Complex Formation in the Ternary Systems $Ca^{II}–H_4SiO_4–H_2O$ and $Mg^{II}–H_4SiO_4–H_2O$

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Calcium(II) and magnesium(II) complexes of partially deprotonated H_4SiO_4 have been investigated at 25 °C in solutions of constant ClO_4^- molarity (1 M) by computer-controlled coulometric titration using a hydrogen electrode. The experimental data could be explained assuming the following equilibria.

$$M^{2+} + H_3SiO_4^- \rightleftharpoons MH_3SiO_4^+;\ K_1 = [MH_3SiO_4^+]/[M^{2+}][H_3SiO_4^-]$$

and

$$M^{2+} + 2H_3SiO_4^- \rightleftharpoons M(H_3SiO_4)_2;\ \beta_2 = [M(H_3SiO_4)_2]/[M^{2+}][H_3SiO_4^-]^2$$

or

$$M^{2+} + H_2SiO_4^{2-} \rightleftharpoons MH_2SiO_4;\ \varkappa_1 = [MH_2SiO_4]/[M^{2+}][H_2SiO_4^{2-}]$$

For the individual equilibrium constants, the following values were obtained:

Ca^{2+}: $\log K_1 = 0{\cdot}39\ (\pm 0{\cdot}03)$; $\log \beta_2 = 2{\cdot}89\ (\pm 0{\cdot}07)$
$(\log \varkappa_1 = 3{\cdot}09)$

Mg^{2+}: $\log K_1 = 0{\cdot}64\ (\pm 0{\cdot}06)$; $\log \beta_2 = 3{\cdot}82\ (\pm 0{\cdot}08)$
$(\log \varkappa_1 = 4{\cdot}17)$

ORTHOSILICIC ACID is a major constituent of natural waters, and therefore a potential ligand for the metal ions present in natural aqueous systems. So far there is, however, little information concerning the ligand properties of deprotonated H_4SiO_4. The occurrence of relatively stable $FeH_3SiO_4^{2+}$ has been reported.[1]

Here we report the results of potentiometric titrations of H_4SiO_4 in the presence of Ca^{2+} and Mg^{2+}. In order to control the activity coefficients of the reacting species, the measurements were carried out in solutions of constant ClO_4^--molarity (1 M) consisting preponderantly of $NaClO_4$. The investigations have been made at 25 °C. The error limits given correspond to 2σ.

EXPERIMENTAL

In elaborating the experimental approach, the following limitations imposed by the system have been considered: In order to avoid the formation of polymer species, such as $Si_4O_6(OH)_6^{2-}$,[2] as well as the precipitation of amorphous silica [3] the total ligand concentration L did not exceed $2{\cdot}3 \times 10^{-3}$ M. Lower values of L were prevented by the presence of comparatively high concentrations of protolytic impurities originating from the inert salt. Regarding the low total concentration of the hydrogen ions present in our systems, coulometric generation of the added base was strongly indicated. In preliminary experiments it was found that the complexes formed are rather weak. Comparatively high concentrations of both the reacting metal ions and the inert salt were therefore required.

In the titration experiments, solutions S of the general composition: $[ClO_4^-] = 1$ M, $[M^{2+}] = B$ M, $[H^+] = H_i$ M, $[H_4SiO_4]_{tot} = L$ M, $[Na^+] = (1 - 2B - H_i)$ M, were reacted with coulometrically generated base. During the titration, the mass balance [equation (1)] is maintained. Since $-\log [H^+]$ did not exceed a value of 8·9, the concentration of $H_2SiO_4^{2-}$ ions could be neglected. The proton balance results in equation (2) where C = concentration (M) of added base, P = concentration (M) of protolytic impurity, $Ka(P)$ = average acid constant of the protolytic impurity (M). Kw = ionic product of water.

$$L = [H_4SiO_4] + [H_3SiO_4^-] + n\sum^{m}\sum^{n}[M_m(H_3SiO_4)_n{}^{(2m-n))+}] + q\sum^{p}\sum^{q}[M_p(H_2SiO_4)_q{}^{2(p-q)+}] \tag{1}$$

$$\begin{aligned} C' &= C - H_i + [H^+] - \frac{Kw}{[H^+]} - P\left(1 + \frac{[H^+]}{Ka(P)}\right)^{-1} \\ &= [H_3SiO_4^-] + n\sum^{m}\sum^{n}[M_m(H_3SiO_4)_n{}^{(2m-n)+}] + 2q\sum^{p}\sum^{q}[M_p(H_2SiO_4)_q{}^{2(p-q)+}] \end{aligned} \tag{2}$$

$$Z = \frac{n\sum^{m}\sum^{n}[M_m(H_3SiO_4)_n{}^{(2m-n)+}] + 2q\sum^{p}\sum^{q}[M_p(H_2SiO_4)_q{}^{2(p-q)+}]}{[M^{2+}] + m\sum^{m}\sum^{n}[M_m(H_3SiO_4)_n{}^{(2m-n)+}] + p\sum^{p}\sum^{q}[M_p(H_2SiO_4)_q{}^{2(p-q)+}]} \tag{3}$$

$$\beta_{n,m} = [M_m(H_3SiO_4)_n{}^{(2m-n)+}]/[M^{2+}]^m[H_3SiO_4]^n \tag{4}$$

$$k_{q,p} = [M_p(H_2SiO_4)_q{}^{2(p-q)+}][H_4SiO_4]^p/[M^{2+}]^q[H_3SiO_4^-]^{2q} \tag{5}$$

$$Z = \frac{n\sum^{m}\sum^{n}\beta_{n,m}[M^{2+}]^m[H_3SiO_4^-]^n + 2q\sum^{p}\sum^{q}k_{q,p}[M^{2+}]^p[H_3SiO_4^-]^{2q}[H_4SiO_4]^{-q}}{[M^{2+}] + m\sum^{m}\sum^{n}\beta_{n,m}[M^{2+}]^m[H_3SiO_4^-]^n + p\sum^{p}\sum^{q}k_{q,p}[M^{2+}]^p[H_3SiO_4^-]^{2q}[H_4SiO_4]^{-q}} \tag{6}$$

The analytical treatment of the experimental data is conventionally made with the aid of the formation function, equation (3). Introducing the stability constants

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[1] W. J. Weber, jr., and W. Stumm, *J. Inorg. Nuclear Chem.*, 1965, **27**, 237.

[2] G. Lagerström, *Acta Chem. Scand.*, 1959, **13**, 722.

[3] S. S. Jørgensen, *Acta Chem. Scand.*, 1968, **22**, 335.

[equations (4) and (5)] one obtains equation (6). Obviously the formation function is not directly accessible from the experimental data since

$$Z = B^{-1}(C' - [H_3SiO_4^-]) = B^{-1}(C' - Ka_1[H_4SiO_4][H^+]^{-1}) = B^{-1}\{C' - Ka_1(L - C' + q\sum^{p}\sum^{q} k_{q,p} [M^{2+}]^p[H_3SiO_4^-]^{2q}[H_4SiO_4]^{-q})[H^+]^{-1}\}$$

(Ka_1: First acid constant of H_4SiO_4).

The assumption $\sum^{p}\sum^{q} k_{q,p} = 0$ permits, however, the calculation of approximate values Z_a and $[H_3SiO_4^-]_a$. From a set of data (Z_a, $[H_3SiO_4^-]_a$), preliminary $k_{q,p}$ values are available. Further refinements are then obtained by iteration.

Solutions.—$NaClO_4$ Stock solution: Equivalent quantities of $HClO_4$ (70%, *p.A.* Merck) and Na_2CO_3 (*sicc.*, *p.A.* Merck) were mixed in a Teflon beaker. After decantation from undissolved Na_2CO_3 the solution was brought to pH 4 by adding excess $HClO_4$. The dissolved CO_2 was then expelled by passage of pure nitrogen.

Stock solutions of $Ca(ClO_4)_2$ were prepared in the same way, using $CaCO_3$ (*p.A.* Merck). Solutions of $Mg(ClO_4)_2$ were obtained from $Mg(ClO_4)_2$ (*p.A.* Merck). Double-distilled water, prepared in an all-quartz column, was used. The ClO_4^--contents of the stock solutions were determined by cation exchange and subsequent titration with standard NaOH solution using a weight burette.

In preparing the solutions S, a measured quantity of SiO_2 (Aerosil 500, 9·78% H_2O, no detectable impurities) was dissolved at 100 °C in a platinum crucible by adding an excess of 1M-NaOH. After addition of the appropriate amount of $NaClO_4$, the volume of the solution was brought to *ca.* 80% of its final volume. Preceding the addition of $M(ClO_4)_2$, the solution was acidified to pH 3. The crucial point of this procedure lies in the correct sequence of dilution and acidification of the concentrated alkaline silicate solution.[4]

Titration Technique.—All titrations were carried out at 25·0 ± 0·1 °C. Details concerning e.m.f. measurements and coulometric generation of acid and base are described elsewhere.[5] Instead of the glass electrode a hydrogen electrode was used consistently. Complications, caused by diffusion of Ag^+ into the test solution, were avoided by replacing the $AgClO_4$ solution in the reference compartment of the generator cell by NaCl.

The course of the titration was controlled with the aid of an on-line digital computer (HP 2114 B). The programs are described elsewhere.[6]

Digital voltmeter readings were taken every 2 min. The solutions were considered to be equilibrated, if six consecutive readings showed the same value. To obtain a further test for true equilibrium the titrations were carried out in such a way, that every addition of base was followed by addition of exactly half the amount of acid. Hence, each point of the titration curve could be approached from the acidic and the alkaline side. The resulting differences generally did not exceed 0·2 mV. Towards the end of the titration the potentials became unstable, indicating the beginning of a precipitation reaction. The occurrence of a solid phase was in some cases visually observable. However, the amount of precipitate obtained was not sufficient for further identification.

The first part of the titration curve which corresponds to the neutralisation of the excess of $HClO_4$ was used to calculate H_i and E_0 by Gran's method.[7]

Determination of Kw, P, *and* Ka(P).—*Kw* in 1M-$NaClO_4$ was obtained from separate titrations of slightly acidified $NaClO_4$ solutions. The figure obtained, log Kw = −13·77 ± 0·01, is in full agreement with reported values.[8] In the course of these titrations, the presence of protolytic impurities amounting to 3·5 (±0·5) × 10^{-5} mol per mol of $NaClO_4$ was detected. The direct determination of the apparent acid constant led to a value of p$Ka(P)$ *ca.* 6. This value, based on measurements in poorly buffered solutions, was, however, found not to be consistent with the first part of the Z– log $[H_3SiO_4^-]$ plots. The best fit could be obtained assuming p$Ka(P)$ = 7·7.

Evaluation of Ka_1 *and* Ka_2.—Ka_1 was evaluated from titrations with solutions of the composition $[ClO_4^-]$ = 1 M, $[H^+] = H_i$ M, $[H_4SiO_4]_{tot} = L$ M, $[Na^+] = (1 - H_i)$ M. Three different solutions, with $L = 2{\cdot}218 \times 10^{-3}$ M, $1{\cdot}548 \times 10^{-3}$ M, and $1{\cdot}043 \times 10^{-3}$ M were used. The resulting value log Ka_1 = −9·471 (±0·004) is very close to the figures obtained in $NaClO_4$ media of different ionic strengths {−9·46 (0·5M-$NaClO_4$ [9]); −9·43 (3M-$NaClO_4$ [2])}. Within this range, Ka_1 is remarkably independent of the prevailing ionic strength.

Ka_2 was estimated from literature data {log Ka_2 = −12·56 (0·5M-$NaClO_4$);[9] −12·71 (3M-$NaClO_4$) [2]}. By linear interpolation one obtains log Ka_2 = −12·59 (1M-$NaClO_4$). With regard to the uncertainty of this figure no error limits are given for values calculated with Ka_2.

RESULTS AND DISCUSSION

In the most general case [equation (6)], Z is a function of the variables $[H_3SiO_4^-]$, $[H_4SiO_4]$, and B. In the course of our titrations $[H_4SiO_4]$ remained, however, almost constant, hence we have equation (6a) where $k_{q,p}' = k_{q,p}[H_4SiO_4]^{-q}$.

$$Z = \frac{n\sum^{m}\sum^{n} \beta_{n,m}[M^{2+}]^m[H_3SiO_4^-]^n + 2q\sum^{p}\sum^{q} k_{q,p}'[M^{2+}]^p[H_3SiO_4^-]^{2q}}{[M^{2+}] + m\sum^{m}\sum^{n} \beta_{n,m}[M^{2+}][H_3SiO_4^-]^n + p\sum^{p}\sum^{q} k_{q,p}'[M^{2+}]^p[H_3SiO_4^-]^{2q}} \qquad (6a)$$

Moreover, in the absence of polynuclear species ($m = p = 1$) Z is a function of $[H_3SiO_4^-]$ only, leading to equation (6b).

$$Z = \frac{n\sum^{n} \beta_n[H_3SiO_4^-]^n + 2q\sum^{q} k_q'[H_3SiO_4^-]^{2q}}{1 + \sum^{n} \beta_n[H_3SiO_4]^n + \sum^{q} k_q'[H_3SiO_4^-]^{2q}} \qquad (6b)$$

Representative data (Z_a, log $[H_3SiO_4^-]_a$) out of 256 (Ca^{2+}), and 95 (Mg^{2+}) data points are shown in Figures

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[4] W. Stumm, H. Hüper, and R. L. Champlin, *Environmental Sci. and Technol.*, 1967, **1**, 221.

[5] H. Gamsjäger, W. Kraft, and P. Schindler, *Helv. Chim. Acta*, 1970, **53**, 290.

[6] U. Keller, J. Padel, H. Gamsjäger, and P. Schindler, *Chimia*, 1973, **27**, 90.

[7] G. Gran, *Analyst*, 1952, **77**, 661.

[8] R. Näsanen and P. Meriläinen, *Suomen Kem.*, 1960, **33** *B*, 149.

[9] H. Bilinski and N. Ingri, *Acta Chem. Scand.*, 1967, **21**, 2503.

1 and 2.* The coincidence of the curves obtained with different values for B confirms the absence of polynuclear complexes. If the functions $y = Z_a/(1 - Z_a)[H_3SiO_4^-]_a$ are plotted against $x = (2 - Z_a)[H_3SiO_4^-]_a/(1 - Z_a)$, straight lines $y = a + bx$ are obtained for both systems:

$$Ca^{II}:\ a = 2{\cdot}45\ (\pm 0{\cdot}15)\quad b = 770\ (\pm 166)$$

$$Mg^{II}:\ a = 4{\cdot}3\ (\pm 0{\cdot}6)\quad b = 6605\ (\pm 1274)$$

(In the course of the regression analysis, each point was weighted by dividing by a factor corresponding to the maximal experimental uncertainty.) The data can thus be explained,[10] assuming the following equilibria (7)—(9). Preliminary values for the individual equilibrium constants are then available from equations (10) and (11).

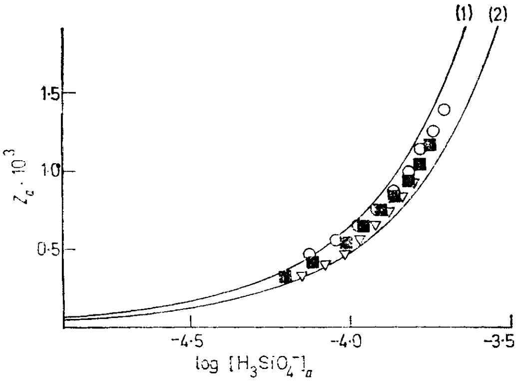

FIGURE 1 Complex formation in the system Mg^{2+}–H_4SiO_4–H_2O. Plot of Z_a as a function of log $[H_3SiO_4^-]_a$. (Every fourth point is shown.) Experimental conditions: 25 °C, $[ClO_4^-] = 1$M; ○ ($[Mg^{2+}] = 0{\cdot}05$M, $L = 2{\cdot}216 + 10^{-3}$M; ■ $[Mg^{2+}] = 0{\cdot}075$M, $L = 2{\cdot}306 \times 10^{-3}$M; ▽ $[Mg^{2+}] = 0{\cdot}10$M, $L = 2{\cdot}234 \times 10^{-3}$M; Curve (1) was calculated with log $K_1 = 0{\cdot}70$, log $\beta_2 = 3{\cdot}90$; curve (2) with log $K_1 = 0{\cdot}58$, log $\beta_2 = 3{\cdot}74$

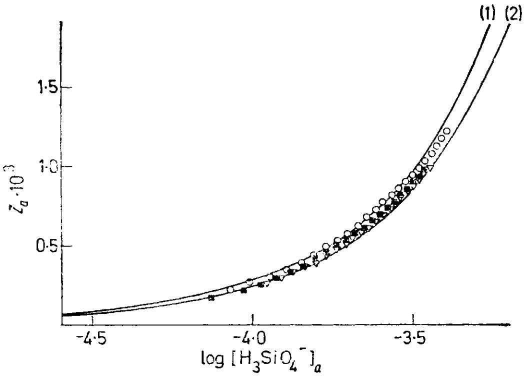

FIGURE 2 Complex formation in the system Ca^{2+}–H_4SiO_4–H_2O. Plot of Z_a as a function of log $[H_3SiO_4^-]_a$. (Every fourth point is shown.) Experimental conditions: 25 °C, $[ClO_4^-] = 1$M; ○ ($[Ca^{2+}] = 0{\cdot}15$M, $L = 2{\cdot}240 \times 10^{-3}$M; ■ $[Ca^{2+}] = 0{\cdot}20$M, $L = 2{\cdot}252 \times 10^{-3}$M; ▽ $[Ca^{2+}] = 0{\cdot}25$M, $L = 2{\cdot}225 \times 10^{-3}$M; Curve (1) was calculated with log $K_1 = 0{\cdot}42$, log $\beta_2 = 2{\cdot}96$, curve (2) with log $K_1 = 0{\cdot}36$, log $\beta_2 = 2{\cdot}82$

$$M^{2+} + H_3SiO_4^- \rightleftharpoons MH_3SiO_4^+$$

$$K_1 = [MH_3SiO_4^+]/[M^{2+}][H_3SiO_4^-] \tag{7}$$

$$M^{2+} + 2H_3SiO_4^- \rightleftharpoons M(H_3SiO_4)_2$$

$$\beta_2 = [M(H_3SiO_4)_2]/[M^{2+}][H_3SiO_4^-]^2 \tag{8}$$

$$M^{2+} + 2H_3SiO_4^- \rightleftharpoons MH_2SiO_4 + H_4SiO_4$$

$$k_1' = k_1[H_4SiO_4]^{-1} = [MH_2SiO_4]/[M^{2+}][H_3SiO_4^-]^2 \tag{9}$$

$$a = K_{1(a)} \tag{10}$$

$$b = (\beta_{2(a)} + k_{1(a)}') \tag{11}$$

On the basis of our measurements it is therefore not possible to estimate the individual contributions of the equilibria (8) and (9) to the formation function. Two limiting situations can, however, be discussed:

Assumption (I): $k_1' = 0$.—This assumption was already used for calculating Z_a and $[H_3SiO_4^-]_a$. Hence

$$K_1 = a \qquad \beta_2 = b \tag{12}$$

Assumption (II): $\beta_2 = 0$.—The assumption $k_{1(a)}' = b$ permits the iterative evaluation of Z and $[H_3SiO_4^-]$. Final values (Z_f, $[H_3SiO_4^-]_f$) were obtained after two cycles. The differences between Z_f and Z_a as well as $[H_3SiO_4^-]_f$ and $[H_3SiO_4^-]_a$ were found to be less than the experimental uncertainty. A graphical presentation of (Z_f, log $[H_3SiO_4^-]_f$) data was therefore omitted. Again plots of $v = Z_f/(1 - Z_f)[H_3SiO_4^-]_f$ against $u = (2 - Z_f)[H_3SiO_4^-]_f/(1 - Z_f)[H_4SiO_4] = (2 - Z_f)Ka_1/(1 - Z_f)[H^+]$ gave straight lines $v = c + du$:

$$Ca^{II}:\ c = K_1 = 2{\cdot}52\ (\pm 0{\cdot}13)\quad d = k_1 = 0{\cdot}943\ (\pm 0{\cdot}173)$$

$$Mg^{II}:\ c = K_1 = 4{\cdot}50\ (\pm 0{\cdot}55)\quad d = k_1 = 11{\cdot}35\ (\pm 2{\cdot}38)$$

k_1 is related to the more familiar stability constant $\varkappa_1$ by

$$\varkappa_1 = \frac{[MH_2SiO_4]}{[M^{2+}][H_2SiO_4^{2-}]} = k_1Ka_1/Ka_2$$

Numerical values for K_1, β_2 and $\varkappa_1$ are collected in the Table. The K_1-values tabulated are averages obtained from assumptions (I) and (II).

Logarithms of equilibrium constants
[25 °C, I = 1M-(Na)ClO$_4$]

	K_1	β_2	$\varkappa_1$
Ca^{2+}	0·39 (±0·03)	2·89 (±0·07)	3·09
Mg^{2+}	0·64 (±0·06)	3·82 (±0·08)	4·17

Although our experiments permit no discrimination of equilibria (8) in favour of (9), there are some indications that (9) is more likely than (8). Considering the relative magnitudes of K_1 and β_2 it turns out that the entering of the second ligand:

$$MH_3SiO_4^+ + H_3SiO_4^- \rightleftharpoons M(H_3SiO_4)_2$$

$$K_2 = [M(H_3SiO_4)_2]/[MH_3SiO_4^+][H_3SiO_4^-] = \beta_2/K_1$$

is largely favoured compared with the addition of the first ligand. This unusual behaviour ($K_2 \gg K_1$) has been observed in the case of Ag^I and Hg^{II} complexes. These cations exhibit a co-ordination number of two, whereas Ca^{2+} and Mg^{2+} are generally six-co-ordinated.

Comparing the preference of $H_3SiO_4^-$ for different cations, the series $Ca^{2+} < Mg^{2+} \ll Fe^{3+} < H^+$ is

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* The complete set of data is available from the authoıs on request.

[10] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, London, 1961.

obtained. The same order is observed with deprotonated surface silanol groups as ligands.[11]

Finally, the evaluated stability constants indicate that in natural water systems ($L \leqslant 10^{-4}$ M, $[Ca^{2+}] \leqslant 10^{-2}$ M, $[Mg^{2+}] \leqslant 5 \times 10^{-2}$ M, pH *ca.* 8·2) the occurrence of Ca^{II} and Mg^{II} complexes with $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ as ligands is negligible.

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[11] K. Kiouplidis and P. Schindler, unpublished data.