

Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 11. Polysilicate Formation in Alkaline Aqueous Solution. A Combined Potentiometric and ^{29}Si NMR Study

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Polysilicate equilibria have been studied in a 0.6 mol dm^{-3} Na(Cl) medium at 25°C . Speciation and formation constants were determined from combined potentiometric (hydrogen electrode) and ^{29}Si NMR methods. Experimental data cover the ranges $11.0 \leq -\log[\text{H}^+] \leq 12.2$ and $0.008 \leq B \leq 0.048 \text{ mol dm}^{-3}$, where B stands for the total concentration of Si. By using NMR-data in a qualitative and quantitative way, nuclearity, charge and stability of a series of polysilicates were determined. Besides a dimer, $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, a cyclic $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ and linear $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$ trimer are formed. However, the prevailing polysilicate is tetrameric, whereas species with higher nuclearities are formed in minor amounts. Furthermore a protonated dimer, $\text{Si}_2\text{O}_2(\text{OH})_5^-$, as well as a cyclic tetramer with the tentative composition $\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$ are formed in less alkaline solutions ($-\log[\text{H}^+] < 11.0$). Formation constants for the different species are given in Table 4. Data were analyzed with the least squares computer program LETAGROPVRID.

The present study forms part of a project comprising equilibrium and structural studies of aqueous silicon(IV) and aluminium(III). In Part 2¹ and 5² of this series, the formation of the mononuclear silicate species $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ was investigated. Using potentiometry (hydrogen electrode, 25°C) conditions for precise determination of pK_1 and pK_2 of $\text{Si}(\text{OH})_4$ were established and the medium dependence of these constants [$0-2.0 \text{ mol dm}^{-3}$ Na(Cl)] were fitted to equations of an extended Debye-Hückel type.

Recently a calorimetric study³ within the same medium range has provided enthalpy as well as entropy values for monosilicate formation.

The aim of the present study is to interpret speciation and equilibria in silicate solutions where polysilicate formation is extensive. By using combined emf and ^{29}Si NMR data, the possibility to evaluate composition and stability of polysilicate species in aqueous solution will be demonstrated.

Due to the complexity of silicate polymerization, the interpretation has been restricted to equilibrium solutions with $Z \geq 1.0$ (Z is defined as the average number of OH^- reacted per $\text{Si}(\text{OH})_4$). Equilibrium studies in solutions with $Z < 1.0$ will be presented in a forthcoming publication.

PREVIOUS WORK

The polymerization of silicate ions in aqueous solution has been studied with a great variety of methods. Out of these, potentiometry and ^{29}Si NMR call for some discussion in view of their direct relevance to the present work.

Some studies have been reported, where equilibrium analysis based on emf data has been applied to interpret silicate formation. In 1959 Lagerström⁴ carried out series of potentiometric titrations in 0.5 and 3.0 mol dm⁻³ Na(ClO₄) media. The average number of OH⁻ reacted per Si(OH)₄, Z , was varied between the limits $0.7 \leq Z \leq 1.0$ [0.5 mol dm⁻³ Na(ClO₄)] and $0.8 \leq Z \leq 1.6$ [3.0 mol dm⁻³ Na(ClO₄)]. The monomeric species Si(OH)₄, SiO(OH)₃⁻ and SiO₂(OH)₂²⁻ together with the tetramer Si₄O₆(OH)₆²⁻ were proposed in 0.5 mol dm⁻³ Na(ClO₄) medium. In 3.0 mol dm⁻³ medium, more alkaline solutions, ($0.5 \leq -\log[\text{OH}^-] \leq 3.0$) were investigated, and the polynuclear species proposed both have an average charge per Si (z) of -1 , viz. Si₂O₃(OH)₄²⁻ and Si₄O₈(OH)₄⁴⁻.

A similar series of titrations was carried out by Ingri (0.5 mol dm⁻³ NaCl)⁵ over the same ranges of Z and silicate concentration. By assuming a single predominating polynuclear species, the best fit to data was obtained with the same model as proposed by Lagerström⁴ in 0.5 mol dm⁻³ Na(ClO₄). Busey and Mesmer⁶ studied polysilicate formation in 1 mol dm⁻³ NaCl solutions at temperatures from 60 to 290 °C with $0.7 \leq Z \leq 1.0$. They found polysilicate formation to decrease with increasing temperature and selected the same scheme of species as Lagerström and Ingri (0.5 mol dm⁻³ media).

It has to be noticed that in these three studies, the intention has been to explain experimental data with as few complexes as possible. Such an approach will lead to simple equilibrium models. However, the results cannot be considered as unique and definite in any way.

Until recently, information about the nature of polysilicate species has been obtained only indirectly, for instance by potentiometry, trimethylsilylation⁷⁻⁹ followed by chromatographic separation and by ultracentrifugation.¹⁰

More direct information seems to be obtained from NMR spectroscopy. During the last decade, the development of ^{29}Si NMR spectroscopy, combined with X-ray structural information on solids, have begun to provide a clearer picture of the speciation in silicate solutions. Pioneering work by Marsmann,¹¹ Engelhardt *et al.*¹² and Harris *et al.*^{13,14} have shown upon the existence of a variety of peaks in the spectra indicating the formation of a great number of polysilicate species in solution. By using solutions enriched in ^{29}Si , Harris *et al.* (A comprehensive review with respect to Si NMR is given in this article.)¹⁴ found evidence of 12 separate species in an alkaline potassium silicate solution ($K:Si=1.0$, and the total concentration of Si, $B=0.65$ mol dm⁻³). Besides the monomer and dimer, silicate species including three-membered and four-membered rings were postulated. Out of these twelve species, six were found in which all silicon atoms are chemically equivalent, giving unsplit peaks: monomer, dimer, cyclic trimer, cyclic tetramer, prismatic hexamer and cubic octamer. Furthermore multiplets indicating the formation of a linear trimer and tetramer were observed. To summarize, these results show upon the formation of a series of polynuclear species with nuclearities two, three, four, five, six and eight. The spectra also show a number of additional peaks for which no assignments were made. Furthermore, Engelhardt *et al.*¹² observed an increase in degree of polymerization with a decrease in pH until gelling occurs. (These findings are in accordance with results obtained using ultracentrifugation¹⁰ and trimethylsilylation methods^{8,9}). Another interesting feature of the NMR-spectra¹² is that the shift values for the mono-, dimer- and cyclotrimersilicate peaks

are dependent on the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio, indicating the formation of proton series of these species.

EXPERIMENTAL

Reagents and preparation of solutions. Sodium chloride (Merck *p.a.*) was dried at 200 °C and used without further purification. Fresh chloride solutions were always used in the measurements to avoid contamination by bacteria. Dilute hydrochloric acid and sodium hydroxide solutions were prepared and analyzed as described elsewhere.¹ Silicic acid solutions were prepared by dissolving $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (Baker *p.a.*) in an acidic medium solution with an H^+ -excess. Preceding the addition of sodium silicate, the volume of the acid medium solution was about 90 % of its final volume. In this way clear solutions with a total concentration of silicic acid, $B \leq 0.05 \text{ mol dm}^{-3}$, could be prepared. Freshly prepared silicic acid solution was used for each experiment and no attempts were made to store a stock solution. Determination of B as well as a carbonate impurity in Na_2SiO_3 , was performed as outlined elsewhere.¹ Omitting the water content, the composition of this sodium silicate was found to be $\text{Na}_2(\text{SiO}_3)_{0.977}(\text{CO}_3)_{0.023}$.

²⁹Si NMR spectra were at first recorded with natural abundance silicate solutions (4.7 % ²⁹Si). It was, however, concluded that, at $B \leq 0.05 \text{ mol dm}^{-3}$, the spectra had a much too low signal to noise ratio to permit any quantitative interpretation. Therefore, ²⁹Si-enriched material has been employed in these measurements. With the form available, SiO_2 (4.7 % ²⁸Si, 95.0 % ²⁹Si, 0.3 % ³⁰Si, Oak Ridge National Laboratory), a special procedure to prepare the solutions without causing carbonate contamination has been employed: To a dry and well-cleaned Pt-crucible approximately 0.1 g of enriched SiO_2 (exactly determined by difference weighing) was transferred. Then, this crucible was placed in an argon filled glovebox and 5.00 ml 0.3525 mol dm^{-3} NaOH-solution was added. A tightly fitting lid made of Teflon was thereafter mounted and secured to the crucible by means of metal wires and the crucible was placed in a semi-tight glass container containing open bowls of concentrated NaOH-solution. The whole arrangement was then placed in a heating cabinet at 90 °C for 15 h. After replacing the arrangement into the glovebox and letting it cool down, the content of the crucible (i.e. a carbonate free $\text{SiO}_2(\text{OH})_2^-/\text{SiO}(\text{OH})_3^-$ -buffer) was quantitatively transferred to a titration vessel in which the required amount of NaCl had been pre-weighed. The correct start volume was finally obtained by adding distilled water to the proper weight (the density was known from pre-experiments with natural abundance SiO_2). Before the solution was taken out of the glovebox for titration, an air tight lid with argon gas in- and outlet was mounted on the vessel. This lid also contained extra, stoppered holes for the hydrogen electrode, the reference electrode, the coulometric electrodes and the H^+ -burette. The titrations were performed as described below, with the exception that in each equilibrium point, 2.50 ml of solution was withdrawn by means of an Oxford-pipette. This amount was quickly transferred to a 10 mm NMR-tube which had been deaerated with argon and, after transferring, the tube was sealed with an ordinary NMR plastic cap.

All equilibrium solutions had the general composition: $[\text{Si}(\text{OH})_4]_{\text{tot}} = B \text{ mol dm}^{-3}$, $[\text{H}^+]_{\text{tot}} = H \text{ mol dm}^{-3}$, $[\text{Na}^+]_{\text{tot}} = 0.6 \text{ mol dm}^{-3}$ and $[\text{Cl}^-]_{\text{tot}} = 0.6 + H \text{ mol dm}^{-3}$. *H* is calculated over the zero-level H_2O , $\text{Si}(\text{OH})_4$.

METHODS

Potentiometric measurements. The measurements were performed at 25.00 ± 0.05 °C in an ionic medium consisting of 0.6 mol dm^{-3} NaCl. As measurements were performed in alkaline solutions ($-\log[\text{H}^+] \leq 12.2$), a hydrogen electrode was used consistently. The potentiometric titrations were performed using an automatic system (Ginstrup 1973¹⁵) and OH^- was added either using a NaOH-solution or coulometrically. The measured emf, *E*, is given by the relation

$$E = E_o + 59.156 \log h + j_{ac}h + j_{alk}k_w h^{-1} \quad (1)$$

where $h = [H^+]$, E_o is a constant, k_w the ionic product of water in $0.6 \text{ mol dm}^{-3} \text{ NaCl}$ and j_{ac} and j_{alk} coefficients in the expression for the liquid junction potential. ($\log k_w = -13.727$, $j_{ac} = -77.1 \text{ mV mol}^{-1} \text{ dm}^3$, $j_{alk} = 42.0 \text{ mV mol}^{-1} \text{ dm}^3$; Sjöberg *et al.* 1981¹).

Each titration started with a degassing of O_2 and CO_2 from the acid ($-\log h \approx 2.5$) silicic acid solution for 1–2 h using argon gas. Then the titration was continued with a slight overpressure of H_2 within the titration vessel, in order to avoid the contamination of CO_2 from the air. The acidic part of the titrations ($-\log h \leq 4$) was used for accurate determinations of the H^+ -excess, H_o , B and E_o of the hydrogen electrode. (In this part OH^- was generated coulometrically). Then $-\log h$ of the solutions was increased to ≈ 12 by one addition of a $NaOH$ -solution from a burette. In this way measurements in the 'instability range' occurring between the limits $4 \leq -\log h \leq 10$ (*cf.* below) could be avoided. The titrations were then continued backwards (decreasing $-\log h$) by the addition of a H^+ -solution until the upper $-\log h$ limit of the instability range was reached. Reversibility of equilibria were fully established within this range by performing both forward (addition of OH^-) and backward (addition of H^+) titrations. Dilution experiments were also performed, where pure ionic medium was added to an equilibrium solution of known h , H , B composition.

Usually stable potentials were established within 1–2 h, provided CO_2 was excluded and measurements were performed outside the 'instability range', otherwise the formation of a precipitate caused a slow drift in the potential.

²⁹Si NMR measurements. All NMR measurements were performed at $295 \pm 1 \text{ K}$ using a Bruker WM-250 spectrometer with a 10 mm multinuclear probehead. During the measurements, an inner concentric tube (o.d. 2 mm) with D_2O was used for instrumental lock. The chemical shifts were recorded with respect to $Si(CH_3)_4$ (tetramethylsilane, TMS) using the high-frequency-positive convention. The spectra (recorded with 16 K data) covered the region $(-50) - (-130) \text{ ppm}$ (4000 Hz) and the chemical shift zero was regularly checked by running TMS between each experimental solution. The spectra were recorded in a quantitative manner, *i.e.* 90° pulses and pulse repetition times longer than $5T_1$'s, were used. The spin lattice relaxation times, T_1 's, were evaluated by the inversion-recovery method and the following values were obtained: monomer 25 s, dimer 26 s and cyclotrimer 21 s. Furthermore, in order to obtain absolute concentration information, the instrument was calibrated against a $0.504 \text{ mol dm}^{-3}$ silicate solution in $15 \text{ mol dm}^{-3} \text{ NaOH}$ [all silicon present as $SiO_2(OH)_2^{2-}$] and used in the absolute intensity mode. Peak integration of spectra was performed manually as (peak height \times half line width)/2 taking the half line widths from highly expanded parts of the spectra. Instrument integrals were not used as they have been found to underestimate the area of small peaks (Pettersson *et al.*¹⁶). In order to obtain an approximately constant signal to noise ratio in all spectra, the number of transient collected (NS) were varied so that $B^2 \cdot (NS)$ was constant.

Data treatment. The equilibria which must be considered in the present study can be divided into groups as follows:

(i) ionization of H_2O and $Si(OH)_4$ according to the equilibria



Accurate values for these formation constants were evaluated from a separate study (Sjöberg *et al.* 1981¹). The following results were obtained: $\log \beta_{-10} = -13.727$, $\log \beta_{-11} = -9.472$, $\log \beta_{-21} = -22.07$.

(ii) polysilicate formation of the general type



The complexes are, for brevity, often given the notation (p, q) .

Using potentiometric data, the quantity

$$Z = (h - H - k_w h^{-1}) / B \quad (6)$$

may be calculated as a function of $-\log h$. Z is here defined as the average number of OH⁻ reacted per silicic acid or, in other words, as the average negative charge per silicon atom (z).

With respect to ²⁹Si NMR data the convention that all silicate anions (and silicic acids) can be described as a combination of Q units has been adopted. This symbol is used to represent a silicon atom bonded to four oxygen atoms forming a tetrahedron. The superscript shows the number of other Q-units attached to the silicon tetrahedron under study. Thus Q⁰ denotes monosilicates, Q¹ disilicates and chain end groups, Q² middle groups in chains and cyclic polymers, Q³ chain branching sites and Q⁴ three-dimensional crossed-linked framework. A given subscript denotes the number of similar Q-units found in the complex in question. The degree of protonation of the different species is ignored in this description.

Computer programs. In the evaluation of the experimental data, the least-squares computer program LETAGROPVRID,¹⁷ version ETITR^{18,19} (potentiometry) was used. p, q -integers and corresponding equilibrium constants that 'best' fit the experimental data were determined by minimizing the error squares sum $U = \sum (E_{\text{calc}} - E)^2$. Calculations and plotting of distribution diagrams were performed using the program SOLGASWATER.²⁰

Potentiometric data. Experimental emf-data comprise 24 titrations with 327 data points. The following concentration ranges were studied: $0.003 \leq B \leq 0.048 \text{ mol dm}^{-3}$, $-0.060 \leq H \leq 0.005 \text{ mol dm}^{-3}$, $0 \leq Z \leq 1.1$ and $2.5 \leq -\log h \leq 12.2$. A part of these data is visualized in Fig. 1 as $Z(-\log h)$ -curves. The upper limit of the Z -curves is set by the uncertainty in Z , caused by high [OH⁻], which implies that the numerator in (6) tends to become the difference between two large figures. The lower limit ($Z \approx 0.7$, $B > 0.003 \text{ mol dm}^{-3}$) is caused by the instability range where drifting potentials were obtained. With $B > 0.003 \text{ mol dm}^{-3}$ different Z -curves for different B are obtained. This means that polynuclear complexes are formed. Furthermore no intersection point is found, instead all curves are found on the alkaline side of the mononuclear wall. This implies that data cannot be explained with one polynuclear complex. Several species with different average charges must be formed. The increased steepness of the Z -curves with decreasing $-\log h$, indicates that the nuclearity of the different species increases when H⁺ is added.

NMR data. Two combined potentiometric and ²⁹Si NMR titrations were performed. 16+19 experimental solutions were studied, covering the ranges $0.010 \leq B \leq 0.048 \text{ mol dm}^{-3}$, $0.83 \leq Z \leq 1.10$, $10.35 \leq -\log h \leq 12.02$, respectively. A typical spectrum for these solutions is

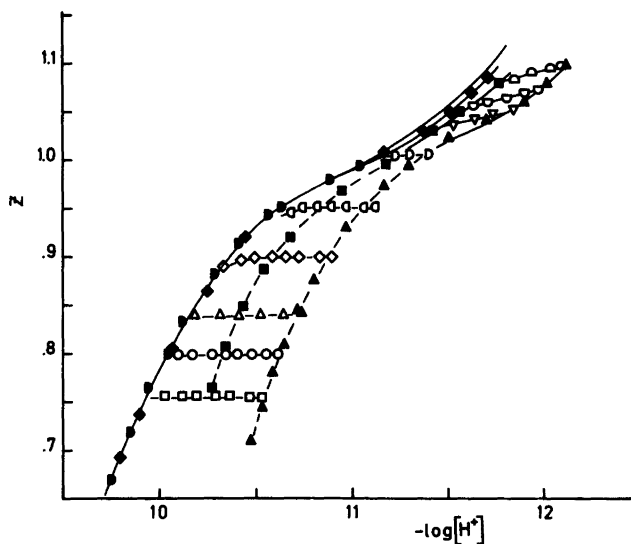


Fig. 1. A part of experimental potentiometric data plotted as curves $Z(-\log[H^+])$. Filled symbols are from titrations with H^+ or OH^- added. Open symbols represent titrations at constant H/B -ratios (dilution experiments). The symbols stand for the following starting concentrations in B: \square 3, \blacklozenge 8, \blacksquare 15, \blacktriangle 40, \square 31, \square 32, ∇ 34, \square 37, \diamond 36, \triangle 46, \circ 37, \square 47 mmol dm^{-3} resp. The full curves have been calculated using the set of proposed constants in Table 4.

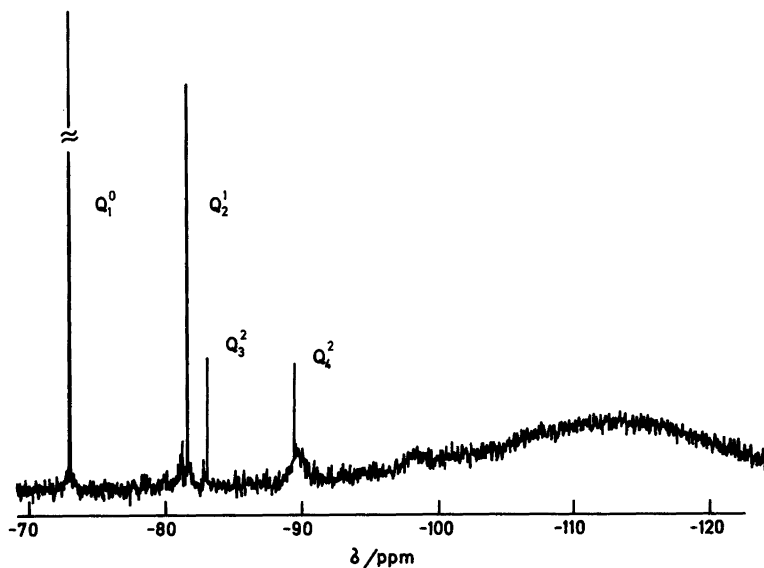


Fig. 2. ^{29}Si NMR spectrum from an alkaline solution with $B=0.028 \text{ mol dm}^{-3}$, $Z=0.98$, and $-\log[H^+]=11.16$. Different assignments are according to Harris.¹⁴ The broad band at about -100 – 120 ppm was found to originate from the NMR-tube which is made out of glass.

Table 1. NMR-characteristics for different silicates.

Species	NMR-assignment	$\Delta\delta^a/ppm$	$\Delta\delta^b/ppm$
Monomer	Q_1^0	0.00	0.00
Dimer	Q_2^1	-8.62	-8.70
Cyclic trimer	Q_3^2	-10.19	-10.11
Cyclic tetramer	Q_4^3	-16.10	-16.50

^a According to Harris *et al.*¹⁴ ($B=0.65 \text{ mol dm}^{-3}$, K:Si=1:1. ^b This work. Values taken from Fig. 2.

given in Fig. 2. The different peaks have been assigned to monomer, dimer, cyclotrimer, and cyclotetramer. These assignments are mainly based on conclusions drawn by Harris *et al.*¹⁴ A comparison between shift values of the different species obtained in this work and those given by Harris *et al.* are compiled in Table 1. As can be seen, the agreement is good. Though additional species were found by Harris *et al.*, no well-defined signals due to these were found, probably due to the low B studied in this work.

The total concentration of measurable Si, given by the monomer, $B(Q_1^0)$, dimer, $B(Q_2^1)$, cyclotrimer, $B(Q_3^2)$ and cyclotetramer, $B(Q_4^3)$ peaks was calculated for each spectrum. These values show the monomer to predominate ($\geq 40\%$ of B), while Si_2 , Si_3 (cyclo) and Si_4 (cyclo) species are only formed in minor amounts ($\leq 10, 4$ and 3% of B , respectively). This implies that the major part of existing polysilicates are to be found in additional species. Furthermore, the relative amount of mono-, di- and trimer decrease with decreasing $-\log h$. This implies that highly polymerized silicates are formed at the expense of mono-, di- and trimers as $-\log h$ is decreased. These findings are in accordance with the potentiometric data.

So far possible protonation of the different silicate species has not been commented. As $B(Q_1^0)=[Si(OH)_4]+[SiO(OH)_3^-]+[SiO_2(OH)_2^{2-}]$ it is likely to expect the corresponding shift value (Q_1^0) to be $-\log h$ dependent. This is also found (*cf.* Fig. 3). In a similar way the chemical shift values of Q_2^1 , Q_3^2 and Q_4^3 depend upon $-\log h$, indicating proton series to be formed.

CALCULATIONS AND RESULTS

A preliminary equilibrium analysis of present emf-data clearly showed upon the complexity of polysilicate formation. A great number of species, with varying degree of nuclearity (q) and z , had to be added to the equilibrium model to get an acceptable fit to data. This implies that calculations based on emf-data solely, cannot provide a unique explanation of data. Instead several equilibrium models are to be expected, each one of them describing data equally well.

However, the following general conclusions could be drawn: i) With $Z \geq 1.0$ and $11.0 \leq -\log h \leq 12.2$ one or several polynuclear complexes all with $z = -1$ seem to be formed. Species with $z < -1$ could not be included in the equilibrium model (the corresponding formation constants always turned out to be zero or negative in the calculations). ii) With $Z < 1.0$ the nuclearity of the species increases with a subsequent lowering of the average charge as $-\log h$ is decreased. Close to the instability range species with $q \geq 50$ and $z \approx -0.5$ seem to be formed. iii) The great number of existing species implies that in practice it is

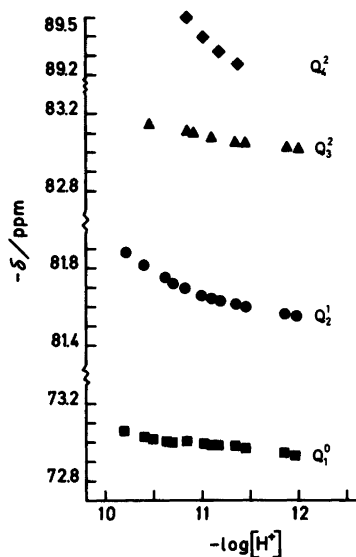


Fig. 3. Chemical shifts, δ , as a function of $-\log[H^+]$.

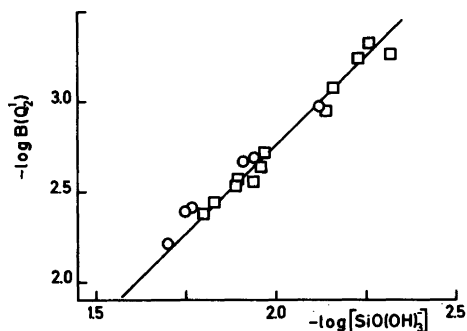


Fig. 4. A plot of $B(Q_1^-)$ versus $-\log[SiO(OH)_3^-]$. The symbols denote two different titrations. The line is drawn with the slope 2.

impossible to determine individual formation constants for each one of them. Instead polymerization according to a two-parameter behaviour was found to be applicable.

To get as 'true' equilibrium model as possible, the need for supplementary methods, able to give more direct information about composition and stability of the different species, is obvious. By performing combined emf and ^{29}Si NMR measurements, experimental data are obtained, which seem to be very promising in describing polysilicate formation. The evaluation of these data will now be presented in detail.

NMR-data. From available $\log h$ and $B(Q_1^-)$ -data it has become possible to calculate the concentration of each of the mononuclear species $Si(OH)_4$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$. In these calculations the relations $[Si(OH)_4] = \alpha_0 B(Q_1^-)$, $[SiO(OH)_3^-] = \alpha_1 B(Q_1^-)$ and $[SiO_2(OH)_2^{2-}] = \alpha_2 B(Q_1^-)$ were used. ($\alpha_0 = 1/(1 + \beta_{-11}h^{-1} + \beta_{-21}h^{-2})$; $\alpha_1 = \beta_{-11}h^{-1}/(1 + \beta_{-11}h^{-1} + \beta_{-21}h^{-2})$; $\alpha_2 = \beta_{-21}h^{-2}/(1 + \beta_{-11}h^{-1} + \beta_{-21}h^{-2})$).

Knowing α_1 and α_2 , the average charge of the polynuclear silicates, $z(\text{poly})$, can be calculated by using the relation

$$z(\text{poly}) = -(BZ - B(Q_1^-)Z(Q_1^-))/(B - B(Q_1^-)) \quad (7)$$

where $Z(Q_1^-) = \alpha_1 + 2\alpha_2$.

Within the range $11 \leq -\log h \leq 12$, $z(\text{poly}) = -0.98 \pm 0.04$ was found, thus confirming statement (i) above.

Assuming the average charge per Si of the polysilicate complexes to be -1 , the nuclearity, q , defined according to the equilibria



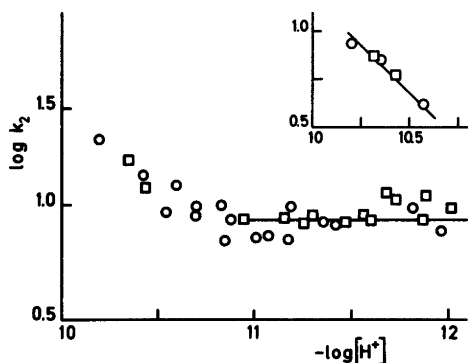


Fig. 5. The $-\log[\text{H}^+]$ dependence of $\log k_2$. The full line is drawn with $\log k_2=0.92$ (calculated from data with $-\log[\text{H}^+] \geq 11.0$). The small figure gives $\log(B(Q_2^1)/2) - \log(-2,2) - 2 \log(-1,1)$ as a function of $-\log[\text{H}^+]$. The line is drawn with the slope set equal to -1.0 using data with $-\log[\text{H}^+] \leq 10.6$.

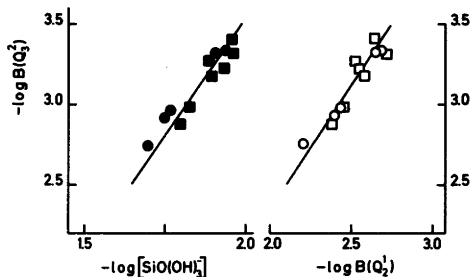


Fig. 6. $-\log B(Q_3^2)$ as a function of $-\log[\text{SiO}(\text{OH})_3^-]$ (left half) and $-\log B(Q_2^1)$ (right half) resp.

is obtained by plotting the logarithm of the Si-concentration given by the different peaks of the spectra against $\log[\text{SiO}(\text{OH})_3^-]$. Such a plot will give a straight line with the slope equal to q and an intercept $= \log k_q + \log q$ as $\log [B(Q_q)/q] = q \cdot \log [\text{SiO}(\text{OH})_3^-] + \log k_q$.

This approach will be used in order to evaluate the possibility of using combined emf and ^{29}Si NMR data in a qualitative and quantitative way.

Dinuclear silicates. Composition and stability of the dinuclear complex $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ was evaluated from a $\log B(Q_2^1) - \log[\text{SiO}(\text{OH})_3^-]$ plot (Fig. 4). A linear regression analysis showed upon a slope $= 1.8 \pm 0.06$, which confirms the dinuclearity of the complex. The line in the figure is drawn with the slope 2 to show the fairly good agreement of the experimental point and the integer value. With this slope $\log(k_2 \pm 3\sigma) = 0.92 \pm 0.05$ was obtained.

As indicated in Fig. 3, the shift value of the Q_2^1 -peak shows a $-\log h$ dependence. This is confirmed in Fig. 5 where $\log k_2$ clearly is increasing with $-\log h \leq 11$. This fact indicates the formation of a $\text{Si}_2\text{O}_2(\text{OH})_5^-$ and/or $\text{Si}_2\text{O}(\text{OH})_6$ complex. The existence of these species was tested by plotting $\log(B(Q_2^1)/2) - \log(-2,2) - 2 \log(-1,1)$ against $\log h$. The slope of this linear relationship (cf. Fig. 5) $= 0.8 \pm 0.06$, shows upon the formation of a $\text{Si}_2\text{O}_2(\text{OH})_5^-$ complex with $\log k(2\text{SiO}(\text{OH})_3^- + \text{H}^+ \rightleftharpoons \text{Si}_2\text{O}_2(\text{OH})_5^- + \text{H}_2\text{O}) = 11.20 \pm 0.09(3\sigma)$. (The slope was set equal to 1.0).

Trinuclear cyclic silicates. The Q_3^2 -peak of the different spectra was interpreted in the same manner as with the Q_2^1 -peak, i.e. $\log B(Q_3^2)$ was plotted against $\log[\text{SiO}(\text{OH})_3^-]$ (Fig. 6). The slope came out as 2.4 ± 0.2 , a value somewhat low to fully confirm the existence of a trinuclear species. (It has to be recognized that the rather steep slope of this line makes the different points sensitive to an error in $\log[\text{SiO}(\text{OH})_3^-]$). With the slope set equal to three, $\log(k_3 \pm 3\sigma) = 1.99 \pm 0.08$ was obtained.

Alternatively, the Q_3^2 -peak was interpreted by plotting $\log B(Q_3^2)$ against $\log B(Q_2^1)$ (Fig. 6). (This implies that $\log h$ data are not used.) The slope 1.4 ± 0.15 is close to 1.5 given by a trinuclear complex and confirms the existence of a $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ complex with $\log k(3(-2,2) \rightleftharpoons 2(-3,3)) = 1.26 \pm 0.07$. This value recalculated gives $\log k_3 = 2.02$, thus in good

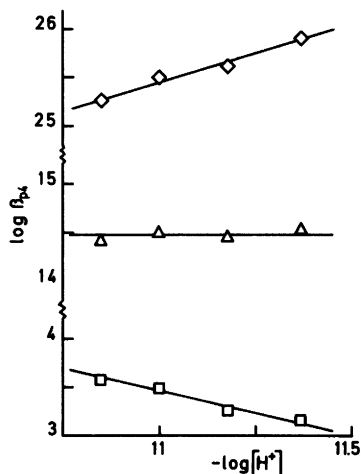


Fig. 7. $\log(B(Q_4^2)/4) - 4 \log[-11] - p \log[H^+] = \log \beta_{p4}$ versus $-\log[H^+]$ for $p=0$ (\square), 1 (\triangle) and 2 (\diamond). β_{p4} is defined according to (9).

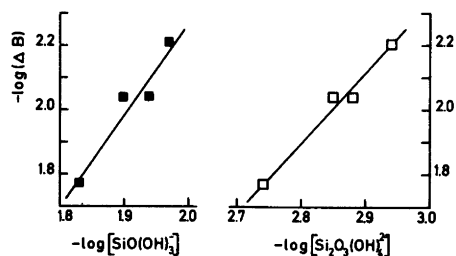


Fig. 8. $-\log(\Delta B)$ as a function of $-\log[SiO(OH)_3^-]$ (left half) and $-\log[Si_2O_3(OH)_4^{2-}]$ resp. (right half). The slopes of the lines are 2.9 and 2.2 resp.

agreement with 1.99 obtained from the combined $\log h$ -NMR data.

Though the chemical shift value of the Q_3^2 -peak shows a $-\log h$ dependence, the present experimental data do not allow for any evaluation of possible trinuclear species with $z > -1$.

Tetranuclear cyclic silicates. The Q_4^2 -peak is, according to Harris *et al.*, due to a cyclic tetramer. This is formed in minor amounts ($\approx 2.5\%$ of B) and could only be quantified from four different spectra at the highest B -values studied. The following $B(Q_4^2)/(\text{mmol dm}^{-3})$, $-\log h$ values were found: 0.94, 11.366; 0.71, 11.182; 1.05, 11.007; and 1.13, 10.845. Using available $B(Q_4^2)$, $-\log h$ and $-\log[-1,1]$ data, formation constants defined according to the equilibrium



was calculated for $p=0, 1$ and 2. As can be seen from Fig. 7, a constant value of $\log \beta_{14} = 14.47 \pm 0.06$ was obtained, showing the $Si_4O_7(OH)_5^{3-}$ species to be predominating. Whether this species represents a mean composition of two or more tetramers (indicated by the $-\log h$ dependence of the chemical shift), *e.g.* $Si_4O_8(OH)_4^{4-}$ and $Si_4O_6(OH)_6^{2-}$ is difficult to predict from present data. Measurements at higher B -values, where the Q_4^2 -peak can be quantified within a broader $-\log h$ range, is necessary to evaluate a possible series of protonated cyclic tetramers.

Additional polysilicates with $q \geq 3$. Though a trisilicate of chain type as well as additional tetrasilicates probably exist we have not been able to quantify these species from available NMR-spectra. This is also valid for proposed penta-, hexa- and octamers. However, it is important to realize that with $B \geq 0.02 \text{ mol dm}^{-3}$, the sum $B(Q_1^0) + B(Q_2^1) + B(Q_3^2) + B(Q_4^2)$ accounts for $\leq 45\%$ of B when $-\log h$ is decreased to ≈ 11 . This means that significant amounts of additional polysilicates with $q \geq 3$ exist.

The average nuclearity (\bar{q}) of these silicates was determined by plotting $\log(\Delta B) = \log(B - (B(Q_1^0) + B(Q_2^1) + B(Q_3^2) + B(Q_4^2)))$ against $\log[-1,1]$ and $\log[-2,2]$, respectively (Fig. 8).

At the highest B -values studied, the slope of these lines gave $\bar{q}=2.9\pm 0.6$ and 4.3 ± 0.4 , respectively. The difference in these \bar{q} -values once more shows $[-1,1]$ -data to underestimate the nuclearity of the polysilicates. (This was also found in the evaluation of the dimer and cyclo trimer, *cf.* above). At lower B -values ($B\leq 0.02$ M) and the highest $-\log h$ values the uncertainty in B is too great to allow a determination of \bar{q} . However, it seems likely to assume a tetramer to be predominating at high B . The following formation constants were calculated: $\log k(2(-2,2)\rightleftharpoons(-4,4))=3.10\pm 0.04$ and $\log K(4(-1,1)\rightleftharpoons(-4,4))=5.02\pm 0.07$. These values correspond to $\log \beta_{44}=-33.00$ and -32.87 , respectively. Preliminary calculations also show that polysilicates with $q=3$ and 5 or 6 exist in minor amounts. However, present NMR-data are too few to allow a precise determination of their stability constants. Instead potentiometric data comprising a greater number of data points are used. In these calculations values of $[-1,1]$, $[-2,2]$ and $[-3,3(\text{cyclo})]$ given by the NMR-measurements are compared with corresponding ones given by the equilibrium model. In this way a model in agreement with the two data sets is searched for. The results of these calculations are presented below.

Potentiometric data. The potentiometric data cover the following concentration ranges: $1.0\leq Z\leq 1.1$, $11.0\leq -\log h\leq 12.2$ and $0.008\leq B\leq 0.048$ mol dm⁻³ (6 titrations, 65 experimental points).

To determine the stability of additional tri- and pentamers, these species were tested one at a time with a subsequent refinement of their formation constant (β_{pq}). As there is a strong correlation between β_{-21} and β_{pq} with $Z>1$, these constants were covaried. Furthermore, an error square sum $U_{\text{NMR}}=\sum(\log[-1,1]_{\text{calc}}-\log[-1,1])^2$ was calculated for each scheme of polysilicates tested, using combined emf-NMR data. The results of these calculations are given in Table 2. The results can be summarized as follows: i) The existence of a linear trimer is clearly demonstrated. A significant decrease in $U(\text{pot})$ and $U(\text{NMR})$ was obtained with $\sigma(E)=0.18$ mV and $\sigma(\log[-1,1])=0.007$. ii) The formation of the $(-3,3)$ and $(-4,4)$ species could very well be explained by a 'core+links' mechanism, where the dimeric species $(-2,2)$ is acting as the core and with a $\text{SiO}(\text{OH})_3^-$ link. The formation constants are given by the expression

$$\log \beta_{pq}=\log \beta_{-22}+(q-2) \log k(\text{link}); \text{ where } -p=q=3,4 \quad (10)$$

With $\log \beta_{-22}=-18.00\pm 0.06$ and $\log k(\text{link})=-7.41\pm 0.01$, a formation constant for the (-33) and (-44) complexes is obtained with high precision. It can be noted that this 'core+links' series gives values of $\log \beta_{-22}(-18.00)$ and $\log \beta_{-44}(-32.82)$ in good agreement with corresponding values obtained from combined NMR-emf data (-18.03 and -32.87 , -33.00 respectively). Attempts were also made to describe polysilicate formation by a polymerization of $\text{SiO}(\text{OH})_3^-$. However, an acceptable fit to data was not obtained in this case. iii) With regard to the existence of a pentamer (and/or higher polysilicates), the results are somewhat contradictory. An improvement of the fit to potentiometric data was obtained by assuming the pentamer to belong to the 'core+links' series with $\log \beta_{-55}=-40.24$. However, $U(\text{NMR})$ was increased unless $\log \beta_{-55}\leq -41.5$. This disagreement may be due to several reasons. This complex is formed in small amounts ($\leq 5\%$ of B) at the highest $-\log h$ values studied. Here the uncertainty in the potentiometric data are greatest. As $\sigma(E)\approx 0.2$ mV, the effects are small and are susceptible to small changes in k_w or j_{alk} . Using $[-11]$ data from the NMR measurements is also risky, as a small error in this concentration will cause a large error in β_{-55} due to the high nuclearity of this complex. Tentatively $\log \beta_{-55}\leq -41.5$ is

Table 2. Results of calculations on different schemes of polysilicates tested. In the calculations a modified version of the ETTR program was used. This version allows the testing of different 'core+links' mechanisms. The constants β_{pq} are defined in (5) and the errors given are $3\sigma(\log \beta_{pq})$. If no 3σ is given the corresponding constant has not been varied.

$\log \beta_{-22}$	$\log \beta_{-33}$	$\log \beta_{-44}$	$\log \beta_{-55}$	$\log \beta_{-21}$	U(POT)	$\sigma(E)/mV$	$U(NMR) \cdot 100$	$\sigma(\log[-11])$
-18.03 ^a	-	-33.00 ^a	-	-22.16(2)	3.80	0.22	11.9	0.090
-18.03	-25.30(16)	-33.00	-	-22.14(2)	2.27	0.18	6.7	0.068
-18.00(6)	-25.41	-32.82	-	-22.13(1)	1.89	0.17	7.0	0.069 ^b
-18.00	-25.41	-32.82	-40.62(22)	-22.12(1)	1.40	0.15	7.9	0.073
-18.00	-25.41	-32.82	≤ -41.5	-22.12(1)	1.76	0.16	7.0	0.069 ^c

^a Values calculated from combined emf-NMR data. In the calculation $\log \beta_{-12} = -7.75$, $\log \beta_{-33}(\text{cyclo}) = -25.40$ and $\log \beta_{-34}(\text{cyclo}) = -23.42$ were included.
^b Values according to a 'core+link' mechanism with $\log \beta_{-22} = -18.00 \pm 0.06$ and $\log k(\text{link}) = -7.41 \pm 0.01$ (cf. eqn. (10)).
^c Values given by a minimum in $U(\text{POT}) + U(\text{NMR}) \cdot 100$.

Table 3. A comparison between calculated and experimentally found values of Z , $[-1,1]$, $[-2,2]$ and $[-3,3(\text{cyclo})]$ in mmol dm^{-3} (combined emf-NMR data).

$B/\text{mmol dm}^{-3}$	$-\log h$	Z_{exp}	Z_{calc}	$[-1,1]_{\text{exp}}$	$[-1,1]_{\text{calc}}$	$[-2,2]_{\text{exp}}$	$[-2,2]_{\text{calc}}$	$[-3,3]_{\text{exp}}$	$[-3,3]_{\text{calc}}$
38.4	11.60	1.012	1.024	14.8	12.7	1.8	1.43	0.3	0.20
37.2	11.30	0.980	1.003	13.0	12.6	1.5	1.40	0.2	0.20
27.5	11.16	0.981	1.000	10.6	11.2	1.0	1.10	0.2	0.14
26.4	11.47	1.022	1.020	12.7	11.0	1.3	1.06	0.2	0.13
24.9	11.73	1.049	1.048	11.5	10.6	1.4	0.99	0.2	0.12
22.0	12.02	1.084	1.103	11.0	9.8	1.1	0.85	0.1	0.09
16.4	11.89	1.092	1.088	7.2	8.6	0.6	0.65	-	0.06
15.6	11.56	1.048	1.038	6.9	8.5	0.4	0.64	-	0.06
10.0	11.26	1.016	1.013	5.5	6.7	0.3	0.39	-	0.03
9.4	11.68	1.039	1.067	5.7	6.3	0.3	0.35	-	0.02
23.8	11.46	1.008	1.021	11.6	10.5	1.0	0.97	0.2	0.11
20.3	11.99	1.064	1.100	12.2	9.4	1.0	0.79	0.2	0.08
14.4	11.85	1.055	1.085	8.6	8.0	0.5	0.56	-	0.05
12.6	11.22	1.007	1.007	6.9	7.7	0.5	0.52	-	0.04

proposed, a value given by a minimum of $(U(\text{pot}) + U(\text{NMR}) \cdot 100)$, cf. Table 2. A careful study of stability and composition of polysilicates with $q > 4$ calls for a broader B -range to be studied. Using more concentrated ionic media, e.g. $3.0 \text{ mol dm}^{-3} \text{ NaCl}$, this will be possible. Measurements in such media are planned.

Table 3 shows the fit of the final model with experimentally $[-11]$, $[-22]$ and $[-33(\text{cyclo})]$ values.

DISCUSSION

A qualitative and quantitative description of polysilicate formation in alkaline ($11.0 \leq -\log h \leq 12.2$) solutions is presented. By means of combining potentiometric and ^{29}Si NMR methods, composition and stability of a series of polysilicates with the average charge per Si, $z = -1$ and nuclearities, $q = 2, 3, 4$ and 5 , were evaluated. The stability of a cyclic trimer, $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$, as well as a cyclic tetramer $\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$, were determined. Furthermore experimental data clearly show upon the existence of a dimer $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ and its protonated form $\text{Si}_2\text{O}_2(\text{OH})_5^-$. However, these species account for a minor part of existing polysilicates. Within the concentration ranges studied, the main polysilicate complex is tetrameric, tentatively of chain and branched forms as well as being a substituted cyclic trimer. Furthermore, a linear trimer $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$ and a pentamer are formed in small amounts. Due to the unfavourable experimental conditions the uncertainty of the stability constant of this pentamer is high. To show the speciation of the different silicates, distribution diagrams given in Fig. 9 were calculated. In these calculations, proposed speciation and equilibrium constants given in Table 4 were used.

As can be seen from these diagrams the prevailing species are the tetramer and the monomer $\text{SiO}(\text{OH})_3^-$. These findings are in accordance with the results obtained by Lagerström⁴ in $3.0 \text{ mol dm}^{-3} \text{ Na}(\text{ClO}_4)$ medium, where a tetramer also prevails. It can be noted that $\log \beta_{-22}$ and $\log \beta_{-44}$ from this study ($-18.00, -32.82$) and those given by Lagerström ($-18.12, -32.48$) are of the same magnitude.

The structural information obtained from the NMR-spectra makes it possible to comment on the stability of different forms of polysilicates. According to Table 4, the linear trimer is more stable than the cyclic form. For the equilibrium



Table 4. Proposed silicate species with corresponding formation constants β_{pq} defined according to the equilibrium $p\text{H}^+ + q\text{Si}(\text{OH})_4 \rightleftharpoons (\text{H}^+)_p(\text{Si}(\text{OH})_4)_q^{p+}$

p	q	Proposed formula	$\log(\beta_{pq} + 3\sigma)$
-1	1	$\text{SiO}(\text{OH})_3^-$	-9.473 ^a
-2	1	$\text{SiO}_2(\text{OH})_2^{2-}$	-22.12(1)
-2	2	$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$	-18.00(6)
-1	2	$\text{Si}_2\text{O}_2(\text{OH})_5^-$	-7.75(9)
-3	3	$\text{Si}_3\text{O}_6(\text{OH})_3^{3-}(\text{cyclo})$	-26.43(8)
-3	3	$\text{Si}_3\text{O}_5(\text{OH})_5^{3-}(\text{linear})$	-25.40(7)
-3	4	$\text{Si}_4\text{O}_7(\text{OH})_5^{3-}(\text{cyclo})$	-23.42(7)
-4	4		-32.81(8)
-5	5		≤ -41.5

^a Value from Ref. 1.

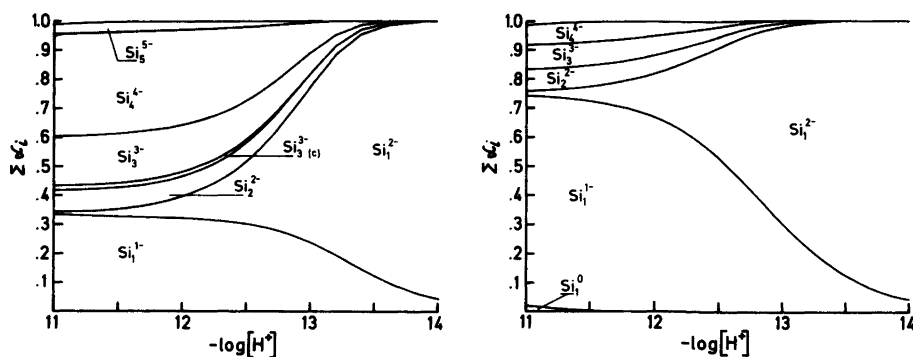


Fig. 9. Distribution diagrams for $B=0.01$ (a) and 0.05 mol dm^{-3} (b). The lines denote $\sum \alpha_i$ of the different species, α_i is obtained as the difference between successive lines. $-\log[\text{H}^+] > 12.2$ denote an extrapolated range. For brevity the species are written without O and OH. (c) denotes cyclic form. Furthermore species with $\alpha_i \leq 0.02$ have been omitted.

log $k=1.0$ is obtained. This is in accordance with data from the trimethylsilylation technique, where the cyclic trimer derivative seemed to be difficult to prepare in larger amounts even from crystalline solids known to contain Si_3O_9 rings (Dent Glasser *et al.*⁸).

As more than two different forms of the tetramer probably exist, it is impossible from present data to compare the stability of these. It can be concluded that the cyclic form is not the dominating tetramer. Probably the substituted cyclotrimer is less stable than chain and branched forms due to strain effects as postulated in the cyclotrimer (O'Keefe and Hyde²¹). This hypothesis is supported by the 'core+links' mechanism found to fit data so well with respect to the dimer, linear trimer and tetramer.

In less alkaline solutions $10.2 \leq -\log h < 11$, the $-\log h$ dependence of the Q_2^1 peak was used to evaluate the average charge per Si and stability of a protonated dimer. With log $\beta_{-12} = -7.75$, $pK_a(\text{Si}_2\text{O}_2(\text{OH})_5^-) = 10.3$ is obtained. Recently Cary *et al.*²² claim the existence of a disilicic acid. In dilute, nearly neutral aqueous solution, ^{29}Si NMR data show $B(Q_2^1)$ to be 6% of a 1.62 mM $\text{Si}(\text{OH})_4$ -solution. Using these data $\log k(2\text{Si}(\text{OH})_4 \rightleftharpoons \text{Si}_2\text{O}(\text{OH})_6 + \text{H}_2\text{O}) = 1.3$ is obtained, which gives $pK_a(\text{Si}_2\text{O}(\text{OH})_6) = 9.05$. This implies that the disilicic acid is an acid stronger than monosilicic acid ($pK_a = 9.47$). This behaviour is in accordance with findings by Schindler and Kamber,²³ who reported a pK_a value of 6.8 ± 0.2 for surface silanol groups of silica gel.

In Part 2¹ of this series log $\beta_{-21} = -22.07$ was reported. This value was obtained from data at low B ($B \leq 0.008 \text{ mol dm}^{-3}$) where effects due to the existence of polysilicates were neglected. Due to this, as well as to difficult experimental conditions, the uncertainty in log β_{-21} was estimated to ± 0.05 logarithmic units. In the present study β_{-21} has been determined at high B where polysilicate formation is extensive. Bearing in mind the complexity of equilibria on polysilicate solutions, the present value log $\beta_{-21} = -22.12 \pm 0.01$ is considered in good agreement with the value obtained at low B .

In a forthcoming publication an equilibrium analysis in less alkaline silicate solutions, close to the instability range (*cf.* Fig. 1) will be presented. Calculations of enthalpy values of the different polysilicates, based on precise calorimetric titrations are also in progress.

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