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

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Experimental Methods

TMAOH (99.9999% in 25 wt% aqueous solution, from Alfa Aesar), SiO_2 (> 99.5% amorphous fumed CAB-O-SIL M5, from CABOT), ultrapure H_2O and D_2O (99.9%, from Sigma Aldrich) were mixed in a Teflon container and heated in an oven at 60 °C overnight to obtain a clear solution. The solution was transferred to a clean 5 mm Teflon tube liner, with its cap sealed using a soldering iron. In a boil-freeze-thaw procedure, the tube liner was heated in a sand bath on a hot plate at 150 °C for 3 minutes, inserted into liquid nitrogen for 3 minutes, thawed at room temperature with all air bubbles removed and then inserted into the magnet immediately at a preset temperature. All solution-state NMR measurements were performed on a Varian DDRS spectrometer with a 17.6 T magnet using a broad-band (BBO) probe. The 90˚ pulse widths were 13 μs for ^{1}H, 140 μs for ^{2}H, 23 μs for ^{17}O, and 12 μs for ^{29}Si. ^{29}Si spectra were collected using 30° pulses with a recycling delay of 20 s for quantitative analysis. T_1 and T_2 relaxation time constants were measured using inversion-recovery and CPMG methods, respectively. ^{1}H and ^{29}Si diffusion coefficient were measured using a bipolar pulse pair stimulated echo pulse sequence with convection compensation. The typical parameters for ^{1}H DOSY experiments were gradient $g = 1.6 – 34.5$ G/cm, number of increments = 18 (for kinetics measurements) and 32 (at equilibrium), diffusion gradient duration $\delta = 2$ ms, diffusion delay $\Delta = 200$ ms, gradient stabilization delay = 2 ms, number of scans = 2 (for kinetics measurements) and 32 (at equilibrium), number of scans for steady state = 16. ^{29}Si DOSY experiments were conducted for solutions after reaching equilibrium using the same gradient strength, but the diffusion gradient duration, diffusion delay, number of scans were increased to 5 ms, 1500 ms, and 256 when $T \leq 25$ °C, and 3 ms, 800 ms and 1024 when $T > 25$ °C, respectively. To track the initial changes in the reaction, each T_1, T_2, diffusion and ^{29}Si experiment was designed to take 5 minutes or less.

40 wt% D_2O was used to reduce proton radiation damping but to maintain a reasonably short ^1H T_1 for relaxation and diffusion measurements within the 5 minute time window.

Typical data analysis of relaxation and diffusion experiments were done directly in VNMRJ software. To confirm that true single-component relaxation and diffusion were observed instead of being forced to fit into a single-component decay in VNMRJ, we exported data to excel spreadsheet and use both the least-squares and linear-regression methods for data fitting. For unrestricted and isotropic diffusion, signal attenuation is a function of gyromagnetic ratio γ, gradient strength g, gradient duration δ, diffusion time Δ, and diffusion coefficient D according to Stejskal-Tanner equation:[1]

$$I = I_0 exp(-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)) = I_0 \exp(-Db) \tag{S1}$$

$$ln(I_0/I) = -Db \tag{S2}$$

Here b is the Stejskal-Tanner parameter, $b = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$. The Stejskal-Tanner plot of $ln(I_0/I)$ vs. b yields a straight line with a slope of $-D$ for single-component diffusion. As an example, Figure S1 shows ^1H T_2 relaxation curves (A-B), ^1H diffusion Stejskal−Tanner plots (C-D) and ^{29}Si diffusion Stejskal−Tanner plots (E-F) of H_2O, TMA and Q^3_8 for the solution containing 1M SiO_2 and 1M TMAOH reaching equilibrium at 25 °C. The straight lines with $R^2 > 0.99$ in the bottom panels demonstrate that single-component fittings are valid.

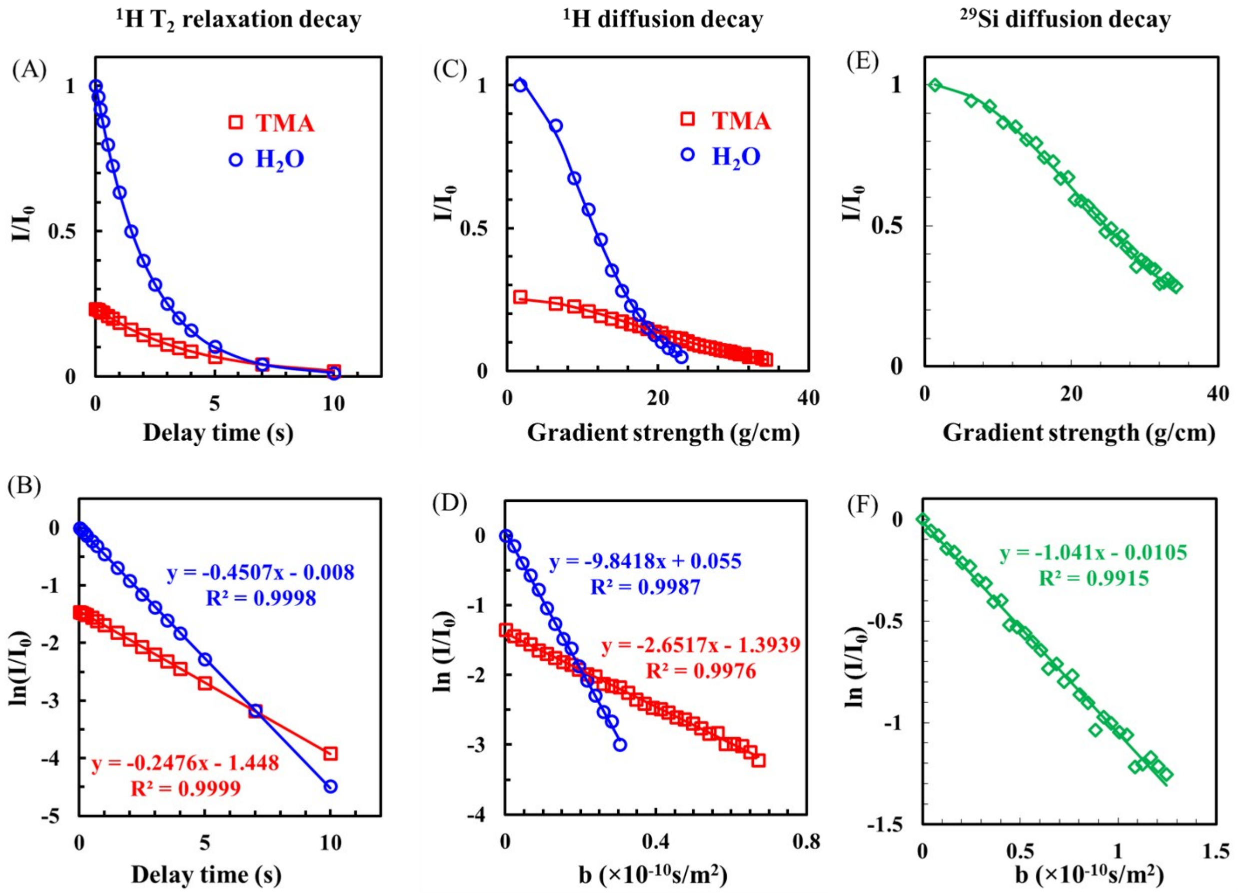

Figure S1. Relaxation and diffusion data fitting. (A-B) ^{1}H T_2 relaxation decay curves of H_2O and TMA. (C-D) ^{1}H diffusion Stejskal-Tanner plots of H_2O and TMA. (E-F) ^{29}Si diffusion Stejskal-Tanner plots of Q^3_8. The markers are the experimental data points and the solid lines are the fits using least-squares (upper panels) and linear-regression (bottom panels).

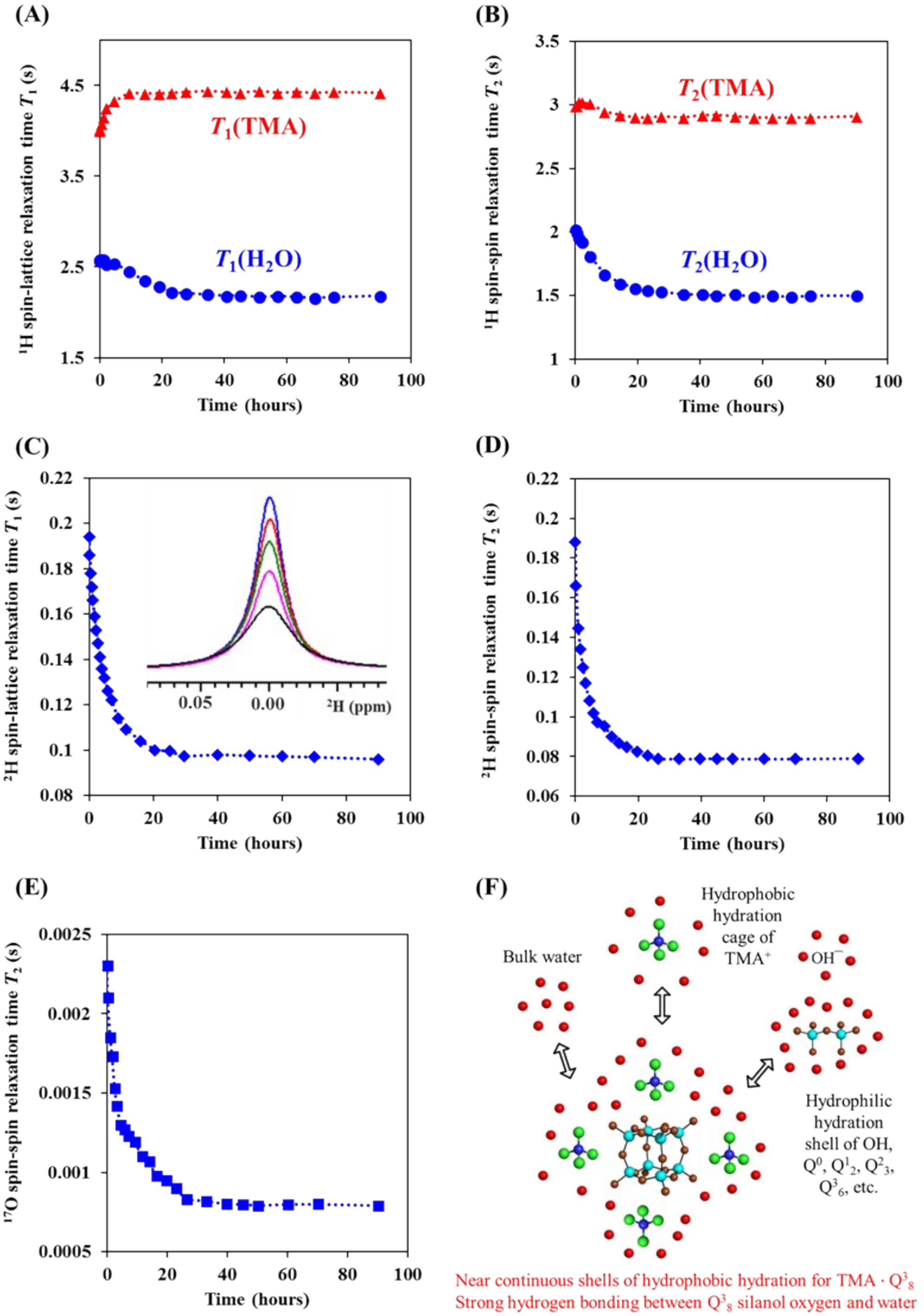

Figure S2. NMR relaxation measurements as a function of time following the boil-freeze-thaw process. (A) ^{1}H spin-lattice relaxation time T_1 of TMA and H_2O, (B) ^{1}H spin-spin relaxation time T_2 of TMA and H_2O, (C) ^{2}H T_1 and (D) ^{2}H T_2 of D_2O, and (E) ^{17}O T_2 of water. The inset in (C) is

^2H spectra acquired at 5 min, 40 min, 90 min, 4 hours and 72 hours after thawing at 15 °C. (F) States of water in TMA silicate solutions during Q^3_8 growth.

As shown in Figure S2A to S2E, while T_1 and T_2 of ^1H, ^2H and ^{17}O of water, and ^1H T_2 of TMA all follow the similar monotonically decreasing curve, time dependent of TMA ^1H T_1 shows an opposite trend, suggesting that the dominant relaxation mechanism for TMA methyl proton T_1 is spin rotation, where the correlation time is not determined by molecular motion but by the lifetime of rotational quantum states.

When referenced to pure water, the ^2H chemical shift $\delta(^2H)$ remains at 0 ppm in TMA silicate solutions, but the ^{17}O chemical shift $\delta(^{17}O)$ decreases from 2.99 ppm in 1 mol/kg TMAOH to 1.86 ppm in a mixture of 1 mol/kg TMAOH and 1 mol/kg SiO_2. Similar to the ^1H and ^{13}C chemical shift, $\delta(^2H)$ and $\delta(^{17}O)$ exhibit little change during the formation of silicate oligomers. Generally speaking, a change in pH or hydrogen bonding strength between water molecules will cause a detectable change in $\delta(^{17}O)$.[2] Here the fast exchange between different water sites in solution (Figure S2F) yields an overall constant $\delta(^{17}O)$, probably because the change in $\delta(^{17}O)$ caused by merging hydrophobic hydration shells between neighboring TMA cations compensates for the change caused by hydrogen bonding between the silanol oxygens of the polysilicate species and surrounding water molecules. A more detailed analysis of water structures and its average coordination numbers around TMA· Q^3_8 complex using a combination of NMR techniques and other analytical tools will be the focus of further studies.

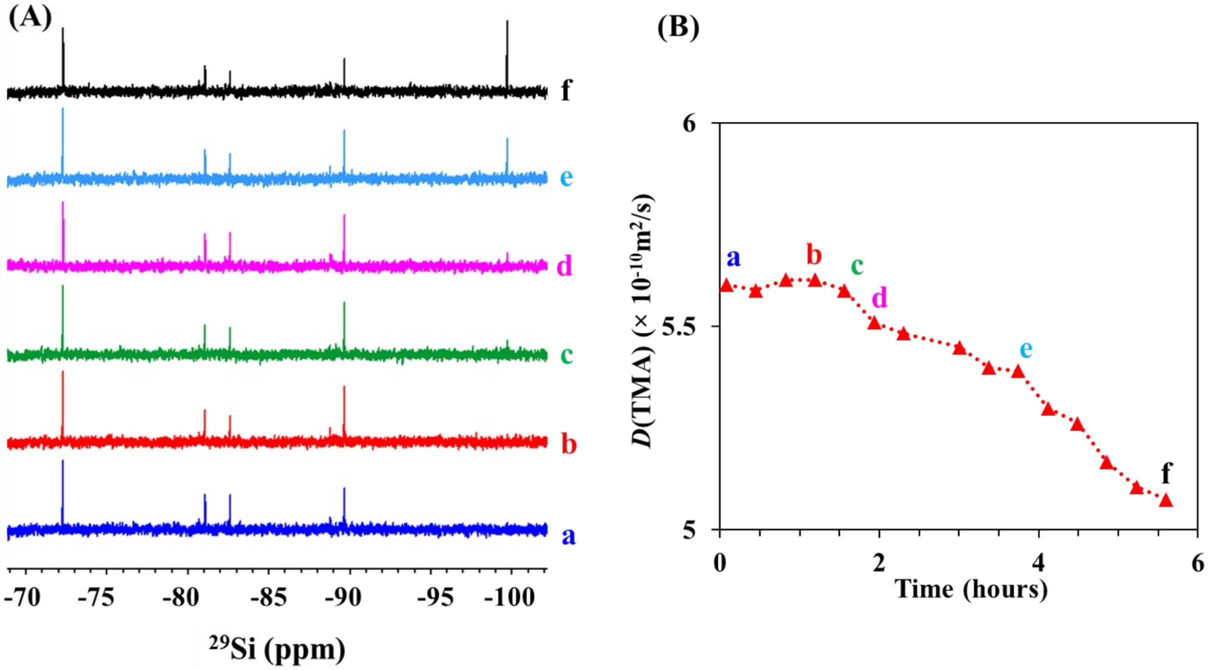

Figure S3. (A) ^{29}Si NMR spectra of TMA silicate solution (0.5 mol/kg SiO_2 and 0.5 mol/kg TMAOH) collected at varying time intervals after the boil-freeze-thaw process at 15 °C. (B) Self-diffusion coefficients of TMA measured by ^{1}H NMR as a function of time after the boil-freeze-thaw process. ^{29}Si spectrum a-f in (A) was taken right before the corresponding time point a-f in (B) when *D*(TMA) was measured.

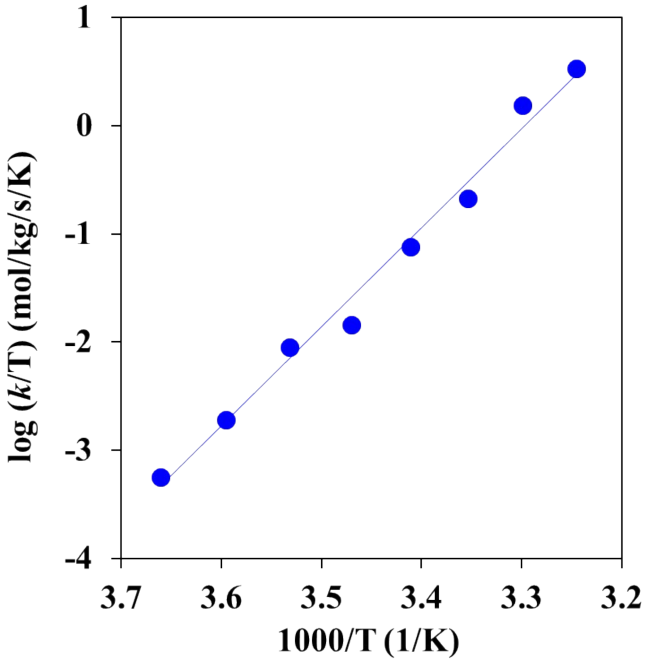

Figure S4. Q^3_8 formation rate as a function of temperature leads to an activation energy of 76 ± 5 kJ/mol.

1. (a) Stejskal, E. O.; Tanner, J. E., Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *The Journal of Chemical Physics* **1965,** *42* (1), 288-292; (b) Tanner, J. E., Use of the Stimulated Echo in NMR Diffusion Studies. *The Journal of Chemical Physics* **1970,** *52* (5), 2523-2526.

2. Castiglione, F.; Mele, A.; Raos, G., Chapter Four - 17O NMR: A “Rare and Sensitive” Probe of Molecular Interactions and Dynamics. In *Annual Reports on NMR Spectroscopy*, Webb, G. A., Ed. Academic Press: 2015; Vol. 85, pp 143-193.