Q^3_8 is accompanied by reduced water mobility and increasing TMA coordination number per Q^3_8, which reaches an equilibrium value of 4.5 at 15 °C. Temperature-dependent measurements further reveal that the increased control over speciation by TMA at lower temperatures results from the more stable ion associations via slower solvent motions.

The development of novel materials with tailorable properties is advanced by increased understanding of the fundamental principles involved in their formation over different length- and timescales. With widespread industrial applications in catalysis, gas separation, and ion exchange, zeolites are an area of intense focus as control of their function can be achieved through hierarchical synthesis using various precursors.[1] Organic molecules, such as tetraalkylammonium (TAA), used in zeolite synthesis have long been recognized as structure-directing agents (SDA) that organize solution components and facilitate the formation of final zeolite architectures.[2-4] However, a fundamental understanding of how the molecular-level interactions between the organic molecules, silicate species, and the solvent combine to affect the final overall structures remains elusive. More generally, interest in defining and quantifying pathways of ion association, cluster formation and the onset of nucleation has intensified in recent years with the realization that hierarchical assembly processes not captured in traditional models of nucleation, like those fundamental in zeolite formation, are pervasive in synthetic and natural systems.[5-7] Herein we use a small-scale system that includes only the silicate source, SiO_2, and an organic SDA, tetramethylammonium hydroxide (TMAOH), in water as a model system to investigate dynamic processes involved at the onset of zeolite formation.

It has been established that two symmetric cage-like silicate species are dominant in highly alkaline TMA silicate solutions, the cubic octamer Q^3_8 (consisting of 8 Q^3 silicon sites) as the major species and the prismatic hexamer Q^3_6 (consisting of 6 Q^3 sites) as the minor species,[8-10] which are in stark contrast to those detected in alkali-metal silicate solutions where a much wider range of small, structurally similar but asymmetric silicate anions emerge in dynamic equilibrium.[11-16] The ability to control silicate speciation with quaternary ammonium ions has recently become an area of intense interest and has been explored both experimentally and theoretically.[17-29] Kinrade et al. employed ^{29}Si NMR, one of the most powerful tools for identifying silicate species in solution, to explore the dependence of Q^3_8 equilibrium concentrations and the polymerization kinetics of Q^3_8 formation with a variety of TAA^+ cations. Their study demonstrated that TAA^+ ions played a critical role in the growth and subsequent stabilization of Q^3_8 and that the stoichiometric ratio of TMA to Q^3_8 was approximately 8:1 for solutions with $[OH]:[Si] \geq 1$.[18, 19] Kinrade et al. hypothesized that hydrophobic hydration spheres of TAA^+ cations (where the water hydrogen-bonding network is disrupted to form a short-lived expanded low-entropy cage) surrounding the symmetrical Q^3_8 or Q^3_6 overlap and create continuous or near continuous shells of water/TMA^+ clathrate structures that isolate the polysilicate anions from the aqueous environment.[18] Cartzoulas et al. employed molecular dynamics to explore the finer details of the aqueous TMA-silicate solution structures and obtained a TMA:Q^3_8 coordination number of six, wherein each TMA cation occupied one face of the cubic octamer.[22] These simulation

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Electronic Supplementary Information (ESI) available: experimental methods; ^{1}H, ^{2}H and ^{17}O NMR relaxation time constants measured as a function of reaction time; states of water in TMA silicate solutions during Q^3_8 growth; ^{29}Si NMR spectra and self-diffusion coefficients of TMA as a function of reaction time for TMA silicate solutions with lower concentrations; and Arrhenius plot to obtain activation energy of Q^3_8 formation. See DOI: 10.1039/x0xx00000x results supported the external scaffolding hypothesis originally proposed by Kinrade et al. where organocations serve as external scaffolds organizing the solvent surrounding cage-like species and stabilizing hydrogen bonds between water and anionic sites of the polysilicates.[19, 23, 24] However, changes in the structure and dynamics of water and the ion associations between TMA and silicates during the process of Q^3_8 formation have not been explicitly studied experimentally, primarily because conventional experimental approaches such as NMR chemical shift, X-ray crystallography, and AFM are not sensitive to these subtle and dynamic changes in solution.

In this study we adopt the boil-freeze-thaw procedure created by Knight et al. to bring the system to the starting point of Q^3_8 formation from SiO_2 and TMAOH.[30] In this procedure the boil step breaks down all stable silicate oligomers into monomers, the freeze step halts chemical exchange, and the thaw step brings us to the initial time point for Q^3_8 growth from its constituent monomers. The thaw step is carried out at several different temperatures. Multiple NMR methodologies were utilized to monitor changes in the aqueous system during Q^3_8 formation: 1) standard single-pulse ^{29}Si NMR to identify polysilicate species and quantify their concentrations; 2) ^{1}H, ^{2}H, and ^{17}O spin-lattice relaxation (T_1) and spin-spin relaxation (T_2) time constants to capture changes in water dynamics; and 3) ^{29}Si and ^{1}H chemically-specific diffusion ordered spectroscopy (DOSY) to detect the formation of ion complexes between the organocation and octahedral silicate Q^3_8 cage, and to obtain the average TMA coordination number per Q^3_8 cage.

^{29}Si NMR spectra in Figure 1A demonstrate the slow growth of the resonance arising from Q^3_8 species with time at 15 °C in a TMA silicate solution containing 1 mol/kg SiO_2 and 1 mol/kg TMAOH after the boil-freeze-thaw process. Note that Q^3_8 species, if present, are below the detection limit in the first few minutes. On the other hand, the measured chemical shifts of ^{1}H, ^{13}C, ^{2}H and ^{17}O NMR spectra exhibit little change with time, as the Q^3_8 growth primarily affects the dynamics of water and TMA. To monitor changes in solvent dynamics during Q^3_8 formation, ^{1}H, ^{2}H and ^{17}O NMR spin-lattice relaxation time constant (T_1) and spin-spin relaxation time constants (T_2) were measured as a function of reaction time. The dominant relaxation mechanisms in aqueous solution are dipole – dipole interactions for ^{1}H and quadrupolar interactions for ^{2}H and ^{17}O; both interactions are highly affected by water molecular correlation time.[31] As shown in Figure 1B and Figure S2, all NMR relaxation time constants of water exhibit an initial steep drop followed by reaching a plateau after 30 hours, suggesting that water reorientation is significantly restricted due to Q^3_8 formation; the remarkable decrease in T_1 primarily results from rotational restriction of water. The observations are consistent with the hypothesis by Kinrade et al.[18, 19] and MD simulations by Caratzoulas et al.[22-24] in which the hydrophobic hydration shells of adjacent TMA molecules inevitably merge to generate a symmetrical shield of water layers around Q^3_8, leading to decreased solvent mobility near the cage. Our results provide the direct experimental evidence of reduced water motion during silicate oligomerization and further support the external scaffolding hypothesis.[18, 22]

Similarly, as shown in Figure 1C, the self-diffusion coefficient of TMA, D(TMA), displays a dramatic drop initially and subsequently reaches a plateau, while the self-diffusion coefficient of H_2O, $D(H_2O)$, remains constant during Q^3_8 formation, confirming an unchanged solution viscosity. Figure S3 shows that no significant change in D(TMA) is observed in the initial time points when Q^3_8 is undetectable after the same boil-freeze-thaw process for a TMA silicate solution of 0.5 mol/kg SiO_2 and 0.5 mol/kg TMAOH. Note that a non-negligible fraction of TMA may loosely associate with other silicate polyanions species, especially with Q^3_6, but the observed D(TMA) does not change during the formation of Q^3_6, indicating that the diffusion coefficients of TMA binding with other silicate polyanions are comparable and the exchange between them is fast enough that the ensemble average D(TMA) remains unaltered (Figure S3). Therefore, the decrease in D(TMA) can be unambiguously attributed to the formation of the relatively more stable ion associations between TMA and Q^3_8.

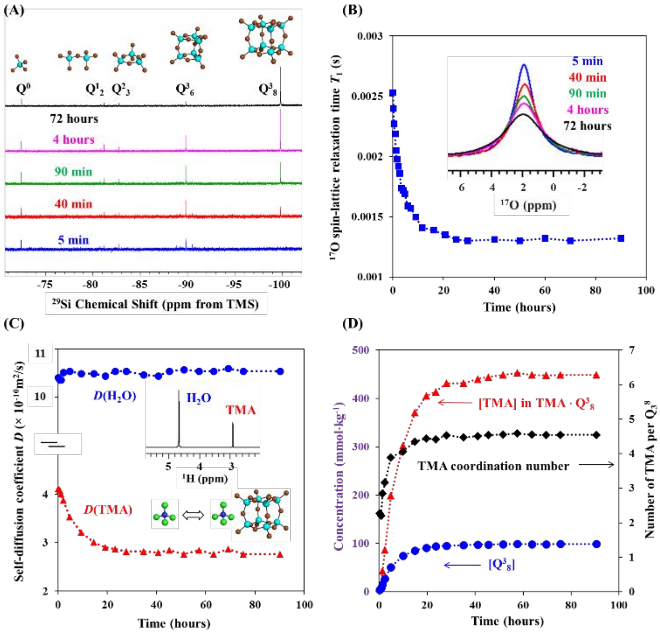

Figure 1. Time series NMR measurements of a TMA silicate solution containing 1 mol/kg SiO_2 and 1 mol/kg TMAOH after the boil-freeze-thaw process at 15 °C. (A) ^{29}Si NMR spectra collected at varying time intervals; (B) ^{17}O spin-lattice relaxation time T_1 of water, with ^{17}O spectra acquired at varying time intervals; (C) self-diffusion coefficients of H_2O and TMA measured by ^{1}H NMR; and (D) concentration of Q^3_8, concentration of TMA in the ion complex $TMA{\cdot}Q^3_8$, and TMA coordination number per Q^3_8 calculated using Eq. 2.

Considering a two-site model for TMA diffusion, where TMA exchanges between a "bound" site in which TMA is associated with Q^3_8 and a "free" site consisting of TMA solvated by water or involved in the short-lived weakly-bound ion complexes with other anions, the observed diffusion coefficient $D_{\text{TMA - }obs}$ is the weighted sum of the diffusion constants of both sites:

$$D_{\text{TMA - }obs} = D_{\text{TMA - }free}\left(1 - f_{\text{TMA}\cdot\text{Q}_8^3}\right) + D_{\text{TMA}\cdot\text{Q}_8^3}\, f_{\text{TMA}\cdot\text{Q}_8^3} \qquad (1)$$

Here $D_{\text{TMA - }free}$ and $D_{\text{TMA}\cdot\text{Q}_8^3}$ are the diffusion coefficients of free and bound TMA, respectively, and $f_{\text{TMA}\cdot\text{Q}_8^3}$ is the fraction of

TMA associated with Q^3_8. As noted earlier the formation of Q^3_8 occurs within a few minutes of the boil-freeze-thaw process, therefore the diffusion measurement at the first time point only involves free TMA, $D_{\text{TMA - }free} = D_{\text{TMA - }t0}$. Assuming that TMA and Q^3_8 diffuse together in the ion associates, $D_{\text{TMA}\cdot Q_8^3}$ can be obtained from ^{29}Si NMR diffusion measurements of Q^3_8 at equilibrium, $D_{\text{TMA}\cdot Q_8^3} = D_{Q_8^3}$. With $f_{\text{TMA}\cdot Q_8^3}$ estimated from Eq. 1, the coordination number of TMA for Q^3_8 can be calculated from:

$$\text{Number of TMA per } Q_8^3 = \left. f_{\text{TMA}\cdot Q_8^3} \times [\text{TMA}] \middle/ f_{Q_8^3} \times [\text{SiO}_2]/8 \right. \quad (2)$$

Here $f_{Q_8^3}$ is the fraction of the total Si concentration existing as Q^3_8 determined from ^{29}Si NMR spectral integration. Figure 1D shows the changes in the concentration of Q^3_8 species obtained from ^{29}Si spectra (blue circle), the concentration of TMA associated in TMA·Q^3_8 complexes obtained from ^{1}H NMR diffusion measurements (red triangle), and the coordination number of TMA per Q^3_8 calculated from Eq. 2 (black diamond). Observation of the Q^3_8 species occurs first at a low TMA coordination number of 2.2, suggesting that a few TMA cations may participate in silicate oligomerization potentially via electrostatic interactions with silicate monomers and then remain proximal to the newly formed octamer. The slow increase of TMA coordination number that matches well with the slow decrease in the solvent dynamics and the Q^3_8 growth curve reveals that the adsorption of TMA around Q^3_8 is a slow kinetic process where nearby TMA molecules are constantly changing positions and finally reach an equilibrium configuration as a result of the combined effects of thermal fluctuations, electrostatic interactions between TMA and Q^3_8, and van der Waals interactions between TMA and water. An equilibrium coordination number of 4.5 at 15 °C is smaller than the value obtained from MD simulations where each face of Q^3_8 is occupied by one TMA molecule on average,[22] suggesting that the symmetrical configuration determined from simulations does not precisely represent the ion complex structures found under our experimental conditions.

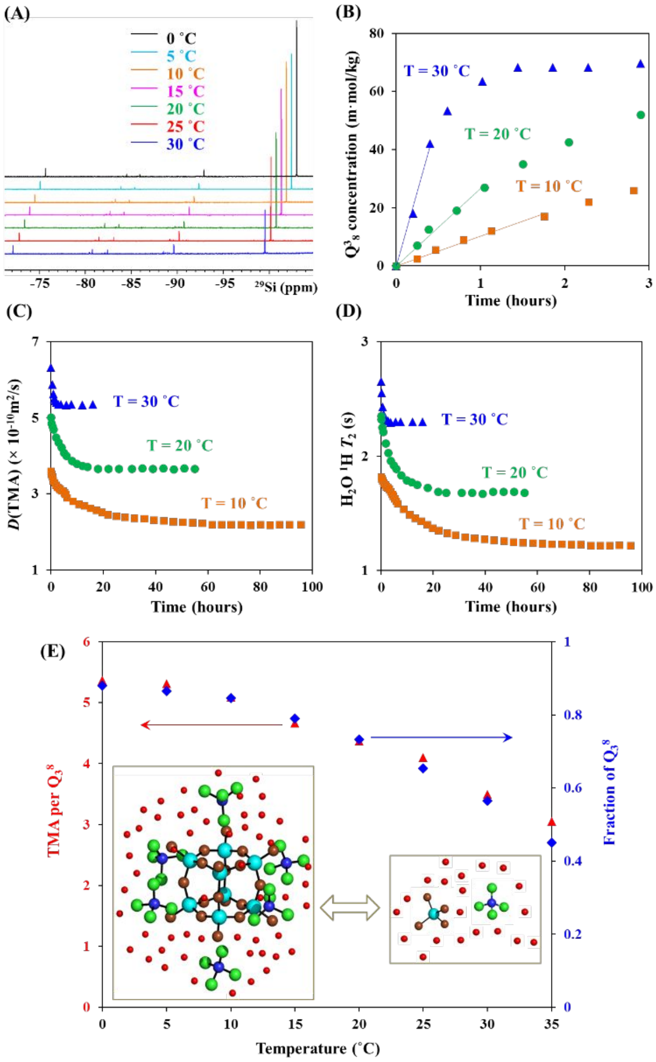

Figure 2. (A) ^{29}Si NMR spectra of TMA silicate solution containing 1 mol/kg TMAOH and 1 mol/kg SiO_2 equilibrating at various temperatures. The peak intensity is normalized to that of Q^0. The formation rate of Q^3_8 calculated from the initial few time points (B), self-diffusion coefficients of TMA (C) and ^{1}H T_1 of water (D) following the boil-freeze-thaw procedure at various temperatures. (E) Strong correlation between the concentration of Q^3_8 at equilibrium and the coordination number of TMA per Q^3_8 at various temperatures

As reported by Kinrade and Haouas, control over silicate speciation by organocations is especially sensitive to temperature.[18, 32] Consistent with these findings, Figure 2A shows that the yield of Q^3_8 in the solution decreases significantly as temperature increases. In Figure 2B, the initial Q^3_8 formation rate k is obtained by fitting the first few data points of Q^3_8 concentration vs. time following the boil-freeze-thaw procedure to a linear equation $[Q^3_8] = k\,t$, as $[Q^3_8] = 0$ at $t = 0$. The reaction rates obtained at various temperatures lead to an activation energy of 76 ± 5 kJ/mol (Figure S4). The greater initial Q^3_8 formation rate followed by the smaller Q^3_8 equilibrium concentration at a higher temperature can be explained by the dynamics and structures of TMA, water and TMA·Q^3_8 complex demonstrated in Figure 2C to 2E. At lower temperature, due to the slow translational motion of TMA and slow exchange between the bound and bulk TMA, as well as the slow growth of Q^3_8, TMA has more time to further adjust its position to fit into a more stable structure of TMA·Q^3_8 (Figure 2C). Concurrently, due to the slow motion of water, and specifically the slow rotational motion, water molecules are prone to be reorganized by TMA and to form a more ordered continuous shell of hydrophobic hydration surrounding TMA and Q^3_8 (Figure 2D). The coordination number of TMA per TMA·Q^3_8 complex increases as temperature decreases and exhibits a strong correlation with the fraction of Q^3_8 at equilibrium (Figure 2E). As discovered by Wiebcke et al.,[33, 34] the local environment of Q^3_8 in crystalline TMA silicate clathrate $[\text{TMA}]_8[Q^3_8]\cdot 65H_2O$ is a very stable finite cluster $[(\text{TMA})_6(Q^3_8)\cdot 24H_2O]^{2-}$, with TMA located at the center of each Q^3_8 face and water molecules forming strong hydrogen bonds with the terminal oxygen atoms from the silicate. Our results show that the similar hydrate clathrate structure exists in TMA silicate solution, $[(\text{TMA})_x(Q^3_8)\cdot nH_2O]^{(x-8)}$ ($x < 6$), which is less symmetric and less stable due to thermal fluctuation and fast exchange with bulk liquids but moves towards the six-fold coordination seen in the basic structural unit of crystal as the temperature is decreased.

In conclusion, time series NMR measurements after initiation of silicate growth demonstrate a direct experimental evidence that the increase in Q^3_8 concentration (quantified by ^{29}Si NMR) is accompanied by reduced water mobility (detected by ^{1}H, ^{2}H and ^{17}O NMR relaxation). In contrast to the stoichiometric ratio [TMA]:[Q^3_8] = 8:1 obtained from direct equilibrium measurements[13] and the average TMA coordinating number of 6 per Q^3_8 estimated from MD simulations[22, 23], the typical Q^3_8 species is found to be surrounded by 4.5 TMA cations at 15 °C calculated from ^{1}H and ^{29}Si diffusion measurements. Increased control over speciation by TMA at lower temperatures is related to a more stable TMA·Q^3_8 complex with a higher TMA coordination number and a stronger hydrogen-bond network due to the average slower translational and rotational motions of TMA and water. This change in the structure and dynamics of ion associations and solvent molecules as a function of temperature may play a vital role in cluster formation and the onset of nucleation in hierarchical assembly processes.

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Conflicts of interest

There are no conflicts to declare.

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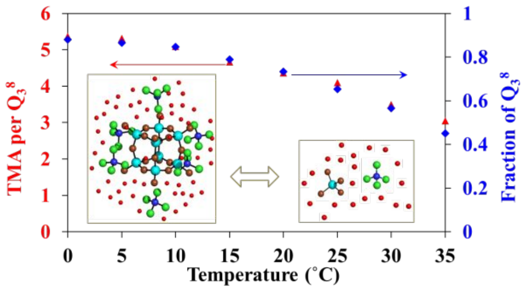

Solvent dynamics and ion associations were monitored during the formation of cubic octamer polysilicate using multiple NMR methods.