The diffusion coefficient of dissolved silica revisited
Laura Rebreanu⁎, Jean-Pierre Vanderborght, Lei Chou
Laboratoire d'Océanographie Chimique et Géochimie des Eaux, Université Libre de Bruxelles, Campus Plaine, CP208, Boulevard du Triomphe, B-1050 Brussels, Belgium

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A B S T R A C T
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 (H₄SiO₄) 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 cm² 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 (H₄SiO₄) 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...
The cell equation is given by Robinson and Stokes (1968):

\[
\ln \left( \frac{C_i^f - C_i^0}{C_i^f - C_i} \right) = \frac{A}{I} \left( \frac{1}{V_i^e} + \frac{1}{V_i} \right)
\]

(1)

where \( C_i^f \) and \( C_i^0 \) in mol L\(^{-1}\) are the dissolved silica concentrations of the external solution at the beginning and at the end of the experiment, respectively, \( C_i^f \) and \( C_i^0 \) 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 \( \text{cm}^2 \text{s}^{-1} \), \( t \) is the time in s, \( V_i^e \) and \( V_i \) in \( \text{cm}^3 \) are the volumes of the external and internal solutions, respectively. The filter constant \( A/I \), in cm, is a parameter characteristic of the filter: it is the ratio between the effective total area of the diaphragm pores (\( A \), in \( \text{cm}^2 \)) 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):

\[
\frac{D_f}{T_1} \eta_i = \frac{D_f}{T_2} \eta_i
\]

(2)

where \( D_f \) and \( D_f \) are the coefficients of molecular diffusion for temperatures \( T_1 \) and \( T_2 \) respectively, \( \eta_i \) and \( \eta_i \) being the corresponding viscosity values. The viscosities of freshwater and salt water of salinity 35 for the different temperature values were obtained from the data in Robinson and Stokes (1968). The values for the different salinities and temperatures were calculated using a relation derived from the Einstein–Stokes equation (Li and Gregory, 1974):

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than 8%. The temperature of the internal solution was also monitored; experiments showing a variation exceeding \( \pm 0.5 \) °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 \( A/\lambda \), 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, (102.0±0.2) × 10\(^{-3}\) cm\(^2\) s\(^{-1}\), is essentially identical to that obtained by Wollast and Garrels (1971), (1.00±0.05) × 10\(^{-3}\) cm\(^2\) s\(^{-1}\).

Table 1 shows also the values of the membrane constant, \( A/\lambda \). The overall average \( A/\lambda \) 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 \( A/\lambda \) values vary very slightly and there is no correlation between \( A/\lambda \) and the temperature or salinity values. This relative constancy of \( A/\lambda \) 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\(_4\)SiO\(_4\)). The variation with salinity of the diffusion coefficients obtained in our study was relatively small. However, the average 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:

\[
D = \frac{kT}{6\pi\eta r_f} \tag{4}
\]

where \( k \) is the Boltzmann's constant, \( T \) the absolute temperature, \( \eta \) 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.

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 \( T/\eta \). Fig. 2 shows that the data are well fitted by the following linear relationship, consistent with the Einstein–Stokes equation:

\[
D = \frac{3.33 \times 10^{-12} T/\eta}{(T/\eta)^2} \tag{5}
\]

where \( D \) is expressed in cm\(^2\) s\(^{-1}\), \( T \) is in K and \( \eta \) 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; \( D_{\text{KCl}} = 6.04 \times 10^{-12} T/\eta \), \( n=5, R^2=0.97 \)). This last relationship could have been used, instead of Eq. (2), to compute \( D_{\text{KCl}} \) at various temperatures and to estimate the membrane constant \( A/\lambda \). 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 \( T/\eta \) 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\(_4\)SiO\(_4\) is present as negatively charged H\(_3\)SiO\(_4\) (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.
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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