^{29}Si N.M.R. Spectroscopy reveals Dynamic SiO_4^{4-} Group Exchange between Silicate Anions in Aqueous Alkaline Silicate Solutions

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Temperature dependent line broadening is observed in the ^{29}Si n.m.r. spectra of sodium silicate solutions which indicates dynamic exchange of SiO_4^{4-} groups between different silicate anion species with the free SiO_4^{4-} anion life time in the order of milliseconds.

^{29}Si N.m.r. spectroscopy has been shown to be a very powerful tool for the study of the silicate anion species and the structural units present in silicate solutions. Characteristic ranges of ^{29}Si chemical shifts have been determined for the different types of silicate structural units Q^n (Q represents a silicon atom bonded to four oxygen atoms and n is the number of ≡Si–O–Si≡ bridges attached[1]) and from a detailed analysis of the spectra a series of distinct species of silicate anions can be identified.[1—3] Since, in general, narrow n.m.r. peaks are observed for the various Q^n units in different structural environments it has been concluded that the rate of exchange between the anion species is slow on the n.m.r. time scale. However, in the course of our ^{29}Si n.m.r. investigations of alkaline silicate solutions we observed, under certain condi-

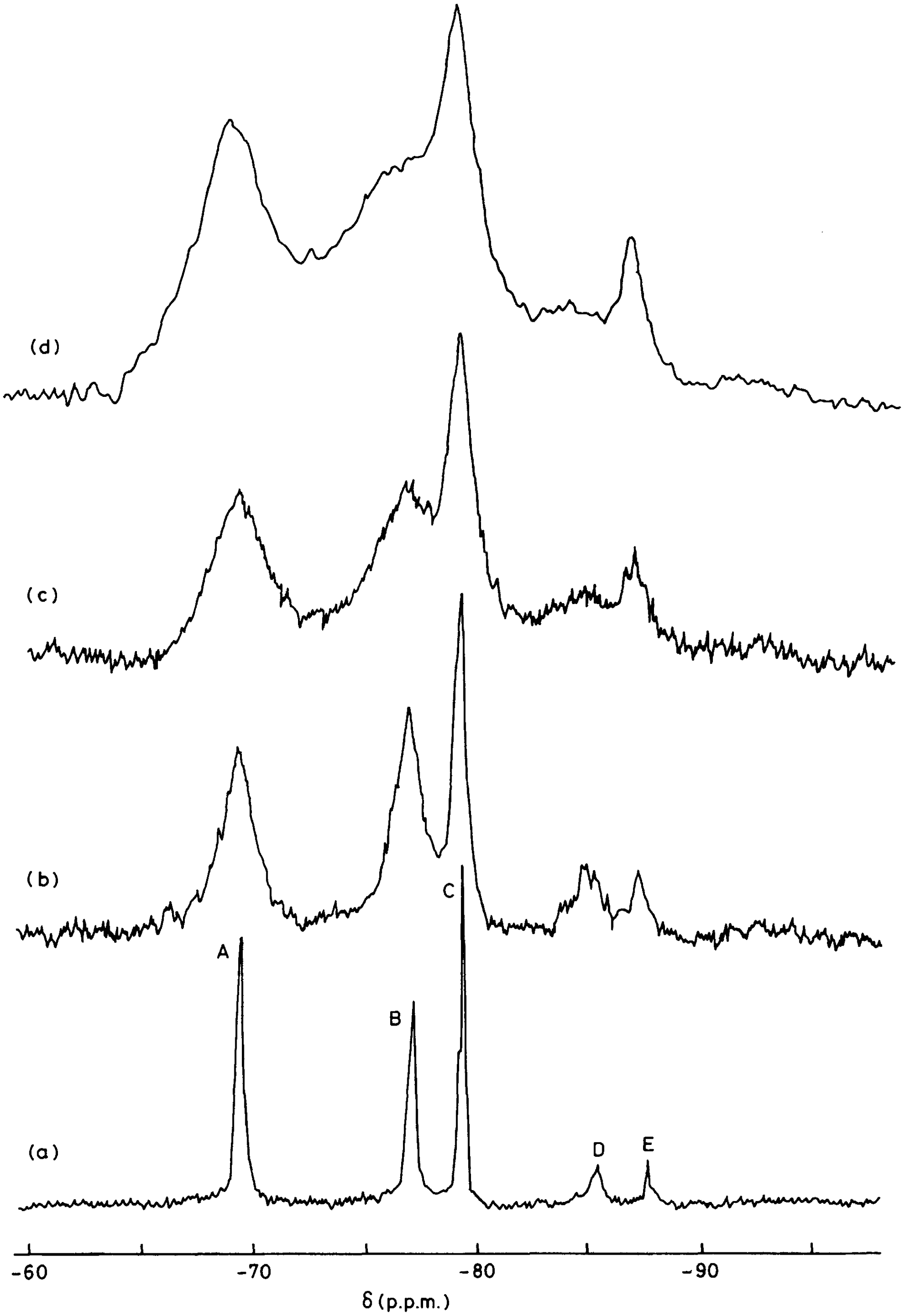
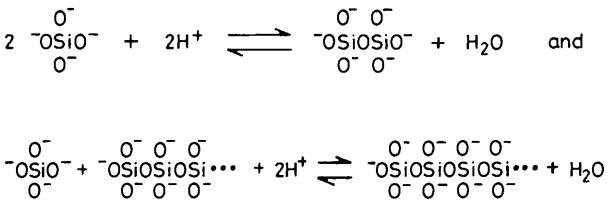


Figure 1. ^{29}Si N.m.r. spectra of a sodium silicate solution with [SiO$_2$] = 4 M and Na:Si = 2.0, prepared from sodium water glass solution (Na:Si = 0.6) at (a) 4, (b) 26, (c) 45, (d) 60 °C. Jeol PS-100/PFT-100, 19.87 MHz, pulse repetition 4 s, pulse width 12 μs corresponding 60° flip angle, number of scans: (a) 960, (b) 3050, (c) 13450, (d) 15060, δ with respect to tetramethylsilane.

tions, unusual temperature dependent line broadening of selected signals which indicates the dynamic exchange of Q groups between different silicate anion species.

Figure 1 shows the ^{29}Si n.m.r. spectra obtained at different temperatures from a sodium silicate solution with [SiO$_2$] = 4 M and a Na:Si molar ratio of 2.0, prepared from a sodium water glass solution with Na : Si = 0.6 and sodium hydroxide. At 4 °C their are five rather narrow peaks [Figure 1(a)]: the monomer silicate anion Q^0 (peak A), dimer and other end groups Q^1 (peak B), cyclic trimers Q^2_3 (peak C), middle groups of chain and cyclic silicate anions Q^2 (peak D), and prismatic hexamer Q^3_6 (peak E).[1,3] With increasing temperature considerable line broadening, especially of peaks A, B, and D, is clearly visible [Figure 1(b)—(d)]. As peaks A, B, and D are broadened to the greatest extent we conclude that a dynamic exchange of SiO_4^{4-}, *i.e.* Q^0 groups takes place between monomeric, dimeric, and oligomeric chain silicates (predominantly trimeric and tetrameric species) in the silicate solution at higher temperatures and this can be described schematically by the exchange equilibria (state of protonation



$$2\ {}^{-}\overset{\mathrm{O^-}}{\underset{\mathrm{O^-}}{\mathrm{OSiO}}}{}^{-} + 2\mathrm{H^+} \rightleftharpoons {}^{-}\overset{\mathrm{O^-\,O^-}}{\underset{\mathrm{O^-\,O^-}}{\mathrm{OSiOSiO}}}{}^{-} + \mathrm{H_2O} \quad \text{and}$$

$${}^{-}\overset{\mathrm{O^-}}{\underset{\mathrm{O^-}}{\mathrm{OSiO}}}{}^{-} + {}^{-}\overset{\mathrm{O^-\,O^-\,O^-}}{\underset{\mathrm{O^-\,O^-\,O^-}}{\mathrm{OSiOSiOSi}}}\cdots + 2\mathrm{H^+} \rightleftharpoons {}^{-}\overset{\mathrm{O^-\,O^-\,O^-\,O^-}}{\underset{\mathrm{O^-\,O^-\,O^-\,O^-}}{\mathrm{OSiOSiOSiOSi}}}\cdots + \mathrm{H_2O} \quad (1)$$

is ignored) shown in equation (1). Peaks C and E are comparatively less broadened and therefore it can be concluded that the cyclic trimer and prismatic hexamer silicate anions are not involved in the exchange process to the same extent.

An approximate kinetic evaluation[4] based on the line width of the Q^0 peak A leads to values for the life time of the free SiO_4^{4-} anion of $\tau = 60$ ms at 4 °C and $\tau = 4$ ms at 60 °C with corresponding rate constant k of 16.7 and 250 s^{-1}, respectively, and a free activation enthalpy $\Delta G^{\ddagger}$ of 77—85 kJ mol^{-1}.

Comparing the ^{29}Si n.m.r. spectra of various solutions of the same SiO_2 concentration and Na : Si ratio and of equal viscosity but prepared from different sources of silica, we found, at a given temperature, considerable differences in the line widths and consequently in the exchange rates. This quite puzzling observation is demonstrated clearly by the spectrum shown in Figure 2 which was measured at 26 °C for a sodium silicate solution of the same concentration and Na : Si ratio as used in Figure 1 but prepared from amorphous silica and sodium hydroxide solution. The lines of the spectrum shown in Figure 2 are much narrower than those of the spectra at 26 °C and even at 4 °C in Figure 1 and show the expected splittings of the peaks B, C, and D.[2]

Similar results have been obtained for a series of sodium and tetra-alkyl ammonium silicate solutions of different SiO_2 concentrations and cation : Si ratios. In general, the solutions prepared from sodium water glass solution or silica sol exhibit broad A, B, and D peaks at room temperature, whereas solutions prepared from amorphous silica or tetramethoxysilane show comparatively narrow peaks which become broader at higher temperatures. At present we have no convincing explanation for these findings but it may be possible that the rates of the exchange processes are affected by different numbers or sorts of hydrogen bridge bonds between silicate anions in the solutions.

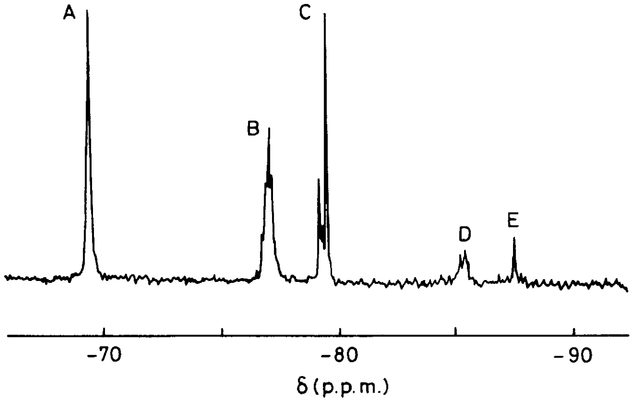


Figure 2. ^{29}Si N.m.r. spectrum at 26 °C of a sodium silicate solution with $[SiO_2] = 4$ M and Na : Si = 2.0, prepared from amorphous silica. For experimental conditions see Figure 1 caption, 1050 scans.

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