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The diffusion coefficient of dissolved silica revisited

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ABSTRACT

The diffusion coefficient of dissolved silica was determined for two different salinities, 36 and 0, at temperatures ranging from 2 °C to 30 °C and at an average pH value of 8.1. Our results show limited influence of salinity and a variation by a factor of 2 to 3 of the silica diffusion coefficient within the temperature range considered in this study. The values obtained at 25 °C are in agreement with previous work carried out at room temperature for seawater and freshwater. The dependency on temperature and viscosity of the diffusion coefficient agrees well with the Einstein–Stokes equation. The composition of the solvent appears to be an important factor because it modifies the viscosity and allows for the complexation of the dissolved silica with less mobile ions, while its pH controls the dissolved silica speciation. In seawater, the higher viscosity and the presence of dissociated and polymeric species result in a decrease of the diffusion coefficient compared to freshwater systems.

1. Introduction

The diffusion coefficient of dissolved silica (H_4SiO_4) has been relatively little studied, although it is an essential parameter for the assessment of diffusive fluxes of this constituent, in particular across the water–sediment interface. It is not only a key parameter for diagenetic modelling, but also is needed for studying the dissolution of silicate minerals in the sedimentary environment. Wollast and Garrels (1971) determined its value, 1.00×10^{-5} cm^2 s^{-1}, for seawater of salinity 36.1 at 25 °C. This value has been applied by a number of authors with a correction for salinity and temperature, whenever necessary, according to the method described by Li and Gregory (1974). Applin (1987) studied the diffusion coefficient as a function of dissolved silica concentration at 25.5 °C and a pH of 5.5. The resulting value was twice that of Wollast and Garrels (1971), but this discrepancy was mainly attributed by the author to the difference in experimental conditions (pure water, acidic pH). To our knowledge, there exist no other values of the silica diffusion coefficient determined experimentally. With the growing interest in the biogeochemical cycle of silica in various environments, a new and more thorough study of this parameter is necessary. The aim of the present work is to reinvestigate the diffusion coefficient of dissolved silica in seawater and freshwater at different temperatures, ranging from 2 to 30 °C, for an average pH value of 8.1, which is encountered in many natural systems.

2. Materials and methods

For the purposes of this study, we used the porous diaphragm technique as described in Robinson and Stokes (1968), which is also the method used by Wollast and Garrels (1971). It is based on the diffusion of the chemical species (H_4SiO_4) through a porous membrane. We used a 0.45 μm nitrate cellulose filter (Millipore) fixed at the end of a plastic tube (diameter 4.5 cm) by means of a plastic filter holder. This system of fixation allows an easy replacement of the filter, while reducing the risks of bulk streaming which could interfere with the diffusive flux. The tube was suspended in the centre of a plastic beaker so that the level of 700 ml of external solution corresponded to the level of 125 ml in the tube (Fig. 1). Both solutions, external and internal, were stirred at a constant rate with magnetic stirring bars, the one in the central tube being placed directly on the filter. This magnetic bar had a smooth surface and a light weight, with a length of 15 mm and a diameter of 1.5 mm; due to its small size, only 11% of the membrane surface was covered while in motion. In addition, given the low stirring rate (50 rpm), we assume that its effect on the membrane properties was negligible. This aspect of the procedure is discussed in more detail later. Preliminary experiments of Rhodamine-B diffusion were first conducted, during which the stirring rate was varied between 25 and 100 rpm. Based on the results, a stirring rate of 50 rpm was chosen in order to assure homogeneity of the solutions and to prevent the formation of an important diffusive layer at the surface of the filter, without however

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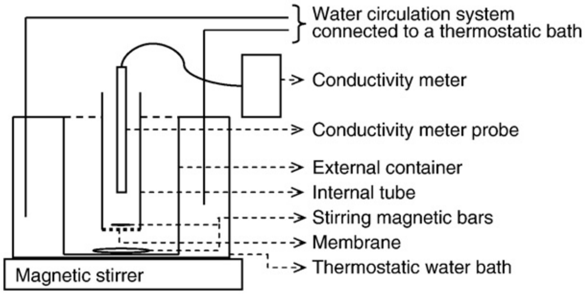

Fig. 1. Schematic diagram showing the experimental set-up.

inducing any advective fluxes. The entire system was placed in a regulated temperature water bath.

The cell equation is given by Robinson and Stokes (1968):

$$\ln\left(\frac{C_e^0 - C_i^0}{C_e - C_i}\right) = Dt\frac{A}{l}\left(\frac{1}{V_e} + \frac{1}{V_i}\right) \tag{1}$$

where C_e^0 and C_e in mol L^{-1} are the dissolved silica concentrations of the external solution at the beginning and at the end of the experiment, respectively, C_i^0 and C_i in mol L^{-1} are the concentrations of the internal solution at the beginning and at the end of the experiment, D is the diffusion coefficient in $cm^2\ s^{-1}$, t is the time in s, V_e and V_i in cm^3 are the volumes of the external and internal solutions, respectively. The filter constant A/l, in cm, is a parameter characteristic of the filter: it is the ratio between the effective total area of the diaphragm pores (A, in cm^2) and their effective average length (l, in cm) along the diffusion path. It is specific to each individual filter and may be determined from Eq. (1) by performing a diffusion experiment using a solute with a known diffusion coefficient.

For this purpose, we used a solution of KCl as an internal standard, which allowed us to measure simultaneously the diffusion of KCl and that of dissolved silica. Average values of the diffusion coefficient of KCl at 25 °C for different KCl concentrations in distilled water were obtained from the data in Robinson and Stokes (1968). The values for the different salinities and temperatures were calculated by using a relation derived from the Einstein–Stokes equation (Li and Gregory, 1974):

$$\frac{D_{T_1}\eta_{T_1}}{T_1} = \frac{D_{T_2}\eta_{T_2}}{T_2} \tag{2}$$

where D_{T_1} and D_{T_2} are the coefficients of molecular diffusion for temperatures T_1 and T_2 respectively, η_{T_1} and η_{T_2} being the corresponding viscosity values. The viscosities of freshwater and salt water of salinity 35 for the different temperature values were obtained from the ITTC — Recommended Procedures (1999). We assumed that the variation of viscosity between salinity 35 and salinity 36, the working value in this study, is negligible (less than 0.3% deviation — derived from Horne, 1969). Given the much higher Cl^- concentrations in our solutions, and particularly in seawater, the diffusion of KCl can be assumed to be that of K^+. However, in order to maintain solution electro-neutrality, the diffusion of K^+ in these multi-component electrolyte solutions is enhanced by that of the counter-ion, Cl^-, which has a higher coefficient of diffusion than K^+ (Robinson and Stokes, 1968). Based on data from Li and Gregory (1974), the diffusion coefficient of K^+ in seawater is about 3% greater than that at infinite dilution. From the above we assumed therefore that the use of the KCl diffusion coefficient, measured in distilled water and corrected for salinity and temperature by means of Eq. (2), is adequate for the purpose of this study.

The diffusion of KCl was recorded by measuring the conductivity of the internal solution, relying on the linear relationship between conductivity and KCl concentration within the concentration range considered here. In order to determine this linear relationship for each temperature and for each run, we measured the conductivity of a number of solutions with KCl concentrations chosen to cover the entire range investigated during the experiment. These solutions were similar to the experimental medium, with salinities of either 0 or 36 and containing the same concentrations of buffer and dissolved silica. While this technique is easy to use and accurate in Milli-Q® water, it can be less precise in seawater, as small variations in conductivity can be obscured by the high natural value of the initial solution. In order to avoid this problem and to increase the precision of the measurements, we increased the KCl concentration of the internal standard for seawater (10 mmol L^{-1} KCl versus 5 mmol L^{-1} for Milli-Q® water).

The value of A/l for each membrane was calculated from the cell equation (Eq. (1)) and the KCl diffusion coefficient, and the diffusion coefficient of dissolved silica could then be determined. This method is more accurate compared to the determination of the filter constant in a separate experiment. Also, it facilitates the usage of a new filter for each run, thus preventing potential problems due to the alteration of the membrane with time. The preliminary Rhodamine experiments conducted to optimise the experimental set-up indeed showed that A/l remained constant for up to 60 h, after which it exhibited a relatively rapid decrease with time. This was the main reason why we chose to use a new filter for each different experiment.

The diffusion coefficient was measured for two different salinities, 36 and 0, at different temperatures. In practice, 700 ml and 125 ml of either filtered seawater from the Gulf of Biscay (North Atlantic) or Milli-Q® water were placed in the external container and in the central tube, respectively, and were left to equilibrate overnight. The external solution was then spiked with dissolved silica of 0.36 mmol L^{-1} (10 mg Si L^{-1}) and with KCl of 10 mmol L^{-1} (salinity 36) or 5 mmol L^{-1} (salinity 0). At the same time, filtered seawater or Milli-Q® water was added to the internal solution to maintain equal water levels in both containers. The entire system was then left to equilibrate during 2 h before sampling. Dissolved silica was added as a sodium metasilicate ($Na_2SiO_3{\cdot}9H_2O$) solution. The pH was kept at an average value of 8.1 by means of a buffer solution, composed of 50 mL of 0.025 mol L^{-1} $Na_2B_4O_7{\cdot}10H_2O$ (borax) and 22.5 mL of 0.1 mol L^{-1} HCl, for 1 L of either seawater or Milli-Q® water, and added to both internal and external containers. The pH varied very little during an individual experiment, and for all experiments it was between 8.0 and 8.3.

Aliquots of 2.025 ml were withdrawn from the internal solution, while 10 ml was removed at the same time from the external solution. These volumes were chosen in order to maintain the solutions in both containers at the same level and thus to prevent advective transfer of solution driven by small pressure difference. Samples were taken simultaneously in both internal and external containers, 2 h and 6 h after the start of the experiment. The initial and final concentrations of dissolved silica were analysed following the colorimetric method described in Grasshoff et al. (1983). The mass conservation of silica was checked for each run and the variations observed between the initial and final total concentrations of silica in the system were on average less than 4%. The KCl concentration in the central tube was continuously recorded by following its conductivity, while in the external solution only the final conductivity value was measured. From the recorded values, the initial KCl concentration of the external solution was calculated using the following expression based on mass conservation:

$$C_e^0 = C_e + \left(C_i - C_i^0\right)\left(\frac{V_i}{V_e}\right) \tag{3}$$

where the terms in the equation are defined above (modified from Robinson and Stokes, 1968, for a negligible membrane volume). Similarly to silica, the mass balance of KCl was also maintained, with maximum variations between the initial and final concentrations less than 8%. The temperature of the internal solution was also monitored; experiments showing a variation exceeding ±0.5 °C were discarded. Three individual determinations of the diffusion coefficient were conducted for each temperature.

Although the principle of the method used to measure the diffusion coefficient is the same as that described in Wollast and Garrels (1971), the experimental protocol and set-up in our study are slightly different. Firstly, in order to measure the cell constant A/l, Wollast and Garrels (1971) conducted six distinct calibrations using a 0.1 mol L^{-1} KCl solution, four before and two after the silica diffusion experiment, while we used KCl as an internal standard. Secondly, their external solutions contained 0.71 mmol Si L^{-1} (20 mg Si L^{-1}), compared to 0.36 mmol Si L^{-1} (10 mg Si L^{-1}) in our experiments. Thirdly, the internal solution was mechanically stirred from above with a rod, while we used a magnetic stirring bar that assures a constant stirring rate directly at the surface of the membrane.

3. Results and discussion

The results obtained at different salinities and temperatures are summarised in Table 1. The first observation is that the diffusion coefficient of dissolved silica measured at salinity 36 and 25 °C in our study, $(1.02 \pm 0.02) \times 10^{-5}$ cm^2 s^{-1}, is essentially identical to that obtained by Wollast and Garrels (1971), $(1.00 \pm 0.05) \times 10^{-5}$ cm^2 s^{-1}.

Table 1 shows also the values of the membrane constant, A/l. The overall average A/l value obtained here, 284±22 cm (calculated from the entire set of individual values, $n = 36$), is comparable to the one measured by Wollast and Garrels (1971), 240±10 cm. Individual A/l values vary very slightly and there is no correlation between A/l and the temperature or salinity values. This relative constancy of A/l is an important feature of our experiments because it shows that this parameter does not depend on external factors, such as the temperature or the KCl concentration, but only on the internal structure of the filter. We can therefore assume that it is not influenced by the nature of the diffusing species, being either ionic (KCl) or neutral (H_4SiO_4). The variation with salinity of the diffusion coefficients obtained in our study was relatively small. However, the averaged variation observed at a constant temperature, between D at salinity 0 and that at salinity 36, 12%, is slightly higher than the one predicted by the correction method described in Li and Gregory (1974). According to these authors, a maximum variation of 8% based on the Einstein–Stokes equation (Eq. (4)) should be observed:

$$D = \frac{kT}{6\pi\eta r} \tag{4}$$

where k is the Boltzmann's constant, T the absolute temperature, η the viscosity of the solvent, and r the hydrodynamic radius of the molecule. Seawater has a viscosity of about 8% higher than that of freshwater, which leads to a decrease in the mobility of the different chemical species (Applin, 1987); the diffusion coefficient is thus expected to be lower in seawater than in freshwater. The small difference observed between our results and the theoretical approach of Li and Gregory (1974) can probably be attributed to the experimental conditions, and mainly to the composition of our solution.

Table 1
The diffusion coefficient of dissolved silica at different temperatures and salinities

Temperature (°C)	A/l (cm)		D (10^{-5} cm^2 s^{-1})	
	Salinity 0	Salinity 36	Salinity 0	Salinity 36
2	n.d.	276	n.d.	0.47±0.01
4.2	255	296	0.58±0.05	0.51±0.01
10	263	265	0.74±0.01	0.65±0.01
15	274	257	0.85±0.03	0.80±0.01
20	304	300	1.00±0.10	0.91±0.04
25	295	299	1.17±0.07	1.02±0.02
30	n.d.	322	n.d.	1.14±0.04

Each value is the average of three distinct determinations with the variation range indicated. Each individual D value was computed using the specific A/l value of the filter used, and determined using KCl (5 or 10 mmol L^{-1}) as internal standard. The average values of the filter constant A/l for each temperature and salinity are also shown.
n.d. = not determined.

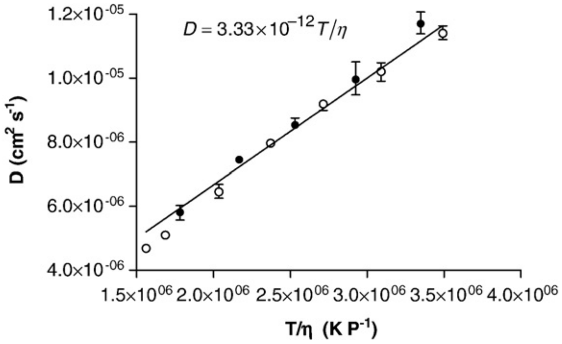

Fig. 2. Variation of D as a function of T/η for salinities 0 and 36, where T is the absolute temperature (K), and η the viscosity expressed in poises (P; 1 $P = 1$ g cm^{-1} s^{-1}). Filled symbols (●) correspond to results for salinity 0, while open circles (○) correspond to those for salinity 36. Data represented are the average diffusion coefficients based on three distinct determinations; the variation range with respect to the mean is also shown. Data are fitted by the relation $D = 3.33 \times 10^{-12} T/\eta$, with $n = 12$ and $R^2 = 0.98$.

Our results show that the diffusion coefficient of dissolved silica increases strongly with temperature, with a doubling between 4 °C and 25 °C. This finding was predicted by Li and Gregory (1974), based on the Einstein–Stokes relation (Eq. (4)). This relation shows that the dependency of D on temperature is not only direct, but also indirect through the viscosity term, which is a function of salinity and temperature. To include the dependency of the diffusion coefficient on the viscosity, the values of D determined in this study for both salinity values (0 and 36) are plotted against T/η. Fig. 2 shows that the data are well fitted by the following linear relationship, consistent with the Einstein–Stokes equation:

$$D = 3.33 \times 10^{-12} \frac{T}{\eta} \tag{5}$$

where D is expressed in cm^2 s^{-1}, T is in K and η is in poises (P). The same is also true for values of the diffusion coefficient of KCl for different temperatures and salinities obtained from the literature (Li and Gregory, 1974; $D_{KCl} = 6.04 \times 10^{-12} T/\eta$, $n = 5$, $R^2 = 0.97$). This last relationship could have been used, instead of Eq. (2), to compute D_{KCl} at various temperatures and to estimate the membrane constant A/l. However, given the fact that we worked with two different KCl concentrations, we chose to use Eq. (2) because it allows the use of a reference diffusion coefficient value (at 25 °C) depending on the KCl concentration. Eq. (5) illustrates the real dependency of the diffusion coefficient of dissolved silica on η and T and therefore it may be used to estimate D for different temperatures and salinities, if the corresponding viscosities are known. Viscosity values can be obtained either from existing tables or calculated using an equation relating them to temperature, salinity and pressure, as for example the relationship given by Richards (1998).

As mentioned previously, the pH varied only between 8.0 and 8.3 for the entire set of experiments. Within this range, a small fraction of H_4SiO_4 is present as negatively charged $H_3SiO_4^-$, a species less mobile than the neutral molecule as it is subject to hydration (Applin, 1987). Given our working pH values, at 25 °C and 0 salinity about 2 to 4% of H_4SiO_4 is dissociated, while at 36 salinity, 3 to 7% is in the dissociated form $H_3SiO_4^-$ (Stumm and Morgan, 1996; Millero, 1996). It has also been shown that polymeric forms of silicic acid appear at pH values higher than 7 (Cary et al., 1982). Due to their larger size, the polymers have a reduced mobility compared to the monomer, and thus their presence could slow down the diffusion.

Dissolved silica can also react with metallic ions like Na^+, Ca^{2+} and Mg^{2+} that are naturally present in seawater, leading to the formation of different complexes with a relatively low mobility, as shown by the values of their tracer diffusion coefficients (Li and Gregory, 1974; Applin, 1987). In addition, we also introduced different ions (Na^+, K^+, Cl^-) in our experimental solutions (either seawater or Milli-Q® water), owning to the use of sodium metasilicate, potassium chloride (internal standard), and borax/HCl buffer. The presence of these ions could lead to the complexation of dissolved silica for both salinities studied. Considering the fact that higher concentrations of ions are present and that dissolved silica might also form a complex with sulphate (Marshall and Chen, 1982), an enhanced effect of complexation in seawater is expected. This conclusion is however difficult to quantify.

4. Conclusions

The results of this study are in agreement with the previous work of Wollast and Garrels (1971), and Li and Gregory (1974). They show that the diffusion coefficient of dissolved silica varies by a factor of 2 with temperature ranging between 4 and 25 °C, while the influence of salinity remains relatively small. The relation between temperature and the diffusion coefficient is consistent with the Einstein–Stokes equation, if the dependency of viscosity on temperature is taken into account. Although we did not study the influence of the pH of the solution (seawater or pure water), it is an important factor affecting the diffusion coefficient, because it determines the dissolved silica speciation, and therefore this parameter has to be carefully controlled in any diffusion study. At the pH values considered here, which are characteristic of many natural waters, dissociated and polymeric forms of silicic acid can be present, resulting in a slowing of the diffusion process. The composition of the solutes also influences diffusion by modifying the viscosity and by allowing complexation of the dissolved silica with less mobile ions. Thus, in seawater, the higher viscosity and the presence of dissociated and polymeric species could result in a decrease of the diffusion coefficient compared to freshwater systems. This decrease is probably even more important in hypersaline solutions, as those characterising some interstitial waters of marine and saline lake sediments, which generally have a very complex and rich composition. This aspect should be carefully considered when diffusive fluxes are evaluated between sediments and the overlying water column.

We have obtained a complete set of values for the diffusion coefficient of dissolved silica, for two salinities and for a series of temperatures ranging from 2 to 30 °C. From these results we derived an expression linking the diffusion coefficient to temperature and viscosity that can be used to calculate this parameter for different salinities and/or temperatures when working in environments where the variation of these factors is an important characteristic, such as estuaries. The experimental set-up developed in this study can also be used to directly measure the diffusion coefficients of other substances of interest in aquatic systems.

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