Longitudinal ²⁹Si Nuclear Magnetic Relaxation in Aqueous Alkali-Metal Silicate Solutions Revisited

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We report the results of a wide ranging ²⁹Si longitudinal (spin–lattice) relaxation study of aqueous alkalimetal silicate solutions. Measurement and interpretation of relaxation rates for the many chemically distinct Si centers found in these solutions is complicated by (a) Si–Si chemical exchange during the inversionrecovery pulse sequences, (b) persistent paramagnetic impurities, and (c), in the case of moderately concentrated low-temperature solutions, the inapplicability of the extreme narrowing condition. The situation is therefore complex but nonetheless amenable to analysis. Our findings indicate that the primary causes of ²⁹Si longitudinal relaxation are interactions (dipolar and contact) with adventitious paramagnetic ions, dipole–dipole relaxation by solvent protons, and an *apparent* spin rotation interaction. The relative importance of these mechanisms at the individual Si centers is a function of solution composition and purity, along with the size and structure of the corresponding silicate anions. Analysis of the ²⁹Si–¹H dipole–dipole contribution to relaxation for the hydrated silicate monomer anion yielded an activation energy for isotropic tumbling (between 275 and 375 K) of 18 ± 3 kJ mol⁻¹. Contrary to an earlier suggestion, there was no measurable contribution from dipole–dipole interactions with alkali-metal nuclei.

Introduction

The substantial gains made over the past 20 years in understanding the speciation and physical chemistry of aqueous silicate solutions have been almost entirely due to the advent of high-resolution, Fourier transform ²⁹Si NMR spectroscopy.^{1–4} Knowledge of the pertinent ²⁹Si relaxation characteristics is crucial to optimizing information available from NMR analysis, and, indeed, considerable effort has been devoted over the years to measuring longitudinal relaxation rates (T_1^{-1}) for aqueous silicates.^{5–10} Reported rates span over 2 orders of magnitude (from 0.04 to 6.71 s⁻¹),^{5.6} but there is as yet no real consensus regarding the primary mechanisms of relaxation.

The first thorough analysis of ²⁹Si relaxation in aqueous silicate solutions was reported by Harris and Newman⁶ in 1977. Although their observations were based on limited data and, at the time, some doubt existed as to the structures of anions giving rise to ²⁹Si NMR spectra, they ruled out Engelhardt's earlier suggestion⁵ that longitudinal relaxation could be caused by proton chemical exchange and instead proposed that unknown paramagnetic contaminants in their samples were the primary cause of anomalously rapid longitudinal and transverse (spin–spin) ²⁹Si relaxation. Additionally, they noted smaller but nonetheless significant longitudinal relaxation contributions from ²⁹Si–¹H dipole–dipole interactions.

Kinrade and Swaddle⁴ later demonstrated that, if precautions are taken to minimize paramagnetic contamination of alkali-

metal silicate solutions, temperature-dependent transverse relaxation is due mainly to rapid Si-Si chemical exchange. At moderately elevated temperatures, the exchange process also causes gross averaging of longitudinal relaxation rates as measured by the inversion-recovery procedure, so that the data for individual anions are rendered meaningless.⁸ Furthermore, they demonstrated that at elevated concentrations and low temperatures the extreme narrowing condition may not be applicable (i.e., the rate of random molecular tumbling does not sufficiently exceed the Larmour frequency), making conventional relaxation analysis difficult.8 Nevertheless, they determined that longitudinal relaxation is apparently influenced by both ²⁹Si-¹H dipole-dipole and spin rotation interations as evidenced, respectively, by a small ²⁹Si-{¹H} nuclear Overhauser effect (NOE) and by a rise in T_1^{-1} as the temperature is increased. Because the relaxation rates of individual solutions were found to be roughly proportional to $R = \sum [\eta \gamma_M^2 S(S + \gamma_M^2)]$ 1)], where η is the fractional abundance of an isotope of spin S for a given alkali-metal cation M, they suggested that ²⁹Si-M dipole-dipole interactions also play a significant role. (The authors noted that proof for this tentative hypothesis could be obtained through ²⁹Si-{M} NOE experiments but lacked access to the necessary equipment to carry these out.)

McCormick *et al.*⁹ reported that they were unable to find any correlation between the cation dipole moment and ²⁹Si longitudinal relaxation rates and dismissed the possibility of a ²⁹Si-M dipole-dipole relaxation process. By default, relaxation by unidentified paramagnetic impurities was invoked as the primary cause of longitudinal relaxation. Spin rotation was not considered, and scalar coupling was proposed as the

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principal mechanism governing transverse relaxation. The applicability of this group's findings unfortunately is limited since the solutions used to compare cation effects varied widely in composition (from $[Si^{IV}] = 1.8-3$ mol% and $[Si^{IV}]$:[MOH] = 1:2-1:5), were prepared with reagent grade materials, and were placed in unprotected glass NMR tubes (a procedure known to contaminate samples very rapidly⁶). Moreover, they made no mention of the temperature at which their measurements were undertaken and therefore failed to rule out the possibility of T_1^{-1} exchange averaging.

The nature of longitudinal ²⁹Si relaxation in alkali-metal silicate solutions remains largely unresolved. This paper describes an extensive reevaluation of the problem. Our data reveal that, depending upon solution composition and anion morphology, the main relaxation contributions are (a) an *apparent* spin rotation mechanism, (b) ²⁹Si⁻¹H dipole–dipole interactions, and (c) unpaired electrons of an unknown paramagnetic impurity. We note moreover the lack of any measurable ²⁹Si⁻{²³Na} NOE which indicates, contrary to an earlier suggestion,⁸ that dipole–dipole interactions between ²⁹Si and alkali-metal nuclei do *not* contribute appreciably to ²⁹Si relaxation.

Experimental Section

Over the course of our silicate research, we have measured relaxation rates in approximately 120 silicate solutions of varying composition. The solutions, in all cases, were prevented from ever coming into contact with glass surfaces. All stock solutions and samples were prepared directly in low-density polyethylene bottles or specially prepared Teflon FEP/TFE NMR tube liners. These vessels were each presoaked in successive solutions of nitric acid, hydrochloric acid, and Na₂-EDTA so as to mitigate external contamination from paramagnetic impurities.

Amorphous silica was either prepared by the hydrolysis of SiCl₄ (Aldrich, 99.999%) or obtained directly as ²⁹Si-enriched SiO₂ (U.S. Services, 95 atom %; Isotech, 67 atom %). Alkalimetal hydroxides were obtained from various commercial suppliers, with reported purities ranging from 99.9 to 99.99% semiconductor grade. These were generally used as received, with stock solutions being standardized against potassium hydrogen phthalate. In some cases, the hydroxides were analyzed by ICP and/or treated with Chelex 100 cation exchange resin (BDH) that had been preexchanged with the appropriate M^+ alkali-metal cation.

All solutions were prepared using freshly boiled type-I deionized water and D₂O (Aldrich, 99.8 atom %) for the NMR lock. The chelating agent 4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo[8.8.8]-hexacosane or "cryptand 2.2.2" (Aldrich; none of 27 potential contaminants detected by ICP) was added to a few sodium silicate solutions. Since cryptand 2.2.2 effectively sequesters alkali-metal cations, its presence may be used to determine their influence on ²⁹Si relaxation.

Silicon-29 NMR experiments were conducted on Bruker AC-E 200, Varian XL200 (each at 39.7 MHz), Nicolet 300 (59.6 MHz), and Bruker AMX 500 (99.4 MHz) spectrometers, using probe inserts (except the Nicolet) and sample tubes¹¹ that had been constructed from Si-free materials. Ninety degree pulses were used with an interpulse delay of at least 5 times the longest T_1 value. All ²⁹Si peak assignments were taken from previous studies.¹⁻³ Transverse relaxation rates were estimated from half-height line widths ($T_2^{-1} = \pi \Delta v_{1/2}$) under solution conditions that excluded any possibility of line broadening caused by rapid Si–Si exchange.⁴ Longitudinal relaxation rates were measured by the $180^{\circ} - \tau - 90^{\circ}$ -acq inversion recovery method. The



Figure 1. Temperature dependence of ²⁹Si longitudinal relaxation rates for a solution containing both 2.2 mol kg⁻¹ SiO₂ (95 atom % ²⁹Si) and NaOH. (Solvent enriched 75 atom % in ²H.) The silicate anions represented are the monomer ($H_{4-q}SiO_4^{q-}$, Q⁰), dimer ($H_{6-q}Si_2O_7^{q-}$, Q¹₂), cyclic trimer ($H_{6-q}Si_3O_9^{q-}$, O²₃), cyclic tetramer ($H_{8-q}Si_4O_{12}^{q-}$, Q²₄), tetrahedral tetramer ($H_{4-q}Si_4O_{10}^{q-}$, Q³₄), prismatic hexamer ($H_{6-q}Si_6O_{15}^{q-}$, Q³₆), and cubic octamer ($H_{8-q}Si_8O_{20}^{q-}$, Q³₈).

precision of T_1^{-1} and T_2^{-1} measurements was typically $\pm 5\%$ or better. Gated ¹H or ²³Na decoupling was used in the NOE experiments.

All ²⁹Si-{²³Na} experiments were conducted on the AMX 500 using a home-built, double-tuned probe head. The optimum decoupler settings for power and duration of ²³Na saturation were directly determined by presaturating the sample under investigation—on and off the ²³Na resonance—and detecting the resultant ²³Na signal using the observe channel. The ²⁹Si-X dipole—dipole relaxation contribution to longitudinal relaxation rate is given by¹²

$$T_{1,\text{DDX}}^{-1} = [2\gamma(^{29}\text{Si})/\gamma(X)]T\eta T_1^{-1}$$
(1)

where γ is the magnetogyric ratio, *T* is temperature, and η is the measured nuclear Overhauser enhancement factor which has a maximum value of -2.52 for ${}^{29}\text{Si} - \{{}^{1}\text{H}\}\)$ and -0.66 for ${}^{29}\text{Si} - \{{}^{23}\text{Na}\}\)$.

Precautions were generally taken to remove dissolved oxygen, although the corresponding unpaired electron relaxation contribution has been shown to be small (less than $0.01-0.04 \text{ s}^{-1}$).^{6,8}

Results and Discussion

We show in Figure 1 the characteristic temperature dependence of the ²⁹Si longitudinal relaxation rate for various silicate anions in a solution containing both 2.2 mol kg⁻¹ SiO₂ and NaOH. As mentioned above, gross averaging of T_1^{-1} due to rapid Si–Si exchange during the delay time τ of the inversion recovery sequence limits the temperature range over which reliable data can be obtained.⁸ For the solution represented in Figure 1, measurements are therefore accurate only up to about 320 K. The exchange process is slower for solutions with $[OH^-]:[Si^{IV}] > 1:1$ (*i.e.*, as pH is raised)⁴ and, under these conditions, T_1^{-1} measurements are reliable to somewhat higher temperatures. We consider each of the possible contributions to ²⁹Si longitudinal relaxation, according to the following equation:¹²

$$T_1^{-1} = T_{1,SA}^{-1} + T_{1,SC}^{-1} + T_{1,DD}^{-1} + T_{1,UE}^{-1} + T_{1,SR}^{-1}$$
(2)



Figure 2. Temperature dependence of the ²⁹Si⁻¹H dipole–dipole (DDH) contribution to the longitudinal relaxation rates for the monomer, dimer, and cyclic trimer anions in a solution containing 2.2 mol kg⁻¹ SiO₂ (95 atom % ²⁹Si) and 8.7 mol kg⁻¹ MOH, where $M^+ = Na^+$ (\bigcirc), K^+ (\square) or Rb⁺ (\triangle). (Solvent-enriched 75 atom % in ²H.)

Shielding Anisotropy $(T_{1,SA}^{-1})$. Any significant contribution from the shielding anisotropy mechanism would be evident by its dependence on the square of the external magnetic field B_0 .¹² As shown elsewhere,⁸ this is not the case for silicates. For concentrated solutions at low temperature, the relaxation rates of individual anions actually *decrease* upon increasing B_0 , indicating that the extreme narrowing condition ceases to hold. It is essential, therefore, to interpret relaxation data obtained from viscous solutions with this in mind.

Scalar Coupling $(T_{1,SC}^{-1})$. For the scalar coupling mechanism (of the *first* or *second* kind) to affect ²⁹Si longitudinal relaxation efficiently, either the resonance frequency of a coupled nucleus must be close to that of ²⁹Si or the spin-spin coupling constant must be very large.¹² As noted elsewhere,^{6,8} neither of these criteria is met and therefore this mechanism can be ignored.

Dipole-**Dipole** $(T_{1,DD}^{-1})$. Dipole-dipole interactions, either with other nuclei or with electrons (dealt with separately below), typically dominate the relaxation of spin-1/2 nuclei.¹² The dipole-dipole relaxation contribution of neighboring ¹H nuclei (DDH), readily determined from ²⁹Si-{¹H} NOE measurements, has been reported^{6,8} to be of only minor significance for alkali-metal silicate solutions. In the present study, the fractional DDH contribution, $T_{1,\text{DDH}}^{-1}/T_1^{-1}$, ranged from zero for a fully deuterated solution to over 60%, although the upper limit was only reached when the overall relaxation rate was low (i.e., when more efficient mechanisms were virtually inoperative) and at low temperatures. Figure 2 shows that the absolute contribution, $T_{1,\text{DDH}}^{-1}$, decreases as the temperature is raised owing to an increase in molecular motion. Figure 3 shows an Arrhenius plot of $T_{1,\text{DDH}}^{-1}$ for the monomeric anion in solutions with widely varying compositions, but with constant deuterium enrichment. The correlation is reasonably good, with remarkably little scatter, despite the fact that the data are derived from a large range of solution conditions (Na, K, Rb, and Cs silicate solutions containing 0.3-2.2 mol kg⁻¹ SiO₂ and [OH⁻]:[Si^{IV}] concentration ratios ranging from 1:1 to 5:1). Assuming that all DDH interactions are intramolecular, i.e., for a fully hydrated anion, the data yield an activation energy for isotropic molecular rotation of 18 ± 3 kJ mol⁻¹ (between 275 and 375 K), which is comparable to the value 16.9 ± 0.6 kJ mol⁻¹ determined for the isotropic tumbling of water molecules in a solution containing both 0.25 mol kg⁻¹ SiO₂ and KOH.¹³ Accordingly, the estimated rate of tumbling $(\tau_c^{-1})^{14}$ for the monomer is about 1.6×10^{10} s⁻¹ at 298 K and 1.0×10^{11} s⁻¹ at 400 K which, being significantly greater than the ²⁹Si Larmor frequency for each spectrometer employed, assures the applicability of the extreme narrowing assumption under these solution conditions.

As demonstrated in Figures 2 and 4, $T_{1,DDH}^{-1}$ is virtually unaffected by variations in the silicon concentration,



Figure 3. Arrhenius plot (33 data points) of the DDH contribution to the longitudinal relaxation of the silicate monomer for 10 alkali-metal silicate solutions having a wide range of compositions (M = Na, K, or Rb; $[Si^{IV}] = 0.3-2.2$ mol kg⁻¹; and $[OH^-]$: $[Si^{IV}]$ concentration ratios ranging from 1:1 to 4:1). (Solvent-enriched 75 atom % in ²H for each solution.)



Figure 4. DDH contribution to the longitudinal relaxation rates for a solution containing both 0.08 mol kg⁻¹ SiO₂ (95 atom % ²⁹Si) and MOH, where $M^+ = Na^+$ or [Na•cryptand]⁺. (Solvent-enriched 20 atom % in ²H.)

the $[OH^-]$: $[Si^{IV}]$ ratio, the anion structure, or the type of alkalimetal cation in solution. However, the picture may change in the presence of organic bases (such as tetramethylammonium hydroxide, TMAOH)^{10,15} or when the alkali-metal cation is chelated with an organic complexing agent such as cryptand 2.2.2.¹⁶ For instance, the DDH mechanism is a somewhat greater contributor to T_1^{-1} in solutions containing [Na•cryptand]⁺ (Figure 4). Selective presaturation of the ¹H signals corresponding to either free or complexed cryptand failed to perturb the ²⁹Si NMR spectrum, indicating that the cryptand hydrogens are not directly responsible for the increased DDH relaxation.



Figure 5. 29 Si $-{}^{23}$ Na} NMR spectra at 280 K for a solution containing 0.3 mol kg⁻¹ SiO₂ and 1.5 mol kg⁻¹ NaOD in 100 atom % D₂O: (a) 23 Na saturation (10 W, 25 s) 100 kHz off-resonance; (b) 23 Na saturation on-resonance; (c) difference spectraum (a) – (b).

Two remaining dipole-dipole relaxation mechanisms are possible: ${}^{2}H-{}^{29}Si$ (DDD) and M $+-{}^{29}Si$ (DDM). (The 0.037 atom % natural abundance of oxygen-17 is too low for it to be a factor.) It has been shown⁸ that DDD interactions are necessarily less important than DDH interactions owing to the smaller magnetogyric ratio of deuterium. Indeed, for a solution that is 50% enriched in deuterium, $T_{1,\text{DDD}}^{-1} = 0.063T_{1,\text{DDH}}^{-1}$. As a definitive test for the importance of the DDM relaxation mechanism, we conducted ²⁹Si-{²³Na} NOE measurements. The experiments were designed to ensure that (a) the sample had a significant sodium to silicon ratio, (b) any chance of ²⁹Si-{¹H} NOE was eliminated, and (c) the ²³Na saturation signal was of appropriate power and duration. Ultimately, we determined that ²³Na irradiation has no effect whatsoever on the resulting ²⁹Si NMR spectrum (see Figure 5), indicating that DDM interactions are insignificant in these solutions. In retrospect, this is not surprising given the lower concentrations, smaller magnetogyric ratios and larger internuclear separations expected for alkali-metal nuclei relative to protons.

Unpaired Electron $(T_{1,UE}^{-1})$. Trace impurities of unspecified transition metal ions have been held responsible for the wide range of ²⁹Si relaxation rates observed in silicate solutions.^{6,9,10} and, in particular, for anomalously high relaxation rates in industrial solutions.⁵ Similarly, phosphorus-31 relaxation in orthophosphate solutions is dominated by paramagnetic contaminants unless rigorous measures are taken to exclude them.¹⁷ By substituting reagents, we determined that paramagnetic contaminants in the present study originated principally from the alkali-metal hydroxides. (Paramagnetic contaminants also are leached from glass surfaces.⁶ We have measured as much as a 3-fold increase in longitudinal relaxation rates for samples stored for 48 h at room temperature in conventional borosilicate glass NMR tubes.) Figure 6 demonstrates how significantly the longitudinal and transverse relaxation rates decreased in this study when reagent grade NaOH (99.9%) was replaced with semiconductor grade (99.99%) material. The effects appear structure specific for the three resonances observed, being most pronounced for the dimer and least for the cyclic trimer. Any additional relaxation contributions from residual *cationic* paramagnetic contaminants in the high-purity NaOH were removed by treating the corresponding silicate solution with Na⁺ exchanged Chelex 100 resin. ICP analysis failed to detect any change in the solution's metal content following this treatment. Nonetheless, Figure 6 shows that relaxion rates were affected. Longitudinal relaxation rates decreased only slightly, again the effect being most pronounced for the dimer and least for the cyclic trimer. Transverse relaxation rates decreased rather more significantly; here, the relative effects are reversed with the cyclic trimer being most affected and the dimer least.

The observations above, and those reported by previous researchers,^{6,9} beg the question of which paramagnetic ion or ions are responsible. Harris and Newman⁶ ruled out both Cr^{3+} and Mn^{2+} as contenders since, even when added in quantities that imparted a distinct color to their solutions, both metal ions produced only a modest increase in relaxation rates. They also disregarded Fe³⁺ on the grounds that it could not be detected by atomic absorption analysis.

We added 0.0045 mol kg⁻¹ CrCl₃·6H₂O to the high-purity, Chelex-treated sodium silicate solution, giving it a bright green color. The effects on longitudinal and transverse relaxation rates are shown in Figure 6. Although longitudinal relaxation rates increased significantly, more or less returning to values obtained for the sample prepared with reagent-grade NaOH, transverse relaxation was virtually unaffected. Harris and Newman⁶ made similar observations and suggested that there is insignificant scalar coupling between ²⁹Si and the unpaired electrons associated with Cr³⁺ to affect the rate of transverse relaxation. In other words, ²⁹Si-electron spin interactions arising from the presence of Cr³⁺ are primarily *dipolar* (outer-sphere) in character, whereas interactions involving the unknown paramagnetic contaminants, which do markedly affect transverse relaxation, appear to have significant *contact* character, that is, they are directly associated with unpaired electrons delocalized at the ²⁹Si nucleus.¹⁸ Thus, in all likelihood, the unknown metal ions are sequestered by silicate anions. Indeed, evidence has been reported of silicates forming dissolved, colorless complexes in alkaline solution with both manganese and iron, their concentration being dependent on the sequence in which the reagents are combined.19,20

As noted above, paramagnetic O₂ dissolved in aqueous silicate solutions makes a very minor contribution to $T_{1,\text{UE}}^{-1.6,8}$

Spin Rotation Interactions $(T_{1,SR}^{-1})$. As shown in Figure 1, longitudinal relaxation rates increase with temperature between 300 and 320 K for all Si centers in a solution containing both 2.2 mol kg⁻¹ SiO₂ and NaOH. It is evident from the figure itself that exchange averaging of T_1^{-1} is insignificant over this temperature range (calculated inverse spin site lifetimes are ≤ 10 $s^{-1 8,13}$) and, as discussed above, rates of isotropic tumbling at $T \ge 298$ K are sufficiently high to be in accordance with the extreme narrowing condition. The observed temperature dependence of T_1^{-1} is genuine, therefore, and is consistent with a significant contribution from the spin rotation relaxation mechanism, since this is the only mechanism generally considered to have a positive activation energy.^{8,12} Spin rotation relaxation has been reported for nuclei in other aqueous ions, such as ⁹Be in Be(H₂O)₄²⁺(aq)²¹ and ¹⁹⁵Pt in PtCl₄²⁻(aq).²² McCain and Markley¹⁷ reported an analogous temperature dependence of ³¹P longitudinal relaxation rates for aqueous orthophosphates. They rejected the spin rotation mechanism, however, stating that the $H_2PO_4^{2-}$ ion must be "locked into the local water structure by numerous hydrogen bonds" and is unable therefore to spin freely. They proposed an alternative mechanism, termed "quasirotation", in which the site of hydrogen bonding rapidly "rotates" about the PO₄ center rather than the ion itself physically rotating. An equivalent case could be made for ²⁹Si relaxation in aqueous silicates, yet the data seem easier to rationalize in accordance with the conventional mechanism. The rate of isotropic tumbling by small silicate anions indeed is quite high, as shown



Figure 6. Rates of (a) longitudinal and (b) transverse ²⁹Si relaxation for the monomer, dimer and cyclic trimer in solutions at 294 K containing 2.18 mol kg⁻¹ SiO₂ and 8.70 mol kg⁻¹ NaOH. Solutions (i) and (ii) were prepared, respectively with 99.9 and 99.99% purity NaOH. Solution (iii) is solution (ii) after treatment with Chelex 100 cation exchange resin. Solution (iv) is solution (iii) after the addition of 0.0045 mol kg⁻¹ CrCl₃· $6H_2O$. (Solvent-enriched 75 atom % in ²H.)



Figure 7. Temperature dependence of longitudinal ²⁹Si relaxation rates for a solution containing 2.18 mol kg⁻¹ SiO₂ and 8.70 mol kg⁻¹ NaOH. (Solvent-enriched 75 atom % in ²H.)

above. In general, the apparent SR contribution correlates with molecular size, being greater for Si centers in small ions (see Figure 1). Yet the dimer and acyclic trimer, which are free to rotate internally, consistently exhibit faster relaxation than the monomer, especially at higher viscosities when whole-body rotation would be comparatively hindered (see Figures 1, 6, 7, and 8). This is consistent with reports of SR-enhanced ²⁹Si relaxation at polysiloxane chain end groups.^{23,24} The terminal silicons of the acyclic trimer exhibit the highest measurable relaxation rates in solutions that are free of paramagnetic impurities (3.4 s⁻¹ for a solution at 300 K with 2.2 mol kg⁻¹ SiO₂ and 8.7 mol kg⁻¹ NaOH), presumably owing to this ion's greater freedom of internal rotation. Finally, in Figure 8, we show that addition of cryptand 2.2.2 to a sodium silicate solution can yield a marked increase in SR relaxation as revealed by the steep rise in T_1^{-1} as temperature is increased. Very likely, Na⁺ chelation frees silicate anions from strong association with the hydrated cation¹⁶ and thereby enhances the rate of isotropic molecular rotation. The relative importance of this apparent SR relaxation contribution has previously been overlooked. The evidence is insufficient, however, to identify the mechanism unequivocally.

Conclusion

Silicon-29 longitudinal relaxation in aqueous alkali-metal silicate solutions is governed by three main processes, the relative proportions of which are determined by a host of



Figure 8. Temperature dependence of longitudinal ²⁹Si relaxation rates for a solution containing 1.0 mol kg⁻¹ SiO₂ and 2.0 mol kg⁻¹ MOH, where $M^+ = Na^+$ (solid symbols) or [Na•cryptand]⁺ (open symbols). (Solvent-enriched 20 atom % in ²H.)

variables including anion size and structure, along with overall solution composition. These processes are as follows: (1) relaxation by paramagnetic impurities, which are difficult to exclude and provide very efficient relaxation, indicating that some of the aqueous silicate anions effectively sequester metal ions; (2) an apparent spin rotation contribution, which is important for all species at elevated temperatures, but is of greatest consequence for small anions that, in addition to whole-molecule rotation, are able to rotate internally; (3) ²⁹Si⁻¹H dipole–dipole relaxation, which dominates systems in which the silicate anion is in a formal and long-lived association with solvent molecules, such as appears to be the case in organic base silicate solutions. This, however, is generally not of primary importance for alkali-metal silicate solutions.

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- (14) Calculated using the equation¹² $T_{1,\text{DDH}}^{-1} = (\mu_0/4\pi)^2 \gamma_{\text{Si}}^2 \gamma_{\text{H}}^2 \hbar^2 / r^6$, where *r* is estimated to be 2.2 nm.
- (15) The relative DDH contribution $T_{1,\text{DDH}}^{-1}/T_1^{-1}$ is highly structure specific in organic base solutions. Indeed, Harris and Knight¹⁰ have proposed ¹H-presaturation as a simple ²⁹Si NMR assignment tool for such

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