The third resonance, at 55.7 ppm, also behaves like the resonance of a bound species. The $^{13}C-^{1}H$ dipolar coupling corresponding to this resonance is inhomogeneous, which can be the case only if there is no appreciable ^{1}H spin diffusion from the methyl protons to other protons in the system. Each molecule of this species must therefore be in a region that is relatively isolated from protons not part of the molecule itself. Adsorption of a series of alcohols on HY indicates that there is a steric restriction associated with the site corresponding to the 55.7-ppm resonance in the methanol system. Access to this site is denied in zeolite samples activated at 500 and 600 °C, arguing against identifying the 55.7-ppm peak with a defect $Al-O-CH_3$ species. We interpret these data as indicating the adsorption of methanol and ethanol into the β cages of HY zeolite. Adsorption into the β cage probably requires a distortion of the 6-ring aperture, which has a diameter of approximately 2.2 Å,[12] to pass the alcohol. It is known that the framework of a zeolite can become distorted during the adsorption of a species with which it has a strong interaction.[12,13] The diameter of methanol, calculated from the Stockmayer potential,[12,14] is 2.4 Å; this compares to 2.6 Å for ammonia, which we know can exit the β cage.[12] We expect that the critical dimension perpendicular to the C–C bond axis of ethanol would be similar to the critical dimension of methanol. The higher alcohols, having bent C–C–C arrangements, will have substantially larger effective diameters. Methanol moieties interacting with the β-cage site are not desorbed by evacuation at 140 °C, a fact that also (1) argues for the isolation of the 55.7-ppm CH_3O species and (2) is consistent with the energetics one would expect for the 6-ring distortion that would be required for CH_3OH or CH_3OCH_3 desorption from a β cage, even if the 55.7-ppm CH_3O species were not mutually isolated.

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Mechanisms of Longitudinal ^{29}Si Nuclear Magnetic Relaxation in Aqueous Alkali-Metal Silicate Solutions

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Abstract: Silicon-29 longitudinal NMR relaxation times (T_1) have been measured by the inversion-recovery method over a range of solution compositions and temperatures (0 to +100 °C) for several of the silicate species which occur in solutions of silica in H_2O-D_2O alkali-metal hydroxide (MOH) solutions. At sufficiently high temperatures, Si–Si chemical exchange causes gross averaging of the apparent T_1 values so obtained, this becoming evident at ~20 °C for $[M^+]:[Si^{IV}] = 1.0:1$ and at higher temperatures for higher $[M^+]:[Si^{IV}]$ ratios. The predominant relaxation process evidently involves dipole–dipole interactions between ^{29}Si and M^+ nuclei (M = Na, K, Rb), with minor contributions from the $^{29}Si-^{1}H$ dipole–dipole mechanism. Contributions to T_1^{-1} from the spin-rotation mechanism are apparent for the smaller silicate species, but in general are of minor importance. These observations explain why previously reported T_1 values for ^{29}Si in aqueous alkali-metal silicates were much shorter than for other silicon compounds, such as organosilanes, and varied markedly from study to study because of differing experimental conditions.

An understanding of the dependence of the longitudinal nuclear magnetic relaxation time T_1 on sample composition and conditions is essential if quantitative NMR spectra are to be obtained, and can also provide useful information concerning molecular structure and dynamics. In the case of ^{29}Si NMR of $(HO)_3SiO^-$ and its polymers in aqueous alkaline solution, reported T_1 values are unusually short for silicon compounds[1,2] and range from about 0.5 s in a solution containing 2 mol kg^{-1} of Si^{IV} and 6 mol kg^{-1} of Na^+[3] to 26 s in one containing <0.05 mol L^{-1} of Si^{IV} and 0.6 mol L^{-1} of Na^+[4] for the dimer at 25 °C. This paper explores the reasons for this relative shortness of T_1 in aqueous silicates and for its variability.

Early on, it was suggested[3] that such efficient ^{29}Si relaxation could arise from rapid interchange between protonated and deprotonated silanol groups which, having different chemical shifts, should generate an appropriate fluctuating magnetic field. Harris and Newman,[5] however, noted that this field would be parallel to the external field B_0 and so could not cause longitudinal relaxation. Instead, they concluded from their observations of "aging" effects in silicate solutions contained in unlined glass NMR tubes that unidentified paramagnetic contaminants, introduced during sample preparation and/or by leaching from the NMR tubes, were probably the dominant factors controlling transverse (T_2) and longitudinal ^{29}Si relaxation.[2,5] Recently,[6] we demonstrated that temperature-dependent transverse relaxation of ^{29}Si in aqueous alkali-metal silicate solutions is due primarily to Si–Si chemical exchange mediated by $H_3SiO_4^-$. We now report evidence

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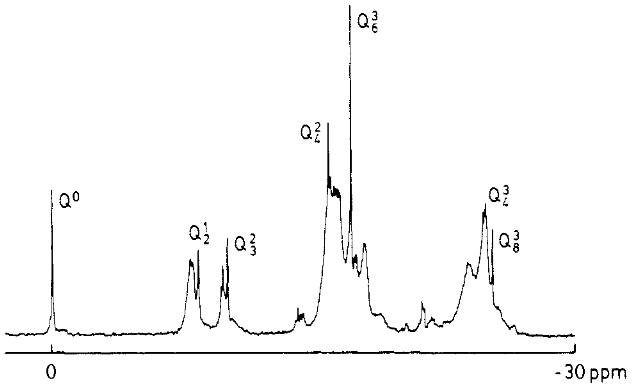

Figure 1. ^{29}Si NMR spectrum of a solution 2.17 mol kg^{-1} in Si (95% ^{29}Si-enriched) with Na$^+$:Si^{IV} = 1.0:1; recorded at 22.4 °C using 300 46.5-μs (90°) pulses and a recycle time of 110 s (>5 $T_{1,\max}$). Silicate anions represented are monomer (Q^0), dimer (Q^1_2), cyclic trimer (Q^2_3) and tetramer (Q^2_4), prismatic hexamer (Q^3_6),tetrahedral tetramer (Q^3_4; see text), and cubic octamer (Q^3_8).

to indicate that dipole–dipole interactions involving ^{29}Si and the alkali metal nuclei are primarily responsible for longitudinal ^{29}Si relaxation in these solutions, and that paramagnetic contaminants are unimportant in this respect if reasonable precautions are taken to exclude them.

Experimental Section

Samples were prepared directly in Teflon FEP® NMR tube liners by dissolving silica (obtained by hydrolysis of redistilled SiCl$_4$ or purchased from U.S. Services as 95% ^{29}Si-enriched SiO$_2$) in MOH (M = Na, K, or Rb) solutions at 100 °C for 1 h. Since the sole source of M$^+$ was MOH, these solutions are conveniently characterized by the concentrations of Si^{IV} and M$^+$. Unless noted otherwise, the solvent contained 75 wt % D$_2$O. Samples were inserted into a pressurizable NMR tube constructed from silicon-free materials,[6] purged with nitrogen gas to minimize dissolved oxygen, and pressurized with nitrogen to 1.0 MPa. All ^{29}Si NMR spectra were obtained at 39.75 MHz on a Varian XL200 spectrometer with the exception of a single series acquired at 59.61 MHz on a Nicolet 300. Glass coil supports in the Varian probehead were replaced with equivalent parts machined from Vespel polyimide resin to ensure a flat spectral baseline. Longitudinal relaxation times were measured by the inversion recovery method, and gated ^{1}H decoupling was employed in nuclear Overhauser enhancement (NOE) measurements. Among the forest of signals that can appear for ^{29}Si-enriched solutions,[7] singlets corresponding to the totally symmetric species are the easiest to follow over varying sample conditions (Figure 1). The Q^y_z symbol is used to denote a Si center with y coordinated bridging oxygens and $(4 - y)$ terminal hydroxy groups, and, when applicable, z indicates the number of equivalent centers in a totally symmetric anion.

Even at the lowest temperatures employed, Si–Si exchange was sufficiently rapid[6] that T_2 was less than T_1 in all solutions. Small increases in T_1 were observed when air-saturated solutions containing 2.17 mol kg^{-1} of each of Si^{IV} and Na$^+$ were purged of O$_2$ with pure N$_2$; the corresponding unpaired electron (UE) relaxation contribution, $T_{1UE(O_2)}{}^{-1}$, was calculated from the T_1 differences and ranged from 0.04 s^{-1} for the monomer to ≤0.01 s^{-1} for the largest species, and is similar in magnitude to findings with organosilicon compounds saturated in O$_2$.[8] Dissolved oxygen was removed for all other NMR experiments.

Results and Discussion

Table I and Figure 2 present T_1 data as a function of temperature for a solution in which [Na$^+$] = [Si^{IV}] = 2.17 mol kg^{-1} (i.e., concentration ratio 1.0:1). Gross averaging of T_1 values for the various Si centers is evident above 20 °C, and this is attributable to rapid Si–Si exchange during the inversion-recovery pulse sequence, as revealed by line-broadening observations.[6] When exchange averaging can be disregarded, e.g., in these 1.0:1 solutions below 20 °C, T_1 is seen to increase with temperature for the larger and less flexible silicate anions, most notably for the symmetric Q^3-containing species, which molecular models show to be the most rigid. In accordance with the special stability expected for a silicate anion consisting exclusively of (SiO)$_3$ rings,[7] the previously unidentified singlet at about −25.6 ppm relative to Q^0 is tentatively assigned to the tetrahedral tetramer Si$_4$O$_{10}{}^{4-}$ (Q^3_4, which models show to be very rigid but unstrained), as is consistent with the location of the singlet slightly downfield of the cubic octamer (Q^3_8) peak as well as with the marked increase in T_1 (Figure 2) and rapid shift of the line to higher field relative to Q^0 as the temperature is increased.

Table I. ^{29}Si Longitudinal Relaxation Rates ($T_1{}^{-1}$)[a,b]

temp/°C	Q^0	Q^1_2	Q^2_3	Q^2_4	Q^3_6	Q^3_4	Q^3_8
3.3	0.16	0.17	0.13	0.14	0.10	0.10	0.10
15.2	0.21	0.23	0.16	0.14	0.08	0.08	0.08
22.4	0.26	0.26	0.22	0.17	0.06	0.08	0.08
30.6	0.29	0.30	0.27	0.20	0.07	0.10	0.08
38.8	0.32	0.34	0.32	0.26[c]	0.10	0.13	0.11
55.0	0.37	0.36	0.36	0.31[c]	0.21	0.23[c]	0.15
68.0	0.31	0.31[c]	0.32[c]	0.31[c]	0.29	0.29[c]	0.21
86.7	0.28	0.29[c]	0.29[c]	0.29[c]	0.29	0.29[c]	[c]

[a] In seconds^{-1} with error typically ±5%. [b] For a solution 2.17 mol kg^{-1} in Si (95% ^{29}Si-enriched) with Na$^+$:Si^{IV} = 1.0:1. [c] Peak indistinct from nearest neighbors.

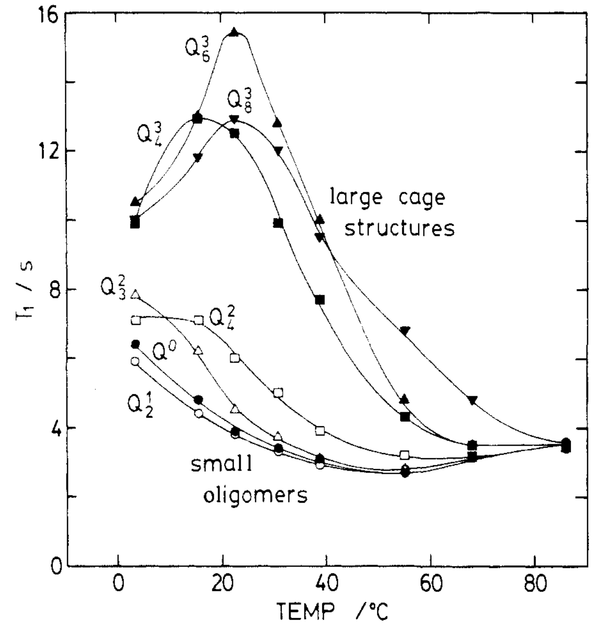

Figure 2. Temperature dependence of longitudinal relaxation time for a solution 2.17 mol kg^{-1} in Si (95% ^{29}Si-enriched) with Na$^+$:Si^{IV} = 1.0:1.

When the averaging effect of Si–Si chemical exchange is allowed for, it should be possible to account for the observed values of $T_1{}^{-1}$ in terms of contributions $T_{1UE}{}^{-1}$ from the presence of species with unpaired electrons, $T_{1SC}{}^{-1}$ from scalar coupling, $T_{1SA}{}^{-1}$ from shielding anisotropy, $T_{1SR}{}^{-1}$ from the spin-rotation mechanism, and $T_{1DD}{}^{-1}$ from nuclear magnetic dipole–dipole interactions.[1,9,10]

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

As noted above, dissolved oxygen makes at most a trivial contribution to $T_{1UE}{}^{-1}$, and was in any case removed from the solutions. Contributions to $T_{1UE}{}^{-1}$ from other paramagnetic species were negligible; the solutions were prepared and handled in Teflon equipment to obviate leaching of contaminants, and consistent T_1 data were obtained from solutions made with silica from different sources. The T_1 data reported here are also consistent with those listed by Harris,[2] once the influences of solution composition and temperature, as analyzed below, are taken into account.

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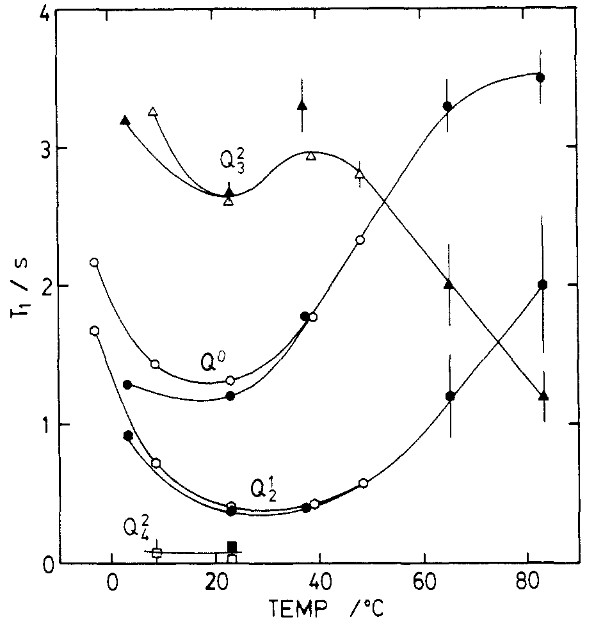

Figure 3. Temperature dependence of longitudinal relaxation for a solution 2.17 mol kg^{-1} in Si with Na$^+$:Si^{IV} = 4.0:1; B_0 = 4.70 T (solid symbols) and 7.10 T (open symbols).

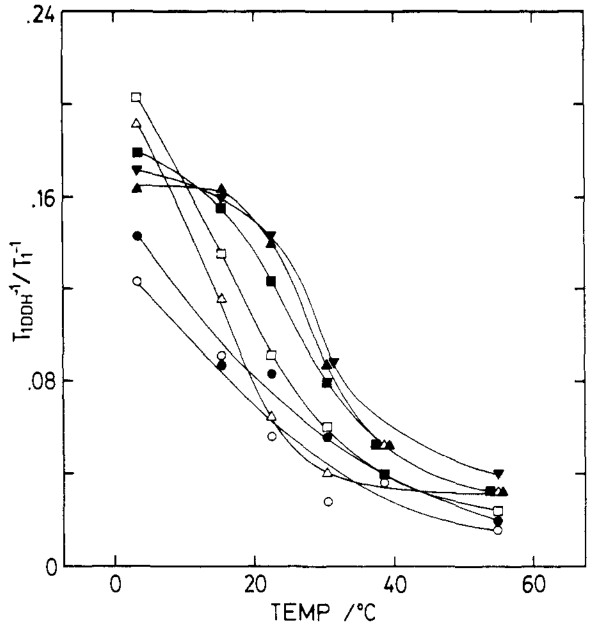

Figure 4. Temperature dependence of the proportional DDH contribution to T_1 relaxation. Solution composition and symbols are as in Figure 2.

Scalar coupling can be disregarded as a source of longitudinal relaxation, since no nuclei with resonant frequencies near that of ^{29}Si were present.[5,8] Any significant contributions to T_1^{-1} from shielding anisotropy would be detectable through its second-power dependence on B_0,[9,10] but in no case was the ^{29}Si relaxation rate increased when B_0 was increased from 4.70 to 7.05 T (Figure 3). On the contrary, relaxation rates T_1^{-1} were slightly *reduced*, below 20 °C, as a result of this increase in B_0, which suggests that, whatever the principal relaxation mechanism, the extreme narrowing condition (correlation time << reciprocal of the Larmor precession frequency)[9,10] ceases to be strictly valid for these solutions at low temperatures.

For the less condensed species, the modest shortening of T_1 with rising temperature (cf. Figure 2, discounting T_1 averaging above 20 °C) evidently reflects a contribution from the spin-rotation mechanism, since this is the only mechanism that would of itself give this kind of temperature dependence.[9,10] For the larger silicate species, this effect is greatly reduced, which is in accordance with expectations for the spin-rotation mechanism since whole-molecule rotation is limited, and internal rotation is, in the case of Q^3 centers at least, impossible.

This leaves the dipole–dipole mechanism as the probable chief cause of ^{29}Si longitudinal relaxation in alkaline aqueous silicate solutions. The only nuclei present in these solutions that could be responsible for these processes are ^{1}H and ^{2}D from the H_2O/D_2O solvent and the M$^+$ nuclei (^{23}Na, in our initial experiments). The fractional contribution T_{1DDH}^{-1}/T_1^{-1} of ^{29}Si–^{1}H dipole–dipole relaxation (DDH) to the total longitudinal relaxation rate, calculated from the NOE data, was significant only at low temperatures, decreasing eight-fold from 0 to 60 °C (Figure 4). In absolute terms, T_{1DDH}^{-1} was smallest for the silicate oligomers of high molar mass and decreased with rising temperature for all silicate species. It was not possible to determine whether the DDH process was intra- or intermolecular,[10] but in any case it was never a major contributor to T_1 relaxation of ^{29}Si, as the close similarity of T_1 values in 75 and 99% D_2O/H_2O proved. If the contribution of the DDH process was not important, that of the deuterium dipole–dipole (DDD) mechanism was necessarily even less so, since, whether the dipole–dipole interaction is inter- or intramolecular, the ratio of the DDD and DDH contributions at mole fractions f_D and f_H is determined largely by the squares of the respective magnetogyric ratios γ_D and γ_H:[10]

$$T_{1DDD}^{-1}/T_{1DDH}^{-1} = 8\gamma_D^2 f_D/3\gamma_H^2 f_H = 0.189 \text{ for } 75\%\ D_2O \quad (2)$$

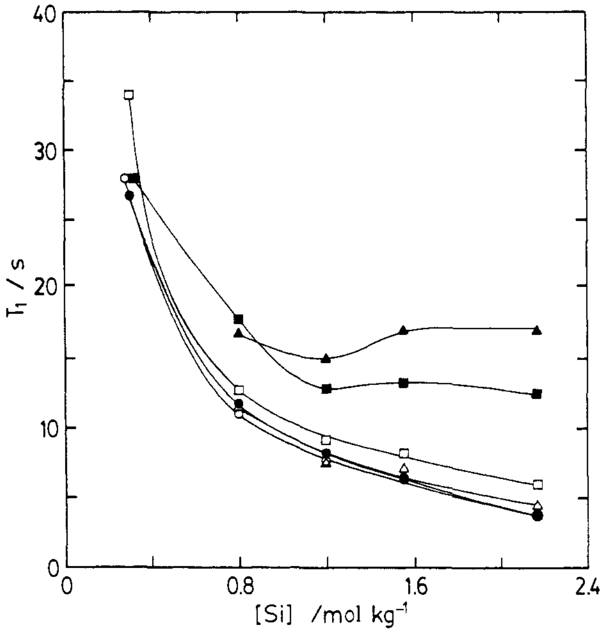

Figure 5. Si concentration dependence of longitudinal relaxation at 22.4 °C for ^{29}Si-enriched solutions with Na$^+$:Si^{IV} = 1.0:1. Symbols are as in Figure 2.

When, however, the concentrations of Na$^+$ and Si^{IV} were increased with a fixed concentration ratio of 1.0:1, longitudinal relaxation was clearly accelerated (Figure 5). Although some of this additional relaxation was demonstrably due to DDH interactions, especially in the smaller silicate anions, the *proportional* contribution of DDH relaxation to T_1^{-1} actually decreased at the higher Si^{IV} concentrations (Figure 6). When the Na$^+$:Si^{IV} concentration ratio was increased from 1.0:1 to 4.0:1 at constant [Si^{IV}] = 2.17 mol kg^{-1}, T_1 was shortened for all four species studied, especially the dimer Q_2^1 and the cyclic tetramer Q_4^2 (Figures 3 and 7; cf. Figure 2). Clearly then, the sodium ion concentration exerted a major influence on T_1. It may also be noted that, since Si–Si chemical exchange is slower at higher pH because of secondary deprotonation of the silicate anions,[6] the onset of exchange averaging of T_1 values occurs at higher temperatures in Figure 3 than in Figure 2. It is significant that, of the four species under consideration here, those (Q^0 and Q^3) for which the

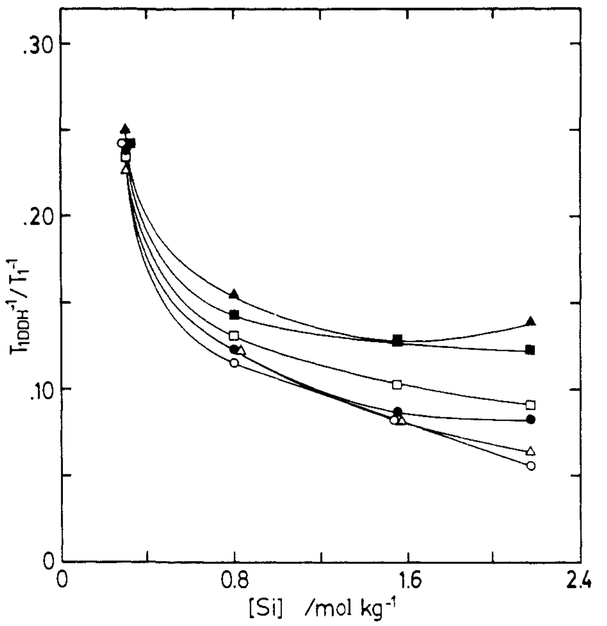

Figure 6. Si concentration dependence of the proportional DDH contribution to T_1 relaxation at 22.4 °C. Solution composition and symbols are as in Figure 5.

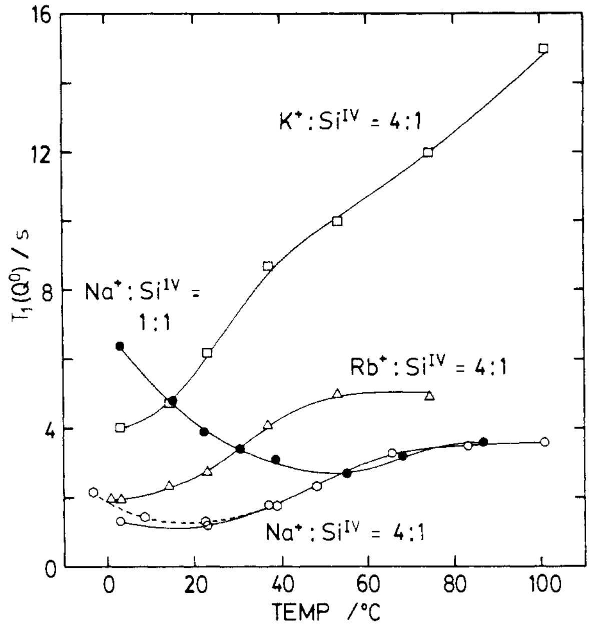

Figure 7. Temperature dependence of longitudinal relaxation time for the monomer Q^0 in solutions containing 2.17 mol kg^{-1} of Si and with M^+:Si^{IV} as indicated. Broken line represents increase of B_0 to 7.05 from 4.70 T.

least T_1 shortening was observed were also those which appear to be most susceptible to secondary deprotonation.[6]

Thus it becomes apparent that the primary cause of the relatively rapid longitudinal relaxation in aqueous alkali-metal silicate solutions is dipole–dipole interaction between ^{29}Si and the nuclei of the counterion Na$^+$ or, more generally, M$^+$ ("DDM" mechanism).

$$T_1^{-1} \sim T_{1DD}^{-1} = (T_{1DDH}^{-1} + T_{1DDM}^{-1}) \sim T_{1DDM}^{-1} \qquad (3)$$

This was substantiated by the observation of very different values and temperature dependences of T_1 when Na$^+$ was replaced by M$^+$ = K$^+$ or Rb$^+$ (Figure 7). Incontrovertible proof of the predominance of the DDM mechanism could be obtained through appropriate NOE experiments, but a decoupler operable at the resonance frequencies of the various M$^+$ is not available to us, and in this respect our conclusion remains tentative.

The relative efficacy Na$^+$ > Rb$^+$ >> K$^+$ in producing longitudinal relaxation of ^{29}Si remains to be explained. Calculations based on an assumed intermolecular dipole–dipole relaxation mechanism[10] gave values of T_{1DD} that were some 10^5-fold too long, so an "intramolecular" process involving (entirely reasonably) a silicate–M$^+$ ion pair that is long-lived on the T_1 time scale must be invoked. Several factors combine to make a realistic calculation of T_{1DDM}^{-1} on this basis impossible; M$^+$ ion-pair formation constants K_{IP} for the various silicate anions are unknown, as are the structures of the ion pairs and the M$^+$–Si distances within them (upon which T_{1DDM} has a sixth-power dependence[10]). There is evidence, however, that M$^+$–anion "contact" distances in water vary surprisingly little,[11] and, furthermore, crude Fuoss-type calculations[12] suggest K_{IP} is nearly the same (6–7 L mol^{-1}) for the Na$^+$–, K$^+$–, and Rb$^+$–$H_3Si_4^-$ pairs. We can therefore expect[10] that the relative T_{1DDM}^{-1} values will be roughly proportional to $R = \sum[n\gamma_M^2 S(S+1)]$, where n is the fractional abundance of an isotope of spin S for a given M. For M = ^{23}Na, (^{85}Rb + ^{87}Rb), and (^{39}K + ^{41}K), the respective values of $10^{-15}R$ are 19, 12, and 0.6, and these explain the qualitative trend in T_1^{-1} (Figure 7) satisfactorily.

Conclusion

The available evidence leaves little doubt that the major mechanism of longitudinal ^{29}Si relaxation in aqueous alkali-metal silicate solutions is a dipole–dipole interaction involving the counterion M$^+$, probably through an intramolecular process within a silicate–M$^+$ ion pair. Thus, measured T_1 values are influenced by both the nature and concentration of M$^+$, as well as the temperature. Furthermore, at higher temperatures, chemical Si–Si exchange leads to apparent averaging of the T_1 values of the individual silicate species, and, since both the relative abundances of these species and the rates of Si–Si exchange are markedly temperature- and pH-dependent,[6] the apparent T_1 values given by the inversion recovery method can vary considerably with conditions when averaging is occurring.

In retrospect then, it is not surprising that aqueous silicate ^{29}Si T_1 data in the literature are inconsistent, and the involvement of the cations in the DDM process explains why these T_1 values are shorter than for most other silicon compounds in the pure liquid state or in solutions not containing alkali-metal ions. The results of Harris and co-workers[2,5] can be seen to be consistent with ours on the basis of the foregoing conclusions, without the need to invoke the presence of paramagnetic contaminants in the silicate solutions. Indeed, experiments in which paramagnetic contaminants were deliberately introduced into silicate solutions revealed only a minor influence of these solutes on T_1.[5]

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