Preliminary kinetic data of silicic acid species prior to the formation of exoskeletal structures

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ABSTRACT

This report shows preliminary information on the presence of silicic acid species for formation of exoskeletons in order to mimic diatomaceous shell structures. Equilibrium constants (K_p) determined by electro-spray ionisation mass spectrometry (ESI-MS) are denoted as $lnK_{p,ESI-MS}$. They provide reasonable consistency to established UV–Vis results ($lnK_{p,UV-Vis}$). $lnK_{p,UV-Vis}$ is determined by the UV–Vis active silico-molybdate complex. Measurements done are at 25 °C and 60 °C and pH = 12 and 13 for each temperature. Based on these results, time-dependent evolution of prominent silicic acid species is determined by means of its equilibrium molar fraction Si^{x-T-pH}, with x being the number of silica atoms in the species of concern. The report also presents forward and reverse rate constants based upon the Euler numerical integration convergence towards equilibrium molar fractions. This report considers five species from monosilicic acid, Si^{1-T-pH} to a branched pentasilicic acid Si^{5-T-pH}.

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1. Introduction

Diatoms require monosilicic acid ($Si(OH)_4$) prior to its uptake to build exoskeletal shells (Sullivan, 1976) and capture a significant amount of human annual carbon emissions (Khatiwala et al., 2009). Only monosilicic acid is able to bind and build ornate hierarchical structures, which facilitate the capture of carbon emissions (Coradin and Lopez, 2003; Currie and Perry, 2007; Schaefer, 1989). Polymerization of silicic acid to a size of 1 to 3 nm exerts a negative charge on the diatom wall. This leads only to an encapsulation of the organic substance with respect to charge attraction and impair the facilitation of carbon capture.

Mimicking the further carbon capture situation in a synthetic manner may provide a method to reduce human carbon emissions. Monosilicic acid has never been isolated perfectly due to its instability (Marsh et al., 1975) and polymerization occurs rapidly, which attains equilibrium concentrations in the form of mixed species. Equilibrium time is extremely long to achieve high amounts of $Si(OH)_4$ at conditions of ocean waters (Krauskopf, 1956). Ocean water conditions are mild and hence the low global solubility of 200 μM (Tréguer et al., 1995). In these conditions, monosilicic acid is in abundance. However, at higher concentrations, polymerization to polymeric silicic acid species occurs (see Fig. 1) (Iler, 1979; Marsh et al., 1975).

Kinetic data to monitor the silicic acid condensation is hence vital to facilitate diatoms for $Si(OH)_4$ uptake and mimic natural carbon emission sequestration conditions. The first challenge is to elucidate the number of prominent species occurring in the solution. In order to get enough silicic acid concentration, higher pH-values are chosen (Sefcik and McCormick, 1997). The electro-spray ionisation mass spectrometry (ESI-MS) method proves to be a good method to elucidate individual silicic acid species at equilibrium (Pelster, 2007; Pelster et al., 2006, 2007a, 2007b).

Results of reactive silico-molybdate are also used to acquire consistent results (Iler, 1979). However, the individual species are destroyed upon solution preparation and only indirect kinetic data are available (Marsh et al., 1975). These indirect data are however useful for further determination of kinetic data in this report, which is the second challenge. After much research (Icopini et al., 2005; Marsh et al., 1975; O'Connor and Greenberg, 1958), the rate constant is known to be of the fourth order (Icopini et al., 2005).

This report hence considers four polymeric species in addition to monosilicic acid, which is confirmed by electro-spray ionisation mass spectrometry (ESI-MS) results. The temperature dependence on silicic acid polymerization is also useful and taken into account for each pH-value considered. As equilibrium conditions exist, consideration of forward and reverse reactions is compulsory.

2. Procedures

2.1. Experimental

2.1.1. ESI-MS procedure

0.1 M NaOH is consistently mixed with distilled water to attain aqueous solutions of pH = 12 and 13. The respective solution is added

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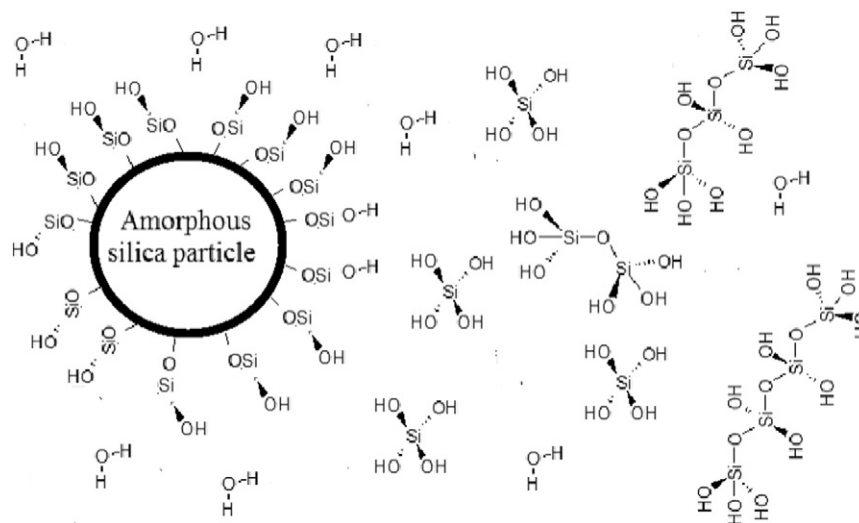(J. Tamahrajah).

Fig. 1. The general scheme of the dissolution and polymerization, which is of importance in this work, is shown. Due to the abundance in the silanol group on the surface of amorphous silica (Zhuravlev, 1987, 2000), the activity of $SiO_{2(am)}$ and $Si(OH)_4$ is taken as unity as in ideal cases (see Supplementary Fig. 5 for water sorption data of $SiO_{2(am)}$).

in an autoclave. Its temperature is controlled with a JUMO temperature controller to 25 °C and 60 °C. Amorphous silica (acquired by heating LUDOX AS-40 at 105 °C for 24 h and calcining it further at 550 °C for 12 h) is added to the solution and sealed with the Teflon-lined autoclave cover. One week is allowed to pass with rigorous stirring for equilibrium conditions (Krauskopf, 1956; Greenberg and Price, 1957; Elmer and Nordberg, 1958). An optimal stirring condition was attained to allow the reduction of the boundary layer between the solid ($SiO_{2(am)}$) and liquid phases (H_2O) to reduce the barrier of the dissolution kinetics, while keeping the alteration of the polymerization to a minimum. It is found by comparing phase concentrations of this work at pH = 12 with data at similar conditions by Alexander et al. (1954) and Sefcik and McCormick (1997) which correspond to values of this work. Upon equilibrium, 5 mL of sample volume is drawn from the autoclave and 2 mL of the sample is used for reactive silico-molybdic measurements, made by photospectrometry. Descriptions of the measurement are detailed by Iler (1979). 2 mL is used for ESI-MS measurements and diluted with methanol (MeOH). 250 μL is taken by a precision-syringe. The solution is injected to the ESI-MS chamber at 120 °C at the tip cone, at 3 kV voltage difference between the poles and at 24 kV at the receiving tip to ensure complete arrival of all species.

The base-catalysed TEOS (tetraethylorthosilicate)/H_2O rapid hydrolysis reaction is considered for the case of equilibrium alteration. It well represents the increased hydrolytic effect by temperature for the system in the injection port. Brinker mentioned the hydrolysis time of 5 min in an alkaline system of TEOS/H_2O (Brinker, 1988). The residence time in the injection port is in the order of a few microseconds at most, being well below the reaction time mentioned by Brinker (1988). Therefore, alterations are considered to be minimal.

Further concerns in the change of equilibrium are eliminated by dilution with methanol (MeOH) to retain equilibrium conditions upon injection (Tamahrajah, 2015; Tamahrajah and Brehm, 2015). It is done by hindering the further equilibrium alteration through minimal hydrolysis effects by minimal esterification (Alexander et al., 1954) during the time of injection and time of flight.
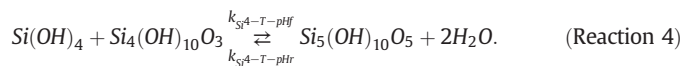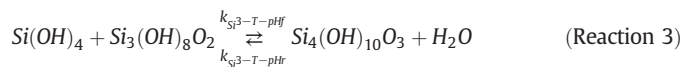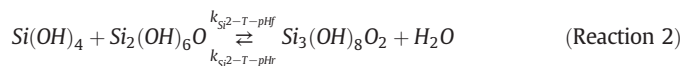
We obtained nearly identical data at $t_{MeOH} = 0.5$ min and at $t_{MeOH} = 8$ min (surpassing the time of Brinker), with t_{MeOH} being the reaction time. However, there mainly exist minimal condensation effects due to MeOH at $t_{MeOH} = 8$ min for pH = 13 for $Si^{4-25-13}$ to $Si^{5-25-13}$. At pH = 12, $Si^{4-25-12}$ increased from $Si^{5-25-12}$ due to further hydrolysis by H_2O at 8 min.

The period of injection together with the encapsulation time of the solvent (MeOH) around the molecule of interest is of essence in this

case. MeOH acts as a catalyst and retains the equilibrium condition during injection time and encapsulation time according to the charge residue model or the ion evaporation model upon injection at $t_{MeOH} = 0.5$ min. Therefore, the most representative equilibrium data at $t_{MeOH} = 0.5$ min is taken to maintain the integrity of the solution.

Intensity of the dissociated silicic acid species is equivalent to the intensity of neutral silicic acid species due to their similarly low dissociation constants (Busey and Mesmer, 1977; Tamahrajah, 2015).

The equilibrium constants from ESI-MS measurements are determined by taking the sum product of the individual silicic acid species by considering Reactions 1 to 4. Simple proof of reaction mechanisms is necessary here. After much research and trial of different mechanisms, convergence of kinetic data is achieved with Reactions 1 to 4, which are derived from equilibrium data. Further complexities can always follow upon these reactions.

$$2Si(OH)_4 \underset{k_{Si1-T-pHr}}{\overset{k_{Si1-T-pHf}}{\rightleftarrows}} Si_2(OH)_6O + H_2O \qquad \text{(Reaction 1)}$$

$$Si(OH)_4 + Si_2(OH)_6O \underset{k_{Si2-T-pHr}}{\overset{k_{Si2-T-pHf}}{\rightleftarrows}} Si_3(OH)_8O_2 + H_2O \qquad \text{(Reaction 2)}$$

$$Si(OH)_4 + Si_3(OH)_8O_2 \underset{k_{Si3-T-pHr}}{\overset{k_{Si3-T-pHf}}{\rightleftarrows}} Si_4(OH)_{10}O_3 + H_2O \qquad \text{(Reaction 3)}$$

$$Si(OH)_4 + Si_4(OH)_{10}O_3 \underset{k_{Si4-T-pHr}}{\overset{k_{Si4-T-pHf}}{\rightleftarrows}} Si_5(OH)_{10}O_5 + 2H_2O. \qquad \text{(Reaction 4)}$$

The equilibrium constants of each reaction (Eq. (1)) are the ratio of the products and reactants (Eq. (2)):

$$K_{p,ESI-MS} = \prod_i^n K_{p,i-ESI-MS} \qquad (1)$$

$$= Si^{1-T-pH} \left(\prod_{i>1}^{n-1} \frac{[Si^{i-T-pH}]}{[Si^{(x-1)-T-pH}][Si^{1-T-pH}][H_2O]} \right) \frac{[Si^{5-T-pH}]}{[Si^{1-T-pH}][Si^{4-T-pH}][H_2O]^2} \qquad (2)$$

for $i > 1$ and $n = 5$.

The relation of the individual silicic acid concentration at a given temperature T and pH to the sum (Eq. (3)) of all silicic acid species