The Constitution of Aqueous Silicate Solutions

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The distributions of anions in solutions of lithium, sodium, potassium, rubidium, caesium, and tetramethyl-, tetra-n-propyl-, and tetra-n-butyl-ammonium silicate solutions have been determined by trimethylsilylation and gas chromatographic analysis of the resulting volatile derivatives over a range of concentrations, temperatures, and silica–base ratios; and with sodium silicate solutions, the effects of adding salts and other alkalis were also studied. With the exception of tetramethylammonium silicate solutions, which at low temperatures and low silica–base ratios contained substantial quantities of the double-four-ring anion $Si_8O_{20}^{8-}$, two values were sufficient to characterise the anion distributions: the fraction of total silicon present found as monomer, and the fraction found in the form of anions with charges of -10 or more. The degree of polymerisation increased with increasing cation radius, silica–base ratio, and concentration, and decreased with temperature; of these, the concentration had much the largest effect. In sodium silicate solutions, addition of alkali metal salts increased the degree of polymerisation but tetramethylammonium chloride had almost no effect; addition of alkali metal hydroxides reduced the degree of polymerisation, NaOH having a greater effect than KOH.

Alkali metal silicates are raw materials for a number of products, such as synthetic zeolites. Since they are polymeric in solution, to understand their behaviour in chemical reactions it is necessary to know how the distribution of the various anions present is affected by changes in composition, concentration, temperature, and the presence of other solutes.

Previous studies of anion distribution in silicate solutions, for example by Lentz,[1] Hoebbel and co-workers,[2-6] and Dent-Glasser *et al.*,[7,8] were mainly confined to sodium silicate solutions at ambient temperatures. In this work, the analysis has been extended to include all the alkali metal silicates, together with tetramethyl-, tetra-n-propyl-, and tetra-n-butyl-ammonium silicates over the temperature range 8—90 °C, at concentrations from 0.01 to *ca.* 5 mol dm^{-3}, and silica–base mol ratios from less than unity to *ca.* 20 : 1. The effects of adding alkali metal and tetra-alkylammonium salts, as well as alkali metal hydroxides have also been studied. The procedure employed was essentially that used by Dent-Glasser *et al.*,[7,8] namely trimethylsilylation of the silicate solution under conditions designed to freeze the anion distribution by rapid quenching into a considerable excess of acid at 0 °C, followed by a high-resolution gas chromatographic analysis of the volatile derivatives obtained.

Experimental

Preparation of Alkali Metal Silicate Solutions.—All the solutions were prepared by adding with stirring an appropriate quantity of an aqueous silica solution (' 1 034–AW,' from Nalfloc Ltd., Northwich, Cheshire) containing SiO_2 (33), H_2O (67), and Na_2O (0.005% w/w) with particle size range 16—22 nm and pH = 3.1, to the calculated amount of alkali metal hydroxide dissolved in enough water to make a stock solution of 3—4 mol dm^{-3} SiO_2. Then, except in the case of lithium silicate, the mixture was heated at 80—90 °C for 8—24 h, cooled, centrifuged at 5 000 r.p.m., and decanted from any residue. Stock solutions of lithium, sodium, potassium, rubidium, caesium, and tetramethyl-, tetra-n-propyl-, and tetra-n-butyl-ammonium silicates were prepared in this way with SiO_2–base mol ratios from 1 to 20, and their exact compositions were ascertained by elementary analysis. For each cation there was a critical silica–base ratio, above which the solutions were opalescent, and below which they were clear. The critical ratio increased with the size of the cation; for example, with sodium the critical ratio was 3.6, with tetramethylammonium 8.5, and with tetrabutylammonium 10. Although solutions with silica–base ratios greater than the critical ratio obviously contained colloidal silica in suspension, preliminary analyses showed no evidence of any discontinuities in the relationships between anion distribution and silica–base ratio, and the results obtained on these solutions have therefore been included without distinction.

Trimethylsilylation Procedure.—The reagent was prepared by mixing hexamethyldisiloxane (20 cm^3), propan-2-ol (30 cm^3), water (12.5 cm^3), and hydrochloric acid (15 cm^3 of 12 mol dm^{-3}), and stirring at 20—25 °C for 1 h. This reagent was cooled to 0 °C, and a sample of the solution to be analysed (containing *ca.* 5 mmol SiO_2) was added with vigorous stirring during 5 min; the cooling bath was then removed and the mixture stirred more gently for 3—4 h while the temperature rose to ambient. A solution of n-tetradecane in hexamethyldisiloxane (1 cm^3 of 0.065 mol dm^{-3}) was added as an internal chromatographic standard, then the organic layer was separated, washed with water (3 × 30 cm^3), and stirred for 16—19 h with Amberlyst 15 ion-exchange resin (2 g). The clear solution was decanted and analysed by gas-liquid chromatography using one of two similar Carlo-Erba model 2151 AC(G) gas chromatographs equipped with fused-quartz capillary columns (15 m × 0.3 mm bore) coated with polysiloxane OV1 (Phase Separation Ltd.) and flame-ionisation detectors. The sample (0.5—1.0 mm^3) was injected with a split ratio of 20 : 1; after a 2-min hold at 120 °C, the column temperature was raised at a rate of 7.5 °C min^{-1} to 325 °C, and then held at this temperature to the end of the chromatogram (*ca.* 30 min). A typical chromatogram is shown in Figure 1. Retention times were measured with a precision of 0.15 s, and corrected for any error in setting the zero time by subtracting the difference between the retention time of the internal standard and a fixed reference time. By reference to a table of standard retention times the identity of each peak was determined and its area multiplied by the appropriate response factor to obtain the corresponding weight of silicon contained in the anion from which that the trimethylsilylated derivative was obtained. The total weight of silicon recovered, and hence by difference the weight unaccounted for, were also calculated.

Identification of Peaks and Determination of Response Factors.—The nomenclature used here is that proposed by

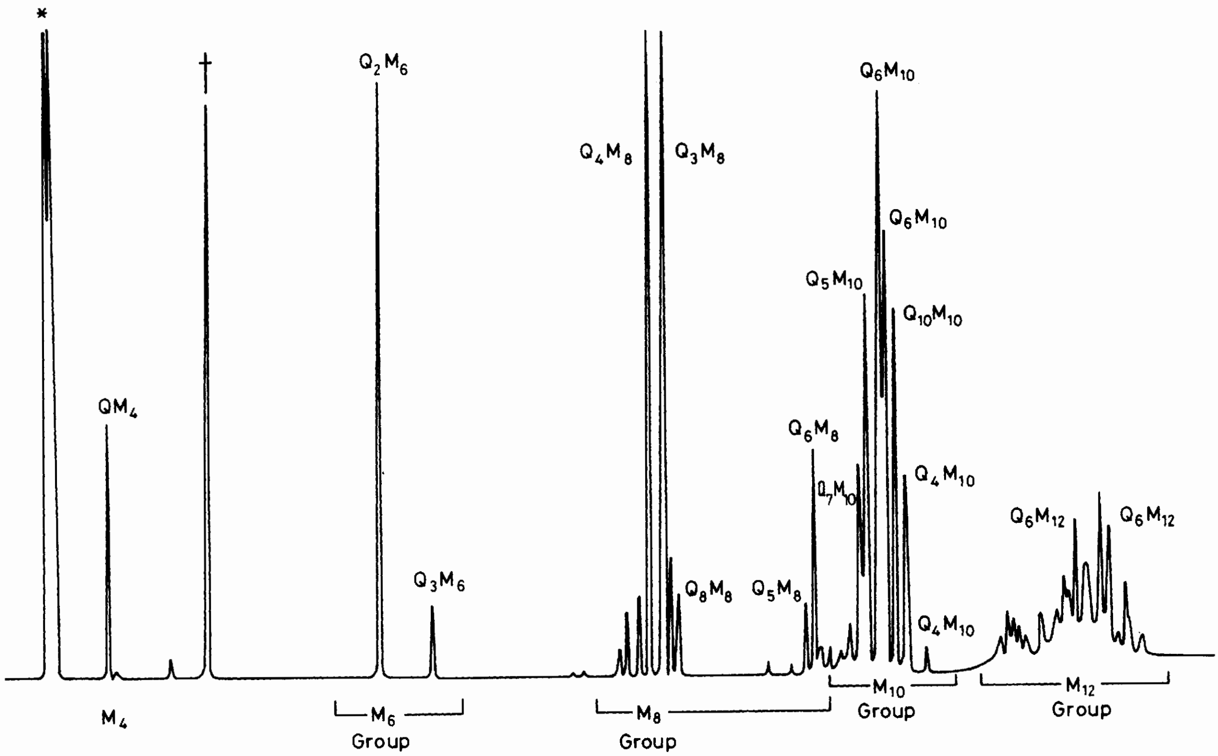

Figure 1. Typical chromatogram of trimethylsilylated silicate ions. Peaks denoted by * and † correspond to the solvent and internal standard respectively

Garzo and Hoebbel[2] and which has been widely adopted by other workers in this field. Any fully trimethylsilylated silicate anion is designated by a symbol of the form Q_xM_y, where x is the number of Si atoms in the original anion ($Q = SiO_2$) and y is the number of trimethylsilyl groups attached to it ($M = Me_3SiO_{0.5}$). The number of possible trimethylsilyl derivatives increases rapidly for values of x greater than four, and not all the individual isomers can be separated; however, the number, n, of possible x values within a group of peaks with the same value of y is given by $n(x) = y/2 + 2$ for $16 > y > 4$, and up to $y = 12$, all of the different x values give rise to distinguishable peaks. The identities of the marked peaks in Figure 1 were established as follows. (*i*) QM_4, Q_2M_6, Q_6M_{12} (two isomers), and Q_8M_8: by injection of the trimethylsilylation products of olivine, hemimorphite, dioptase, and the crystalline tetramethylammonium silicate $(NMe_4)_8Si_8O_{20}{\cdot}36H_2O$, respectively. (*ii*) Q_3M_6, Q_4M_8, Q_3M_8, and Q_4M_{10}: by comparison with literature values of retention times.[2,3] (*iii*) Q_5M_{10} and $Q_{10}M_{10}$: from the trimethyl silylation products of tetra-n-butylammonium silicate.[4] (*iv*) Q_7M_{10}: as the major impurity in the product of trimethylsilylation of tetramethylammonium silicate.[5] (*v*) Q_6M_{10} (two isomers): by elimination of the remaining possibilities on the M_{10} group.

Flame-ionisation detector response factors with n-tetradecane as internal standard have been determined for a number of trimethylsilylated silicate anions by Garzo *et al.*,[6] and six replicate determinations on each of the two columns used in this work of the response factor for QM_4 gave a mean value of 2.5 (standard error of mean 0.02), which is identical to the value found by Garzo *et al.* Using the published response factors, silicon recoveries approaching 100% were obtained from dilute solutions of sodium silicate with the number of average degrees of polymerisation <3; but with solutions of tetramethylammonium silicate which contain a relatively high concentration of the double-four-ring anion $Si_8O_{20}^{8-}$, the calculated recoveries of Q_8M_8 using the published response factor were obviously incorrect. For this reason, a separate determination of the response factor for Q_8M_8 was made as follows.

Tetramethylammonium hydroxide solution (300 cm^3 of 25% w/w) was added to a silica solution (Nalfloc 1034-AW, 168 cm^3 of 33% w/v) and the mixture heated at 90 °C for 5 h. The resulting clear solution was cooled to 0 °C and the crystalline material which separated was filtered off, washed with acetone and diethyl ether, and dried *in vacuo* at ambient temperature; additional material was recovered from the mother-liquors by continued cooling and filtration, giving octakis(tetramethylammonium) pentacyclo-octasilicate hexatriacontahydrate (210 g, 98%) (Found: C, 22.95; H, 9.1; N, 6.35; Si, 12.1. $C_{32}H_{168}N_8O_{56}Si_8$ requires C, 21.5; H, 9.5; N, 6.3, Si, 12.6%). Weighed samples of this compound were trimethylsilylated by the procedure described and the products analysed. Replicate samples were also trimethylsilylated without addition of the internal chromatographic standard and the resulting solutions were evaporated to constant weight at 90 °C. The residues were weighed and analysed; in six such determinations the yield of octakis(trimethylsilyl) pentacyclo-octasilicate was 99—100%. The mean response factor for Q_8M_8 found from eight repeat determinations was 6.28, with 95% confidence limits of 5.78—6.79. This is almost twice the value (3.3) reported by Garzo *et al.*,[6] but they did not isolate the pure tetramethylammonium salt of this anion. Accordingly, a value of 6 was used for the response factors for both Q_8M_8 and the analogous double-five-ring derivative $Q_{10}M_{10}$.

Results

Reproducibility.—In replicate determinations of the anion distribution in samples of sodium silicate solutions covering a

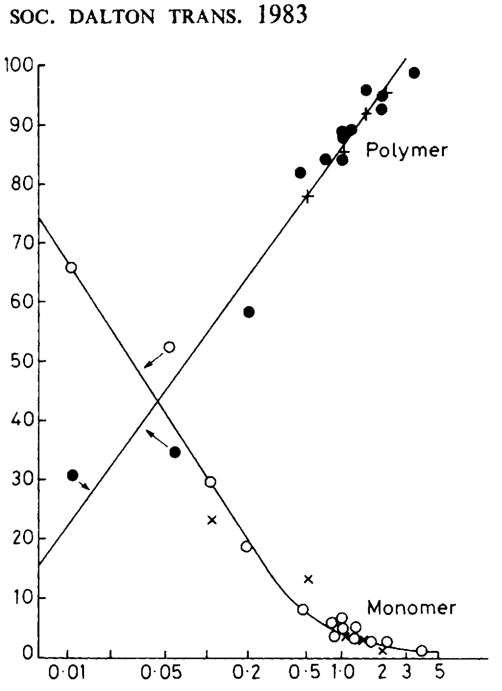

Figure 2. Distribution of anions in sodium silicate solutions (SiO_2–Na_2O = 2.8—3.6) as a function of SiO_2 concentration from this work (●,○) and that of Dent-Glasser[7] (×,+)

range of concentrations and SiO_2–Na_2O ratios, an analysis of variance gave a residual mean square of 0.188, corresponding to a standard deviation of 0.43 units of per cent. This means that the 95% confidence limits around any particular result are approximately ±0.9 units of per cent, so that a difference between any two results exceeding 2 units of per cent is to be regarded as significant.

Method of Presentation.—With the exception of the tetramethylammonium silicate solutions, which at low temperatures contained substantial amounts of the double-four-ring anion $Si_8O_{20}^{8-}$, it was found that the variations in the proportions of anions containing from two to eight silicon atoms was comparatively small, and that the most significant changes occurred in the proportions of monomeric ions, and of ions with charges of −10 or more. It is therefore possible to summarise the results in the form of graphs showing the changes in % monomer and % polymer (meaning anions with charge −10 or more), together with an additional plot for the $Si_8O_{20}^{8-}$ anion in the special case of tetramethylammonium silicate.

Sodium Silicate Solutions.—The distribution of anions in solutions of sodium silicate was measured over a range of SiO_2 concentrations from 0.01—3.5 mol dm^{-3} for SiO_2–Na_2O ratios of 2.86 and 3.55, over a range of SiO_2–Na_2O ratios from 2.86 to 20 at a SiO_2 concentration of 1 mol dm^{-3}, and over a range of temperatures from 8—90 °C (at the same concentration) for SiO_2–Na_2O ratios of 3 and 6. The results are given in Figures 2—4.

In Figure 2 (which includes some results obtained by Dent-Glasser *et al.*[7]) the amounts of silicon present as monomer and polymer are plotted against the logarithm of the concentration for solutions of SiO_2–Na_2O ratios 2.86 and 3.55. The amounts of monomeric and polymeric silicate ions present in these solutions are almost linear functions of the logarithm of the silica concentration up to *ca.* 1 mol dm^{-3}, and can be closely approximated by equations (1) and (2) where $0.001 < c < 4$ in both cases, and c is the concentration of SiO_2 in mol dm^{-3}. The standard deviations of the measured

$$\%\ \text{monomer} = -1.48 - 15.28 \ln c + 6.35c \qquad (1)$$

$$\%\ \text{polymer} = -88.26 + 14.17 \ln c + 0.84c \qquad (2)$$

values from those predicted are for the monomer, 3.6 units of per cent and for the polymer, 4.6 units.

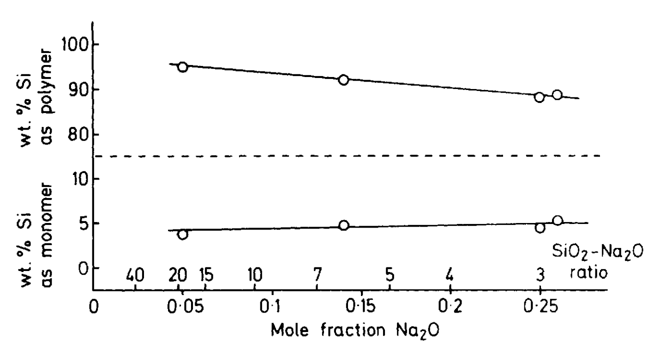

Figure 3. Anion distribution in 1 mol dm^{-3} sodium silicate solutions as a function of SiO_2–Na_2O ratio

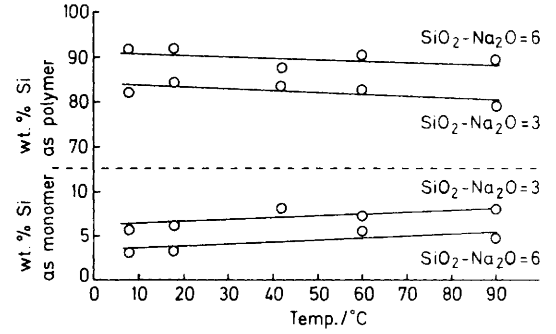

Figure 4. Effect of temperature on distribution of anions in sodium silicate solutions

Since Figure 2 contains results obtained with SiO_2–Na_2O ratios of 2.86, 3.04,[7] and 3.55, it is evident that the effect of changing the SiO_2–Na_2O ratio within this range is small in comparison with the effect of concentration. In Figure 3, the concentrations of monomer and polymer in 1 mol dm^{-3} (in SiO_2) solutions with SiO_2–Na_2O ratios ranging from 2.86 to 20 are plotted against the mole fraction $[Na_2O]/[SiO_2 + Na_2O]$. This shows that both the monomer and polymer concentrations are linear functions of this mole fraction; that is, they are linearly dependent on $1/(1 + R)$, where R = mol ratio SiO_2–Na_2O, and equations (3) and (4) can be derived

$$\%\ \text{monomer} = 3.7 + 4.88/(1 + R) \text{ for } 2.8 < R < 6 \qquad (3)$$

$$\%\ \text{polymer} = 97.6 - 38.11/(1 + R) \qquad (4)$$

for the % monomer and % polymer in 1 mol dm^{-3} sodium silicate solutions with SiO_2–Na_2O ratio = R. The standard deviations of the measured values from those predicted by these equations were for % monomer, 0.7 units of per cent, and for % polymer, 2.2 units of per cent.

Combining these equations with equations (1) and (2) above, the effects of both concentration and ratio in Na_2O

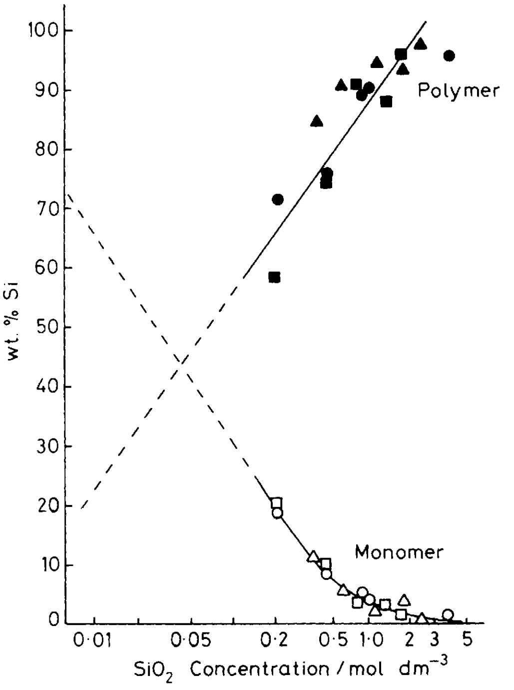

Figure 5. Anion distribution in solutions of lithium (□,■), potassium (○,●), and caesium (△,▲) silicates (SiO_2–Li_2O = 2.7, SiO_2–K_2O = 2.9, SiO_2–Cs_2O = 9.5)

solutions can be described by equations (5) and (6) where $0.001 < c < 4$ and $2.8 < R < 6$.

$$\% \text{ monomer} = -2.65 - 15.28 \ln c + 6.35c + 4.88/(1 + R) \quad (5)$$

$$\% \text{ polymer} = 96.7 + 14.17 \ln c + 0.84c - 38.11/(1 + R) \quad (6)$$

The effect of temperature on the distribution of anions in sodium silicate solutions is shown in Figure 4. Over the range 8—90 °C, the effect is small; the average degree of polymerisation decreases with temperature and the temperature coefficient is approximately the same for SiO_2–Na_2O ratios of 3 and 6. The results fit equations (7) and (8), where M_T and P_T

$$M_T = M_0 + 0.02T \quad (7)$$

$$P_T = P_0 - 0.035T \quad (8)$$

are the percentage of Si present as monomer and polymer respectively at T °C, and M_0 and P_0 are the percentage of Si as monomer and polymer at 0 °C. The standard deviation of all twenty measured values from those predicted by these equations is 1.8 units of per cent.

Other Alkali Metal Silicate Solutions.—The anion distributions in solutions of lithium, potassium, and caesium silicates were measured over a range of concentrations from 0.24 to 3.8 mol dm^{-3}, and for potassium silicate only over a range of SiO_2–K_2O ratios from 0.13 to 3.0 and temperatures from 8—90 °C. A single result was obtained from rubidium silicate at SiO_2–Rb_2O = 3 and SiO_2 concentration 1 mol dm^{-3}. The results are given in Figures 5—7.

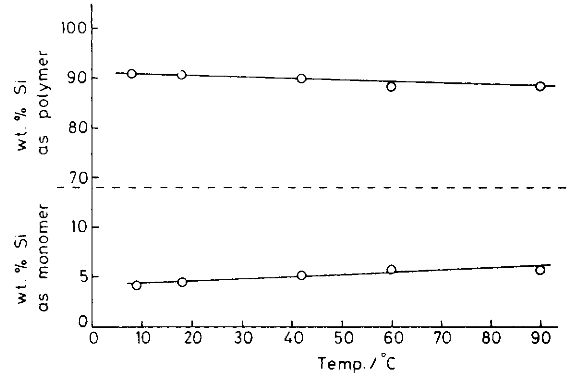

Figure 6. Effect of temperature on distribution of anions in 1 mol dm^{-3} potassium silicate solutions (SiO_2–K_2O = 3)

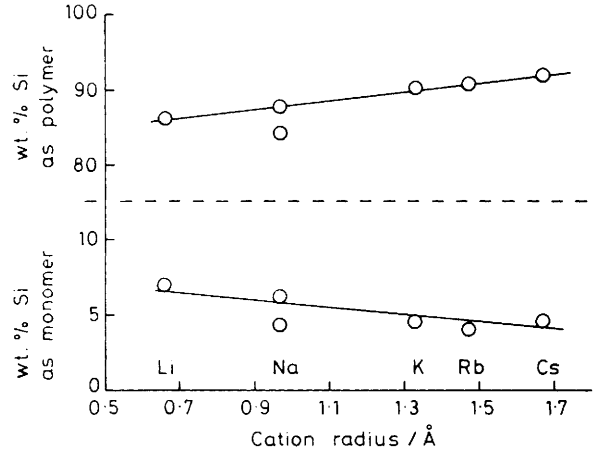

Figure 7. Anion distribution in 1 mol dm^{-3} alkali metal silicate solutions as a function of cation radius (SiO_2–base = 3)

Figure 5 shows the changes in monomeric and polymeric anions with concentration for lithium, potassium, and caesium silicates at SiO_2–R_2O ratios of 2.7 for lithium, 2.9 for potassium, and 9.5 for caesium. Since these curves are directly superimposable on those in Figure 2, the equations (3) and (4) derived above relating the monomer and polymer content in sodium silicate solutions to concentration will also fit all the other alkali metal silicates, with slightly different values of the constant term, K, to adjust for the different SiO_2–R_2O ratios [equations (9) and (10)], with the restrictions that

$$\% \text{ monomer} = K_m - 15.28 \ln c + 6.35c + 4.88/(1 + R) \quad (9)$$

$$\% \text{ polymer} = K_p + 14.17 \ln c + 0.84c - 38.11/(1 + R) \quad (10)$$

$0.001 < c < 4$ and $2.8 < R < 20$, where R is the SiO_2–base mol ratio, and the values of K_m and K_p are as shown below.

Cation	Li	Na	K	Rb	Cs
K_m	−2.71	−2.65	−2.64	−2.6	−1.91
K_p	96.99	96.7	96.54	96	91.34

(The values given for rubidium are based on only a single result and may not be reliable.) The standard deviation of all the measured values from those predicted by these equations was 3.9 units of per cent for monomer and 7.8 units of per cent for polymer.

The effect of temperature over the range 8—90 °C on the

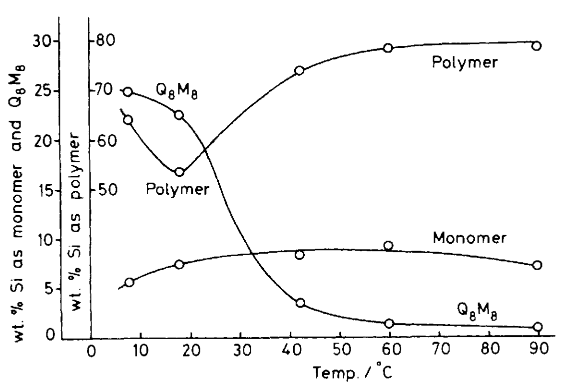

Figure 8. Anion distribution in 1 mol dm^{-3} tetramethylammonium silicate solutions as a function of temperature [SiO_2–$(NMe_4)_2O$ = 3]

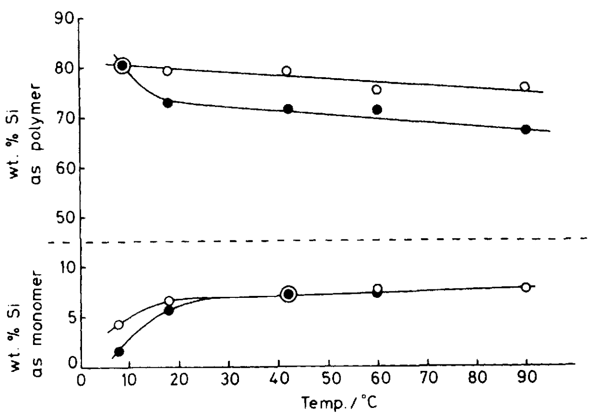

Figure 9. Anion distribution in 1 mol dm^{-3} solutions of tetra-n-propyl- (○) and tetra-n-butyl- (●) ammonium silicates (SiO_2–base = 3)

anion distribution in potassium silicate is shown in Figure 6; the slopes of the lines for monomer and polymer are the same as those found for sodium silicate, and equations (7) and (8) may therefore be taken to apply to potassium silicate as well.

The anion distributions for all five alkali silicates at a silica concentration of 1 mol dm^{-3} and an SiO_2–base ratio of 3 are compared in Figure 7, which suggests that the amounts of monomer and polymer decrease and increase respectively in an approximately linear fashion with cation radius; however, the differences in monomer and polymer contents between lithium and caesium silicate solutions are of similar magnitude to the standard deviations of the measurements, so not much reliance can be put on this correlation.

Tetra-alkylammonium Silicate Solutions.—The anion distributions in tetramethyl-, tetra-n-propyl-, and tetra-n-butyl-ammonium silicate solutions were determined at a silica–base ratio of 3 and silica concentration of 1 mol dm^{-3} over the temperature range 8—90 °C; for tetramethyl- and tetra-n-butyl-ammonium silicates the effect of silica–base ratio was also investigated over a wide range. The results are given in Figures 8—10.

Tetramethylammonium silicate solutions were distinguished from all other alkali metal silicates by the presence of considerable quantities of the double-four-ring anion $Si_8O_{20}^{8-}$, which under certain conditions accounted for more than 30% of the silica present; this anion was rarely found in other alkali metal silicate solutions, and then only in small amounts. However, as shown in Figure 8 this anion is thermally unstable and practically disappears above 50 °C.

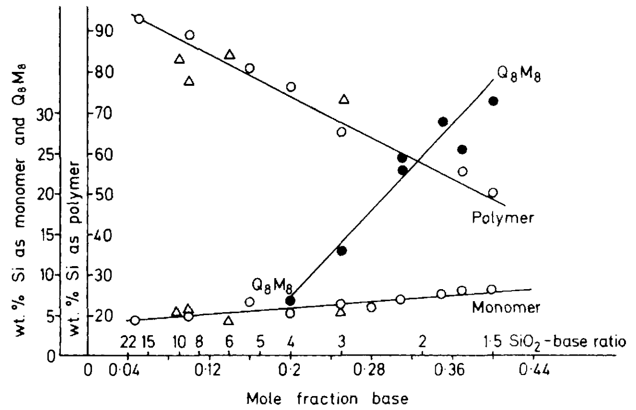

Figure 10. Anion distribution in 1 mol dm^{-3} tetramethyl- (○) and tetra-n-butyl- (△) ammonium silicate solutions and Q_8M_8 (NMe_4 only) (●) as a function of SiO_2–base ratio

At temperatures above 18 °C, and with the exception of the polymeric anion content of tetramethylammonium silicate, all the tetra-alkylammonium silicates exhibited a similar temperature dependence to those of the alkali metal silicates, the temperature coefficients in equations (7) and (8) being shown below.

Cation	Temperature coefficient % Monomer	 % Polymer
Na^+, K^+	0.02	−0.035
NMe_4^+	<0.001	+0.32
$NPr^n{}_4^+$	0.007	−0.07
$NBu^n{}_4^+$	0.02	−0.08

Tetramethylammonium silicate solutions behaved differently from all other alkali metal silicates studied in that their polymer content increased with temperature over the range 18—90 °C, and the proportion of monomeric anions was almost constant in this range. If, however, the silicon present as Q_8M_8 is included in the % polymer, the temperature coefficient of the % polymer becomes −0.02.

Figure 10 shows how the anion distributions in 1 mol dm^{-3} tetramethyl- and tetrabutyl-ammonium silicate solutions varied with silica–base ratio; with only four results for tetrabutylammonium silicate, the difference between these two anions was not significant, and the monomer and polymer contents can be described by equations (11) and (12). The

$$\%\ \text{monomer} = 4.1 + 9.6/(1 + R) \qquad (11)$$

$$\%\ \text{polymer} = 100 - 132/(1 + R) \qquad (12)$$

standard deviations of the measured values from those predicted by these equations were for the monomer, 0.5 units of per cent and for the polymer, 6 units of per cent. Both values of slope were significantly larger than those found for the alkali metal silicates, showing that the degree of polymerisation of the silicate anions is more sensitive to silica–base ratio in tetra-alkylammonium silicate solutions.

Effects of Added Salts and Bases in Alkali Metal Silicate Solutions.—The changes in anion distribution in sodium and potassium silicate solutions resulting from the addition of neutral salts and alkali metal hydroxides are illustrated in Figures 11 and 12. For the neutral salts the differences

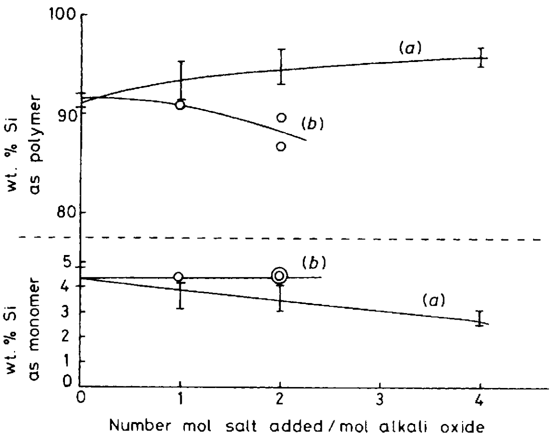

Figure 11. Anion distribution in 1 mol dm^{-3} sodium and potassium silicate solutions (SiO_2–base = 2.9) containing the added salts (*a*) NaCl, NaBr, KCl, CsCl, NPr^n_4Cl and (*b*) NMe_4Cl

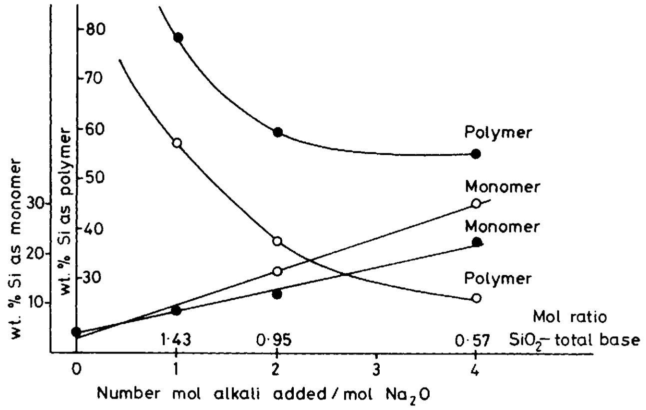

Figure 12. Anion distribution in 1 mol dm^{-3} sodium silicate solutions (SiO_2–Na_2O = 2.86) containing added KOH (●) or NaOH (○)

between the results for sodium and potassium silicate solutions at a silica–base ratio of 2.9 and SiO_2 concentration of 1 mol dm^{-3} were small, and consequently it was possible to plot the results for both cations together in Figure 11. This shows that adding any of the salts tested (NaCl, NaBr, KCl, CsCl, or NPr^n_4Cl), except NMe_4Cl, caused an increase in the proportion of polymeric anions and a corresponding decrease in the proportion of monomeric anion. Tetramethylammonium chloride, however, had the opposite effect; the proportion of polymeric anions was decreased, while the proportion of monomer remained nearly constant. A change in the degree of polymerisation resulting from the addition of a ' neutral ' salt should be accompanied by a change in pH, because the more highly condensed silicic acids are stronger acids than the monomer;[9] consequently an increase in the degree of polymerisation will cause the pH to fall, and *vice versa*. This is demonstrated by the results of pH measurements given in Figure 13; here the pH of a sodium silicate solution of SiO_2–Na_2O ratio 3 was monitored during the gradual addition of 5 mol dm^{-3} aqueous solutions of sodium, potassium, and tetramethylammonium chlorides. The anomalous behaviour of tetramethylammonium chloride is again evident: while sodium and potassium chloride solutions both lower the pH (compared to addition of the same volume of water), tetramethylammonium chloride raises it. (The small pH change observed for addition of water alone is probably attributable to dissolved carbon dioxide.)

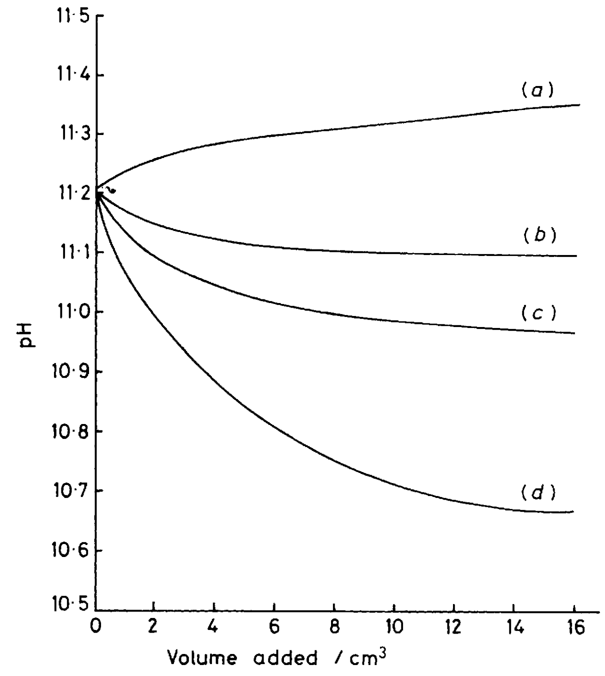

Figure 13. pH Changes of 1 mol dm^{-3} sodium silicate solutions during addition of salt solutions (*a*) NMe_4Cl (5 mol dm^{-3}), (*b*) H_2O, (*c*) KCl (5 mol dm^{-3}), and (*d*) NaCl (5 mol dm^{-3}). The horizontal scale represents the volume of H_2O or solution added to sodium silicate solution (25 cm^3) (SiO_2–Na_2O = 3, initial SiO_2 concentration = 1 mol dm^{-3})

Figure 12 shows the effects of adding sodium and potassium hydroxides to a 1 mol dm^{-3} sodium silicate solution of SiO_2–Na_2O ratio 2.86. In both cases, the proportion of monomer was increased, and the proportion of polymer was decreased considerably more than would be predicted from equations (3) and (4), showing that these equations are not valid for SiO_2–Na_2O ratios less than two. Attempts to fit equations of the same form to these additional results gave, at best, error variances greater than 40, showing that the relationship between % monomer or polymer and mole fraction Na_2O in the silicate is not linear for mole fractions greater than 0.33.

Discussion

Alkali metal silicate solutions contain monomeric and polymeric anions in varying proportions depending upon composition, concentration, and temperature. Except when the cation is NMe_4^+, the bulk of the polymeric silica is present in anions with charges of −10 or greater; tetramethylammonium silicate solutions can contain substantial quantities of $Si_8O_{20}^{8-}$. The five alkali metal silicates studied behaved in a similar way, the proportion of monomer increasing and the proportion of polymer decreasing with rising temperature, increasing dilution, and decreasing silica–base ratio, concentration having the greatest effect. Tetramethylammonium silicate solutions show an apparently different temperature effect, because the double-four-ring anion $Si_8O_{20}^{8-}$ is thermally unstable and practically disappears above 50 °C. If, however, the silicon content of this anion is added to that present as polymer, the proportions of monomer and total ' polymer ' present change with temperature in exactly the same fashion as the other alkali metal silicates.

Addition of neutral salts such as sodium or potassium chloride to a solution of sodium silicate increases the proportion of polymeric anions and reduces the proportion of monomer present, the pH of the solution falling in consequence; however, addition of tetramethylammonium chloride reduces the proportion of polymeric anions without significantly altering the amount of monomer present, and the pH of the solution increases accordingly.

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