Solubility and Dissolution Kinetics of Precipitated Amorphous Silica in 1 M NaClO₄ at 25°C

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When suspended in 1 M NaClO₄, various preparations of precipitated amorphous silica rapidly yielded supersaturated solutions. However, after several months the same solubility, 77.7 ± 1.1 mg SiO₂/l at 25°C, was found for all preparations, and also when starting with supersaturated solutions. Silica previously equilibrated with the solution did not give a supersaturated solution when resuspended. In this case the rate of dissolution was found to be proportional to the cube of $(c_{equilibrium} - c)$. The rate of precipitation from the supersaturated solution formed when suspending silica preheated to 700°C was proportional to the cube of $(c - c_{equilibrium})$. The dissolution-precipitation behaviour observed is concordant with the formation of an ordered surface layer consisting of silica or hydrated silica, the nature of which is unknown.

It was shown by Alexander *et al.*[1] and by other workers [2-4] that amorphous silica dissolves in acid and neutral aqueous solutions at ordinary temperature and pressure in the form of low-molecular silicic acid. "Equilibrium" concentrations in the range of 0.0018—0.0027 M (110—160 mg SiO₂/l) are attained in days, weeks, or months, the time depending mainly on surface characteristics. Judged from its reaction with molybdic acid, the only dissolved species existing at equilibrium is monomeric silicic acid, $Si(OH)_4$.[1,5-7]

In alkaline solution the solubility of silica is much larger than in acid and neutral solution, mainly due to ionization of silicic acid.[1] Equilibria in alkaline 0.5 m NaClO₄, 3.0 m NaClO₄, and 0.5 m NaCl unsaturated in silica were extensively studied by Lagerström [8] and by Ingri [9] by emf methods. Their data were best explained by the existence of only tetranuclear silicate ions in addition to monomeric species.

The present investigation has been undertaken in order to obtain more precise knowledge of the solubility of precipitated amorphous silica and of the dissolution and precipitation processes. The medium — 1 M NaClO₄ — was chosen in order to allow comparison with future experiments in alkaline solution at constant ionic strength.

EXPERIMENTAL

Reagents. Sodium perchlorate was Riedel-de Haën, "rein", once recrystallized from 70 % ethanol. $NaClO_4$ was determined by drying to constant weight at 120°C or by acidimetric titration of a solution which had passed through a H^+-saturated cation exchanger.

All silica preparations were made from sodium silicate ($Na_2SiO_3,9H_2O$, Baker, analyzed reagent). Other chemicals were of analytical grade. Polyethylene utensils were used when possible. Volumetric flasks for silica determinations were kept in 30 % HCl when not in use.

Analytical. Dissolved silica was determined as the unstable β-silicomolybdic acid by the following modification of the method of Govett.[5] To 10 ml 1 M $HClO_4$ in a 50 ml volumetric flask was added 2—10 ml clear silica solution, 10 ml 0.3 M Na_2MoO_4 and deionized water to volume. Extinction of this solution was measured against a reagent blank in a 1 cm cell at 400 nm on a Beckman DU spectrophotometer 2—10 min after addition of molybdate. In some cases extinctions of unknowns and standards were followed for longer periods of time. Also a few determinations as the stable α-silicomolybdate [10] were made. For that purpose the above mentioned acid silicomolybdate solutions were heated on a steam bath for 3 h, cooled, made to volume, and extinctions were measured at 400 nm. Silica standards were made from Merck's "Quarz, gewaschen u. geglüht, zur Analyse". 60.1 mg of a powdered (in agate) and ignited sample was heated with molten NaOH for 30 min in a Ni-crucible and, when cold, dissolved in water, neutralized with $HClO_4$, and filled up to 1000 ml. Preliminary experiments showed that $NaClO_4$ concentrations up to 0.4 M in the final solution had no influence on the extinction at 400 nm.

Gravimetric silica determinations were made in the following way. A known volume (~300 ml) of solution from which the silica precipitate had been removed by centrifugation was passed through a H^+-saturated cation exchanger (Dowex 50 or Amberlite IR 120). Effluent plus washings were evaporated on a steam bath in polyethylene and finally on a hot plate in a platinum or a porcelain crucible. The dry residue was ignited to constant weight at 1200°C. When the volume was about 20 ml (fuming perchloric acid) the liquid turned black (dissolved ion exchanger?). When a platinum crucible was used the residue did not become white on ignition and the Pt was superficially attacked. In porcelain no attack was observed and the ignited residue was perfectly white.

Dissolution experiments were carried out in 250 ml rubber-stoppered polyethylene bottles rotated end-over-end (25 rpm) in a water thermostat at 25.00 ± 0.02°C. Most experiments were made in duplicate.

Supersaturated solutions were prepared in the following way. Sodium silicate was dissolved in water and acidified to pH 4—5 with a known amount of $HClO_4$. Solid $NaClO_4$ and water were then added to give 1 M $NaClO_4$.

Precipitated silica was prepared by the following procedures:

1. 50 mmoles $Na_2SiO_3,9H_2O$ was dissolved in water and neutralized with $HClO_4$. $NaClO_4$ and water were added to obtain 1000 ml solution, 1 M with respect to $NaClO_4$. In this solution silica flocculated within a few hours. After standing at least two months the suspension was centrifuged and the precipitate used for dissolution experiments without further treatment.

2. A Na_2SiO_3-solution was neutralized with $HClO_4$ and the liquid evaporated to dryness

   a. on a steam bath and the residue washed with water and dried for two days at 120°C. Some samples were heated to a higher temperature.

   b. by standing in the air. The air-dry residue was washed on a Büchner funnel with 70 % ethanol, 99 % ethanol, and acetone and was air dried.

3. A 0.050 M Na_2SiO_3-solution was passed through a H^+-saturated cation exchanger (Dowex 50 or Amberlite IR 120). In the effluent Na^+ could not be detected by flame photometry. Effluent + washings were evaporated on a steam bath and heated to the temperature indicated.

RESULTS

Equilibria. In all experiments started from the supersaturated side silica flocculated out within $1-5$ h. After one day silica concentrations were $95-110$ mg SiO_2/l. The highest concentration was obtained where the initial degree of supersaturation was highest. Equilibrium was attained very slowly $(3-5$ months). In Table 1 are given average values of five silica determinations (β-silicomolybdate) on each sample made during another 10 months. Silica determinations as α-silicomolybdate made at the same time as the last of the β-determinations agreed with these. The rest of the equilibrated solutions was then used for gravimetric silica determinations. The agreement between the three analytical methods shows that the equilibrated solutions do not contain polymer silicic acid unable to react with molybdate within 2 min. Samples I and II were kept in the thermostat and occasionally analyzed during further 17 months. Silica concentrations did not alter significantly during this period.

Table 1. Equilibrium concentrations of silica in initially supersaturated solutions.

Experiment No.	Initial concentration mg SiO_2/l	Equilibrium concentration, mg SiO_2/l	
		spectrophotometric	gravimetric
I	600	78.8	
II	600	77.8	
III	1200	78.1	} 78.1
IV	1200	78.1	
V	2400	78.9	} 69.6
VI	2400	78.3	
VII	4800	78.1	} 72.3
VIII	4800	78.1	

Table 2. Equilibrium concentrations of silica in the liquid phase of various suspensions. Solid/solution ratio, 4.8 g SiO_2/l 1 M $NaClO_4$.

Experiment No.	Silica sample			mg SiO_2/l	
	Preparation procedure	Preheating temperature, °C	H_2O %	spectro-photometric	gravimetric
1	2a	1100	0	6.3	
2	2a	1100	0	7.4	
3	2a	120	15.7	77.0	} 64.7
4	2a	120	15.7	74.9	
5	2b	not heated	29.4	77.9	} 78.4
6	2b		29.4	78.7	
7	1		n.d.	78.7	} 74.2
8	1		n.d.	76.4	

n.d. = not determined

In the experiments of Table 2 all the solutions, except 1 and 2, became supersaturated with silica within 2 days (85—100 mg SiO_2/l). Concentrations then decreased slowly and were constant after 6—9 months, 7 and 8 requiring the shortest time. The ignited specimens, 1 and 2, were shown by X-ray diffractometry to be mixtures of cristobalite and tridymite. Constant silica concentrations were here obtained after 4 months. The solubility of cristobalite at 25°C was found by Fournier and Rowe [11] by extrapolation of high temperature data to be 27 mg SiO_2/l. The solubility of tridymite at room temperature does not seem to have been determined.

The precipitates from experiments V and VI were resuspended in 1 M $NaClO_4$ and the dissolution process followed. Here no supersaturated solution was formed and equilibrium was attained in less than 2 months. (V 77.3, VI 76.3 mg SiO_2/l).

The average of the solubility values obtained in experiments I—VIII, 3—8, and V and VI resuspended is 77.7 ± 1.1 mg SiO_2/l.

The dissolution process. The initial phases of the dissolution of various preparations are shown in Figs. 1 and 2. It is seen that in these experiments a supersaturated solution is always formed when a silica, not previously equilibrated with the ionic medium, is suspended. The degree of supersaturation is higher the higher the ratio solid silica/solution. The initial dissolution rate
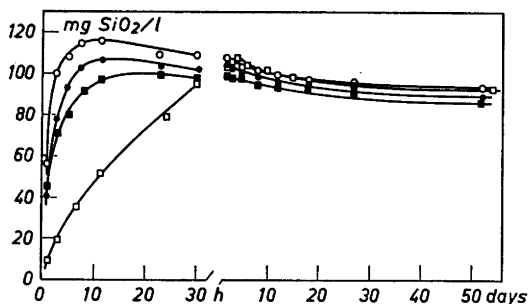

Fig. 1. Dissolution of amorphous silica in 1 M $NaClO_4$. Preparation procedure 3, preheated to 120°C: ■ 4.8, ● 9.6, ○ 19.2 g SiO_2/l. Preparation procedure 1: □ ~2.5 g SiO_2/l.
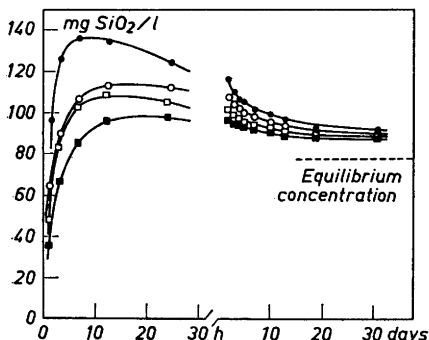

Fig. 2. Dissolution of amorphous silica in 1 M $NaClO_4$. Preparation procedure 3, preheated to 450°C: ■ 4.8, □ 9.6 g SiO_2/l, preheated to 700°C: ○ 4.8, ● 9.6 g SiO_2/l.

and the degree of supersaturation is also increasing with increasing preheating temperature in the range 120—700°C. Also with silica prepared by procedure 1 a supersaturated solution was formed. With silica which had previously been equilibrated with the ionic medium a supersaturated solution was not obtained and the dissolution process was entirely different. When trying to find an expression for the rate of dissolution in this case the best fit was obtained when assuming the following cubic relation (Fig. 3),

$$dc/dt = k_u(c_e - c)^3 \tag{1}$$

$$k_u = \frac{1}{2t}\left[\frac{1}{(c_e - c)^2} - \frac{1}{c_e{}^2}\right] \tag{2}$$

where k_u is the rate constant and $c_e = 77.7$ mg SiO_2/l is the equilibrium concentration. In the present case $k_u = 1.2 \times 10^{-4}$ l^2 mg^{-2} h^{-1} was obtained graphically. A cubic relation did also best fit the descending portion of the dissolution curve of the silica heated to 700°C (Fig. 4),

$$-dc/dt = k_s(c - c_e)^3 \tag{3}$$

$$k_s = \frac{1}{2t}\left[\frac{1}{(c - c_e)^2} - \frac{1}{(c_0 - c_e)^2}\right] \tag{4}$$

where k_s is the rate constant and c_e has the same value as in (1) and (2). c_0 is the hypothetical concentration at the time $t = 0$. In contrast to the initial dissolution rate k_s does not seem to increase with increasing silica/solution ratio. From the curves of Fig. 4, $k_s = 4.4 \times 10^{-6}$ l^2 mg^{-2} h^{-1} (4.8 g SiO_2/l) and $k_s = 3.4 \times 10^{-6}$ l^2 mg^{-2} h^{-1} (9.6 g SiO_2/l) was obtained. In the other experiments the degree of supersaturation was not high enough to verify eqn. (3). According to the values found for k_u and k_s equilibrium should be virtually attained
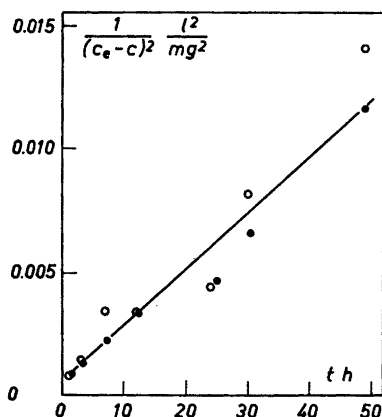

Fig. 3. Dissolution of amorphous silica previously equilibrated with the ionic medium. O and ● are duplicate runs.
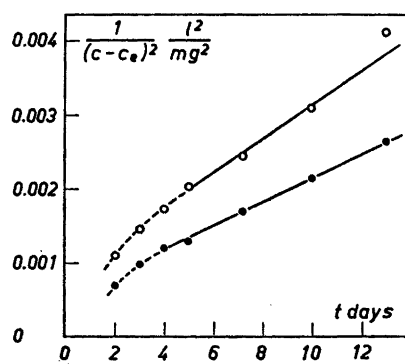
Fig. 4. Precipitation from the supersaturated solution of amorphous silica prepared by procedure 3, preheated to 700°C. O 4.8, ● 9.6 g SiO_2/l.

within one year in the former, but only after at least 20 years in the latter case. Stöber [12] found that the rate of dissolution of quartz and coesite (a very dense, high temperature-high pressure phase of silica [13]) in hydrofluoric acid also followed a cubic equation.

DISCUSSION

The dissolution behaviour observed is to be expected when one solid phase dissolves with the subsequent precipitation of another more stable solid phase. Similar curves are found, for example, in the slaking of lime,[14] *i.e.* when solid CaO is dissolved in water with subsequent formation of crystalline $Ca(OH)_2$. In the present case it does not seem likely that the solid as a whole is changed into another well defined phase. The solids from the equilibrated suspensions showed no trace of an X-ray diffraction pattern, but a definite solubility might well be defined by a much thinner surface layer than is required to give an X-ray pattern. Since the equilibrium concentration does not depend on the solid/solution ratio and is the same whether attained from unsaturated or supersaturated side, it is safe to conclude that the same thermodynamically well defined surface is developed in all the experiments.

From early X-ray measurements and from considerations on the surface density of OH-groups, a cristobalite- or tridymite-like surface structure of amorphous silica has been suggested.[15-17] The solubility data obtained here do, however, not confirm this suggestion, since the solubility of cristobalite, as stated above, is only 27 mg SiO_2/l.[11] The solubility values obtained in experiments 1 and 2 suggest a still lower solubility of tridymite. Keatite, a crystalline silica phase which can be obtained from gelatinous silica under hydrothermal conditions in the presence of small amounts of alkali, has also been suggested as forming a surface layer on amorphous silica in water.[13] The solubility of keatite does not seem to have been determined. Another possibility is that the solubility-defining surface layer consists of an ordered layer of a hydrated silica. Crystalline "silicic acid", $H_2Si_2O_5$, has been prepared by elution of crystalline $Na_2Si_2O_5$ with acid.[18] The solubility of $H_2Si_2O_5$ was not determined.

The initial dissolution rate is found to increase with increasing preheating temperature up to 700°C. At that temperature about two thirds of the chemisorbed water originally present is removed as seen from a thermogravimetric curve. This dissolution behaviour contradicts the opinion of Holt and King,[19] that the rapid initial dissolution is caused by a surface layer of highly hydrated silica. The present results are in better accordance with the view that the solid silica — whether formed by spontaneous flocculation in the liquid or suspended after some drying and heating procedure — is a highly unstable phase, which dissolves rapidly with subsequent formation of a more stable phase. Heating above 120°C causes a loss of surface hydroxyls and is thereby producing strained Si—O—Si bonds. Therefore the surface becomes more and more unstable the higher the temperature and consequently the dissolution rate increases. Heating to 1000°C produces a mixture of crystalline phases, each defining its own solubility and dissolution rate.

There is a marked difference between the dissolution behaviour in 1 M $NaClO_4$ and in pure water. The solubility is much more reproducible and

considerably lower (77.7 mg $SiO_2/l = 1.36 \times 10^{-3}$ mol/kg H_2O) than in water (110—160 mg $SiO_2/l = (1.8-2.7) \times 10^{-3}$ mol/kg H_2O). In preliminary experiments in water [20] equilibrium concentrations of 108—121 mg SiO_2/l were found in initially supersaturated solutions and 135—140 mg SiO_2/l in initially unsaturated solutions. The initial dissolution was not very rapid in these experiments and a supersaturated solution did not develop in the initially unsaturated samples. Greenberg and Price [3] found no appreciable difference in the solubility of amorphous silica when going from pure water to 0.1 M NaCl or 0.1 M Na_2SO_4. Lagerström [8] and Ingri [9] found the same equilibrium constants for silicate equilibria in alkaline 3.0 m $NaClO_4$, 0.5 m $NaClO_4$, and 0.5 m NaCl, where no solid phases were present. A possible explanation might be that either the sodium ion or the perchlorate ion exerts a catalytic effect in the formation of the solubility-defining surface layer. This hypothesis might be tested by making dissolution experiments in other salt solutions.

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