The Temperature Dependence of ^{29}Si Nuclear Magnetic Resonance Linewidths in Aqueous Silicate Solutions and their Effect on Exchange Rate Determinations

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The temperature-dependent ^{29}Si n.m.r. spectra of a range of alkali silicate solutions are reported. Linewidth studies of the silicate monomer resonance give an indication of the rate of exchange with other solution species. However, it is shown that the spin–spin relaxation time (T_2) surprisingly *decreases* with increasing temperature so that exchange rates determined from linewidth alone are invalid. For a 1.0 mol dm^{-3} solution of sodium silicate with $SiO_2:Na_2O = 1.0$ the true monomer exchange rate is calculated to be $\leqslant 2.8$ s^{-1} up to 320 K. A similar solution having $SiO_2:Na_2O = 0.33$ gave values of $\leqslant 24$ s^{-1} at 277 K and 25—44 s^{-1} at 320 K. These rates are lower than those measured by linewidth alone but higher than related values obtained by other workers using selective inversion recovery.

Considerable effort has been devoted to the study of aqueous alkaline silicate solutions.[1,2] Trimethylsilylation with gas chromatography[3,4] and ^{29}Si n.m.r. spectroscopy[5–15] have provided much information about the silicate species present in these solutions, principally as a function of solution composition. Although the effect of temperature on the ^{29}Si n.m.r. linewidths of dissolved silicates has been known for some time,[16–19] it is only recently that it has been reported in the literature.[20,21] Exchange rates (or minimum lifetimes) have been extracted on the assumption that the 'natural' linewidth is the minimum observed (usually at the lowest temperature) and any residual linewidth at higher temperatures is entirely due to exchange. This is an attractive procedure in that the average exchange rate for each resolved species can be obtained from a single spectrum. However, it has been pointed out[21] that in this slow exchange limit[22,23] the n.m.r. linewidth yields only an estimate of the maximum possible rate of exchange, and it has now been shown[24] by selective inversion experiments that the true exchange rates are considerably lower. It would appear that the 'natural' linewidth is increasing with temperature. Since this is an unexpected result which complicates an otherwise simple determination of exchange rate we have determined the spin–spin relaxation time (T_2) for some silicate solutions to test this hypothesis. These results are reported here, together with our earlier[19] linewidth measurements.

Experimental

Silicate solutions were prepared from Nalfloc 1034-AW silica sol and AnalaR (except NMe_4^+) hydroxides as described previously.[4] The aqueous component contained 25% D_2O for field/frequency locking purposes. All solutions were prepared and handled in polypropylene or polytetrafluoroethylene apparatus with minimal exposure to air. The n.m.r. spectra were run in glass n.m.r. tubes (10 mm).

Analyses for solutions 1 and 2 are given in Table 1. The remaining solutions were analysed for iron only: the highest value recorded was 7 p.p.m. Fe.

Occasionally, differences in linewidth were observed from nominally similar solutions. The reason for this is not known, although other authors have reported similar findings.[9,16,20] The values obtained for solution 4 (which was run on one occasion only) may be an aberrant result of this type, as the linewidths seem anomalously large.

Table 1. Concentration of impurities (p.p.m. w v)

	Solution 1		Solution 2	
Impurity	*a*	*b*	*a*	*b*
V	<4.0	<4.0	<4.0	<4.0
Cr	<0.7	<0.7	<0.7	<0.7
Mn	<0.2	<0.2	<0.2	<0.2
Fe	17.0	17.0	10.0	8.0
Co	<0.5	<0.5	<0.5	<0.5
Ni	<0.8	<0.8	<0.8	<0.8

[a] As prepared. [b] After heating in a closed n.m.r. tube for 18 h at 80 C.

Silicon-29 n.m.r. spectra were obtained at 79.5 MHz on a Bruker WM400 spectrometer. The 180 pulse width was determined accurately in each case and was in the range 75—80 μs. The value of T_2 was determined on a static sample *via* the Carr-Purcell-Meiboom-Gill (CPMG). pulse sequence with $\tau = 1$ ms (time between 180 pulses = 2 ms) and a relaxation delay of 5 s.

Values of T_2 were calculated from the natural logarithm of at least four CPMG points with a linear least-squares fitting procedure in which less weighting was given to points of lower absolute intensity. The standard deviation of the slope was calculated on the same basis and the 95% confidence limits taken as mean $\pm 2 \times$ (standard deviation). These confidence limits are based on random error in the CPMG experiment only and do not consider other random or systematic errors.

Linewidths were determined as the width at half-height of a magnetically shimmed spinning sample. The error in this measurement is probably ±0.2 Hz or ±5%, whichever is larger. The linewidth and T_2 were determined on the same sample and on the same day with no adjustment of the temperature.

Linewidths for a wide spread of temperatures and solutions are given in Table 2. Measurements on solutions 1 and 2 were made as described above. The remaining solutions were not run under the same rigorous conditions, *i.e.* they were not necessarily shimmed at every temperature and are subject to larger errors, particularly where heating caused movement of the vortex suppressor.

Results

For the T_2 investigations, only the Si monomer linewidth has been determined. This is largely for convenience since it is the

Table 2. Silicon-29 n.m.r. linewidths (Hz) of monomer resonance in silicate solutions at various temperatures (K)

	Solution composition			Monomer linewidth[a]							
Solution	M	SiO_2:M_2O	[Si]/mol dm^{-3}	277	298 (initial)	298 (final[b])	310	320	330	340	350
1	Na	1.0	1.0	1.4	2.0	2.5	6.5	8.0	16.8	31	41
2	Na	0.33	1.0	11	32	33	54	77	101	109	133
3	K	1.0	1.0	4.2	5.4	6.5	12	21	41	61	
4	Na	1.0	2.0	6	9	14	20		44		117
5	Na	1.0	0.25		1.6		3.0		11		24
6	NMe_4	1.0	0.8		1.0	2.0	2.6	4.0		8.0	11
7	NMe_4–Na (91:9)	1.0	0.8		1.7		3.0		6		14
8	Na	3.5	1.0	1.4	2.0	6.0	4.0		15		42

[a] Values obtained by stepwise increase of temperature. [b] Value obtained on cooling at end of run.

only well resolved peak common to all samples examined. The monomer could in principle exchange with any other silicate species in solution so the exchange rates determined will necessarily be an average. Since it is easy to postulate exchange of silicate species through the monomer, the behaviour of the monomer could be regarded as representative of the solution as a whole.

Two experimental linewidths are quoted: the observed width of a shimmed spinning sample (L_1) and that attributed to the measured T_2 (L_2), equation (1). For the sake of convenience, all

$$L_2 = 1/(\pi T_2) \qquad (1)$$

rate processes are discussed in terms of their equivalent linewidths. The difference between L_1 and L_2 ($\Delta\delta$) is the lower limit of the linewidth due to silicate exchange, whence in the slow exchange limit[22,23] equation (2) applies, where k is the

$$k = \pi(\Delta\delta) \qquad (2)$$

exchange rate. Exchange itself can contribute to the measured T_2. This contribution can be determined[25–27] by equation (3),

$$\frac{1}{T_{2\text{obs.}}} = \frac{1}{T_2} + P_A P_B(\delta w)^2\tau\left[1 - \left(\frac{2\tau}{t_{cp}}\right)\tanh\left(\frac{t_{cp}}{2\tau}\right)\right] \qquad (3)$$

where P_A and P_B are the relative concentrations of exchanging species ($P_A + P_B = 1$), δw is the separation (Hz) of exchanging species, τ is the mean lifetime of exchanging species, and t_{cp} is time between 180° pulses adopted during the CPMG pulse sequence.

This contribution to L_2 is therefore given by equation (4); P_A,

$$L_3 = P_A P_B(\delta w)^2\tau\left[1 - \left(\frac{2\tau}{t_{cp}}\right)\tanh\left(\frac{t_{cp}}{2\tau}\right)\right]/\pi \qquad (4)$$

P_B, and δw are difficult to define for such a complex system while τ is unknown. The upper limit of L_3 can however be calculated. The maximum value of $P_A P_B$ is 0.25 while the maximum of δw is the maximum separation of peaks. Although τ is unknown, its smallest possible value (giving rise to a maximum L_3) is given by assuming the whole of the observed linewidth (L_1) to be due to exchange, *i.e.* $\tau = 1/(\pi L_1)$. We can therefore define the lower and upper 95% confidence limits of the contribution (X) of exchange to linewidth as in equations (5) and (6) respectively,

$$X_{\text{min.}} = L_1 - L_2(\text{b}) \qquad (5)$$

$$X_{\text{max.}} = L_1 - L_2(\text{a}) + L_3 \qquad (6)$$

where L_2(a) and L_2(b) are the lower and upper 95% confidence limits of L_2.

Discussion

Observed Linewidths.—All of the solutions examined show some degree of line broadening with increasing temperature. Possible sources of this effect could include (*a*) viscosity variation, (*b*) presence of paramagnetic impurities, (*c*) presence of chemically active impurities (*e.g.* B, Al), (*d*) exchange of silanolic protons, and (*e*) exchange reactions between silicate anions.

Literature data[28] appear unanimous in ascribing decreasing viscosity to silicate solutions with increasing temperature, which would tend to produce the converse of the observed result. Factors (*b*) and (*c*) may broaden peaks, but seem unlikely to produce the temperature-variable effects recorded, especially as the changes are reversible. Proton exchange occurs on a time-scale many orders of magnitude above that under discussion.

If silicate exchange reactions are regarded as the sole source of temperature-dependent line broadening, exchange rates and activation energies may be calculated from the n.m.r. data. However, the apparent lack of chemically significant correlations in the results suggests that such an analysis is premature. Nevertheless, the fact that the broadest peak at ambient temperature is found in the solution of highest base:silica ratio does suggest that silicate anion exchange reactions are contributing to the effect: equations (7) and (8).

$$OH^- + {}^{29}Si\text{–}O\text{–}Si \rightleftharpoons HO\text{–}Si + {}^{29}Si\text{–}O^- \qquad (7)$$

$${}^{29}Si\text{–}O^- + Si\text{–}O\text{–}Si \rightleftharpoons {}^{29}Si\text{–}O\text{–}Si + Si\text{–}O^- \qquad (8)$$

The tetramethylammonium silicate solution[29] differs from sodium and potassium silicate solutions in possessing an unusually high concentration of the cubic octamer $[Si_8O_{20}]^{8-}$. The singlet resonance of the cubic octamer itself (not tabulated) shows no appreciable line broadening in the temperature range 298—350 K, but decreases in intensity from 35 to 1% of the total visible silicon signal even with pulse delays of 30 s (*cf.* monomer which is approximately constant at 15%). This suggests that the octamer is not involved in exchange processes, but is held in a hydrogen-bonded clathrate structure involving water molecules linked by NMe_4^+ cations. Such a structure is known[30] to exist in the hydrate $[NMe_4]_8[Si_8O_{20}]\cdot 69H_2O$, which itself crystallises out on cooling the present solution below 298 K. It seems likely that the structure persists in solution at low temperatures, but collapses as the temperature is raised, as evidenced by the loss of intensity in the ^{29}Si resonance. Substitution of 9 mol% of sodium ion in the system halves the octamer signal intensity. Presumably this is a structure-breaking effect of the Na^+ ion.

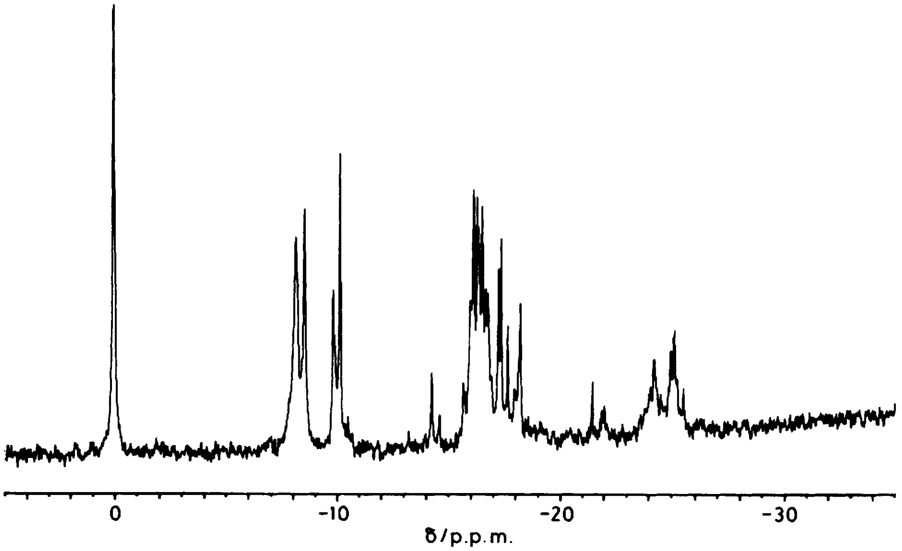

Figure 1. ^{29}Si N.m.r. spectrum of sodium silicate solution (SiO_2: Na_2O = 1.0, [Si] = 1 mol dm^{-3})

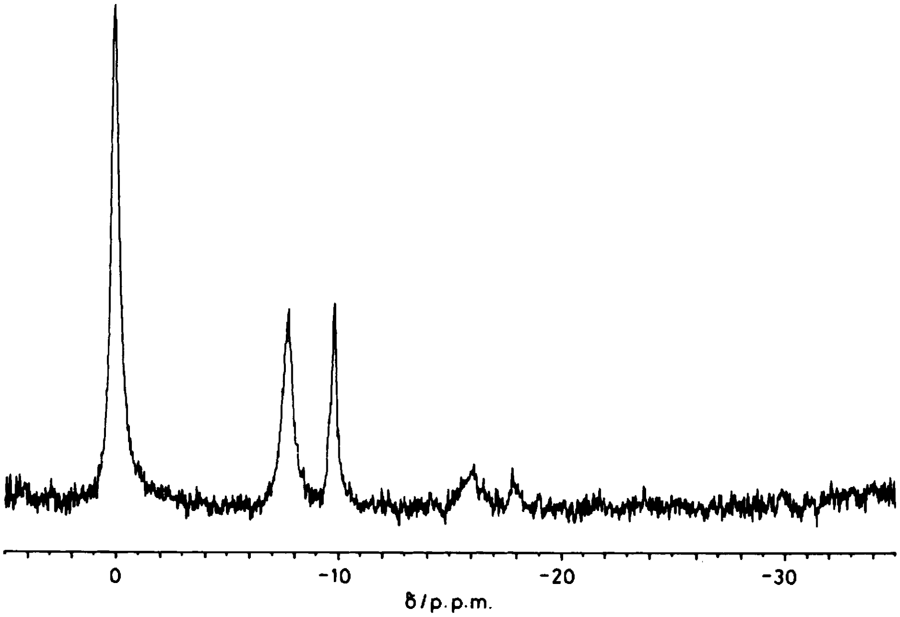

Figure 2. ^{29}Si N.m.r. spectrum of sodium silicate solution (SiO_2: Na_2O = 0.33, [Si] = 1 mol dm^{-3})

Table 3. Linewidths and exchange contributions for solution 1 (SiO_2:Na_2O = 1.0, [Si] = 1.0 mol dm^{-3})[a]

T/K	L_1	L_2(a), L_2(b)	L_3	$X_{min.}$	$X_{max.}$	k/s^{-1} [b]
298	2.0	1.9, 2.2	0.8	−0.2	0.9	0—2.8
320	8	10.5, 12.2	3.1	−4.2	0.6	0—1.9

[a] Maximum peak separation = 27 p.p.m. (2 160 Hz). [b] Range of values.

Silicate Exchange.—Solution 1 (SiO_2:Na_2O = 1.0) exhibits a complex spectrum (Figure 1) but the monomer peak shows no significant exchange rate, at 95% confidence, at either 298 or 320 K (Table 3). At 320 K, L_2 is larger than L_1 at 95% confidence which is clearly incorrect. If a revised value of L_3 = 0.2 Hz is calculated on the basis of $X_{max.}$ (which is more reasonable than the original calculation based on the whole linewidth) and this subtracted from L_2, then L_2 and L_1 are still divergent. This must be seen as a measure of a 1 in 20 occurrence or a systematic error. Furthermore it is chemically unreasonable for the exchange rate at 320 K to be smaller than that at 298 K.

Although silicate exchange for solution 1 cannot be ruled out, it is obviously small ($\leqslant$2.8 s^{-1} up to 320 K). Measurements of T_2 at higher temperatures would make extremely large demands on spectrometer time.

Solution 2 (SiO_2:Na_2O = 0.33) exhibits a much simpler spectrum (Figure 2) but the monomer resonance is 16 times broader at room temperature. Although exchange is not significant at 277 K, it is at room temperature (298 K; Table 4).

It should be noted that the exchange rates are considerably lower than would be calculated from linewidth alone ($\leqslant$0.4 times at room temperature and $\leqslant$0.2 times at 320 K). However

Table 4. Linewidths and exchange contributions for solution 2[a] (SiO_2:Na_2O = 0.33, [Si] = 1.0 mol dm^{-3})

T/K	L_1	L_2(a), L_2(b)	L_3	$X_{min.}$	$X_{max.}$	k/s^{-1}[b]
277	11	4, 13	0.6	−2.0	7.6	0—24
298	32	21, 26	1.6	6	12.6	19—40
320[c]	69	56, 61[d]	0.9	8	13.9	25—44

[a] Maximum peak separation = 9.8 p.p.m. (784 Hz). [b] Range of values. [c] Repeat preparation of that in Table 2. [d] τ = 0.5 ms.

the rates are considerably higher than determined by Creswell *et al.*[24] in an equivalent potassium silicate solution. Using selective inversion recovery no observable exchange was found below 353 K.

As pointed out previously L_3 is an overestimate, and hence so also is $X_{max.}$, partly because it is calculated from L_1 rather than $X_{max.}$ but also in this case because $P_AP_B \neq 0.25$ since the monomer peak (at 0 p.p.m.) is much larger than either of the other two peaks in the spectrum. Despite this the contribution is still small and one is still led to invoke exchange even at room temperature.

Spin–Spin Relaxation Times.—In both solutions in this study, significant decreases take place in T_2 with increased temperature. This is contrary to the general rationale in which decreased correlation times would be predicted. This throws into question the validity of silicate exchange rates determined from linewidth alone.

The most obvious mechanism for increased relaxation rates at higher temperatures is that of spin-rotation relaxation.[31] Since this mechanism is more important in smaller molecules or ions, one would expect it to be greatest for the monomer species. We observed comparative insensitivity of the linewidth of the cubic octamer to temperature which is consistent with this assertion.

Another possibility in explaining decreasing T_2 values is by invoking the presence of dissolved paramagnetic species. The solutions are extremely alkaline and any contact with glass increases the probability of dissolved paramagnetics. However, after studying a wide range of silicate solutions, we have found no evidence that paramagnetics are directly responsible. First, all the temperature induced broadenings are reversible* by cooling, which would require dissolution of paramagnetics at elevated temperature and precipitation at lowered temperature. Secondly, the effects are immediate and no time dependence of linewidth is observed immediately after elevation of temperature or, more importantly, after introducing the solution to the n.m.r. tube. Analyses for paramagnetic impurities are given in the Experimental section.

It is conceivable that reversible complexation of paramagnetic species would lead to a second type of exchange in solution. This could be in either the fast or slow exchange limit. In the fast exchange limit there would be no direct contribution to linewidth but T_2 would be decreased by a weighted contribution of the complex. The measured T_2 value, however, would be anomalously large as calculated by equation (3) and the observed temperature dependence would not necessarily be expected. If paramagnetic exchange was in the slow exchange limit then there would be an increasing contribution to linewidth with temperature. To account for the increase of 50 Hz in L_2 for solution 2 between 277 and 320 K, allowing for a maximum Si:Fe (paramagnetic) ratio of 1.8×10^{-4}, a minimum paramagnetic shift of 222 kHz or 2 793 p.p.m. would be required.

Conclusions

Alkali silicate solutions have been shown to exhibit reversible temperature-dependent line broadening in their ^{29}Si n.m.r. spectra. From a study of the silicate monomer resonance, the effect is ascribed partly to silicate anion exchange reactions and part to a dependence of the spin–spin relaxation time (T_2) upon temperature. Therefore, the effect cannot be used as a simple quantitative measure of exchange rates. The observed T_2 values in this study were found to decrease with increased temperature, and some possible reasons for this have been discussed.

Derived silicate exchange rates were considerably lower than those measured by linewidth alone but higher than those measured by other workers with selective inversion recovery. There remains the possibility that some of the exchange ascribed to silicates could be between silicates and paramagnetic complexes.

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* It can be seen from Table 2 that in all cases there is a small discrepancy between the initial and final linewidths measured at 298 K. The value obtained at the end of the experiment is always larger. Whilst this may be due, in part, to chemical reaction between the solution and the glass of the n.m.r. tube, it is more probable that the difference reflects changes in field homogeneity (see Experimental section). This conclusion is supported by (*a*) the chemical analyses given in the Experimental section, and (*b*) the very small difference between the two 298 K values for solution 1: in this experiment the n.m.r. spectrometer was re-shimmed at each measurement temperature.

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