Silicate Species in Solution. Part 2.[1] The Structure of Polymeric Species

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The following rules are formulated concerning the structure of polymeric species in solution: (1) connectivity is maximised consistent with a lower ring size of four tetrahedra (except possibly in trimeric species); (2) all tetrahedra in a given species show as nearly as possible the same degree of connectivity. Both these rules are consistent with the idea that the lability of silicate groups in solution decreases with increasing connectivity.

PART 1 of this paper[1] described the results of studies on the distribution of silicate species in solution; in this paper we consider the possible constitution of these species and deduce some principles that govern their structures.

Attempts to formulate all possible silicate species, either by abstract pencil-and-paper chemistry or through building models, produce a bewildering variety of structures and at first sight the task of rationalising these seems hopeless. However, the experimental results indicate that surprisingly few species actually occur in solution, and the problem then looks more tractable.

Figure 1, which is explained in detail below, illustrates this. Each point marks a possible composition for a finite silicate species. Those that are believed to occur in sodium silicate solutions are distinguished as squares with formulae written beside them; other observed species, mainly those found in crystals, are marked as solid circles. The total number of observed finite species is quite small, and the number of finite species identified in solution is very small indeed.

REPRESENTATION OF SILICATE SPECIES

Each point on Figure 1 represents a possible, in general hypothetical, low-molecular-weight (*i.e.* finite) silicic acid $m\mathrm{H_2O}\cdot n\mathrm{SiO_2}$ where m and n are integers. The acid form is used merely for convenience; the species actually present in alkaline solution are the corresponding more-or-less deprotonated ions, and those found in solids are usually totally deprotonated. From here on the term ' species ' will be used to mean a given silicic acid or any ion derived from it; that is, to refer to the Si–O skeleton only.

It is assumed that the normal rules of silicate chemistry are obeyed: each silicon is co-ordinated tetrahedrally by four oxygen atoms and these tetrahedra may share corners but not edges. Thus the lowest-molecular-weight species is that with $m = 2$ and $n = 1$, *i.e.* H_4SiO_4, orthosilicic acid or ' monomer ' (Si_1 in Part 1). The next member is that with $m = 3$, $n = 2$, *i.e.* $H_6Si_2O_7$, pyrosilicic acid or ' dimer ' (Si_2 in Part 1). Beyond this we reach either $m = 4$, $n = 3$, *i.e.* $H_8Si_3O_{10}$, linear trimer (Si_3 in Part 1), or $m = 3$, $n = 3$, *i.e.* $H_6Si_3O_9$, cyclic trimer or three-membered ring.† Note that these are molecular, not empirical, formulae: they all represent possible finite species. Infinite chains, $(H_2SiO_3)_\infty$, and infinite sheets, $(H_2Si_2O_5)_\infty$, are not represented on this diagram. The finite species H_2SiO_3 ($m = 1$, $n = 1$) and $H_2Si_2O_5$ ($m = 1$, $n = 2$) do not exist: their formulae are incompatible with structures built from silicate tetrahedra. The blank areas of the diagram correspond to other formulae for which no reasonable structure can be devised; points in parentheses indicate compositions for which the corresponding structures are so highly strained as to be unlikely.

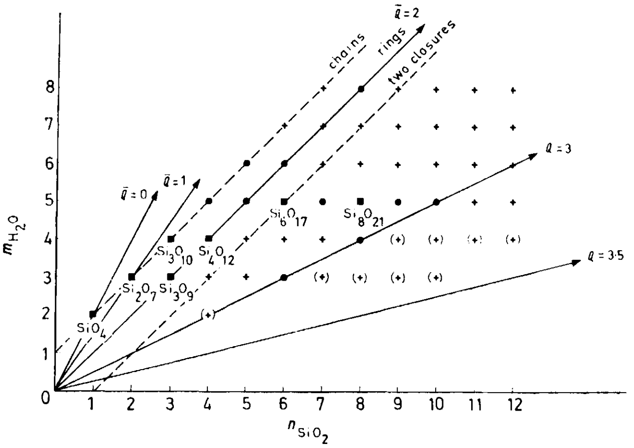

FIGURE 1 A convenient way of representing finite silicate species or the corresponding silicic acids. Squares with formulae attached represent species that have been identified in solution with reasonable certainty, circles other species that have been found, mainly in crystals; crosses represent other possible compositions, enclosed in parentheses where it is felt that the corresponding structure is excessively strained. Dashed lines connect ' families ' with the same number of closures (p), solid lines species of constant $\bar{Q}$

Isomerism is not represented on this diagram; for a given value of n all chain species (for example) have the same molecular formula, irrespective of whether they are straight or branched, being in this respect analogous to the alkanes. However, this deficiency of the diagram proves to be relatively unimportant.

The possible species can be divided into families as shown by the diagonal dashed lines. On the left-hand side are chain species; next come rings, then rings with a bridge across them, and so on. We may define these

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† ' Three-membered ' ring and similar terms here mean rings containing three tetrahedral units, not rings of three atoms. Where these exist as finite entities, we shall refer to them as ' cyclic trimer ' and so on, but these terms are not appropriate for rings that form part of a more extended structure.

as families with no closures, one closure, two closures, and so on, or with $p = 0, 1, 2,$ *etc.* where p is the number of ring closures. Elimination of the elements of water between two silanol groups of a given species produces a closure; on Figure 1 the formula drops by one unit in m and the composition then lies on the line with the next highest p value.

OBSERVED RELATIONSHIPS

For a given silicic acid $mH_2O{\cdot}nSiO_2$ we may write down the following relationships:

Formula: $H_{2m}Si_nO_{(2n+m)}$
Completely ionised form: $[Si_nO_{(2n+m)}]^{2m-}$
$\left.\begin{array}{l}\text{No. of terminal oxygen atoms}\\ \text{No. of silanol groups in acid form}\end{array}\right\} = 2m$
No. of bridging oxygen atoms $= 2n - m$
No. of closures, $p = n - m + 1$

Thus the species with $m = 4$, $n = 4$ is $H_8Si_4O_{12}$ or $[Si_4O_{12}]^{8-}$ (or some intermediate form), having eight terminal oxygen atoms or silanol groups, four bridging oxygen atoms, and one closure. Possible structures for this are cyclic tetramer or cyclic trimer with a single-unit side chain.

We can distinguish between the degree of polymerisation, n, and the mean number of shared corners or *connectivity* of the species, defined as $\bar{Q}$ in Part 1. $\bar{Q}$ can be expressed in terms of m, n, and p as in equation (1).

$$\bar{Q} = \frac{2(2n - m)}{n} = \frac{2(n + p - 1)}{n} \qquad (1)$$

Lines corresponding to various values of $\bar{Q}$ are marked on Figure 1.

The species that have been identified in solution with reasonable certainty lie in a band across Figure 1, with $\bar{Q}$ increasing rapidly with n over the first few members. Thus increase in n beyond 3 or 4 results not in long chains but rather first in rings and then in clusters. The next step is to explore the relationship between n and $\bar{Q}$.

Figure 2 plots $\bar{Q}$ against n. For known species, n is simply the number of silicon atoms; these are distinguished as solid circles. To extend the plot to higher molecular weights, values obtained from mixtures of trimethylsilyl derivatives are included. For these, $\bar{Q}$ was derived from carbon analysis and n from the weight-average molecular weight, $\bar{N}_w$, determined by gel-permeation chromatography (g.p.c.) and expressed as the number of silicon atoms in the parent species. (Weight average was chosen rather than number average, $\bar{N}_n$, since it is the total quantity of silicon atoms with a given connectivity that is significant.) The three points with highest $\bar{N}_w$ values were obtained by solvent–non-solvent fractionation of a large-scale preparation of derivatives from a 1 : 3.41 sodium silicate solution. The other points are taken from a selection of preparations, and those for mixtures with very low $\bar{N}_w$ agree well with the values for a single species.

All the points fit reasonably well on to a smooth curve that has the general appearance of a parabola. If $\bar{Q}^{-1}$ is plotted against $(n - 1)^{-1}$ a fairly good straight line is obtained from which the approximate equation (2) can be derived for the parabola.

$$\bar{Q} = \frac{7(n - 1)}{2n + 3} \qquad (2)$$

This is shown as a dashed line in Figure 2 and gives a fair, although by no means perfect, fit to the experimental curve. Although we have so far been unable to provide a convincing theoretical basis for equation (2), it has nevertheless proved useful. It is difficult to extrapolate graphs such as that in Figure 2, but equation (2) tells us that as n tends to infinity $\bar{Q}$ tends to 3.5, not as might be expected for infinite frameworks, 4. This suggests that even very large silicate particles, of colloidal dimensions, still retain a fair proportion of $\geqslant$Si–OH or $\geqslant$Si–O$^-$ groups. Moreover, combining equation (2) with (1) yields (3).

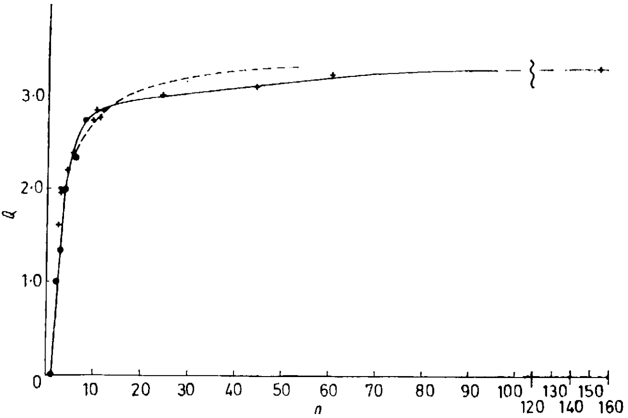


FIGURE 2 The relationship between $\bar{Q}$ and n. Filled circles represent the species whose formulae are given in Figure 1, crosses values determined for mixtures. The solid line is the experimental curve; the dashed line corresponds to equation (2)

$$p = \frac{3(n - 1)(n - 2)}{2(2n + 3)} \qquad (3)$$

Again a theoretical basis is hard to establish, but equation (3) correctly predicts no closures for species with $n = 1$ or 2. For $n = 3$, $p = \frac{1}{3}$, which would be consistent with a mixture of linear and cyclic species in the ratio of 2 : 1. This is in excellent agreement with the figures given by Harris and Newman [2] from interpretation of ^{29}Si n.m.r. spectra. For $n = 4$, $p = \frac{9}{11} \sim 1$, suggesting a preponderance of cyclic species. This value does not agree quite so well with the interpretation of the n.m.r. data, which seem to show roughly comparable amounts of linear and cyclic tetramer: on the other hand trimethylsilylation finds cyclic tetramer but no linear tetramer. In this connexion it must be remembered that the trimethylsilylation technique involves an acidification step, and while it is thought that this does not greatly change the overall degree of polymerisation of the silicate units, it may very well cause rearrangement within individual species. Equally, it should be borne in mind that the assignments of the resonances in the n.m.r. spectra are not yet all established beyond doubt.

Beyond the tetrameric species, p increases more rapidly with n; for $n = 6, p = 2$, and for $n = 8, p \approx 3$, both consistent with the values for the known species. At very large values of n, $p \approx 3n/4$; that is, for every four units added, three new closures are formed.

An empirical approach to fitting the curve in Figure 2 was very successful. From a study of the structures of known species, rules were formulated that should apply to all species. These rules were then tested by building models of larger species according to the rules and comparing the $\bar{Q}$ and n values derived from these with those on the curve.

RULES FOR BUILDING SILICATE POLYMERS

$\bar{Q}$ increases rapidly with n for small values of n because of self-condensation. The results of trimethylsilylation studies suggest that the trimer is a straight-chain species, and that the addition of a fourth unit is accompanied by spontaneous self-condensation to form a ring. This would be in excellent agreement with the observation [3,4] that three-membered rings are strained because their rather short Si–Si distances cause repulsion, whereas four-membered rings are virtually unstrained. On the other hand the results of ^{29}Si n.m.r. spectroscopy [2,5] suggest that ring formation may occur with as few as three units in the polymer, and at the same time suggest that a measurable quantity of linear tetramer also exists. Some possible explanations of these discrepancies were mentioned above. It is quite possible that the rules governing the stable species in alkaline solution are different from those in acid, and it is also possible that the cyclic trimer and linear tetramer, rare in the solid state, are stabilised in solution through interaction with the surrounding water molecules. (A scale model shows that the cyclic trimer can be fitted very neatly into the ice structure.)

However this may be, it seems likely that the three-membered ring plays an insignificant role in the construction of larger units. It has not been identified in any of the larger species found in solutions, nor is it found in extended crystalline structures such as zeolites or felspars. Taking also into account the probable structures of the Si_6 and Si_8 members we can formulate the rule: *connectivity is maximised consistent with a minimum ring size of four tetrahedra.*

Although the evidence of ^{29}Si n.m.r. spectroscopy suggests that this may not hold for small species in very alkaline solutions, it explains very neatly the results of trimethylsilylation studies.

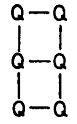
It further appears that large variations in connectivity within any one structure are not tolerated. The Si_8O_{21} species, for example, with $\bar{Q} = 2.75$ is built from a mixture of Q^2 and Q^3. This is entirely consistent with what is observed in crystals,[6] in which equality of connectivity has been explained in terms of the relative basicity of the oxygen atoms in tetrahedra of different connectivity.[7] Once again the interpretation of ^{29}Si n.m.r. spectra from very alkaline solutions conflicts with the rule; we return to this point later.

Equality of Q number may well result from the mechanism of polymerisation. In solution, the tetrahedra of lowest Q number are most heavily protonated. This is mainly because the *number* of terminal oxygen atoms available for protonation is greater for tetrahedra with fewer shared corners. In addition, the basicity of a terminal oxygen atom decreases with increasing Q number [7] and hence the conjugate acid (silanol group) becomes stronger. Since condensation in solution necessarily involves at least one silanol group the tetrahedra with the most protons are most likely to react. Therefore the lower the Q number the greater is the reactivity, and consequently if a species contains a mixture of groups of different connectivity further condensation occurs at the group with the lowest Q number.

Consider, for example, the situation in equation (4) when an additional tetrahedron is added to cyclic

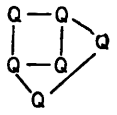
$$\overline{Q^2Q^2Q^2Q^2} + Q^0 \longrightarrow \overline{Q^2Q^2Q^2Q^3}Q^1 \qquad (4)$$

tetramer. The Q^1 group is reactive and rapidly condenses with a further Q^0 group to give $\overline{Q^2Q^2Q^2Q^3}Q^2Q^1$. This new reactive Q group can be eliminated by self-condensation within the species to give a bridged ring as in (I) or (II). These are precisely the two isomers that Hoebbel *et al.*[8] felt to be the most probable for the hexamer, and represent relatively unreactive groupings. The above also suggests why no species with five silicate units has so far been detected in solution. The production of higher polymers can similarly be visualised. A further rule of polymerisation is thus: *connectivity within a given species is as equal as possible, reactivity increases with decrease in Q number, and pendant Q^1 groups form reactive growth points at which further units add preferentially.*



(I)

or



(II)

Again we must note that some species postulated from n.m.r. spectroscopy seem not to be consistent with the above. In addition to cyclic trimer, the group $\overline{Q^2Q^2Q^3}Q^1$ appears to exist in very alkaline solution. However, in such solutions protonation of all groups except Q^0 will be quite low, and this might result in stabilisation of configurations that could not exist at lower pH.

CONSTRUCTION OF MODELS

The validity of these ideas was tested by comparing the $\bar{Q}$ and n values of species conforming to them with the experimental curve in Figure 2. The most elegant way of doing this would be by computer, but in practice it proved easier and quicker to build models. To avoid bias, the task was given to two volunteers with no knowledge of silicate chemistry. They were provided with plenty of tetrahedra and flexible bonds for connecting them, told the rules to be followed and asked to construct as large a variety of structures consistent with them as they could. For each model produced, $\bar{Q}$ and n were determined.

The results are shown in Figure 3, together with the experimental curve from Figure 2. The agreement is very respectable, although the results tend to be slightly high. This may well be a consequence of the mechanical properties of the model-building equipment; it was quite difficult to build large open structures, since they tended to collapse under gravity. Silicate ions in solution presumably would not have this problem; moreover hydrogen bonding of water molecules to the framework might stabilise more open structures. On the other hand it was found that if three-membered rings were permitted the resulting structures all fell well above the experimental curve.

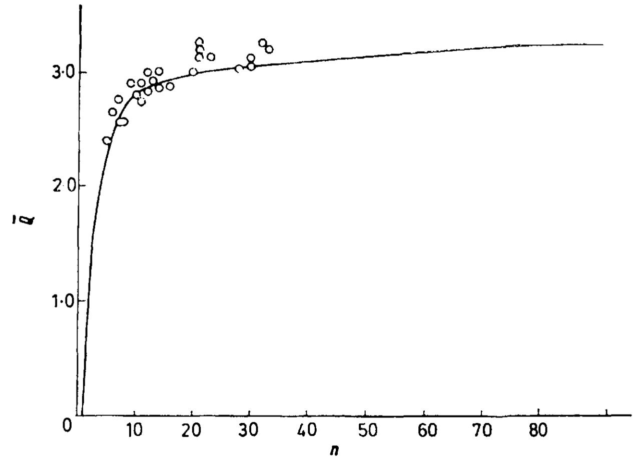


FIGURE 3 Values of $\bar{Q}$ and n, obtained from models built according to the rules given in the text, compared with the experimental curve

A reasonable picture thus emerges of the polymerisation of silicate species in solution and of the structures of the resulting species, although it should be remembered that details may differ with pH. Larger species are definitely not chain-like; on the contrary, they tend to form cage-like structures, probably rather globular, and as highly condensed as possible. Surface Q^1 groups, and to a lesser extent Q^2 groups, provide reactive growth points. Larger species thus tend to contain mainly Q^3 and Q^4 units, with a $\bar{Q}$ value of *ca.* 3.5 for very large values of n. Since the limiting value of $\bar{Q}$ is not 4, even when n tends to ∞, some unattached corners must remain as silanol groups trapped within the structure and unable to condense. Analyses of trimethylsilyl derivatives of high-molecular-weight species invariably give an H : C ratio greater than the 3 : 1 required by methyl groups (Part 1) and this too suggests the presence of unreacted silanol groups within the structure.

Finally we note that the shapes of the larger units are consistent with the appearance noted for the primary particles of silica gel,[9] while the structures postulated for the smaller species bear a striking resemblance to many of the ' secondary building units ' that have been described for zeolites.[10]

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