Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 28. Formation of Soluble Silicic Acid–Ligand Complexes as Studied by Potentiometric and Solubility Measurements

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Öhman, L.-O., Nordin, A., Sedeh, I. F. and Sjöberg, S., 1991. Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 28. Formation of Soluble Silicic Acid–Ligand Complexes as Studied by Potentiometric and Solubility Measurements. – Acta Chem. Scand. 45: 335–341.

Amorphous silica solubilities in the presence of organic (mannitol, oxalate, citrate, catechol) and inorganic (SO_4^{2-}) ligands have been studied in 0.6 M Na(Cl) medium at 25 °C. Apart from the catechol system, the experiments were performed at neutral pH with an equivalent ligand concentration of ≤ 0.6 M. In the presence of mannitol, the solubility of SiO_2(am) was found to decrease with increasing ligand concentration. With oxalate, citrate and sulphate, an increased solubility was observed. However, the effects were small and it was concluded that the formation of soluble Si complexes of these ligands under natural water conditions could be neglected.

With catechol, the measurements were performed under slightly alkaline conditions and a significant solubilization was noticed. Composition and stability of the species causing this solubilization was evaluated from precise potentiometric titration data in homogeneous $Si(OH)_4$–catechol solutions. These data cover the ranges $2 \leq -\log [H^+] \leq 10$; $0.002 \leq B \leq 0.004$ M and $0.002 \leq C \leq 0.015$ M, with C/B ratios of 1, 2, 2.5, 3 and 5 (B and C denote the total concentration of Si and ligand, respectively). With $-\log [H^+] \geq 7$, a hexacoordinated complex, SiL_3^{2-} is formed with log K $[Si(OH)_4 + 3H_2L \rightleftarrows SiL_3^{2-} + 2H^+ + 4\ H_2O] = -10.44 \pm 0.029$ (3σ). The recorded solubilization of amorphous silica was fully explained by the formation of this species.

Owing to the abundance of silicon in crustal rock, silicon compounds are a major component of suspended matter derived from weathering processes. Soluble silicon compounds in natural waters are also fairly abundant, but their concentrations are controlled by processes such as adsorption, precipitation, complexation and biological removal.[1,2] These geo- and biogeochemical processes are far from fully understood. Attempts to understand the mobility, transport and bioavailability of silica in natural waters requires a knowledge of the chemical forms, or species, which are present. Despite this well recognized requirement, it is true to say that for many elements, including silicon, their speciation in the natural environment is still a subject of debate.

With regard to silicon in natural waters, silicic acid, $Si(OH)_4$, is commonly referred to as the prevailing form. Since the pH of most natural waters are well below 9, the dissociation reactions of $Si(OH)_4$ can be neglected.[3] However, the situation is somewhat complicated by the question as to what extent silicic acid is present in polymeric forms and/or complexed to metal ions or organic ligands. The presence of a disilicic acid at total Si-concentrations below the solubility limit of amorphous silica has been established.[4] Furthermore, recent findings by Bennett and Siegel[5] have shown an increase in the solubility of quartz in the presence of dissolved organic compounds. These compounds were produced by the biodegradation of petroleum and consist largely of a complex mixture of aliphatic and aromatic acids as well as of hydroxy- and keto-acids. Based on these observations, Bennett and Siegel[5] proposed that silica was complexed and mobilized by certain organic acids in waters having close to neutral pH.

Later Bennett *et al.*[6] studied the dissolution kinetics of quartz in dilute aqueous solutions containing different well-defined organic ligands. Some of these ligands were found to increase significantly the velocity by which silicon was released from the solid phase. By using UV difference spectroscopy, they also investigated the possibility of $Si(OH)_4$–organic acid complexation in the aqueous phase. From their results they claim that dissolved silica is complexed by citrate, oxalate and pyruvate at pH 7, whereas no complexation was found between $Si(OH)_4$ and acetate, lactate, malonate or succinate. More recently, the possible aqueous interactions between silicic acid and oxalate has also been the subject of an investigation employing laser Raman and FT–IR spectroscopies.[7] Highly supersaturated

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solutions with regard to amorphous silica were used, and the existence of soluble $Si(OH)_4$/oxalate species was interpreted from the occurrence of new product bands in the spectra. It was also reported that the presence of this species delayed the precipitation of gelatinous silica. However, in neither of these investigations were any attempts made to evaluate the composition and/or stability of the aqueous complexes.

The aim of the present work is to identify different ligand classes able to form soluble complexes with dissolved silica. Based upon solubility measurements of freshly precipitated amorphous silica, the ligand types polycarboxylates (oxalate and citrate), polyols (mannitol) and *ortho*-diphenols (catechol) will be studied. Furthermore, a sulphate–silicic acid complex which has been postulated by Marshall and Chen[8] will also be studied. In systems with significant increases in the solubility of SiO_2(am), a detailed equilibrium analysis, based upon potentiometric titrations of $Si(OH)_4$–ligand mixtures, will be performed.

Experimental

Chemicals and analysis. Sodium chloride (Merck p.a.) was dried at 180 °C and used without further purification. Fresh sodium chloride solutions were always used in the measurements.

The dilute hydrochloric acid (Merck p.a.) was standardized against tris(hydroxymethyl)aminomethane (TRIZMA-base, Sigma, p.a.). Dilute sodium hydroxide was prepared from "oljelut" (50 % NaOH and 50 % H_2O) and standardized against acid.

Silicic acid solutions were prepared by dissolving $Na_2SiO_3 \cdot 9H_2O$ (Baker p.a.) in an acidic medium solution with an H^+-excess. Preceding the addition of sodium silicate, the volume of the medium solution was about 90 % of its final volume. In this way clear solutions with a total concentration of silicic acid, $B \leq 0.01$ mol dm^{-3}, were easily prepared. Freshly prepared silicic acid solutions were used for each experiment and no attempts were made to store a stock solution. Determination of the total silicate concentration, as well as of the carbonate impurity in Na_2SiO_3, was performed as outlined elsewhere.[3] Omitting the water content, the composition of this sodium silicate was found to be $Na_2(SiO_3)_{0.977}(CO_3)_{0.023}$.

Suspensions containing ca. 0.03 mol of amorphous silica per dm^3 were prepared from $Na_2SiO_3 \cdot 9H_2O$ and standardized hydrochloric acid. The resulting $-\log [H^+]$ values in these suspensions were 7.4. Before their use in the solubilization experiments, the suspensions were equilibrated under stirring for 48 h.

Sodium oxalate ($Na_2C_2O_4$, Merck p.a.), sodium citrate ($Na_3C_6H_5O \cdot 2H_2O$, Merck p.a.), mannitol ($C_6H_{14}O_6$, Difco certified) and sodium sulfate (Na_2SO_4, Merck p.a.) were all used without further purification.

Pyrocatechol (1.2-dihydroxybenzene, Merck p.a.) was sublimed before use. Stock solutions were prepared by dissolving $C_6H_4(OH)_2$ in standardized HCl and the content checked potentiometrically. The titrated amount was in full agreement (within 0.1 %) with that expected from weighing. After preparation, the solution was used within a few days to avoid effects from the slow oxidation which occurs in acidic solution.

Since pyrocatechol (H_2L) is extremely sensitive to oxidation in neutral and alkaline solution, special efforts had to be made to protect it from oxygen. Therefore, during the titrations, performed in airtight vessels with gas outlet beneath a liquid surface, as stream of argon or hydrogen was bubbled through the solution for stirring and for maintaining an inert or reducing atmosphere. The gas, from a cylinder, was first bubbled through a vanadium (V^{III}, V^{IV}) solution in order to remove traces of oxygen and then through solutions of 10 % NaOH and 10 % H_2SO_4 in order to remove acid and alkaline impurities. Finally, before the gas came into contact with the equilibrium solution, it was passed through solutions of pure ionic medium.

Before the addition of OH^- ions, the vessel was deaerated with argon for at least 2 h. In the case of backward titrations, two burettes containing OH^- and H^+ ions, respectively, were mounted on the vessel before the experiment, and $-\log [H^+]$ was raised to an appropriate value with OH^- ions before the titration with H^+ ions.

With these precautions, no discolouring of the solution due to oxidation could be observed during the measurements. Without them, the solutions immediately turned dark brown in colour and no stable potentials could be obtained.

All equilibrium solutions had the general composition $[Si(OH)_4]_{tot} = B$ M, $[H^+]_{tot} = H$ M, $[H_2L]_{tot} = C$ M, $[Na^+]_{tot} = 0.6$ M and $[Cl^-]_{tot} = 0.6+H$ M. H is calculated over the zero-level H_2O, $Si(OH)_4$ and H_2L.

Methods. All measurements were performed at 25.00 ± 0.05 °C in an ionic medium consisting of 0.6 M Na(Cl).

The solubilization measurements. The experiments were performed using 60 ml Pyrex glass tubes. Various amounts of the different ligands, together with the amount of NaCl needed to give the final suspensions a sodium content of 0.6 M, were directly weighed into the tubes. Thereafter, 50 ml of the silica-containing suspension was added and the tubes were encapsuled using rubber caps. In the experiments employing catechol, the tubes were deaerated with argon gas and the sodium hydroxide added immediately before sealing the tubes. In each system, the solution containing the highest ligand concentration was also prepared using the same volume of distilled water to certify that their solubilities were not exceeded.

The suspensions were then allowed to equilibrate under continous stirring for more than 3 weeks. This was achieved by means of an end-rotation test tube holder running at about 30 r.p.m. At the end of the experiments, the suspensions were centrifuged and the clear solutions analyzed for silicon using an ARL 3410 ICP-spectrometer.

The EMF measurements. The measurements were carried out as a series of potentiometric titrations. The free H^+ concentration, h, was determined by measuring the EMF of cell (I)

$$-\text{Ag,AgCl|0.6 M NaCl||equilibrium solution|glass electrode} + \quad \text{(I)}$$

The EMF of the cell (expressed in mV) may be written as eqn. (1), where E_j is given by eqn. (2) and is the liquid

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

$$E_j = -77h + 42k_w h^{-1} \quad (2)$$

junction potential at the junction 0.6 M NaCl||equilibrium solution.[3] E_0 is a constant which is determined within each titration in solutions of known h or immediately before and after each titration in separate H^+ solutions of known compositions. k_w (1.875×10^{-14} M^2) is the ionic product of water in 0.6 M Na(Cl) medium.[3]

During the titrations, the quotient between the total concentrations of $Si(OH)_4$, B, and catechol, C, was kept constant.

The measurements were performed within the limits $2 \leq -\log h \leq 10$; $0.002 \leq B \leq 0.004$ M; $0.002 \leq C \leq 0.015$ M, covering the C/B ratios: 1, 2, 2.5, 3 and 5. To test the reproducibility and reversibility of equilibria, both forward (addition of OH^-) and backward (addition of H^+) titrations were performed. Furthermore, dilution experiments (titrations in which pure medium solution was added) were also performed.

Data treatment. In order to visualize experimental data, curves showing $Z_B(-\log h)$ were calculated. Z_B is defined as the average number of H^+ released per $Si(OH)_4$ and is given by the relation $Z_B = (h-H-k_w h^{-1})/B$.

The equilibria to be considered in the present study can be divided into three groups:

(i) the binary catechol equilibrium

$$H_2L \rightleftharpoons HL^- + H^+; \qquad \beta_{-1,0,1}$$

(ii) the hydrolytic equilibria of $Si(OH)_4$

$$Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+; \qquad \beta_{-1,1,0}$$

$$Si(OH)_4 \rightleftharpoons SiO_2(OH)_2^{2-} + 2H^+; \qquad \beta_{-2,1,0}$$

$$2Si(OH)_4 \rightleftharpoons Si_2O(OH)_6 + H_2O; \qquad \beta_{0,2,0}$$

$$2Si(OH)_4 \rightleftharpoons Si_2O_2(OH)_5^- + H^+ + H_2O; \qquad \beta_{-1,2,0}$$

$$2Si(OH)_4 \rightleftharpoons Si_2O_3(OH)_4^{2-} + 2H^+ + H_2O; \qquad \beta_{-2,2,0}$$

Table 1. Binary and ternary equilibria in the three-component system H^+–$Si(OH)_4$–pyrocatechol (H_2L). The formation constants $\beta_{p,q,r}$ are defined according to the reaction $pH^+ + qSi(OH)_4 + r(H_2L) \rightleftharpoons H_p(Si(OH)_4)_q(H_2L)_r^p$.

$p\ q\ r$	Proposed formula	$\log(\beta_{p\ q\ r} + 3\sigma)$	Ref.
−1 1 0	$SiO(OH)_3^-$	−9.473	3
−2 1 0	$SiO_2(OH)_2^{2-}$	−22.12	3
0 2 0	$Si_2O(OH)_6$	1.2	4
−1 2 0	$Si_2O_2(OH)_5^-$	−7.75	4
−2 2 0	$Si_2O_3(OH)_4^{2-}$	−18.00	4
−1 0 1	HL^-	−9.198	9
−2 1 3	SiL_3^{2-}	−10.44 ± 0.03	This work
0 1 0	SiO_2(am)	2.76 ± 0.03	This work

For these equilibria, results evaluated earlier in this series[3,4,9] will be used. Equilibrium constants, valid in 0.6 M Na(Cl) medium, are given in Table 1.

(iii) three-component equilibria of the general form

$$pH^+ + qSi(OH)_4 + r(H_2L) \rightleftharpoons$$

$$H_p(Si(OH)_4)_q(H_2L)_r^p; \qquad \beta_{p,q,r}$$

In the evaluation of the three-component experimental data, the binary complex models under (i) and (ii) were considered as known, and all effects above this level were treated as being caused by ternary species. The mathematical analysis of data was performed with the least-squares computer program LETAGROPVRID[10] (version ETITR[11,12]). p,q,r-triplets and corresponding equilibrium constants that "best" fit the experimental data were determined by minimizing the error-squares sum $U = \Sigma(H_{calc} - H_{exp})^2$. The standard deviations $\delta(H)$ and $3\delta(\log \beta_{p,q,r})$, obtained in the LETAGROP calculations, were defined and calculated according to Sillén.[13,14] The computations were performed on a CD CYBER 850 computer.

Results and discussion

Solubilization measurements. The recorded concentrations of aqueous silicon in suspensions equilibrated with various concentrations of mannitol, oxalate, citrate and sulfate are presented in Fig. 1. This figure shows that while high concentrations of oxalate, citrate and sulfate all result in a slight solubilization of the amorphous silica, increasing concentrations of mannitol result in a decreasing concentration of silica in the aqueous phase. The reason for this solubility decrease is unclear; however, since these solutions were all made up from 0.6 M NaCl plus various amounts of uncharged mannitol, a possible reason is that high concentrations of mannitol could influence the activity of water in these suspensions.

The solubility of amorphous silica in the pure 0.6 M NaCl medium was evaluated from six individual samples treated

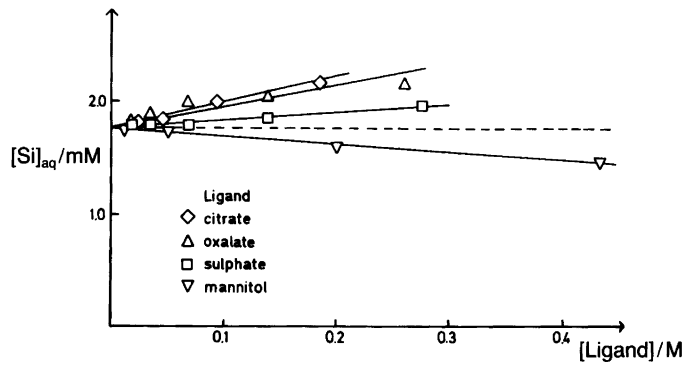

Fig. 1. The solubility of amorphous silica as a function of the total ligand concentration. The broken line denotes the solubility of SiO_2(amorphous). Full lines are calculated using the following log *K* values: 0.11 (citrate), 0.04 (oxalate) and −0.42 (sulfate), respectively.

in an identical manner to the ligand-containing samples. The value found, $(1.77 \pm 0.05)\times10^{-3}$ M, is in fair agreement with the value previously reported by Marshall and Warakomski[15] (1.86×10^{-3} M). As previously shown by Cary *et al.*[16] and Sjöberg *et al.*,[4] small amounts (ca. 3 % of *B*) of a disilicic acid are formed in these saturated amorphous silica solutions. By taking this equilibrium into consideration, log *K* [$2Si(OH)_4 \rightleftharpoons Si_2O(OH)_6 + H_2O$] = 1.2, a solubility product for SiO_2 (am) of log $K_{so} = -2.76 \pm 0.03$ was obtained. This value is in good agreement with literature values.[17]

The increased solubility recorded in the presence of oxalate, citrate and sulfate can be interpreted as due to the occurrence of weak aqueous Si–ligand complexes. With regard to the sulfate ion, such a complex has previously been suggested by Marshall and Chen.[8] Their investigation, which covered the temperature range 25–350 °C, was based on differences in silica solubility between sodium chloride and sodium sulfate solutions of equal sodium ion concentration. They assumed that the difference in solubility was caused by a species $Si(OH)_4{\cdot}SO_4^{2-}$ and calculated that the equilibrium constant for the reaction $Si(OH)_4 + SO_4^{2-} \rightleftharpoons Si(OH)_4{\cdot}SO_4^{2-}$ was $10^{-0.54}$ M^{-1} at 25 °C. When we applied the same hypothesis to the present data, in which the sodium ion concentration was kept constant at 0.6 M and the chloride ions were gradually exchanged for sulfate ions, we obtained an equilibrium constant of $10^{-0.42}$ M^{-1}. Given the very small solubilization effects recorded in the present work (Fig. 1), this value can be regarded as being in full agreement with the value previously reported by Marshall and Chen.[8]

For the suspensions containing oxalate and citrate, somewhat larger effects were recorded. Taking the same approach also for these data, i.e. the assumption that the increased solubility was caused by the formation of a soluble $Si(OH)_4{\cdot}L^{n-}$ species, the resulting equilibrium constants became $10^{0.04}$ M^{-1} and $10^{0.11}$ M^{-1} for oxalate and citrate, respectively.

By applying this equilibrium constant for the species $Si(OH)_4{\cdot}oxalate^{2-}$ to the experimental conditions employed by Marley *et al.*[7] ($[Si(OH)_4]_{tot} = [oxalate]_{tot} = 0.2$ M), a calculated $Si(OH)_4{\cdot}L^{2-}$ concentration of 0.031 M is obtained. Since this concentration is likely to be visible spectroscopically, our findings can be regarded as in qualitative agreement with the spectra presented in their article. However, in view of the low stability of this species, we find it much more probable that it is formed via hydrogen bonding than via ester formation. The assumption of an ester-bonded species $(OH)_3Si{-}O{-}C{=}O(CO_2)^-$, as suggested by Marley *et al.*,[7] was also contradicted by the fact that titrations of a 0.4 M $SiO_2(OH)_2^{2-}$ solution with 0.4 M oxalic acid and with 0.8 M HCl, respectively, yielded identical titration curves, i.e. no extra release of OH^- ions was recorded in the oxalic acid titration.

Also, with regard to the oxalate stabilization of oversaturated silicic acid solutions, our findings are in contradiction to those of Marley *et al.*[7] Thus, while they claim that the amorphous silica gel formation is significantly delayed by the presence of oxalate, we found only small differences in gelling time between solutions neutralized by HCl and those neutralized by oxalic acid. The implication of this observation is, in agreement with the calculation above, that the soluble $Si(OH)_4{\cdot}L^{2-}$ species only constitutes a minor fraction of the total silicon concentration and that the major fraction of silicon in these heavily oversaturated solutions can be found as different mono- and polynuclear silicic acids.

Under natural water conditions, in which the aqueous silicon concentration seldom exceeds the solubility of amorphous silica and in which the total concentration of organic carboxylic acids is of the order of 0.1×10^{-3} M, an inspection of Fig. 1 directly reveals that the weak silicon complexes with oxalate and citrate can be neglected. Also, under the experimental conditions used by Bennett *et al.*,[6] in which an increase in the dissolution kinetics of quartz was recorded, the formation of soluble $Si(OH)_4{\cdot}L^{n-}$ species is of minor importance. It is therefore a likely assumption that the main interactions between silicon and polycarboxylates does not take place in the aqueous phase, but rather on the surface of the dissolving particles. The effects recorded by Bennett *et al.* might also in part have been caused, not by the presence of polycarboxylate ions, but by the presence of the charge-balancing sodium ions. As was recently shown by Dove and Crerar,[18] a sodium (or potassium)ion concentration of 0.05 mol kg^{-1} (at 100–300 °C but with a constant activation enthalpy) increased the dissolution rate of quartz at near-neutral pH by a factor of 30.

With regard to the *ortho*-diphenolic compound catechol, a somewhat different experimental approach was taken. As this ligand has been claimed to form soluble Si-complexes in slightly alkaline solutions,[19] it was decided to perform the solubilization measurements at a constant catechol concentration of 50×10^{-3} M and at variable concentrations of hydroxide ions. The results of these measurements are illustrated in Fig. 2 and show that alkaline catechol-con-

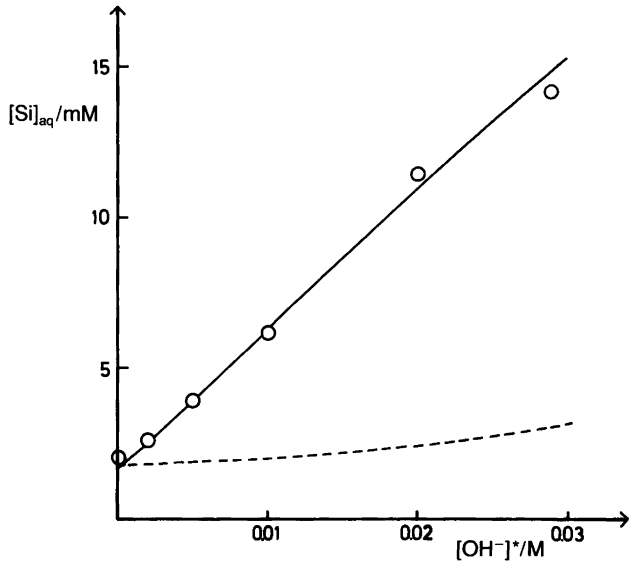

Fig. 2. The results obtained from the solubilization measurements of amorphous silica in the presence of pyrocatechol (at a constant concentration of 50×10^{-3} M) at variable concentrations of hydroxide ions, The broken curve denotes the calculated solubility in absence of complexation between $Si(OH)^4$ and pyrocatechol. The full line was calculated using $\log \beta_{-213} = -10.44$.

taining solutions are much more effective solubilizers for amorphous silica than the previously tested substances.

Since the presence of hydroxide ions, however, does promote the formation of hydrolytic silicate species, these effects cannot, *a priori*, be taken as evidence for the existence of soluble Si–catechol complexes. The potential influence of such hydrolytic effects was therefore modelled by considering the solubility product of amorphous silica, the pK_a of catechol and the hydrolytic equilibria of $Si(OH)_4$. This modelling, which was performed by using the computer program SOLGASWATER,[20] is illustrated by the dashed curve in Fig. 2 and shows that the solubilization recorded in the experiments by far exceed those predicted by the model. It can therefore be concluded that catechol posesses a solubilizing effect of amorphous silica under these circumstances, i.e. that soluble Si–catechol complexes are definitely present in these suspensions. To evaluate the stoichiometries and stabilities of these complexes, a series of potentiometric titrations was undertaken.

Potentiometric measurements in the system H^+–$Si(OH)_4$–catechol. Experimental potentiometric data comprise 11 titrations with 119 points. The total concentration of $Si(OH)_4$ was kept at a low level ($B \leq 0.004$ M) to avoid extensive formation of polysilicic and -silicate complexes. At present detailed information about the composition and stability of such species is not available, hence it is not possible to make corrections for their presence in the mathematical treatment of data.

As can be seen from Fig. 3, the H^+–$Si(OH)_4$–H_2L system is characterized by an instability range ($6 \leq -\log h \leq 8$) in which stable EMF potentials could not be obtained within a reasonable time (< 10 h). At $-\log h \leq 8$, equilibration times of 2–5 h were frequently found.

To determine the composition and stability of the ternary complex(es) a LETAGROP analysis of data was performed as an unbaissed *p,q,r* analysis (systematic testing of different *p,q,r* combinations) with the simple assumption that only one ternary complex is formed. The result of this analysis is given in Fig. 4. As can be seen, the lowest error squares sum, *U*, was found for the complex $H_{-2}[Si(OH)_4](H_2L)_3^{2-}$, with $\log \beta_{-2,1,3} = -10.44 \pm 0.029$. This calculation

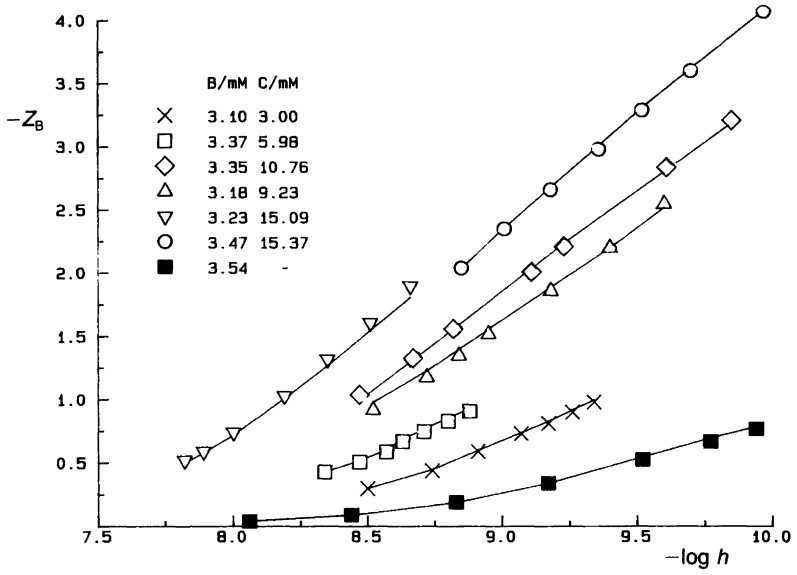

Fig. 3. Part of the experimental data in the H^+–$Si(OH)_4$–pyrocatechol system plotted as curves Z_B ($-\log h$). The solid lines have been calculated with the constants proposed in Table 1.

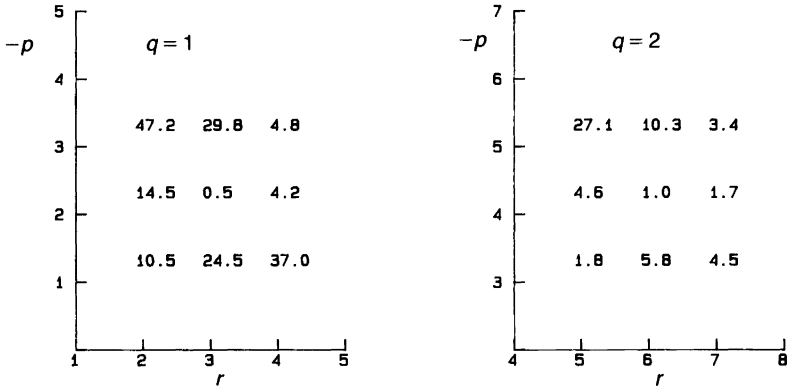

Fig. 4. Results of *p,q,r* analysis on data in the system H^+–$Si(OH)_4$–pyrocatechol. The figure gives error squares sums $U_H(pr)_q \times 10^3$ assuming one ternary complex.

ended at σ(H) = 0.06 mM, indicating a good fit to experimental data. Although the remaining residuals, $H_{calc} - H_{exp}$, showed no systematic trend, speciation models given by the stepwise formation of the complexes (−2,1,*n*) (*n* = 1,2,3), as well as by (0,1,1) and (0,1,2) together with (−2,1,3), were also tested. However, in neither of these cases was any significant improvement of the fit obtained.

Furthermore, when this single species with its corresponding equilibrium constant was added to the speciation scheme for the H^+–SiO_2(am)–catechol system, a full explanation to the solubility data given in Fig. 2 was obtained (cf. the calculated solid curve). These data can therefore be regarded as an independent confirmation of the speciation model.

The anionic species SiL_3^{2-}, which is formed according to reaction (3), was also characterized from ^{29}Si-NMR measurements. The chemical shift observed for this species, −144.7 ppm vs. TMS, is a clear indication of a hexacoordinated complex in which the ligands are bidentately bound.[21] A crystal structure determination by Flynn and Boer[22] has shown the existence of a corresponding complex in the solid phase compound.

$$Si(OH)_4 + 3H_2L \rightleftharpoons SiL_3^{2-} + 2H^+ + 4H_2O \qquad (3)$$

According to the reaction given above, the formation of the SiL_3^{2-} complex is favoured by high −log *h* values. As can be seen from Fig. 5, the complex is mainly formed in aqueous solutions with −log $h \geq 7.5$. This implies that catechol or a catechol-like binding site of a humic substance is a potential complex former to silicic acid in natural waters. However, to obtain significant amounts of the tris-catecholate species, quite high ligand concentrations are needed. This is clearly seen from the predominance area diagram given in Fig. 6. Here, stable solid phases are quartz or amorphous silica, respectively.

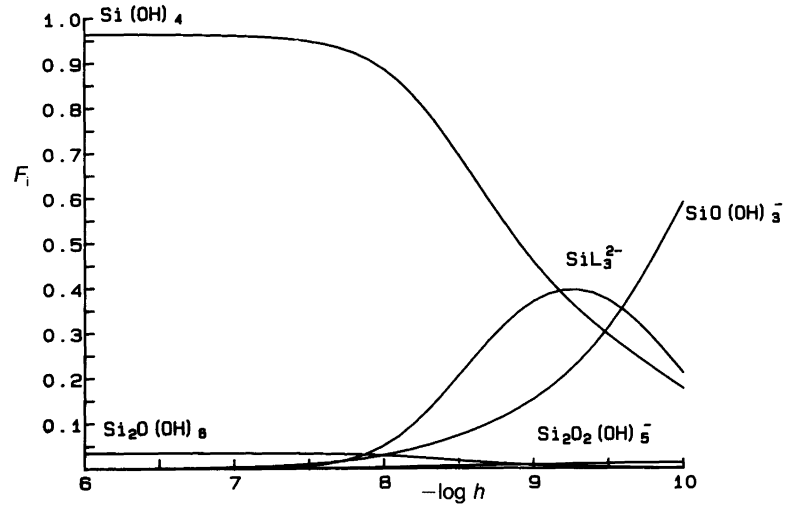

Fig. 5. Distribution diagram F_i(−log *h*) in the H^+–$Si(OH)_4$–pyrocatechol system. F_i is defined as the ratio between Si in a species and the total Si concentration. The calculation was made at *B* = 0.0012 M and *C* = 0.006 M.

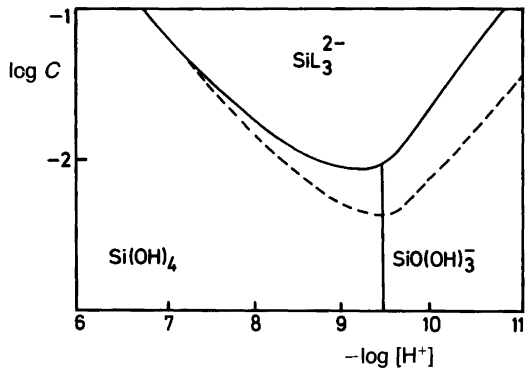

Fig. 6. Predominance area diagram showing predominating species in the presence of quartz (log $K_{so} = -4$, broken curve) and amorphous silica (log $K_{so} = -2.76$, full curve).

Conclusions

The different dissolution experiments performed in the present study have clearly shown an increased solubility of amorphous silica in the presence of sulphate ions and in the presence of the organic ligands catechol, oxalate and citrate. Except for the catechol system, however, the interaction with the different ligands was found to be very weak. Ligand concentrations as high as 0.3 M for SO_4^{2-} and 0.1 M for citrate and oxalate, respectively, were found necessary to yield a 10% increase in the solubility of SiO_2(am) at neutral pH. These same figures will, of course, also apply to yield a 10% increase in the solubility of quartz. It can therefore be implied that the concentration of the corresponding species in natural water environments are probably negligible.

With catechol, the solubilization effect was quite significant. In this system, composition and stability of a SiL_3^{2-} complex was evaluated from precise potentiometric data of homogeneous $Si(OH)_4$–ligand solutions.

From ^{29}Si-NMR spectra, it was concluded that Si is coordinated in an octahedral manner. The complex is formed with $-\log h \geq 7.5$ and indicates that *ortho*-diphenolic binding sites are potential complex formers to silicic acid in natural waters.

Acknowledgements. This work forms part of a program financially supported by the Swedish Natural Science Research Council.

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Received July 13, 1990.