821. *Hydrolysis of Sodium Silicate: Ultracentrifugation in Chloride Solutions*

By J. AVESTON

The hydrolysis of sodium silicate, $Na_mH_{4m}SiO_4$, with m between 0·64 and 1·04 has been studied by equilibrium ultracentrifugation. Weight-average degrees of polymerisation were found to increase rapidly with decrease in m, and increase in concentration. These results conflict with published schemes based on titration results, in which species no higher than tetramers are suggested. It is shown that these results, and also the centrifuge results, are more compatible with the existence of an extended series of polymers with $m = 0·5$ in addition to the tetramer and monomers previously proposed.

THE widespread industrial use of silicate solutions has stimulated much research into the formulæ of the silicate-containing species but, in common with other systems in which complex hydrolytic equilibria exist, the methods used have often been unequal to the problems involved. The limitations of such methods as the measurement of diffusion coefficients and the position of breaks in conductometric titration curves, which have been discussed previously,[1] need not be reiterated, although in fact they are even more pertinent to the present case. The literature on silicate solutions, before 1959, has been reviewed by Lagerström [2] and Ingri,[3] and their Papers call for some discussion in view of their direct relevance to the present work.

Lagerström carried out a series of potentiometric titrations of sodium silicate in 0·5M-(molal) and 3M-sodium perchlorate medium using a hydrogen electrode to measure the acidity. In 0·5M-sodium perchlorate, the average number, m, of OH^- ions bound per Si atom was varied between 0·7 and 1·05; in 3M-sodium perchlorate the range was 0·8—1·6. The range of m was limited at the lower end by the formation of unstable solutions, and at the higher end by the fact that, at high OH^- concentration, m is obtained as the difference between two large quantities, with consequent decrease in accuracy. The monomeric species $Si(OH)_4$, $[SiO(OH)_3]^-$, and $[SiO_2(OH)_4]^{4-}$ together with the polymers $[Si_2O_3(OH)_4]^{2-}$ and $[Si_4O_8(OH)_4]^{4-}$ were assumed in order to fit the calculated titration curves to the experimental points in 3M-sodium perchlorate. In the more dilute medium, neither of these polymeric species is apparently present; $[Si_4O_6(OH)_6]^{2-}$ is postulated instead.

A similar series of titrations was carried out by Ingri [3] over the same range of m and silicate concentration, but with the substitution of 0·5M-sodium chloride as supporting electrolyte. He also postulated the species $[Si_4O_6(OH)_6]^{2-}$ and, moreover, found its formation constant to be virtually unchanged with change in medium. Although this does not necessarily prove that such a species exists, it does indicate that the experimental curves were the same in the two media.

The need to postulate the existence of different species at different concentrations of the same " inert " supporting electrolyte, as found by Lagerström, is a little disturbing. It would perhaps appear more plausible if the results fitted the calculated curves over the whole range of m but in fact deviations occur around $m = 1·0$ for all three sets of data. As both workers stress the need to try other experimental methods it seemed worth while to apply the equilibrium ultracentrifuge to the problem and also to take advantage of the least-squares methods now available to refine, and re-interpret, Lagerström's results by using the species indicated by the ultracentrifuge.

EXPERIMENTAL

Centrifugation.—Centrifugations were carried out with a Spinco model E ultracentrifuge at 25°. Interference optics with 12 mm. cells were used and speeds of rotations varied between

---

[1] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.
[2] G. Lagerström, *Acta Chem. Scand.*, 1959, **13**, 722.
[3] N. Ingri, *Acta Chem. Scand.*, 1959, **13**, 758.

20,400 and 23,160 r.p.m. The centrifugation and computational procedures described by Johnson, Scatchard, and Kraus [4] were used. Computations were carried out on an IBM 7090 computer.

Refractive Index Increments and Volumes.—Densities were measured with a *ca.* 24-ml. pycnometer and refractive-index increments at 546 mμ with a Brice–Phoenix differential refractometer. The apparent molal volumes ϕ_v, and mean refractive-index increments $\Delta n/c$ for the silicate component defined $Na_mH_{(4-m)}SiO_4$ were found to vary linearly with m at constant total sodium concentration. Insufficient results at constant total sodium but varying silicate concentration were available to draw any conclusions about the concentration-dependence of ϕ_v and $\Delta n/c$. However, no significant variation has been observed in the other inorganic systems that have been examined in the ultracentrifuge and where the concentration of the polymeric component is small compared to the supporting electrolyte. The values of $\Delta n/c$ and ϕ_v (divided by the molecular weight of the monomer unit as defined above) given in the Table were therefore used for dn/dc and $\bar{v}$ in the computation of the degree of polymerisation.

Refractive-index increments and apparent molal volumes for $Na_mH_{(4-m)}SiO_4$ in sodium chloride supporting electrolyte

Concentration					
Si	Na^+	m	$-\log[OH]$	ϕ_v (ml. monomole^{-1})	$\Delta n/c$ (l. monomole^{-1})
0·2	2·0	0·642	2·853	50·9	0·00916
0·2	2·0	0·781	2·446	47·9	0·0113
0·2	2·0	0·919	1·805	44·8	0·0128
0·2	2·0	0·986	1·378	43·8	0·0135
0·2	2·0	1·040	1·151	45·3 *	0·0142
0·1	1·0	0·638	3·021	48·9	0·0109
0·1	1·0	0·776	2·641	45·3	0·0124
0·1	1·0	0·969	1·647	40·6	0·0152
0·2	1·0	0·78	2·389	45·8	0·0119
0·2	1·0	0·977	1·350	41·0	0·0144
0·08	0·5	0·639	3·055	47·4	0·0105
0·08	0·5	0·773	2·696	43·7	0·0129
0·08	0·5	0·899	2·111	40·1	0·0146
0·08	0·5	0·952	1·711	38·9	0·0155

* A value of 42·7 was used in the computations; if the experimental value were used, N_w would be decreased by 2%.

Literature values were used for the refractive-index gradients [5] and partial specific volume [6] of the sodium chloride supporting electrolyte. The refractive indices of the silicate solutions were measured by direct comparison with solvent containing the same concentrations of sodium chloride and sodium hydroxide to correct for that produced by hydrolysis of the silicate. The corresponding correction to ϕ_v was computed from literature values for sodium hydroxide [7] at the same total sodium concentration. These corrections were small, except for ϕ_v at the highest value of m, where the deviation of this point probably stems from the inadequacy of this correction rather than any abrupt change in silicate species in the region of $m = 1$.

Acidity Measurements.—The free OH^- concentrations needed to compute the stoicheiometric formula of the monomer unit were measured with a hydrogen electrode, in conjunction with a silver–silver chloride reference electrode and a salt bridge containing sodium chloride at a concentration equivalent to the total sodium-ion concentration of the silicate solution. The electrode system was calibrated with sodium chloride–sodium hydroxide solutions of the same total sodium concentration.

Materials.—A solution of polysilicic acid was prepared by passing a solution of recrystallised (from 5% NaOH) reagent grade sodium metasilicate through a column of Dowex 50W — X8 in the H^+ form. The effluent was analysed for silica by evaporating a sample to dryness, igniting it at 1000°, weighing the residue and then evaporating it to constant weight with hydrofluoric acid in the usual way; no detectable residue was obtained. The low acidity of the solution (pH *ca.* 4·0) showed the absence of anions of strong acids. A stock solution of

---

[4] J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, 1959, **63**, 787. For details of the computational programme (Fortran) used see O. E. Esval, Thesis, University of N. Carolina, 1962.

[5] A. Kruis, *Z. phys. Chem.*, 1936, *B***34**, 13.

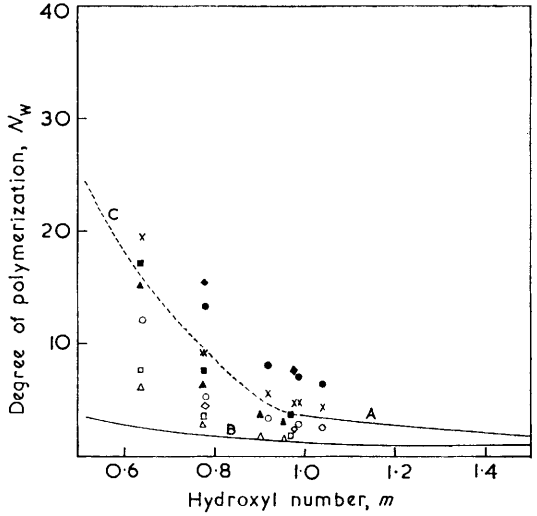
[6] H. Wirth, *J. Amer. Chem. Soc.*, 1940, **62**, 1128.

[7] F. T. Gucker, *Chem. Rev.*, 1933, **13**, 111.

sodium silicate with $Na_2O/SiO_2 = 0{\cdot}266$ was prepared from the silicic acid solution by adding the required weight of saturated (carbon dioxide-free) sodium hydroxide solution. Solutions used in the centrifugations were prepared by weight from the stock silicate and sodium hydroxide solutions and solid (Baker Analysed Reagent) sodium chloride. All alkaline solutions were stored in Polythene bottles under an atmosphere of nitrogen.

RESULTS AND DISCUSSION

Ultracentrifugation.—The sedimentation of a charged polymer in the presence of an excess of supporting electrolyte depends on the effective charge per monomer unit, z' and its concentration c_2', relative to that of the supporting electrolyte. Johnson [4] has shown that by suitable definition of the polymeric component the charge-effect can be split into two terms, only one of which is concentration-dependent. Centrifugation of a monodisperse solute over a range of concentrations will therefore give concordant results for only a single value of z'. For a labile polydisperse solute, the weight-average degree of polymerisation N_w and perhaps z' also, will vary with concentration so that this procedure is inapplicable. However, some information about z' and hence about N_w can still be obtained by varying the concentration of supporting electrolyte but keeping the concentration of the polymeric component constant, so long as it is assumed that the appropriate activity-coefficient quotients and also any counter-ion binding are not too sensitive to moderate changes in supporting electrolyte concentration. In the absence of such assumptions, it is only possible to compute upper and lower limits for the weight-average degree of polymerisation corresponding to the extreme assumptions of maximum charge (no counter-ion binding) and zero charge (complete counter-ion binding), respectively.



Weight-average degree of polymerisation of the silicate species as a function of m computed for maximum charge (solid symbols), zero charge (open symbols), and most probable value of the charge (crosses). Curve A computed for Lagerström's scheme, curve B for Ingri's scheme, and curve C for the scheme suggested in the text.

× ○ ● 0·2M-Si, 2·0M-NaCl
× ◊ ♦ 0·2M-Si, 1·0M-NaCl
□ ■ 0·1M-Si, 1·0M-NaCl
△ ▲ 0·08M-Si, 0·5M-NaCl

Equilibrium ultracentrifugations were carried out for fourteen sodium silicate solutions with m ranging from 0·64 to 1·04 and c_2' between 0·08 and 0·2M. Three separate concentrations of sodium chloride supporting electrolyte were used: 1M and 2M at the higher silicate concentrations, and 0·5M at $c_2 = 0{\cdot}08$M to provide a direct test of Ingri's scheme. All the solutions were found to be highly polydisperse by the criterion that plots of ln. n^* *vs.* x^2 were concave upward (n^* is the difference in refractive index between the solution and background and x is the radius), *i.e.*, N_w increased with the increase in silicate concentration throughout the centrifuge cell. Although all solutions were outside the instability range reported by Lagerström [2] (3M-sodium perchlorate medium) it is possible that this range is displaced with a change in medium. However, no change in molecular weight (within the limits of measurement, about 1%) could be detected from examination of plates exposed on successive days once centrifugal equilibrium had been attained.

The values of N_w computed for the extreme assumptions of zero charge (open symbols) and maximum charge (equal to m, solid symbols), are shown as a function of m in the Figure. The actual value of N_w at a given concentration should lie between these limits, and probably near to the maximum value, since extensive association of sodium ions does not seem very plausible. For the intermediate value of $z = 0{\cdot}75\ m$ concordant values for N_w were obtained in 1M- and 2M-sodium chloride for solutions with $m = 0{\cdot}78$ and $0{\cdot}98$ and $[Si] = 0{\cdot}2$M. These points, together with the remainder of the centrifugations at this concentration computed for a charge of 75% of the maximum, are shown by crosses in the Figure. They are considered the most probable values of N_w at this concentration, but their precise values should not be taken too seriously in view of the approximations involved.

The degrees of polymerisation predicted by the schemes of Lagerström [2] and of Ingri [3] which involve species no larger than tetramers, were computed from the published formation constants. As the values of N_w predicted by either scheme are insensitive to concentration over the range used in the centrifugations, only one curve is shown for each scheme.

The centrifuge results clearly conflict with Ingri's scheme; species much higher than tetramers are needed to interpret the results, even for the extreme assumption of zero charge. As Lagerström's scheme involves no species with $m < 1{\cdot}0$, deviations from his titration figures below this value (outside the instability range) are inevitable. Also values of N_w can only be computed using this scheme up to $m = 1{\cdot}0$ so that no direct comparison can be made with the majority of the centrifugations, although in fact reasonable agreement is obtained in the region of $m = 1{\cdot}0$.

Re-interpretation of Lagerström's Titration Results.—The centrifugation results clearly show that stable silicate solutions with $m < 1{\cdot}0$ can be obtained and also suggest a limiting value for m of 0·5—0·6. It is equally clear that a better fit to Lagerström's data could be obtained by including a species with m in this range. But the existence of a single polymer with a sufficiently high molecular weight to account for the observed values of N_w would be inconsistent with the high degree of polydispersity indicated by the centrifugations and is, in any case, not very likely in the general context of silicate chemistry. A range of polymers with each alternate silicon atom carrying a negative charge is more plausible and is consistent with the steep increase in N_w as m decreases to *ca.* 0·5. This is essentially the "core + link" hypothesis invoked by Sillén [8] to interpret e.m.f. data for some other systems. In this case, the core would be $[SiO(OH)_3]^-$ and the link $[Si_2O_3(OH)_3]^-$. Addition of base to such a system may be visualised as causing ionisation of adjacent silicon atoms with consequent depolymerisation to provide more ionised end-groups.

In order to test this scheme with the existing computer programme, the simplifying assumption of a series of polymers, all with $m = 0{\cdot}5$ and containing 10, 20, 30, 40, and 50 silicon atoms was made.* The tetramer and monomers suggested by Lagerström were also included, but the dimer $[Si_2O_3(OH]_4]^{2-}$ was omitted, as a separate least-squares test with the species suggested by Lagerström indicated that its formation constant was not well determined. As the accuracy of the data clearly did not allow the independent variation of formation constants for five polymeric species, the converged values of the constants obtained when each species was tried separately with the tetramer and monomers were used. In practice, this gave an almost constant value of $\log K = \log \beta_{p,2p}/2p = 4{\cdot}9$ for the addition of each link. The formation constants

$$\beta_{p,q} = [Si_q(OH)^{-p}_{(4q+p)}]/[Si(OH)_4]^q[OH^-]^p$$

---

* The suggested scheme strictly requires species with an odd number of silicon atoms with $p/q = p/2p + 1$, but the difference is immaterial for $q > 10$ with the present data.

[8] L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, 1907.

for the (1,1), (1,2), and (4,4) species were then adjusted by using the O.R.G.L.S. Fortran least-squares programme to give the least-squares deviation in m from the experimental points. The converged values of log $\beta_{1,1} = 4{\cdot}72$, log $\beta_{2,1} = 5{\cdot}95$, and log $\beta_{4,4} = 23{\cdot}75$ were obtained with a standard deviation in $m, \sigma_m = 0{\cdot}022$ which compared favourably with a value of 0·039 obtained with Lagerström's scheme. The improvement of fit with the figures is rather better than that implied by these deviations; as there are fewer experimental points in the region where the high polymers are important, it would be logical, assuming that they are of equal accuracy to those at high values of m, to provide a higher weighting-factor to these points instead of using unit weights throughout.

The value of N_w as a function of m computed for this scheme, shown by the broken curve in the Figure, is also in much better agreement with the experimental results.

This scheme is also supported by recent work of Lentz,[9] in which it was shown that some silicate minerals can be simultaneously acid-leached and the resulting polysilicic acids end-blocked by trimethylsilyl groups to yield derivatives with the same silicate structure as the mineral from which they were derived. With sodium silicate solution the yield of polysilicate derivatives containing more than four silicon atoms increased rapidly as $m \rightarrow 0{\cdot}5$, and also as the concentration increased at constant value of m, in an analogous manner to the increase in N_w shown by the centrifuge results. The disproportionately high yield of a *cyclic* tetramer (relative to dimer and trimer) found with solutions with $m > 1{\cdot}0$ provides a clue to the predominance of tetramers at high value of m.

However, once it is accepted that a wide range of polymers exists, a virtually unlimited number of different schemes are conceivable, and no doubt by postulating sufficient species with separate formation constants as adjustable parameters, both the titration and centrifuge results could be fitted to any desired degree of accuracy. The situation is analogous to polysilicic acid solutions[10] but is further complicated by the presence of charged species and by reversible equilibria, which cause N_w to vary with concentration and prevent any direct measurement of the polymer-size distribution.

Appreciation is expressed to R. M. Rush for supplying Fortran card decks for the centrifuge and least-squares programmes.

NATIONAL CHEMICAL LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, December* 31*st*, 1964.]

---

[9] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

[10] A. Audsley and J. Aveston, *J.*, 1962, 2320.