Exchange Rates between Silicate Anions in Alkaline Aqueous Solution

Clifford J. Creswell, Robin K. Harris,* and Per T. Jageland

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

A variable-temperature study using selective inversion-recovery ^{29}Si n.m.r. spectroscopy yielded the first definitive information on exchange between silicate anions, giving rate constants of the order of 0.5 kg mol^{-1} s^{-1} and a free energy of activation of 93 kJ mol^{-1} for the dimerization of the orthosilicate anion in an alkaline solution of potassium silicate.

It is well known[1—3] that alkaline aqueous solutions of alkali metal silicates contain a variety of anionic silicate species in dynamic equilibrium. The structures of a number of these species have been determined by ^{29}Si n.m.r. spectroscopy (see, for example, refs. 4 and 5). However, the lifetimes of the various species are not easy to determine and have been subject to controversy. Their determination is of relevance to a number of important questions regarding the stability, formation, and use of silicate solutions. In principle ^{29}Si n.m.r. linewidths may give such information, and, indeed, mean lifetimes have been reported[6,7] using variable temperature measurement of line broadening of the various spectral bands.

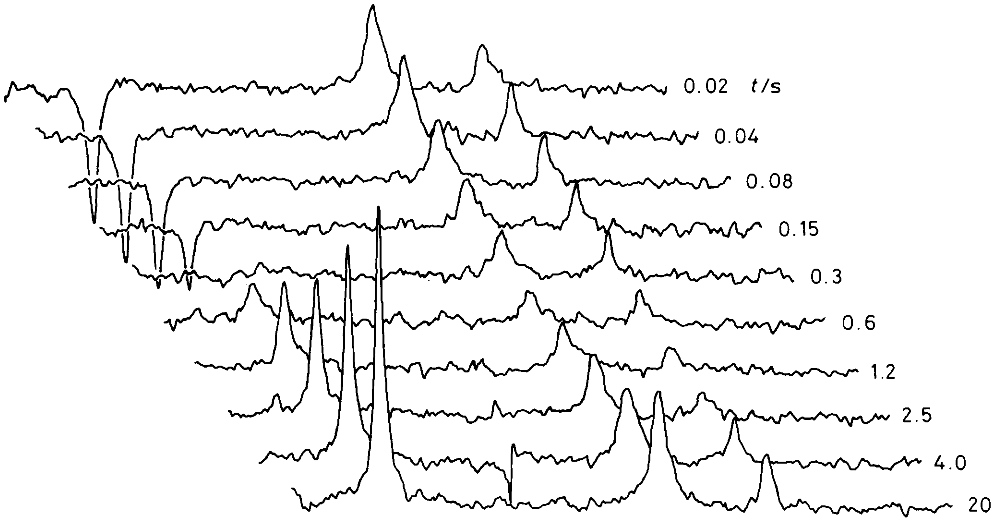

Figure 1. ^{29}Si N.m.r. spectra from a selective inversion-recovery experiment at 96 °C on an alkaline potassium silicate solution. Band A (due to monosilicate) was inverted at the start of the experiment. Bands B and C are also visible (middle and right-hand peaks respectively). The relevant recovery interval is given beside each spectrum.

There is usually a substantial broadening of the bands in the spectra as the temperature is raised from 0 to 60 °C. Rough kinetic evaluations[8] based upon the linewidth of the monomeric (Q^0) band yield lifetimes for the free $[SiO_4]^{4-}$ anion of the order of 10 ms. However, somewhat conflicting evidence has been obtained[7] from a selective inversion-recovery experiment, no magnetization transfer being detected at 38 °C, which indicates an anion lifetime greater than 1 s. Indeed, we have emphasized[7] that lifetimes obtained from linewidths are *minimum* values, since other causes of line-broadening (postulated[9] to be paramagnetic impurities) are known.

In these circumstances, it appeared to us that the selective inversion-recovery experiment was highly valuable. Not only is it free from the ambiguities associated with linewidths, but it is also specific, in that it can yield separate lifetimes for the various possible exchanges between the different species. In this communication we report the results of a series of selective inversion-recovery ^{29}Si n.m.r. experiments which yield exchange rates and a free energy of activation for exchange between species in highly alkaline solution. A potassium silicate solution 2.8 mol kg^{-1} in silica was prepared using silica obtained by hydrolysis of $SiCl_4$. The solution was adjusted to a K:Si ratio of 3.8:1 using 'Aristar' KOH. The ^{29}Si n.m.r. spectrum showed, as expected, a relatively simple situation, with mainly monomer, dimer, linear trimer, and cyclic trimer species definitely revealed by the usual bands[2] associated with the Q^0, Q^1, and Q^2 units. Selective inversion-recovery experiments were carried out at 19.75 MHz using a JEOL FX-100 spectrometer. The monomer band (A)[10] was inverted using the DANTE method,[11,12] and the signals from the monomer (A), dimer (B), and cyclic trimer (C) bands were monitored by a non-selective 90° pulse applied after a recovery interval, *t*. Any exchange occurring during *t* shows as a transfer of magnetization affecting the intensities of those bands corresponding to the species undergoing exchange. Of course, any direct cross-relaxation processes (*i.e.* not involving exchange) would also affect magnetization recovery, but we have neglected such possibilities in our kinetic analysis of the data. This implies the derived rate constants for exchange are actually the maximum possible values. Our experiments were conducted over the temperature range 0 to 107 °C. No transfer of magnetization was observed for temperatures under 80 °C even though appreciable selective line broadening was observed as the temperature was increased from 0 °C. Above 80 °C, transfer of magnetization was observed (Figure 1) to occur between bands A, B, and C, indicating that monomer, dimer, and cyclic trimers were all involved in the exchange. The system was analysed in terms of exchange occurring between all of these species plus the linear trimer (included as an intermediate between dimer and cyclic trimer). The equilibria for the system, ignoring the states of protonation, may be described by equations (1)—(3), where Q^0, $Q^1{}_2$, $Q^1Q^2Q^1$, and $Q^2{}_3$ refer to the monomer, dimer, linear trimer, and cyclic trimer respectively. The use of more sophisticated schemes, involving degrees of protonation or other species, cannot be justified in relation to the experimental data.

$$2Q^0 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Q^1{}_2 \qquad (1)$$

$$Q^1{}_2 + Q^0 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Q^1Q^2Q^1 \qquad (2)$$

$$Q^1Q^2Q^1 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Q^2{}_3 \qquad (3)$$

Second-order rate constants for the reaction (1) were found to vary from 0.21 kg mol^{-1} s^{-1} at 83 °C to 1.06 kg mol^{-1} s^{-1} at 107 °C, corresponding to a free energy of activation of 93 ± 6 kJ mol^{-1} (95 °C). Figure 2 shows the calculated and experimental plots for the ^{29}Si selective inversion-recovery experiment at 91 °C. The fraction, f_n, of the equilibrium magnetization of nucleus n at time *t* is plotted. The calculated curves were obtained by an iterative fitting of the data to the modified Bloch equations, solved by the Runge–Kutta–Merson numerical method.[13] Figures 1 and 2 make it clear that monomer $\rightleftharpoons$ dimer exchange is more rapid than formation and dissociation leading to the cyclic trimer.

Extrapolation of the rate constant to 25 °C would yield a linewidth due to exchange approximately two orders of magnitude smaller than that usually attributed to magnetic field inhomogeneity under normal operating conditions.

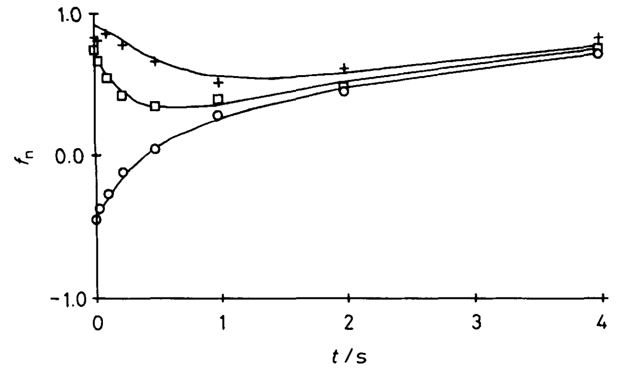

Figure 2. Calculated (solid curves) and experimental (points) plot for the ^{29}Si selective inversion-recovery experiment at 91 °C. The fractions (f_n) of the equilibrium magnetizations for the nuclei of monomer (○), dimer (□), and cyclic trimer (+) are shown at relative recovery times, t.

Therefore, we conclude that for the sample studied the line-broadening observed in bands over the temperature range of 0 to 60 °C is not due to chemical exchange between the various silicate species, but may be attributed to the presence of paramagnetic ions. Studies on enriched ^{29}Si solutions are being carried out to quantify our results further and to extend them to solutions with different pH or concentration.

One of us (P. T. J.) thanks EKA AB, Sweden, for financial support. C. J. C. is on leave from the Department of Chemistry, Hamline University, St. Paul, Minnesota, U.S.A.

Received, 1st June 1984; Com. 763

References

1 R. K. Iler, 'The Chemistry of Silica,' Wiley, New York, 1979.
2 'Soluble Silicates,' ed. J. S. Falcone, Am. Chem. Soc. Symposium Series, vol. 194, 1982.
3 D. Hoebbel, G. Garzo, G. Engelhardt, and A. Tilly, *Z. Anorg. Allg. Chem.*, 1979, **450**, 5.
4 R. K. Harris and C. T. G. Knight, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1525.
5 R. K. Harris and C. T. G. Knight, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1539.
6 G. Engelhardt and D. Hoebbel, *J. Chem. Soc., Chem. Commun.*, 1984, 514.
7 R. K. Harris, J. Jones, C. T. G. Knight, and R. H. Newman, *J. Mol. Liquids*, to be published.
8 G. Engelhardt, H. Jancke, D. Hoebbel, and W. Wieker, *Z. Chem.*, 1974, **14**, 109.
9 R. K. Harris and R. H. Newman, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1204.
10 H. C. Marsmann, *Z. Naturforsch., Teil B*, 1974, **29**, 495.
11 G. Bodenhausen, R. Freeman, and G. A. Morris, *J. Magn. Reson.*, 1976, **23**, 171.
12 G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1978, **29**, 433.
13 G. Bull, 'Computation Methods & Algol,' Harrap, London, 1966.