A Determination of the Formation Constant of $SiO(OH)_3^{-}$*

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Silicate solutions of very low total silicic acid concentration, B, have been studied at 25°C in an ionic medium of 0.5 M $Na(ClO_4)$ by a coulometric titration technique using a hydrogen electrode. The average number of OH^- bound per $Si(OH)_4$, Z, has been varied within the limits $0 \leq Z \leq 0.95$ and B, between 0.32×10^{-3} M and 1.32×10^{-3} M. In this range data could be explained with the equilibrium $Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$ and with log $*\beta_1 = -9.46 \pm 0.02$ (3σ). The calculation has been carried out by using the computer program Letagropvrid.[4] Table 2 gives a survey of the calculations.

In 1959 Lagerström[1] and one of the present authors (N.I.)[2] presented data on equilibrium measurements at 25°C of silicate solutions in the ionic media 0.5 m (molality) Na(Cl), 0.5 m $Na(ClO_4)$ and 3.0 m $Na(ClO_4)$. The hydrogen ion concentration, h, was measured with emf methods using a hydrogen electrode. These data, which covered total silicic acid concentrations, B from 0.0025 to 0.080 m and the Z-range from $Z \simeq 0.75$ up to $Z \simeq 1.4$ indicated, besides the mononuclear species $Si(OH)_4$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$, the presence of polynuclear species with a fairly low number, three or four, of Si-atoms. The equilibrium constants and the formula of the species proposed are given in Table 1. In order to get a "pure" mononuclear $Z(\log h)$-curve in titrations of silicic acid with OH^-, we found it necessary to go down in B-concentrations, at least below 2×10^{-3} M. In attempts to titrate these low B-concentrations by using the usual buret technique we found that the experimental uncertainty made a data spread, and Z could not be determined accurately enough for getting reliable values of the mononuclear equilibrium constants, $*\beta_1$ and $*\beta_2$, so the values given in Table 1 have been obtained by an extrapolation method.

The aim of the present work is to make equilibrium measurements in a series of silicate solutions of very low B-values (0.9471×10^{-3}, 0.9334×10^{-3}, 0.6605×10^{-3}, 0.6730×10^{-3}, 0.4386×10^{-3}, 1.323×10^{-3}, 0.3219×10^{-3} M)

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Table 1. Previously reported equilibrium constants for silicate equilibria (mainly mononuclear).

	0.5 m Na(Cl) (Ref. 2)	0.5 m Na(ClO₄) (Ref. 1)	3.0 m Na(ClO₄) (Ref. 1)
$Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$	$\log *\beta_1 = -\ 9.51 \pm 0.05$	$= -\ 9.46$	$= -\ 9.43$
$Si(OH)_4 \rightleftharpoons SiO_2(OH)_2^{2-} + 2H^+$	$\log *\beta_{21} = -22.12 \pm 0.15$	$= -22.02$	$= -22.14$
$4Si(OH)_4 \rightleftharpoons Si_4O_6(OH)_6^{2-} + 2H^+ + 4H_2O$	$\log *\beta_{24} = -12.37 \pm 0.20$	$= -12.57$	$= \ -$
$4Si(OH)_4 \rightleftharpoons Si_4O_8(OH)_4^{4-} + 4H^+ + 4H_2O$	$\log *\beta_{44} = \ -$	$= \ -$	$= -32.48$
$2Si(OH)_4 \rightleftharpoons Si_2O_3(OH)_4^{2-} + 2H^+ + H_2O$	$\log *\beta_{22} = \ -$	$= \ -$	$= -18.12$

$\log *\beta_1$ and $\log *\beta_{21}*\beta_1^{-1}$ given in *Stability Constants* [9] (emf data): Hägg, -9 and -13; Harman, -9.4 to -9.8 and -16.3; Joseph and Oakley, -10 and -12; Treadwell and Wieland, -9.7 and -12; Flint and Wells, -9.66 and -11.7; Oka, Kawagaki and Kadoya, -9.51 and -11.77; Miedreich (own data and recalculation from data of Boque, Hägg and Harman), -9.4 and -11.4; Greenberg (recalculation from data of Bacon and Wills), -9.85 and -11.8; Greenberg (recalculation from data of Harman), -9.7 and -11.9;

Proposed value in the present work: $\log *\beta_1 = -9.46 \pm 0.02$ (0.5 m Na(Cl)).

by using coulometric and emf methods and from these data try to deduce a reliable value of the equilibrium constant for the equilibrium $Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$. It is very difficult to get an accurate analytical value of the total silicic acid concentration, B, and therefore in the calculation of the equilibrium constant, $*\beta_1$, it was necessary to consider B as an additional unknown constant to be determined (besides $*\beta_1$). Also in this calculation an estimation of the impurity concentration [HX] was necessary. The calculations have been carried out by using the least squares-program Letagropvrid.[4]

For literature data about silicate equilibria in solution the reader is referred to summaries given in our previous papers in these series [1-3] and also recently by Thilo [5] and Aveston.[6]

REAGENTS AND ANALYSES

Sodium perchlorate, silicic acid solutions were prepared and analysed as described in Lagerström's paper.[1] The analytical determination of the silicic acid concentration in our stock solutions has not been carried out to the same extent and accuracy as described in Refs. 1 and 2, in most cases only an estimation has been made. However, in our computer calculation we have considered B as an additional unknown constant to be determined (besides the equilibrium constant), and this calculation has shown that the B-values, obtained in different titrations and with solutions prepared from the same B-stock, all gave (after recalculation) the same B-value for the stock.

The hydrogen electrodes were used as described in Ref. 1. *The Ag, AgCl-electrodes* were prepared according to Brown [7] by electrodepositing Ag on a Pt-foil and afterwards chloridizing the silver as anode in dilute HCl.

In order to prevent *dissolution* of SiO_2 and B_2O_3 from the titration vessels, all surfaces in contact with equilibrium solutions were treated with paraffin wax (*p.a.*).

EXPERIMENTAL METHOD

The hydrogen ion concentration has been measured electrometrically in a number of silicic acid solutions. As usual the measurements were carried out as a series of potentiometric titrations. In each of these the total silicic acid concentration, B, was kept constant; the hydrogen ion concentration, h, was decreased by adding OH^- with a coulometer. The coulometer arrangement was the following one:

$$-\text{Pt-gauze} \mid \begin{array}{c} \text{equilibrium} \\ \text{solution} = S \end{array} \mid \text{0.500 M NaCl} \mid \text{Ag}+ \qquad (A)$$
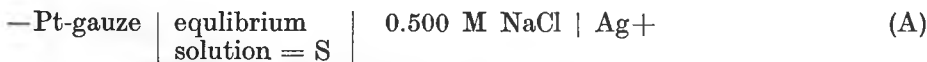
with the anode reaction: $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$, and the cathode reaction: $H^+ + e^- \rightarrow \frac{1}{2}H_2(g)$. The current was measured with a Leeds and Northrup Coulometric Analyzer, Catalogue No. 7960.

In order to keep the activity factors constant all solutions were made 0.5 M in respect to sodium ions by addition of $NaClO_4$. For the determination of the hydrogen ion concentration the following cell was used:

$$-H_2(\text{1 atm}) \mid S \mid RC + \qquad (B)$$

S is here an equilibrium solution of the general composition:

$$S:[Si]_{tot} = B \text{ M}; \quad [H^+]_{tot} = H \text{ M}; \quad [Na^+]_{tot} = 0.500 \text{ M}; \quad [Cl^-]_{tot} = 0.500 \text{ M}$$

where M denotes mole/liter, B the total concentration of Si and H the "analytical" hydrogen-ion excess concentration over $Si(OH)_4$ (a negative value of H means OH^--excess over $Si(OH)_4$). Along with these main components, the equilibrium solutions certainly contain an unknown amount of impurities which also consume OH^- giving an "impurity background" in the solutions. The total concentration of these impurities will in the following be denoted with HX.

As reference half cell (RC)

0.500 M $NaClO_4$ | 0.500 M Na^+, 0.480 M ClO_4^-, 0.020 M Cl^- | AgCl,Ag
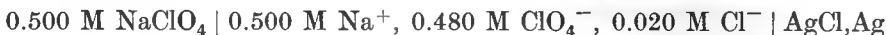
was used, and the salt bridge was of "Wilhelm" type.[8]

The emf of the cell (B) at 25°C can be written:

$$E = E_0 + 59.15 \ \log \ h + j_{alk}K_w h^{-1} + j_{ac}h \tag{1}$$

where E_0 is a constant, K_w the ionic product of water in 0.500 M $Na(ClO_4)$, and j_{alk} and j_{ac} constants in the expression for the liquid junction potential. It has been found [2] that $j_{ac} \simeq 83$ mV mole^{-1} and $j_{alk} \simeq 41$ mV mole^{-1} (valid in 0.5 m Na(Cl)).

From H, the analytical excess concentration of protons over $Si(OH)_4$, and the electrometrically measured h, the quantity:

$$BZ = h - H - K_w h^{-1} \tag{2}$$

may be calculated as a function of $\log h$. In (2) Z is the average number of OH^- bound per $Si(OH)_4$.

The use of these extremely low total silicic acid concentrations requires that the titration must be carried out in a way that prevents introduction of additional OH^--consuming impurities. For that reason the starting solutions in all of our titrations were prepared from distilled (in a distilling-apparatus with a tin cooler) and boiled (in this way free from CO_2) water, sodium chloride, and silicic acid sol. This solution was slightly acidic ($\simeq 1$ mM H^+), and the acidity was decreased by adding OH^- with the coulometer arrangement (A).

CALCULATIONS AND RESULTS

The calculation has been carried out by using the least-squares method and the computer-program Letagropvrid [4] (type 3 in the latest version). Input experimental data are the pairs (E,μ), E is the measured emf, and μ the number of microfaradays added. Together with these data also a set of first estimated or guessed parameters are given. These are:

The ks-parameters ("unknown constants" special for various titrations), H_0 (starting hydrogen excess concentration over $Si(OH)_4$), B (= total silicic acid concentration) and E_0 (= the constant in eqn. (1)), and
the k-parameters ("unknown constants" common to all points), here only *β_1 (= formation constant of $SiO(OH)_3^-$).

We have assumed that E is without error and that all errors are on the analytical excess concentration of protons over $Si(OH)_4$

$$H = H_0 - 0.001 \ \mu \ V^{-1} \tag{3}$$

where V is the volume.

For every point, h was evaluated from (1) and inserted in the equation:

$$H_{calc} = h - K_w h^{-1} - *\beta_1 B(h + *\beta_1)^{-1} \tag{4}$$

Then the quantity $(H_{calc} - H)^2$ was calculated on all experimental points giving the error squares sum:

$$U = \sum (H_{calc} - H)^2 \tag{5}$$

As "best" k- and ks-values we consider those giving the lowest error square sum (U_{min}). Then standard deviations have been determined as outlined in Ref. 10.

In order to estimate the impurity concentration, [HX], the computer calculation for each titration was divided into two parts, one "acid" part where $H_0(ac)$ and E_0 were determined, and one "alkaline" part where $H_0(alk)$, B and $*\beta_1$ were determined. We assumed that the difference $\Delta H_0 = H_0(ac) - H_0(alk) = $ [HX]. $pK_a(HX)$ was found to be $\simeq -5.5$. (A more recent program uses [HX] directly as a parameter). In Table 2 the results of the computer calculations are given.

With the "best" ks-values obtained in the computer calculations, values of $-\log h$ and Z have been calculated. These values for the different B are given in Table 2 and plotted as curves $Z(\log h)_B$ in Fig. 1. From this figure it is seen that all points fall very well on the curve calculated for the mononuclear reaction $Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$ with $\log *\beta_1 = -9.46$. For comparison Lagerström's data have also been given.

Comparing the $*\beta_1$-values of the present study with those reported in Refs. 1 and 2 we find a very good agreement. Other $*\beta_1$-values reported in the
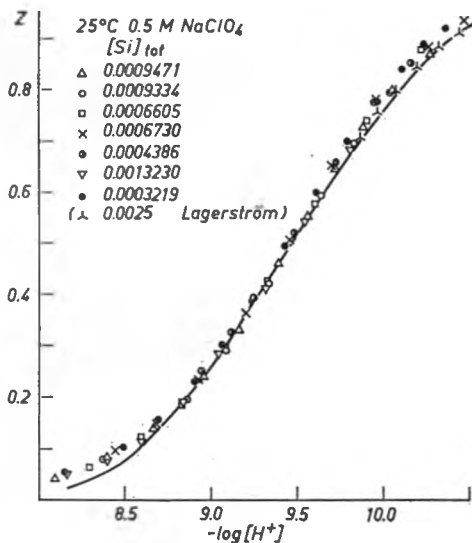

Fig. 1. Experimental data $Z(\log h)_B$ for equilibria of silicate solutions (25°C and 0.5 M Na(ClO$_4$)-medium). The full curve has been calculated for a mononuclear reaction with $\log *\beta_1 = -9.46$.

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Table 2. Result of computer-calculation on silicate data in 0.5 M $Na(ClO_4)$.

Titration No.	ks-Constants with standard deviations (σ)					k-Constants with standard dev.
	$(B \pm \sigma)10^3$ B in mole/liter	$E_0 \pm \sigma$	$(H_0(\text{ac}) \pm \sigma)10^3$	$(H_0(\text{alk}) \pm \sigma)10^{-3}$	$(\Delta H_0 = \text{HX}) \times 10^3$	$(*\beta_1 \pm \sigma)10^{10}$
1	0.9471 ± 0.0011	-355.86 ± 0.13	0.1692 ± 0.0005	0.1788 ± 0.0007	0.0096	3.421 ± 0.016
2	0.9334 ± 0.0005	-355.26 ± 0.13	0.1571 ± 0.0004	0.1661 ± 0.0003	0.0089	3.326 ± 0.008
3	0.6605 ± 0.0009	-355.69 ± 0.13	0.1680 ± 0.0005	0.1747 ± 0.0006	0.0066	3.429 ± 0.020
4	0.6730 ± 0.0036	-355.22 ± 0.18	0.1613 ± 0.0007	0.1653 ± 0.0037	0.0039	3.621 ± 0.089
5	0.4386 ± 0.0028	-354.09 ± 0.14	0.1539 ± 0.0006	0.1545 ± 0.0040	0.0006	3.630 ± 0.122
6	1.3230 ± 0.0027	-355.87 ± 0.10	0.1660 ± 0.0004	0.1761 ± 0.0008	0.0102	3.333 ± 0.020
7	0.3219 ± 0.0005	-356.05 ± 0.21	0.1726 ± 0.0009	0.1814 ± 0.0005	0.0088	3.620 ± 0.028

Proposed $*\beta_1$-value $= (3.483 \pm 0.129(3\sigma))10^{-10}$; $\quad \log*\beta_1 = -9.46 \pm 0.02$

literature (see Ref. 9 and Table 1) are in most cases of very low accuracy and usually not better than ± 0.5 "pH"-units. However, if we assume this error, the $*\beta_1$-value of the present work falls very well within the accuracy range of the most of earlier reported $*\beta_1$-values.

Accurately known $*\beta_1$- and $*\beta_{21}$-values are of greatest importance in silicate studies of higher B-values, where it is, without knowing the mononuclear constants, very difficult to find the composition and the formation constants of the polysilicates present (here the mononuclear reactions must be subtracted). In the future we hope to complete our earlier published silicate data with more data and data over a greater range of concentrations. At present, work is going on [11] in order to obtain mononuclear silicate data at high Z-

Table 3. Equilibrium data for silicates in 0.5 M $Na(ClO_4)$ at 25°C.

$B = 0.0009471$ M; Z, $-\log h$;	0.041,	8.104;	0.459,	9.394;	0.872,	10.268;
	0.080,	8.406;	0.554,	9.556;		
	0.139,	8.673;	0.647,	9.723;		
	0.237,	8.955;	0.727,	9.883;		
	0.332,	9.160;	0.802,	10.054;		
$B = 0.0009334$ M; Z, $-\log h$;	0.079,	8.388;	0.592,	9.639;		
	0.138,	8.668;	0.694,	9.830;		
	0.193,	8.859;	0.795,	10.056;		
	0.290,	9.091;				
	0.421,	9.340;				
$B = 0.0006605$ M; Z, $-\log h$;	0.064,	8.299;	0.578,	9.599;		
	0.120,	8.595;	0.739,	9.901;		
	0.186,	8.827;	0.860,	10.219;		
	0.294,	9.081;				
	0.424,	9.323;				
$B = 0.0006730$ M; Z, $-\log h$;	0.095,	8.450;	0.652,	9.710;		
	0.149,	8.685;	0.779,	9.962;		
	0.236,	8.932;	0.886,	10.260;		
	0.364,	9.203;	0.935,	10.469;		
	0.507,	9.460;	0.960,	10.639;		
$B = 0.0004386$ M; Z, $-\log h$;	0.249,	8.954;	0.777,	9.948;		
	0.324,	9.116;	0.853,	10.164;		
	0.394,	9.250;				
	0.524,	9.479;				
	0.659,	9.715;				
$B = 0.0013230$ M; Z, $-\log h$;	0.046,	8.167;	0.412,	9.324;		
	0.075,	8.407;	0.543,	9.551;		
	0.119,	8.604;	0.683,	9.808;		
	0.190;	8.846;				
	0.274,	9.054;				
$B = 0.0003219$ M; Z, $-\log h$;	0.050,	8.160;	0.392,	9.246;	0.842,	10.106;
	0.103,	8.496;	0.494,	9.426;	0.892,	10.238;
	0.155,	8.698;	0.600,	9.609;	0.923,	10.365;
	0.230,	8.909;	0.699,	9.786;		
	0.301,	9.069;	0.781,	9.955;		

values ($Z > 0.75$) and also to get a better experimental check of B and the impurity concentration, HX. These studies are carried out in 0.5 M Na(Cl) and 3.0 M Na(Cl)-medium.

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