Inorg. Chem. **1988**, *27*, 4259–4264

units in the formation of minerals.[33,34]

Finally, it is significant that, with the care taken to eliminate all sources of silicon other than the solution samples themselves from the probehead, the ^{29}Si spectra of all the silicate solutions examined were completely blank, with zero intergrated intensity, in the Q^4 region (ca. −30 ppm and beyond, relative to the Q^0 resonance). Harris and co-workers,[35] in a two-dimensional ^{29}Si NMR study of aqueous silicates, were similarly unable to detect any sharp peaks in the Q^4 region, although Svensson et al.[20b] reported evidence for Q^4 centers in aged silicate solutions (decanted from a precipitate) with Na$^+$:Si^{IV} < 1.0:1, in which colloidal or suspended silica would be expected to be present. Evidently, the connectivity of silicate centers cannot exceed 3 in true solution in water, although colloidal silica or silicates, if present, may contain Q^4 centers.

Acknowledgment. We thank the Alberta Oil Sands Technology and Research Authority for a scholarship (to S.D.K.) and the University of Calgary Research Grants Committee and the Natural Sciences and Engineering Research Council of Canada for financial assistance.

Supplementary Material Available: Tables of solution compositions, ^{29}Si shifts as functions of temperature and solution composition, and spectral integration data for aqueous alkaline silicate solutions (10 pages). Ordering information is given on any current masthead page.

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Silicon-29 NMR Studies of Aqueous Silicate Solutions. 2. Transverse ^{29}Si Relaxation and the Kinetics and Mechanism of Silicate Polymerization

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For solutions of SiO$_2$ in aqueous MOH (M = Na, K, Rb) with M$^+$:Si^{IV} = 1:1 (in which each Si carries one –O$^-$ group), the temperature-dependent ^{29}Si line broadening is almost entirely due to Si–Si chemical exchange, if contaminants are absent, and is uniform for most resonances. This implies involvement of a common vehicle of intermolecular Si exchange (polymerization)—evidently the neutral form of the monomer, Si(OH)$_4$. The temperature dependence of the inverse spin-site lifetime τ^{-1} is given by $\Delta H^* = 50$ kJ mol^{-1} and $\Delta S^* = -69$ J K^{-1} mol^{-1}. Intramolecular cyclization processes are faster than intermolecular polymerization and result in greater line broadening for a few minor peaks. For solutions with M$^+$:Si^{IV} > 1:1 (high pH), silicate species that have more than one –O$^-$ per Si and that are relatively unreactive in Si–Si exchange form to varying degrees, leading to reduced and nonuniform temperature-dependent line broadening. When this is taken into account, Si–Si chemical exchange is seen to explain both ^{29}Si line broadening and the results of selective inversion-recovery experiments.

Introduction

We have remarked[1,2] that the use of ^{29}Si NMR for the characterization of hydrothermal silicate solutions is limited by the marked broadening of the spectral lines as the temperature is increased. Engelhardt and Hoebbel[3] suggested that this broadening was due to chemical exchange of SiO$_4$ units between the silicate anions at rates within the NMR time frame. Although Harris and co-workers originally put forward a similar suggestion,[4] they later reported[5] spin saturation-transfer experiments that implied exchange rates some 2 orders of magnitude lower than had been estimated from line-width measurements. They noted that line broadening was particularly severe (and not completely reversible) when the samples were heated in the spectrometer in unlined glass NMR tubes[4] and concluded that paramagnetic contaminants introduced during sample preparation and/or by leaching from glass NMR tubes were the most likely cause of both longitudinal relaxation (time constant T_1) and line broadening (transverse relaxation T_2).[5] Both research groups reported that the extent of temperature-dependent line broadening varied from resonance to resonance.[3,4]

Griffiths, Cundy, and Plaisted[6] recently employed the Carr–Purcell–Meiboom–Gill pulse sequence[7] in an attempt to quantify the contribution of Si–Si exchange to ^{29}Si line widths in aqueous silicates. Their conclusions, however, are based upon limited data and are not unequivocal, since unlined glass NMR tubes were used and the possible effect of pseudo-T_2 relaxation arising from field inhomogeneities was not taken into account. Thus, while NMR methods afford unique insights into the complicated aqueous chemistry of silicates, definitive results have been elusive and are likely to remain so.

The present paper reports a detailed study of ^{29}Si line broadening in silicates as a function of temperature (up to 144 °C) and solution composition (expressed as the total concentration [Si^{IV}] of silica dissolved in aqueous MOH, where M is an alkali-metal ion, and the concentration ratio M$^+$:Si^{IV}[1]), with special attention to the avoidance of contamination of the solutions; an ancillary study[8] of longitudinal relaxation in these systems showed that paramagnetic contamination can readily be reduced to insignificance. It will be shown that the temperature-dependent line broadening is indeed due to chemical exchange of silicate units and that this is strongly pH-dependent, which accounts for some of the disagreement in the literature, as was pointed out in a brief preliminary communication.[2] The mechanistic implications will also be considered. Finally, an error in our preliminary communication[2] is corrected.

Experimental Section

The preparation of the solution and the conduct of the NMR experiments are described in the preceding paper.[1] Full details of the sample compositions are given in the supplementary material of ref 1. Several

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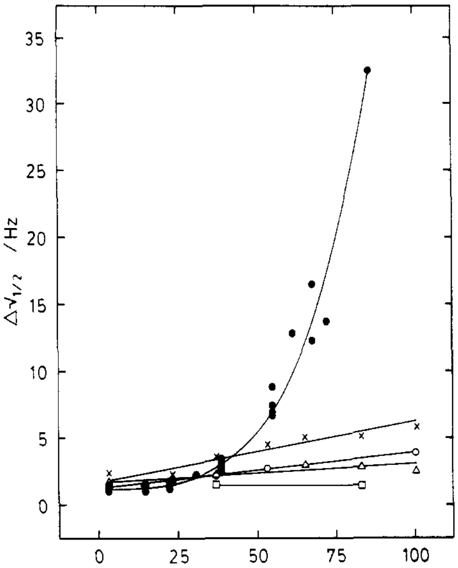

Figure 1. Temperature dependence of the monomer ^{29}Si line width: (filled circles) $Na^+:Si^{IV}$ = 1.0:1 but [Si^{IV}] ranging from 0.80 to 2.17 mol kg^{-1}; (crosses) $Na^+:Si^{IV}$ = 4.0:1; (open circles) $K^+:Si^{IV}$ = 4.0:1; (open triangles) $K^+:Si^{IV}$ = 10.0:1; (open squares) $K^+:Si^{IV}$ = 20:1.

duplicate experiments were made with all chemicals (including the solvent water) from new sources; the spectra were in all cases reproduced to within the experimental uncertainty; i.e., any contamination of the solutions that may have occurred did not affect the results.

Silicon-29 spectra were obtained at temperatures ranging from about −5 to +150 °C and integrated, and the line widths at half peak height ($\Delta\nu_{1/2}$) were recorded for the easily resolved, uncoupled signals. Selective inversion-recovery experiments were conducted on five samples using a DANTE-like pulse sequence as described by Creswell et al.[5]

In an attempt to obtain ^{29}Si spectra under preequilibrium conditions, three solutions ([Si^{IV}] ≈ 1.3–2.3 mol kg^{-1}; $M^+:Si^{IV}$ = 1.2–5.8; M = K, Rb; natural-abundance ^{29}Si) were prepared rapidly at 0 °C and then, beginning 15 minutes from the start of sample preparation, spectra were recorded, still at 0 °C. Rubidium hydroxide was used because it dissolved the silica most rapidly.

Complete band-shape analyses were carried out using the Fortran program GNMR derived from the exchange-modified Bloch equations.[9–17] For each of 14 samples, a low-temperature (<20 °C), unbroadened spectrum was simulated manually by iterating the positions, line widths, and areas of up to 70 computer-generated Lorentzian peaks. Many reaction models were then tested to find appropriate sets of rate equations (kinetic matrix **K**, defined in ref 13) that would replicate the observed temperature-dependent line broadening.

Results and Discussion

Solutions with $M^+:Si^{IV}$ = 1.0:1. Silicon-29 line widths, measured in the lined, pressurizable NMR tube, of solutions with $Na^+:Si^{IV}$ are listed in the supplementary material and were typically 1.0–1.6 Hz at 3 °C; i.e., they were narrower than those reported for similar solutions under comparable conditions in unlined glass tubes.[4,6,18] Temperature-dependent line broadening was insignificant below 20 °C but increased sharply at higher temperatures (Figure 1), and so spectra recorded at temperatures below 20 °C were used as the preexchange basis set in band-shape modeling studies, which were undertaken to determine whether Si–Si chemical exchange can account for the observed line broadening. Line widths were not significantly affected by ^{29}Si abundance (4.6 vs 95%) or sample dilution (Figure 1). A slight dependence of line width on the identity of the counterion (M = Na, K, Rb) was discernible in the absence of temperature-dependent broadening, i.e., below 20 °C.

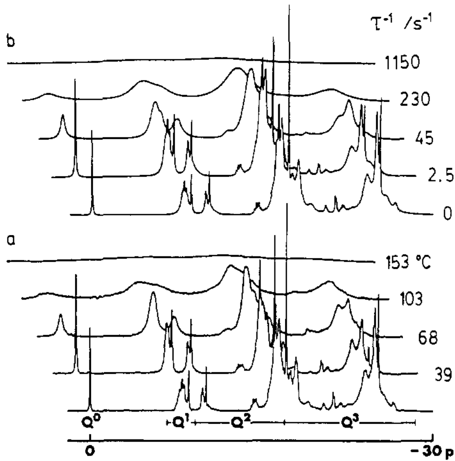

Figure 2. Comparison of (a) experimental and (b) simulated spectra for a sample with [Si^{IV}] = 1.55 mol kg^{-1} and $Na^+:Si^{IV}$ = 1.0:1 (^{29}Si abundance 95%). The simulations are based on the assumption that the spectrum at 3 °C represents infinite spin-site lifetimes. The simulations do not take into account the small variations in resonance frequencies caused by phenomena other than spin-site exchange.[1]

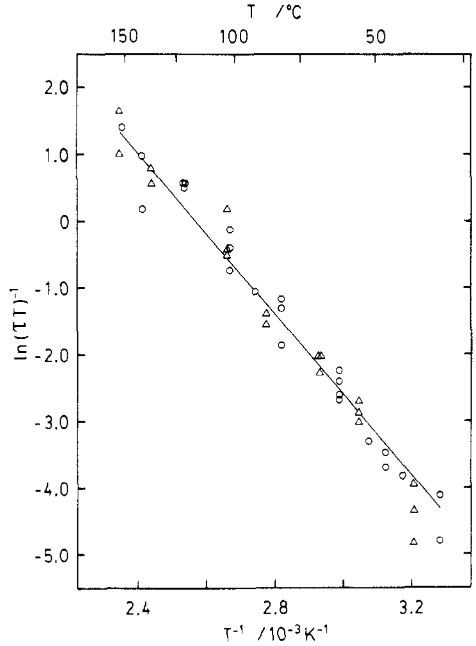

Figure 3. Temperature dependence of the spin-site residence time τ for $Na^+:Si^{IV}$ = 1.0:1 (eq 1). Two independent batches of 95% ^{29}Si-enriched SiO_2 were used (batch A, circles; batch B, triangles).

After many alternative reaction models were tested to find exchange matrices **K** that could replicate the observed temperature-dependent line broadening, it was established that only those **K** in which all the diagonal elements were equal, balanced in accordance with the conditions given by Sack,[13] could reproduce the experimental spectra. This implies that all the principal resonances broaden uniformly with rising temperature (some minor exceptions are noted below), in apparent contrast to some earlier reports.[3,4] The accuracy of band-shape simulations made on this basis (Figure 2) strongly supports the view[2,3] that temperature-dependent ^{29}Si line broadening in aqueous silicates is indeed due to Si–Si chemical exchange. Furthermore, the alternative hypothesis, that the phenomenon is due to contaminants,[5] seems to be ruled out by the reproducibility of the spectra regardless of

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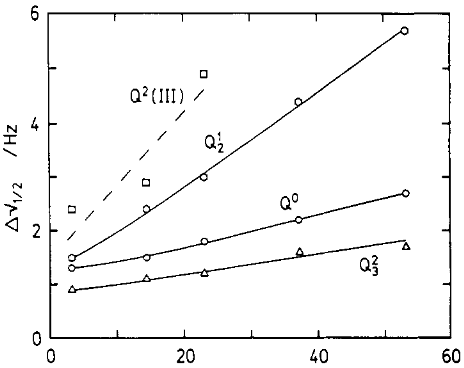

Figure 4. Temperature dependence of line widths for a sample with [Si^{IV}] = 2.17 mol kg^{-1} and K^+:Si^{IV} = 4.0:1. Q^2(III) refers to the Q^2 center in species III (acyclic trimer).[1]

the sources of the reagents and by the care taken to handle the samples only in inert vessels.

The chemical-exchange explanation implies that the ^{29}Si residence times at all the principal spin sites must be equal. This simple fact was missed in preparing our preliminary communication[2] because of faulty data treatment; the table and reaction scheme 1 in that report should therefore be disregarded, although the essential conclusions concerning the role of deprotonation remain unchanged. Inverse spin-site lifetimes τ^{-1} derived by complete band-shape analysis for eight samples with Na^+:Si^{IV} = 1.0:1 are listed in Table I. As Figure 1 shows, these lifetimes appear to be independent of sample concentration. A single least-squares fit (Figure 3) of all the τ^{-1} values of Table I to the Eyring equation

$$\tau^{-1} = (k_BT/h)\exp[(\Delta S^*/R) - (\Delta H^*/RT)] \qquad (1)$$

gives the enthalpy of activation $\Delta H^* = 50.1 \pm 1.4$ kJ mol^{-1} and the entropy of activation $\Delta S^* = -69.0 \pm 3.8$ J K^{-1} mol^{-1} (corresponding to $\tau^{-1} = 2.6$ s^{-1} at 298.2 K; uncertainties are standard deviations) for the process that controls the spin-site lifetimes when M^+:Si^{IV} = 1.0:1 (see below).

There are a few minor resonances that broaden more than the majority; all represent species that can easily cyclize, e.g., the acyclic trimer and tetramer. Because the cyclic and cage structures remain in equilibrium with the smaller silicate units, the slower ring-*breaking* processes must occur at least as rapidly as intermolecular condensation. Since these peaks are relatively weak and are observable only below about 20 °C, however, they do not contribute materially to the line-broadening analysis.

Solutions with M^+:Si^{IV} Greater Than 1.0:1. Line widths measured for 36 solutions with M^+:$Si^{IV} \geq 4.0$:1 (listed in the supplementary material) were again narrower than those reported previously for comparable conditions.[4,6,18] Figure 1 shows that the Q^0 line width, which is 1–2 Hz for *all* solutions below ambient temperature, was virtually independent of temperature for very alkaline solutions (M^+:Si^{IV} = 20:1) but tended increasingly to broaden with rising temperature as the M:Si^{IV} ratio was decreased. The uniformity of $\Delta\nu_{1/2}$ at low temperatures and/or high alkalinity is a further indication that contaminants[5] do not contribute to the temperature-dependent line broadening reported in this paper.

In contrast to the cases with M^+:Si^{IV} = 1.0:1, line broadening at higher M^+:Si^{IV} ratios is no longer the same for all signals (Figure 4), and the counterion M^+ exerts a small but significant effect upon the temperature dependence of $\Delta\nu_{1/2}$ (Figure 5). The latter effect could be due to dissimilarities in viscosity or other solution properties, but the order of T_2 values (K > Rb ≥ Na) correlates with that observed for T_1 relaxation, which is caused primarily by M–Si nuclear dipole–dipole interactions.[8]

The decrease in the overall degree of line broadening as the M^+:Si^{IV} ratio is raised is linked to a decrease in the extent of polymerization (Figure 1). At extreme alkalinity (K^+:Si^{IV} = 20.0:1), almost all the dissolved silicate is monomeric and the Q^0 line width is constant at about 1.5 Hz up to at least 87 °C. Where temperature-dependent line broadening does occur, in solutions of moderately high alkalinity, there can be little doubt that its primary cause is Si–Si chemical exchange, but because the degree of broadening is not the same for all signals, band-shape simulations consistently failed when exchange matrices that had been used successfully for M^+:Si^{IV} = 1.0:1 were employed.

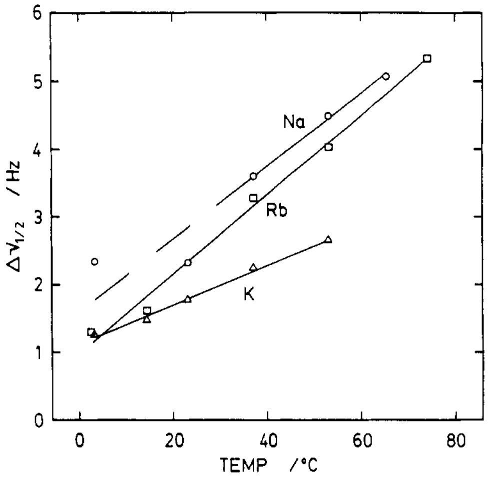

Figure 5. Temperature dependence of the monomer line width in samples with M = Na, K, Rb, each with M^+:Si^{IV} = 4.0:1.

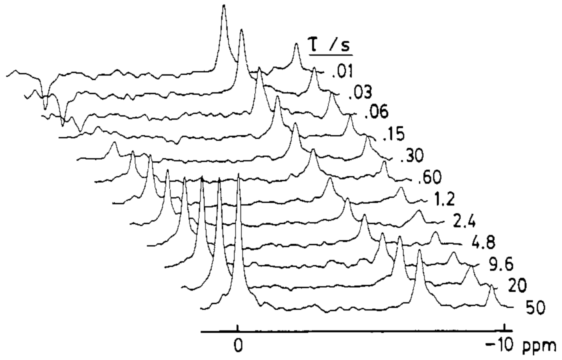

Figure 6. ^{29}Si spectra of a selective inversion-recovery experiment at 92 °C for a sample with [Si^{IV}] = 2.80 mol kg^{-1} and K^+:Si^{IV} = 4.5:1.

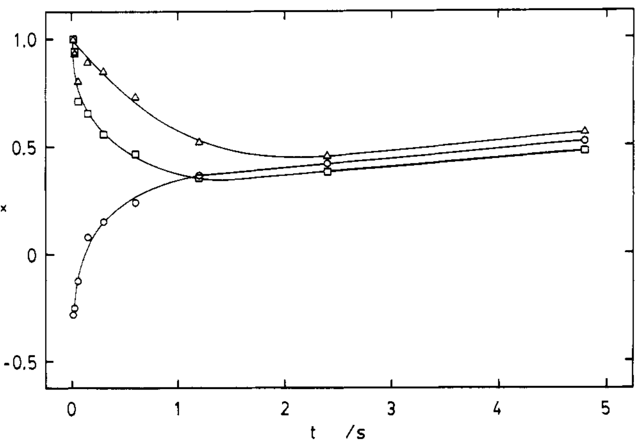

Figure 7. Inversion-recovery data for the same sample as in Figure 6. The fractions f_x of the equilibrium z-magnetization components for the monomer (circles), dimer (squares), and trimer (triangles) nuclei are presented as a function of time t.

Selective inversion-recovery (SIR) experiments, conducted in the manner described by Creswell et al.[5] on solutions containing 2.8 mol kg^{-1} of Si^{IV}, succeeded in demonstrating that spin rates were on the order of T_1^{-1} between 80 and 100 °C for K^+:Si^{IV} = 4.5:1 (Figures 6 and 7) and at 30 °C for K^+:Si^{IV} = 1.0:1. No attempt was made to calculate actual exchange rate constants from the SIR data, for reasons that are explained below. We have shown[8] that, for small oligomers, T_1 values should not vary by more than a factor of 2 or 3 between these two solutions at their respective temperatures. Thus, the SIR experiments reveal that

Table I. Inverse Spin-Site Lifetimes for Samples with $Na^+:Si^{IV}$ = 1.0:1

$[Si^{IV}]$/mol kg^{-1}	temp/°C	τ^{-1}/s^{-1}
1.40	41.5	7 ± 2
	61.5	25 ± 5
	91.5	130 ± 20
	121.5	650 ± 100
	151.5	1700 ± 200
0.70	31.5	2.5 ± 1
	51.5	12 ± 2
	61.5	36 ± 2
	81.5	96 ± 6
	101.5	330 ± 50
	121.5	700 ± 50
0.35	31.5	5 ± 1
	46.5	10 ± 2
	61.5	30 ± 5
	81.5	110 ± 10
	101.5	250 ± 50
	121.5	700 ± 100
	141.5	1100 ± 100
0.18	46.5	8 ± 1
	61.5	23 ± 1
	81.5	55 ± 5
	101.5	180 ± 10
	141.5	500 ± 200
2.70	38.8	4 ± 1
	55.0	22 ± 2
	68.0	35 ± 5
	102.5	250 ± 30
	137.3	900 ± 50
	152.7	2200 ± 400
1.55	38.8	2.5 ± 1
	55.0	16 ± 2
	68.0	45 ± 4
	86.7	76 ± 4
	102.5	230 ± 30
	137.3	720 ± 50
	152.7	1150 ± 100
0.30	38.8	6 ± 2
	55.0	19 ± 1
	68.0	45 ± 3
	86.7	90 ± 4
	102.5	450 ± 60

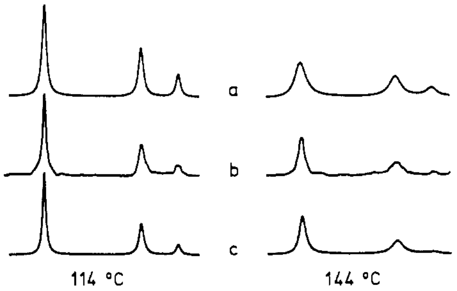

Figure 8. Simulations (a, c) and actual ^{29}Si spectra (b) for a sample with $[Si^{IV}]$ = 2.79 mol kg^{-1} and $K^+:Si^{IV}$ = 3.80:1 (cf. ref 5; spectral width 14 ppm). Simulation c allows for deprotonation, whereas simulation a does not.

Table II. Inverse Spin Lifetimes for a Sample[a] with $K^+:Si^{IV}$ = 3.80:1

temp/°C	τ^{-1}/s^{-1}	temp/°C	τ^{-1}/s^{-1}
83.2	4 ± 1	140.0	82 ± 4
113.8	24 ± 2	144.2	98 ± 4
131.5	47 ± 2		

[a] $[Si^{IV}]$ = 2.80 mol kg^{-1}.

the exchange rates decrease roughly 100-fold as the $K^+:Si^{IV}$ ratio is increased from 1.0:1 to 4.5:1.

Creswell et al.[5] calculated exchange rates from an SIR investigation of a solution containing 2.8 mol kg^{-1} of Si^{IV} with $K^+:Si^{IV}$ = 3.8:1, on the assumption that dimer formation proceeds by straightforward addition of monomer. Arrhenius extrapolation of their published rate data yields a half-period for the monomer–dimer exchange in excess of 2 h at 0 °C. We have, however, been able to obtain, within 15 min of sample preparation at 0 °C, spectra of three samples with nominal $M^+:Si^{IV}$ ratios ranging from 1.0:1 to 6.0:1, and all displayed the equilibrium distributions of peaks. Thus, although the present SIR experiments show that exchange becomes slower as the alkalinity is raised, the exchange rates are much faster than those calculated in ref 5. We have pointed out in a preliminary communication[2] that this apparent discrepancy, along with other features (noted above) of ^{29}Si line broadening in the more alkaline aqueous silicate solutions, can be understood in terms of protonation equilibria.

Protonation Equilibria. Sjöberg et al.[19] determined that pK_a = 9.473 for H_4SiO_4 and 12.65 for $H_3SiO_4^-$ at 298 K and ionic strength I = 0.6 mol L^{-1} but varied somewhat among polymeric species (e.g., pK_a = 10.25 for $(HO)_3SiOSi(OH)_2O^-$) and that the average charge per Si atom in alkaline solutions at pH up to 12.2 (including those with $M^+:Si^{IV}$ = 1.0:1) was −0.98 ± 0.04. Thus, in the present study, each Si center was singly deprotonated at $M^+:Si^{IV}$ = 1.0:1, while, at higher alkalinities, the extent of secondary or further deprotonation depended on the species in which the particular Si center was located. It is convenient to express local charge $x-$ at a Si center of connectivity y by the symbol ${}^xQ^y$, which represents an SiO_4 unit with $4 - y$ terminal –OH groups of which x are deprotonated.

It was shown above that, as the $M^+:Si^{IV}$ ratio (i.e. alkalinity) was raised from 1.0:1, the degree of polymerization was reduced, the ^{29}Si resonances narrowed, and the temperature dependence of the line broadening differed between the resonances. These findings, together with the slow exchange rates calculated by Creswell et al.,[5] may be understood if the doubly deprotonated Si centers ${}^2Q^y$ are much less reactive in the polymerization process than are the corresponding singly deprotonated centers ${}^1Q^y$. Figure 8 shows that accurate spectral simulations for a solution with $K^+:Si^{IV}$ = 3.80:1 (cf. Creswell et al.[5]) can be achieved if, and only if, the rate equation corresponding to the deprotonation reaction

$$ {}^1Q^0 + OH^- \rightleftharpoons {}^2Q^0 + H_2O \qquad (2)$$

is included in the exchange matrix **K**, with the additional assumption that the rate of this reaction is in excess of the fast-exchange limit (which is reasonable) so that two signals—a Si-exchange-broadened ${}^1Q^0$ resonance and a sharp unbroadened ${}^2Q^0$ peak—collapse into a single monomer band. The site lifetimes τ determined by complete band-shape analysis for this sample (Table II; eq 1 gives ΔH^* = 62.1 ± 4.7 kJ mol^{-1} and ΔS^* = −61 ± 11 J K^{-1} mol^{-1}) are much longer than for $M^+:Si^{IV}$ = 1.0:1 (e.g., 100 and 5.3 ms, respectively, at 100 °C), which is in accordance with the SIR observations. From the data of Creswell et al.,[5] τ^{-1} can be estimated to be 0.31 s^{-1} for their conditions at 83 °C; comparison with a value of 3.7 s^{-1} extrapolated from the band-shape analysis data in Table II indicates that only 8% of the monomer was in the reactive ${}^1Q^0$ form at that temperature.

The exact proportions of the various deprotonated forms of the monomeric and polymeric silicate species present in our solutions over the temperature range −5 to +150 °C and widely varying ionic strengths are generally not known, and therefore, we have not attempted to analyze the SIR data (e.g., of Figure 7) quantitatively. Nevertheless, Arrhenius extrapolation of site lifetimes indicates that intermolecular Si–Si exchange has a half-period of 2–3 min at 0 °C, which explains why freshly prepared samples gave spectra corresponding to the equilibrium distribution of silicate species after as little as 15 min at this temperature.

The variations observed between different Si centers in the temperature dependence of $\Delta\nu_{1/2}$ at $M^+:Si^{IV} > 1.0:1$ (Figure 4) indicate that Q^y centers in the polymers (i.e., $y > 0$) generally undergo secondary deprotonation at higher pH than does the monomer Q^0 and that the relative ease of deprotonation is $Q^0 \simeq Q^2{}_3 > Q^1{}_2 \simeq Q^2$ of the acyclic trimer (notation as in ref 1). The Q^3 centers are completely deprotonated after losing just one proton,

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(19) (a) Sjöberg, S.; Nordin, A.; Ingri, N. *Mar. Chem.* **1981**, *10*, 521. (b) Sjöberg, S.; Öhman, L.-O.; Ingri, N. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 93. (c) Svensson, I. L.; Sjöberg, S.; Öhman, L.-O. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3635.

so that they occurred only as $^1Q^3$ in our experiments.

Reaction Mechanism. For solutions with $M^+:Si^{IV} = 1.0:1$, the uniformity of the temperature dependence of line broadening demonstrates that all the silicate centers, except those for which facile cyclization is possible, contribute equally to the dynamics of Si–Si exchange. Such independence of the nature of the reactive sites is typical of diffusion-controlled processes, but aqueous diffusion rates are generally much faster than the entire frequency range of ^{29}Si resonances.

More probably, Si–Si exchange broadening is the result of reversible formation of active silicate sites $^*Q^y$, which attack at the oxygens on other Si centers. If the active $^*Q^y$ site occurs in an easily cyclizable anion, rapid ring closure would be expected, and this is consistent with both the low abundances and excessive NMR line broadening associated with such species.[1,20] If the $^*Q^y$ center is in a noncyclizable silicate species, it will either encounter and bind to another silicate molecule, leading to increased polymerization, or else revert to its original inactive state, in which case no net change is observed. The remarkable uniformity of temperature-dependent line broadening observed for all noncyclizable species when $M^+:Si^{IV} = 1.0:1$ implies that there is one predominant vehicle of intermolecular Si–Si exchange. The obvious candidate, on the grounds of abundance of its precursor and relatively high mobility (small size), is an active form $^*Q^0$ of the monomeric anion $^1Q^0$. At $M^+:Si^{IV} = 1.0:1$, each Si center bears one negative charge[1,2,19] and can be conventionally represented as $\equiv Si—O^-$ (e.g., $(HO)_3SiO^-$ for $^1Q^0$). Our observation that excess OH^- *retards* Si site exchange may therefore be taken to mean that the active species $^*Q^0$ is a form of neutral silicic acid, nominally $Si(OH)_4$:

$$H_3SiO_4^- + H_2O \rightleftharpoons Si(OH)_4 + OH^- \qquad (3)$$

Polymerization could then proceed by electrophilic attack of $Si(OH)_4$ on the $-O^-$ ligands of the various Si^{IV} centers. Recent MNDO calculations on models of $Si(OH)_4$ dimerization[21] as well as general experience in Si^{IV} chemistry[22-24] suggest expansion of the coordination number of $Si(OH)_4$ (associative attack on O in $^-O—Si\equiv$), followed by elimination of H_2O or OH^-, as the most likely pathway:

$$(HO)_4Si + {}^-O—Si\equiv \rightleftharpoons {}^-(HO)_4Si—O—Si\equiv \rightleftharpoons {}^-O(HO)_2Si—O—Si\equiv + H_2O \qquad (4)$$

Since the crucial processes in this mechanism all occur on the attacking Q^0 unit, the rate will be largely independent of the identity of the target silicate species. The reverse of reacton 4 provides for the release of a terminal Q^1 unit; the various Q^y centers can be degraded stepwise to Q^1 and so enter the Q^0 exchange pool. Figure 9 presents a tentative mechanistic interpretation of the polymerization and depolymerization processes on this basis. We stress that our data do not exclude the involvement of neutral species other than $Si(OH)_4$ as vehicles of Si–Si exchange, but these alternative species would be less mobile (bulkier) and invariably less abundant than the neutral monomer.

Direct attack by the anions $H_3SiO_4^-$ and especially $H_2SiO_4^{2-}$ on $^-O—Si\equiv$ is electrostatically improbable, while a $^0Q + {}^2Q$ encounter would result in rapid transfer of a proton to give two mutually repelling ^1Q centers. Thus, Si exchange becomes very slow on the NMR time scale at high pH, where a substantial part of the Q^0 pool is converted to the inactive dianion.[2] This is demonstrated by the lack of *uniformity* of temperature-dependent line broadening for different resonances at the higher alkalinities. Attemps were made to obtain Si–Si exchange rate data at $M^+:Si^{IV} < 1.0:1$, at which formation of $^2Q^y$ species would be totally negligible and the proposed special reactivity of neutral $^0Q^y$ would stand revealed, but such solutions either could not be prepared or were metastable and soon deposited silicic acid gel.[1]

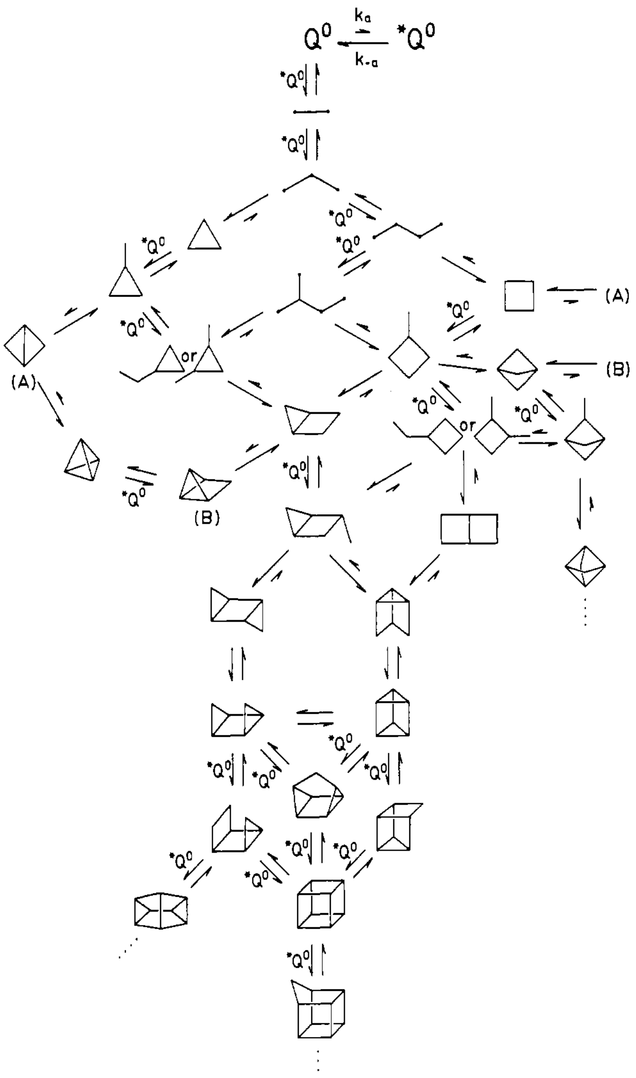

Figure 9. Silicon site exchange through stepwise addition of monomer in the activated form $^*Q^0$. This scheme includes several species that have yet to be identified.

As an alternative to associative electrophilic attack of $Si(OH)_4$ on $^-O—Si\equiv$, a dissociative mechanism can be considered in which $(HO)_3SiO^-$ loses OH^- or H_2O in a thermodynamically unfavorable preequilibrium step to produce $^*Q^0 = H_2SiO_3$ or $HSiO_3^-$, which then either recombines or scavenges $^-O—Si\equiv$ targets indiscriminately according to Figure 9. The hypothetical intermediates H_2SiO_3 and $HSiO_3^-$, analogues of carbonic acid and bicarbonate ion, have a precedent in the occurrence of the silaacetate ion $CH_3Si(O)O^-$ in the alkaline cleavage of $m\text{-}ClC_6H_4CH_2SiCH_3(O^-)_2$,[25] and comparison might be made with the role of PO_3^- in reactions of four-coordinate phosphate species.[26] The distinction between these associative and dissociative mechanisms cannot be made on kinetic grounds, however, although energetic considerations appear to favor the former (eq 3 and 4).

Thus, the inverse site lifetime τ^{-1} represents the sum of the first-order rate coefficients for cleavages of noncyclic Si–OSi bonds, the rates of which, in these equilibrium systems, are matched by those of bimolecular Si–OSi bond formation. In principle, rate coefficients for monomer elimination can be obtained from τ^{-1} and spectral integration measurements, but as noted above, it is generally difficult to extract integrated intensities

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but are adequately represented by $\Delta H_-^* = 51.0 \pm 1.7$ kJ mol^{-1} and $\Delta S_-^* = -51.8 \pm 5.4$ J K^{-1} mol^{-1}, which give $k_- = 14$ s^{-1} at 298.2 K.

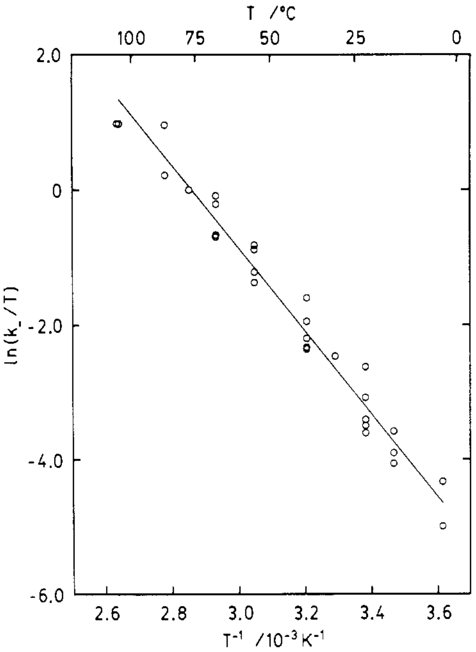

Figure 10. Temperature dependence of the rate coefficient k_- for dissociation of the dimer $H_4Si_2O_7^{2-}$.

for single species (other than the monomer) except at high pH, where the additional complication of unknown degrees of multiple deprotonation of the various silicate species arises. Nevertheless, for solutions with $M^+:Si^{IV} = 1.0:1$, it is possible to estimate roughly the rate coefficient k_- for cleavage of the dimer $H_4Si_2O_7^{2-}$ (${}^1Q^1{}_2$) from eq 5, in which k_+ ($=\tau^{-1}/[{}^*Q^0]$) is the first-order rate coefficient for dimerization and p_m and p_d are the integrated areas of the monomer and dimer resonances, respectively.

$$k_- = k_+[{}^*Q^0][{}^1Q^0]/[{}^1Q^1{}_2] = \tau^{-1}[{}^1Q^0]/[{}^1Q^1{}_2] = 2\tau^{-1}p_m/p_d \quad (5)$$

Figure 10 summarizes the available data for solutions with $Na^+:Si^{IV} = 1.0:1$ in terms of eq 1 and 5. The k_- values refer to widely differing media and carry an uncertainty of about ±20% but are adequately represented by $\Delta H_-^* = 51.0 \pm 1.7$ kJ mol^{-1} and $\Delta S_-^* = -51.8 \pm 5.4$ J K^{-1} mol^{-1}, which give $k_- = 14$ s^{-1} at 298.2 K.

Conclusion. Our findings demonstrate that temperature-dependent line broadening in ^{29}Si spectra of aqueous silicate solutions is indeed the result of Si–Si chemical exchange at rates within the NMR time frame (roughly 1 s to 0.1 ms, from ambient temperature to about 150 °C). For readily cyclizable species such as the acyclic trimer, cyclization is more rapid than intermolecular condensation. For $M^+:Si^{IV} = 1.0:1$, at which each Si normally carries one $-O^-$ group, the rate of intermolecular condensation is essentially the same for all Si centers that are not easily cyclized, implying that there is a common vehicle of Si exchange which is probably an active forrm of the monomer. At higher pH levels, i.e., at $M^+:Si^{IV}$ ratios higher than 1.0:1, substantial fractions of the silicate centers carry two $-O^-$ groups and are relatively unreactive, resulting in a decrease in both polymerization and cyclization rates and a shift in the equilibrium distribution of silicate species toward the monomer and low-molecular-mass oligomers.

Most of the controversy that has arisen over the origin of the temperature-dependent line broadening of aqueous silicates has stemmed from failure to consider the effect of pH or of the leaching of line-broadening contaminants from glass sample tubes. When deprotonation equilibria are taken into account, line-broadening analyses and selective inversion-recovery experiments are seen to be in agreement.

Finally, there is evidence for a small contribution to ^{29}Si line widths from Si–M nuclear dipole–dipole relaxation, but this effect is significant only at temperatures below 20 °C and/or very high pH, i.e., when Si–Si exchange broadening is negligible.

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Registry No. Si, 7440-21-3; $Si(OH)_4$, 10193-36-9; $H_4Si_2O_7^{2-}$, 51931-86-3; SiO_2, 7631-86-9.

Supplementary Material Available: Tables of line widths as functions of temperature and alkalinity and (for the monomer–dimer equilibrium) integrated peak areas and rate coefficients (3 pages). Ordering information is given on any current masthead page.

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The $FeBr_2$–Br_2–H_2O–HBr System. Iron(III) Bromide Hydrate in the Vapor Phase

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Absorbances of vapors generated by $FeBr_2$–Br_2–HBr–H_2O mixtures at temperatures between 400 and 700 K have been measured in the wavelength range 300–480 nm. Evidence is found for substantial concentrations of a hydrate in the vapor phase, along with Fe_2Br_6(g) and $FeBr_3$(g). $Fe(H_2O)Br_3$(g) is assumed to be the dominant hydrate vapor molecule. Molar absorptivities at various wavelengths and thermodynamic constants are derived. For $Fe(H_2O)Br_3$(g) at 500 K, $\Delta H° = -508$ kJ mol^{-1} and $S° = 502$ J K^{-1} mol^{-1}.

Introduction

The recent finding of iron(III) chloride hydrate molecules[1,2] in the vapor phase has motivated a search for similar hydrate molecules in the iron bromide system. In the presence of solid iron(II) bromide, the concentrations of iron(III) bromide dimer, Fe_2Br_6(g), and monomer, $FeBr_3$(g), are fixed by the concentration of bromine, Br_2(g). Equilibrium reactions 1 and 2 have been

$$2FeBr_2(s) + Br_2(g) = Fe_2Br_6(g) \quad (1)$$

$$FeBr_2(s) + 0.5Br_2(g) = FeBr_3(g) \quad (2)$$

studied in previous work.[3-6] If the addition of water vapor to a mixture of solid iron(II) bromide and bromine forms a volatile hydrate, as in reaction 3, then the total concentration of iron(III)

$$FeBr_2(s) + 0.5Br_2(g) + H_2O(g) = Fe(H_2O)Br_3(g) \quad (3)$$

bromide molecules in the vapor, and hence the vapor phase absorbance, should be enhanced.

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