Silicon-29 Multiple Quantum Filtered N.M.R. Spectroscopic Evidence for the Presence of Only Six Single Site Silicate Anions in a Concentrated Potassium Silicate Solution

Christopher T. G. Knight,* R. James Kirkpatrick,[a] and Eric Oldfield

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801, U.S.A.

[a] Department of Geology, University of Illinois at Urbana-Champaign, 1301 West Green Street, Urbana, IL 61801, U.S.A.

Silicon-29 multiple quantum filtered n.m.r. spectroscopy of a (nominally) 1.5 M, 1 : 1 (K : Si), ^{29}Si isotopically enriched potassium silicate solution shows that only six 'single site' silicate anion structures are present, these being the monomer, dimer, cyclic trimer, cyclic tetramer, prismatic hexamer, and, perhaps, the tetrahedral tetramer.

Both chemical[1] and spectroscopic[2] techniques have shown that concentrated aqueous alkaline silicate solutions, such as those used in the synthesis of some highly siliceous zeolites, contain a variety of small silicate anions in dynamic equilibrium. Silicon-29 n.m.r. spectroscopy, in particular, has been successful in determining the structure of many of these anions, and, using ^{29}Si isotopic enrichment together with 'spin perturbation' techniques (such as ^{29}Si-{^{29}Si} decoupling[3,4] and two dimensional shift correlated ^{29}Si homonuclear magnetic resonance experiments[5—7]) eighteen silicate anion structures have been identified, and four more have been tentatively proposed.[7] There exists, however, a class of structures for which isotopic enrichment and spin perturbation techniques provide no structural insights. These are the anions in which all the silicon sites are chemically equivalent. These 'single site' silicate anions yield only a singlet in the ^{29}Si n.m.r. spectrum, even after full isotopic enrichment. Examples of such species include the monomer and dimer, together with all the unsubstituted cyclic and regular cage anions. Because of both the congested nature of ^{29}Si n.m.r. spectra of concentrated silicate solutions, and because 'single site' species are not affected by isotopic enrichment, it has to date been
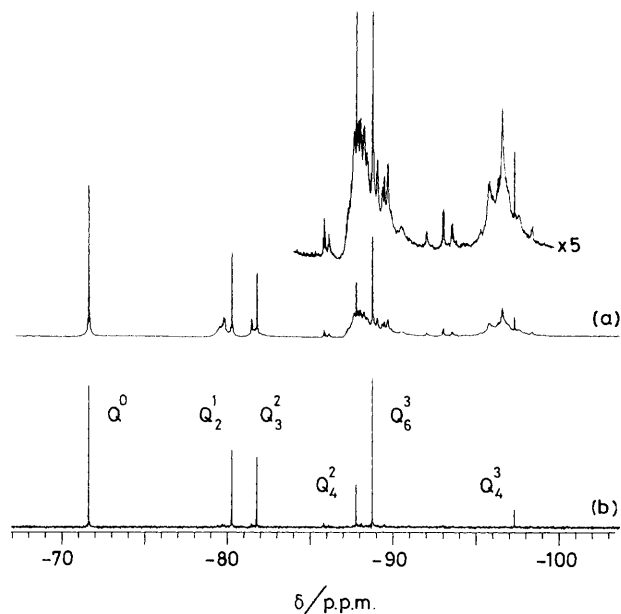
Figure 1. The 99.3 MHz (11.7 Tesla) ^{29}Si n.m.r. spectrum of a (nominally) 1.5 M, 1:1 potassium silicate solution prepared with isotopically enriched ^{29}SiO$_2$ at 22 °C. (a) Conventional single-pulse Fourier transform spectrum; 128 39 μs (90°) pulses, 3.65 kHz sweepwidth, 32K points, acquisition time of 4.5 s, interpulse delay of 15 s. (b) The 'one spin' filtered ^{29}Si n.m.r. spectrum of the same solution, acquired using the same operating parameters as in (a), with the exception that 1280 pulses were accumulated, and the interpulse delay was set to 25 s. The 'filter' was set to exclude the signals of all multisite silicate anions and was achieved using the pulse sequence of Sorensen et al. [13] The chemical shift scale is referenced externally to the signal of tetramethylsilane in [^{2}H$_6$]acetone (50 : 50 v/v), high frequency signals being positive (IUPAC δ-scale).

Figure 2. Expansion of the ^{29}Si n.m.r. spectra shown in Figure 1, for the region ascribed to Q^3 groups in regular cages. The spectral and solution conditions are the same as those given in the caption to Figure 1.

difficult to determine how many such species are present in a given solution. Although signals from the monomer, dimer, and cyclic trimer are usually unmistakable, signals from larger rings and regular cages may go unnoticed, owing to the severe spectral overlap of the Q^2 (cyclic) and Q^3 (cage) regions. Thus, it is impossible to determine whether or not species such as the five- and six-membered rings, and their double ring analogues, the pentagonal decamer and the hexagonal dodecamer, are present in concentrated solutions. The question of whether or not these particular structures exist in solution is of some importance, since their presence has recently been claimed,[8,9] and indeed all four are recognized zeolite secondary building units (the six-membered ring and the hexagonal dodecamer were included in Meier's original list of zeolitic secondary building units,[10] and the five-membered ring was later added to the list by Barrer[11]).

In order to try to overcome the problem of spectral overcrowding, we have made use of multiple quantum filtered ^{29}Si n.m.r. spectroscopy. This technique allows the imposition of a 'filter' upon the spectrum, sensitive to the number of scalar coupled, non-equivalent silicon sites present in the molecules studied.[12,13] By applying a 'one spin filter' to the spectrum, signals from all anions with more than one silicon site are removed, and thus only the signals of the 'single site' species are observed. The results are illustrated in Figure 1. Figure 1(a) shows the conventional 99.3 MHz ^{29}Si n.m.r. spectrum of a potassium silicate solution, nominally 1.5 M in both SiO$_2$ and KOH, prepared using silica enriched to 95% in ^{29}Si. Figure 1(b) illustrates the 'one spin filtered' ^{29}Si n.m.r. spectrum of the same solution, acquired using the 'p-spin
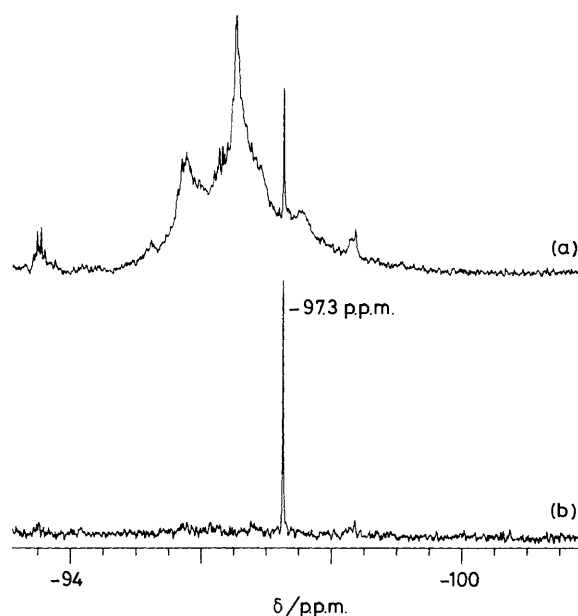
filter' pulse sequence of Sorensen et al.[13] Only six signals remain, indicating that only six 'single site' silicate anions exist in this solution (at least to within the limits of detection of the experiment, estimated here to be ca. 3% of the intensity of the monomeric signal). Five of these signals can be immediately assigned.[3—7] The two highest frequency resonances, at −71.6 and −80.2 p.p.m., have long been associated with the monomer, Q^0, and the dimer, Q$^1_2$, respectively. The peak at −81.8 p.p.m. arises from the cyclic trimer, Q$^2_3$, that at −87.7 p.p.m. is due to the cyclic tetramer Q$^2_4$, and the signal at −88.8 p.p.m. arises from the double three-membered ring, or prismatic hexamer, Q$^3_6$. (This last assignment has been confirmed elsewhere by observing the splitting patterns caused by lifting the chemical shift degeneracy of the molecule by the isomorphous replacement of a silicate tetrahedron with either a germanate[6,14] or an aluminate[15] tetrahedron.) Assignment of the lowest frequency singlet is more difficult, and expanded scale spectra are shown in Figure 2. At −97.3 p.p.m., the signal lies in the spectral region characteristic of Q^3 units in unstrained cages. It was originally assigned[3] to the double four-membered ring or cubic octamer, but comparison with ^{29}Si n.m.r. spectra of equivalent tetramethylammonium silicate solutions, which are known to contain this anion, showed[4] that the cubic octamer resonates approximately 2 p.p.m. to lower frequency, thereby leaving the signal unassigned. Recently, however, Kinrade and Swaddle,[16] examining the effects of temperature upon the chemical shift and ^{29}Si spin–lattice relaxation times of the signals of silicate anions in solution, concluded that the unassigned peak was that of an 'unusually strain-free but rigid molecule.'[17] They proposed the tetrahedral tetramer Q$^3_4$ as the most likely candidate, noting that regular cages with ten or more silicate sites were 'quite flexible and, because of O · · · O interactions, strained as well.' Preliminary experiments in our laboratory designed to test Swaddle and Kinrade's assignment by the isomorphous replacement of a silicate tetrahedron by a germanate tetrahedron proved unsuccessful, and consequently this assignment must remain tentative. If correct, however, the double five- and double six-membered rings are specifically ruled out.

No other signals are apparent in the multiple quantum filtered spectrum, suggesting that neither five nor six membered rings are present (at least to within the limits of detection of the experiment). The lack of larger rings and cages in this solution is perhaps not particularly surprising, considering the structures of the anions already known to exist. Open, flexible structures, containing five- and six-membered rings, are not common. On the contrary, most silicate anions are highly condensed, many containing the three-membered silicate ring. The presence of the double five-membered ring has been claimed in concentrated, low N : Si ratio, tetralkylammonium silicate solutions.[18] In this case, however, it appears that high proportions of an organic solvent are required in order to stabilize the anion.

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