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Experimental Determination of the Diffusion Coefficient of Dimethylsulfide in Water

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Estimates of the sea-to-air flux of dimethylsulfide (DMS) are based on sea surface concentration measurements and gas exchange calculations. Such calculations are dependent on the diffusivity of DMS (D_{DMS}), which has never been experimentally determined. In this study the diffusivity of DMS in pure water was measured over a temperature range of 5°–30°C. The measurements were made using a dynamic diffusion cell in which the diffusing gas flows over one side of an agar gel membrane and the inert gas flows over the other side. The diffusion coefficient can be estimated from either time dependent or steady state analysis of the data, with an estimated uncertainty of less than 8% (1σ) in each measurement. A best fit to all the experimental results yields the equation D_{DMS} (in $\text{cm}^2 \text{sec}^{-1}$) = $0.020 \exp(-18.1/RT)$, where $R = 8.314 \times 10^{-3} \text{ kJ mole}^{-1} \text{ K}^{-1}$ and T is temperature in kelvin. The values of D_{DMS} obtained in this study were 7–28% larger than estimates from the empirical formula of Hayduk and Laudie (1974) which has previously been used for DMS in gas exchange calculations. Applying these values to seawater results in an increase of less than 5% in the global oceanic flux of DMS.

INTRODUCTION

The sea-to-air exchange of dimethylsulfide (DMS) is a major component of the global atmospheric sulfur budget. Current estimates of this flux are based on the measurement of sea surface DMS concentrations and various parameterizations of gas exchange across the sea surface [Andreae, 1990; Bates et al., 1987]. These parameterizations take the general form of

$$\text{Flux} = K_l(C_l - C_g/\alpha) = K_g(C_l\alpha - C_g) \quad (1)$$

where K is the gas exchange coefficient or piston velocity (expressed on a liquid or gas phase basis), C is the concentration in the liquid or gas phase, and α is the dimensionless solubility of the gas in seawater [Liss and Slater, 1974]. The gas exchange coefficient contains both liquid and gas phase components (k_l and k_g) as follows:

$$\frac{1}{K_l} = \frac{1}{k_l} + \frac{1}{\alpha k_g} \quad (2)$$

Experimental studies have shown that $k_g \gg k_l$ under natural conditions [Liss, 1973]. Therefore gas exchange is dominated by resistance in the liquid phase for slightly soluble gases. This is also the case for DMS, which has intermediate solubility in water. It has also been demonstrated experimentally that k_l is dependent on the diffusivity of the diffusing gas D with a functional form of

$$k_l = f(S c^{-n}) = f(D^n) \quad (3)$$

where n may vary from 1/2–2/3 depending on the sea state [Liss and Merlivat, 1986; Jähne et al., 1987b]. The magni-

tude of the gas exchange coefficient has been deduced from a variety of artificial and natural tracer experiments utilizing ^{14}C , Rn, SF_6 , and ^3He [Peng et al., 1979; Smethie et al., 1985; Wanninkhof et al., 1985; Watson et al., 1991], and the results are extrapolated to DMS using the above relationships. The diffusivity of DMS has not previously been measured. Instead, it has been estimated from the diffusivities of other nonelectrolytes using various empirical formulae relating diffusivity to molar volume, viscosity, and temperature [Wilke and Chang, 1955; Hayduk and Laudie, 1974].

In this study we experimentally determine the diffusion coefficient for DMS, compare the measured and calculated values, and discuss the implications for the global flux of DMS. We also determined the diffusion coefficient of methane in order to evaluate systematic errors introduced by the experimental apparatus and to compare our results to diffusivities reported in the literature for other gases.

EXPERIMENTAL METHOD

The experimental approach used in this study is a variation on the method of Barrer [1941], and the apparatus was modified from the design of Jähne et al. [1987a]. The diffusion cell consists of a stainless steel housing with two chambers on either side of an aqueous gel membrane (Figure 1a). At the onset of the experiment, a flow of DMS in nitrogen is introduced on the "high-concentration" side of the membrane (referred to as chamber 1), while pure nitrogen flows on the "low-concentration" side of the membrane (referred to as chamber 2). The experiment consists of measuring the ratio of the DMS concentrations in the gas flows from each chamber as a function of time from the start of the experiment or after equilibration of the membrane. In this section we briefly discuss the use of diffusion theory to model the experimental results and describe the experimental procedure.

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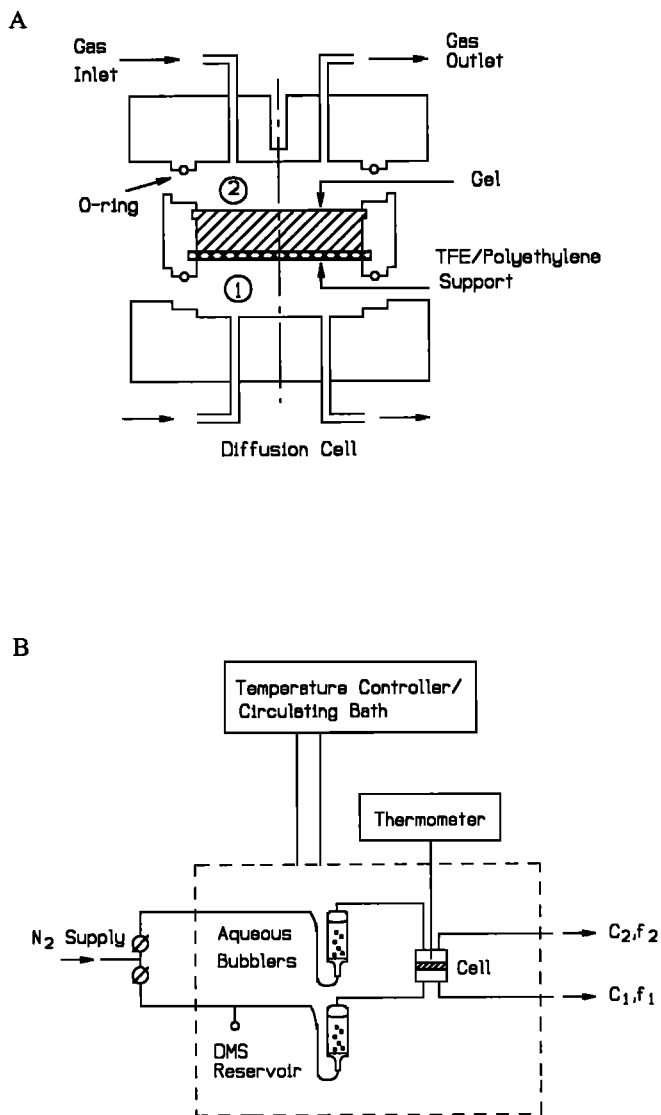


Fig. 1. (a) Schematic cross section of the diffusion cell. The high- and low-concentration chambers are labeled as 1 and 2, respectively, as in (4). (b) Schematic of the experimental apparatus. The gas flows from the cell are labeled as in (10).

Theoretical Analysis

Crank [1975] gives the following expression for the concentration of a diffusing substance (C) in an infinite sheet or membrane:

$$C = C_1 + (C_2 - C_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \cdot \sin \frac{nx\pi}{l} \exp - (Dn^2\pi^2t/l^2) + \frac{4C_0}{\pi} \sum_{m=1}^{\infty} \frac{1}{2m+1} \cdot \sin \frac{(2m+1)\pi x}{l} \exp - [D(2m+1)^2\pi^2t/l^2] \quad (4)$$

where l is the membrane thickness, C_1 and C_2 are the concentrations at $x = 0$ and $x = l$, respectively, and C_0 is the concentration in the sheet at $t = 0$, which is assumed to be uniform throughout the sheet.

The flux across the membrane is obtained by taking $-D(\partial C/\partial x)$, which yields

$$\Phi = -D \frac{\partial C}{\partial x} = -D \frac{(C_2 - C_1)}{l} - \frac{2D}{l} \cdot \sum_{n=1}^{\infty} (C_2 \cos n\pi - C_1) \cos \frac{nx\pi}{l} \exp - (Dn^2\pi^2t/l^2) - \frac{4DC_0}{l} \sum_{m=1}^{\infty} \cos \frac{(2m+1)\pi x}{l} \exp - [D(2m+1)^2\pi^2t/l^2] \quad (5)$$

At $x = l$ this expression reduces to

$$\Phi = -D \frac{\partial C}{\partial x} = -D \frac{(C_2 - C_1)}{l} - \frac{2D}{l} \cdot \sum_{n=1}^{\infty} (C_2 \cos n\pi - C_1) \cos n\pi \exp - (Dn^2\pi^2t/l^2) - \frac{4DC_0}{l} \sum_{m=1}^{\infty} \cos (2m+1)\pi \exp - [D(2m+1)^2\pi^2t/l^2] \quad (6)$$

Assuming that C_2 and C_0 are both equal to zero gives

$$\Phi = -D \frac{\partial C}{\partial x} = +D \frac{C_1}{l} + \frac{2DC_1}{l} \cdot \sum_{n=1}^{\infty} \cos n\pi \exp - (Dn^2\pi^2t/l^2) \quad (7)$$

In our experiments the concentration ratio of the diffusing gas in contact with either side of the diffusion membrane (C_{2g}/C_{1g}) can be determined more accurately than absolute concentrations. Thus we do not determine the absolute flux through the membrane but, rather, the ratio of the flux through the membrane at $x = l$ to C_{1g} . C_{1g} can be converted to C_1 if the solubility is known. We can solve the theoretical expression for the flux for this ratio:

$$\frac{\Phi}{C_1} = \frac{D}{l} \left[1 + 2 \sum_{n=1}^{\infty} \cos n\pi \exp - (Dn^2\pi^2t/l^2) \right] \quad (8)$$

At steady state ($t \rightarrow \infty$) this becomes simply

$$\frac{\Phi}{C_1} = \frac{D}{l} \quad (9)$$

Measurement

As described above, the experimental quantity of interest is the ratio of the gas flux through the "low-concentration" surface of the membrane to the gas concentration at the "high-concentration" side of the membrane. This is given by

$$\frac{\Phi}{C_1} = \frac{C_{2g}f_2}{C_{1g}\alpha A} \quad (10)$$

where Φ is the flux out of the membrane, C_{2g} and C_{1g} are the gas phase concentrations on either side of the membrane, f_2 is the gas flow on the low-concentration side of the membrane, α is the dimensionless Ostwald coefficient for DMS in water (ratio of aqueous phase to gas phase concentration), and A is the cross-sectional area of the membrane.

The experimental apparatus is shown in Figure 1b. The cell is immersed in a stirred, thermostated water bath which was varied at 5° intervals from 5° to 30°C over the course of the experiments. The nitrogen gas supplies were passed through glass-fritted bubblers immersed in the water bath to saturate them with water vapor prior to entering the cell. The temperature of the cell was monitored using a thermocouple sensor placed in a well drilled near the center of the cell. DMS was introduced into chamber 1 by passage over a small glass bulb containing liquid DMS (purity >99%, Aldrich, Milwaukee, Wisconsin). The concentration on this side of the cell is therefore slightly undersaturated with respect to pure DMS. For methane runs, the glass bulb was removed, and the pure gas (purity 99.0%, Liquid Carbonic, Chicago, Illinois) was introduced into the bubbler in place of the nitrogen. Gas flow rates of 10 cm³ min⁻¹ and 20 cm³ min⁻¹ were used on the high- and low-concentration sides of the membrane, respectively, during the experiments.

The membrane is an agar gel (0.5%) which is 3.8 cm in diameter and approximately 0.6 cm thick. Agarose gels have been used in many previous studies of diffusion through a liquid membrane [Schantz and Lauffer, 1962; Spalding, 1969; Langdon and Thomas, 1971]. Jähne *et al.* [1987a] compared gas diffusion through agarose gels to wetted frit diaphragms. Their results demonstrated agreement between the two methods, with more reproducible results from the gels. This is presumably because convective or other turbulent motion is inhibited in the gels. Two small corrections must be accounted for when calculating aqueous diffusion coefficients from measurements made in gel membranes. The first is the reduction of solubility of the diffusing gas due to the lowering of the activity of water. Second, there is a hindrance to the diffusion path due to the formation of a three-dimensional network not found in pure water. Langdon and Thomas [1971] estimated that both effects reduce the diffusion coefficient for a substance through a gel in comparison to pure water by 1.36% for a 0.5% gel.

The gel in our apparatus rests directly on a sheet of porous polytetrafluoroethylene filter membrane 0.13 mm thick with mean pore size 10–20 μm (Zitex, Norton Company, Wayne, New Jersey). The sheet is supported by a porous polyethylene sheet 1.59 mm thick with mean pore size 15–45 μm (X-4900, Porex Corporation, Fairburn, Georgia). The porosity of both sheets is sufficiently large that they make a negligible contribution to the resistance of the membrane to gas diffusion. The gel is cylindrical in shape, but for a small portion of its total length the gel diameter is slightly increased by the presence of a small (0.79 mm × 0.40 mm) groove machined in the cell wall. This groove provides friction for the gel to prevent it from sliding upward in the event of a slight pressure gradient between the two sides during setup. The presence of a groove of these dimensions has a negligible effect on the diffusion of gases through the cell, as demonstrated by Barrer *et al.* [1962].

The gel thickness used in each experiment was calculated from the gel weight and the known diameter of the cell. The gel density was determined experimentally to be 0.992 g cm⁻³ (1σ = 0.05%) at 25°C. The uncertainty involved in determining the gel thickness has two components. The first is the uncertainty in the physical measurement of the thickness, which is largely due to the uncertainty in the determination of the density of the gel. The second results from the loss of some of the gel to evaporation during the course of the experiment, which was greatest at the higher temperatures. The combined uncertainty in the measured thickness is less than 5%. For steady state calculations the latter uncertainty was removed through the measurement of the gel thickness at the conclusion of the experiment.

The concentrations of DMS on either side of the membrane are determined by withdrawing samples from their respective outlet tubing with gastight syringes using perfluoroalkoxy needles. Thus samples contact only glass and Teflon during sampling. Samples from the high-concentration side are diluted by a factor of roughly 10 (500 for methane) in the syringe by adding pure nitrogen. The samples are then loaded into the injection loops of a 10-port gas injection valve and analyzed by gas chromatography with flame ionization detection. Two different volume loops (30 and 300 μL) are used for the high (C_{1g}) and low-concentration (C_{2g}) sides of the membrane, respectively. As a result, the amount of DMS (or methane) injected on column from both sides of the cell is similar once the cell reaches steady state. Linearity in detector response was tested (using DMS) by successive dilutions of the effluent from the low-concentration side of the cell to cover the range of concentrations observed during time-resolved measurements. A linear relationship between peak area and dilution factor was obtained. A least squares linear regression to the data gave a slope of 1.01 ± 0.05 (1σ); thus no corrections for detector linearity are needed. The absolute concentrations of the gas streams are not determined; instead, the ratio of the peak areas is taken as the ratio of their concentrations. The analyses were done on an HP5890 gas chromatograph with a 2-m Chromasil 330 column, an oven temperature of 50°C, and nitrogen carrier gas at a flow rate of 30 cm³ min⁻¹. Chromatographic data was acquired and integrated using a PC-based data acquisition system.

The gas flow rate on the low-concentration side of the membrane (f_2) was determined using a soap bubble flow meter corrected for temperature and water vapor variations. The gas flow on the high-concentration side of the membrane (f_1) was also monitored to insure constant flow during the course of each experiment, but this flow rate is not used in the calculation of the diffusion coefficient.

The Ostwald coefficient of DMS in water was obtained from Dacey *et al.* [1984]. A linear regression was fit to their data and yielded the equation

$$\ln \alpha = -10.1794 + 3761.33(1/T) \quad (11)$$

where T is temperature (in kelvin). The estimated uncertainty in this fit is 2.52% (1σ). The uncertainty in the coefficient, however, was due mainly to the variations in the temperature of the cell. The accuracy of the thermocouple used for temperature measurement in this experiment is ±0.4°C. This results in an uncertainty of less than 2% (1σ) in the Ostwald coefficient.

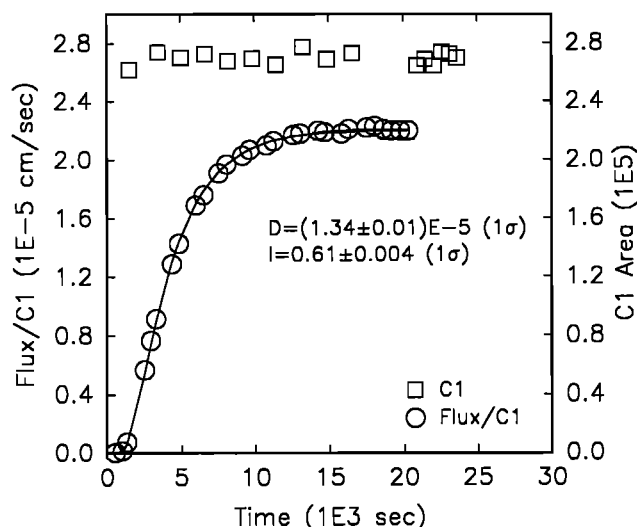


Fig. 2. Experimental results (circles) plotted as a function of time for dimethylsulfide experiment at 25°C. The curve is the best fit of (8), which yields the values shown for D and l . Also plotted are the high-concentration values (squares) obtained during the course of the experiment.

Data Analysis

There are two approaches to calculating the diffusion coefficient from the experimental data. The first is simply to allow the experiment to run until the membrane approaches a steady state condition, that is, constant flux. In this case, (9) and (10) apply, and if l (in centimeters) is known accurately, D (in $\text{cm}^2 \text{s}^{-1}$) can be solved for directly. Alternatively, the diffusion of DMS through the membrane can be followed as a function of time, in which case, (8) applies. An example of a time dependent experiment is shown in Figure 2. In this case a nonlinear fit of (8) to the data was carried out, allowing both D and l to vary [Marquardt, 1963]. The values of D and l obtained from the time-resolved measurements are within the estimated uncertainties of the steady state values. The range and estimated uncertainty of various parameters are given in Table 1.

The diffusivities reported in this paper include only the steady state values. The steady state proved to be more reproducible than the time-resolved diffusivities. The time-resolved method provided confirmation that the experiment was proceeding correctly and that the gel was intact during the experiment. Both the steady state and time-resolved diffusivities have been corrected for the gel effects discussed earlier. Each value was increased by a factor of 1.36% [Langdon and Thomas, 1971].

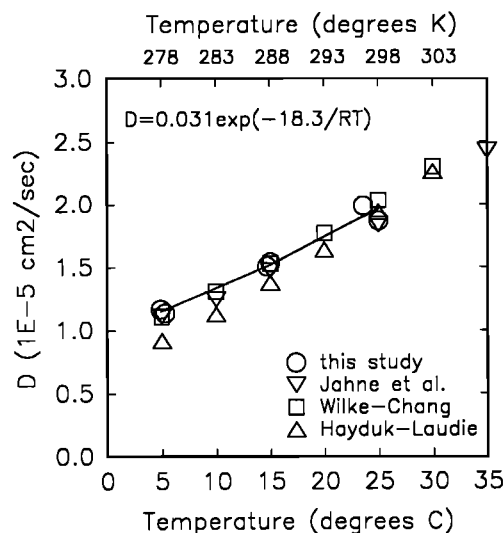


Fig. 3. Diffusion coefficient of CH_4 measured in this study, measured by Jähne *et al.* [1987a], and based on the empirical estimates of Wilke and Chang [1955] and Hayduk and Laudie [1974] relationships. The curve is a plot of the equation $D = 0.031 \exp(-18.3/RT)$, where T is temperature (in kelvins), fit to the data in this study.

RESULTS AND DISCUSSION

Methane

In order to test the reliability of our technique we first measured the diffusion coefficient of methane. Methane was chosen because (1) it enabled us to use the same flame ionization detector that we would use for DMS and (2) Jähne *et al.* [1987a] recently published diffusivities for methane with very good precision. Our results for methane are plotted with data from Jähne *et al.* [1987a] against temperature in Figure 3. For the purposes of this comparison we used the solubility data of Wiesenburg and Guinasso [1979] in our diffusivity calculations. This data set was used by Jähne *et al.* [1987a].

The measured diffusivities can be expressed as a function of temperature by fitting our data to the equation

$$D = A e^{-E_a/RT} \quad (12)$$

where E_a is the "activation energy" for diffusion in water (in kJ mole^{-1}), $R = 8.314 \times 10^{-3} \text{ kJ mole}^{-1} \text{ K}^{-1}$, and T is temperature in kelvin [Eyring, 1936]. A least squares fit of this function to the data obtained in this study yields a preexponential (A) factor of $0.031 \text{ cm}^2 \text{ sec}^{-1}$ ($1\sigma = 6.7\%$) and an E_a of $18.3 \text{ kJ mole}^{-1}$ ($1\sigma = 14.6\%$). The mean estimated uncertainty of this fit to the experimental data is

TABLE 1. Typical Values and Estimated Uncertainties of Experimental Parameters Used in the Calculation of the Diffusion Coefficient

Parameter	Range	Absolute Uncertainty	Relative Uncertainty %
Flow rate, f_2 (in $\text{cm}^3 \text{ min}^{-1}$)	20	0.15	0.76
Concentration ratio, C_2/C_1	0.008–0.015	0.0003–0.0004	2.7–3.9
Temperature, T (in degrees celsius)	5–30	0.4	n/a
Ostwald coefficient, α	9–28	0.15–0.58	1.6–2.0
Gel thickness, l (in centimeters)	0.5–0.7	0.006	1.0
Gel area, A (in cm^2)	11.51	0.002	0.02
Total			6.1–7.7

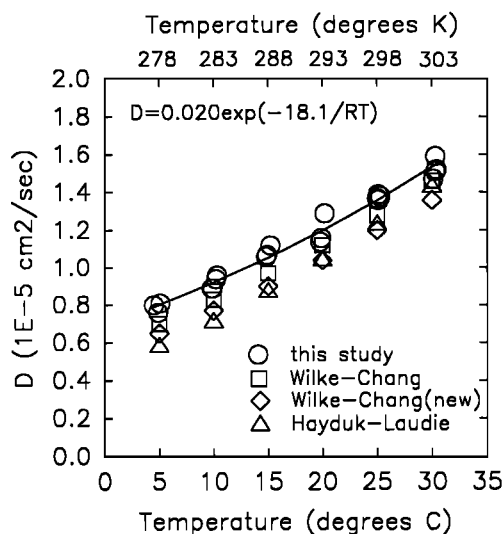


Fig. 4. Diffusion coefficient of dimethylsulfide measured in this study and empirical estimates based on the Wilke and Chang [1955] and Hayduk and Laudie [1974] relationships. Also plotted are the estimates using the Wilke-Chang relationship with the association factor recommended by Hayduk and Laudie. The curve is a plot of the equation $D = 0.020 \exp(-18.1/RT)$, where T is temperature (in kelvins).

7.48% (1σ). Our values of D for methane are within 5% (1σ) of those published by Jähne *et al.* [1987a], which is within the stated uncertainty of both sets of measurements.

Dimethylsulfide

The measurements of D_{DMS} are shown in Figure 4. A least squares fit of our diffusion data to the function given in (12) yields a preexponential (A) factor of $0.020 \text{ cm}^2 \text{ sec}^{-1}$ ($1\sigma = 1.0\%$) and a value of Ea of $18.1 \text{ kJ mole}^{-1}$ ($1\sigma = 6.5\%$). The mean estimated uncertainty of this fit is 14.68% (1σ).

Previous estimates of D_{DMS} have been made using the empirical expressions of Wilke and Chang [1955] and Hayduk and Laudie [1974]. These expressions are derived from a mathematical correlation of existing diffusivities for a variety of substances in several different solvents. The common parameters used in both correlations are the molar volume of the solute and the viscosity of the solvent. In these expressions the difference in diffusivity between substances is controlled by the molar volume. This implies that for a given solvent, the temperature dependence of the diffusivity is the same for all substances. These two empirical relationships differ in their treatment of the temperature dependence. As shown below, the Wilke-Chang expression includes temperature as an explicit parameter, while the Hayduk-Laudie expression does not:

$$D_{\text{W-C}} = \frac{7.4 \times 10^{-8} (\phi M_B)^{1/2} T}{\eta_B V_A^{0.6}} \quad (13)$$

$$D_{\text{H-L}} = \frac{13.26(10^{-5})}{\eta_B^{1.4} V_A^{0.589}} \quad (14)$$

where ϕ is a dimensionless "association factor" equal to 2.6 for water, M is the molecular weight of solvent B , T is temperature (in kelvins), η is the viscosity of solvent B (in centipoise), and V is the molar volume (the volume of a mole

of the pure liquid at its boiling point in $\text{cm}^3 \text{ mole}^{-1}$) of the solute A . The calculated values of D_{DMS} using these expressions are shown in Figure 4. In these calculations we used the viscosity of pure water from Korson *et al.* [1969] and a molar volume of DMS of $75.82 \text{ cm}^3 \text{ mole}^{-1}$ at 37.3°C . The molar volume of DMS at its boiling point was calculated from an equation developed by Rackett [1970] and modified by Spencer and Danner [1972]. This value for the molar volume is slightly different from that previously used to estimate D_{DMS} in the gas exchange literature ($73.96 \text{ cm}^3 \text{ mole}^{-1}$), which was taken from the density at 20°C [Bates *et al.*, 1987; Andreae, 1990].

Figure 4 demonstrates that the diffusivities obtained in this study are larger than those predicted by Wilke and Chang [1955] and Hayduk and Laudie [1974]. A discrepancy of 7–28% is observed between this study and the Hayduk-Laudie study. The magnitude of the disagreement with the Wilke-Chang results depends on the value of the association factor chosen. Hayduk and Laudie, using a larger data set, recommended an adjustment of the association factor for water from 2.6 to 2.26. The diffusivities calculated using this new association factor are 12–20% lower than this study, but the values obtained using the original association factor are only 6–14% lower. Another difference is the temperature dependence of the diffusivities. As expected, the Wilke-Chang correlation gives a better agreement with the temperature dependence observed in this study than the Hayduk-Laudie correlation. The results for methane were similar, with the Wilke-Chang expression using the original association factor providing the best agreement of the three estimations with the data from this study.

The diffusion coefficients determined in this study were measured using gels made with pure water. A correction is needed in order to apply these results to seawater for the calculations of the sea-to-air flux of DMS. Jähne *et al.* [1987a] measured the diffusivities of H_2 and He in pure water and 35.5% NaCl gels and found the diffusivities in NaCl to be lower by 6%. We made a similar comparison for methane, which is much closer in molar volume and diffusivity to most gases of atmospheric interest. Three runs made with a 35% NaCl gel at 15°C gave a mean D_{CH_4} of 1.47×10^{-5} ($1\sigma = 0.02 \times 10^{-5}$), and the four pure water 15°C runs (shown in Figure 3) gave a mean of 1.53×10^{-5} ($1\sigma = 0.02 \times 10^{-5}$). These results suggest that D_{CH_4} in seawater is $3.9 \pm 1.4\%$ lower than that in pure water, a difference which is significant at the 98% confidence level according to the t test [Havilcek and Crain, 1988]. This factor was used to calculate D_{DMS} in seawater. We obtained the appropriate Schmidt numbers for diffusion of DMS in seawater using the kinematic viscosity, ν (in $\text{cm}^2 \text{ sec}^{-1}$) of seawater as a function of temperature. The kinematic viscosity (viscosity/density) is calculated using the viscosity of seawater from Millero [1974] and the density of seawater from Millero and Poisson [1981]. The resulting Schmidt numbers are given in Table 2 for the temperature range $5^\circ\text{--}30^\circ\text{C}$. A least squares third-order polynomial fit to the data gave the equation

$$Sc = 2674.0 - 147.12t + 3.726t^2 - 0.038t^3 \quad (15)$$

where t is temperature (in degrees Celsius). The mean estimated uncertainty of this fit is 0.27% (1σ).

In previous global flux studies [Bates *et al.*, 1987; Erickson *et al.*, 1990; Andreae, 1990] the diffusivity of DMS has been estimated using molar volume and viscosity in the Hayduk-

TABLE 2. Schmidt Numbers for Dimethylsulfide in Seawater of 35 Parts-per-Thousand Salinity

Temperature, degrees Celsius	Schmidt Number, $Sc (\nu/D)$
5	2027
10	1537
15	1173
20	920
25	720
30	577

Laudie correlation. Despite the large differences between those estimates and the experimentally determined diffusivities (7–28%), the global flux of DMS is not greatly affected. Since the square root of the diffusivity is used in the flux calculation, the global flux should increase on the order of 4–5%. A correction to the global flux estimate of these studies cannot be made with only a single calculation, because the difference in diffusivity is temperature dependent. The correction must be made for the flux at individual locations and then factored into the global flux estimate.

SUMMARY

In this study the diffusion coefficient of DMS in pure water was experimentally determined in order to provide a basis for sea-to-air gas exchange calculations. The measured diffusivities agree reasonably well with empirical estimates, with the closest agreement provided by the Wilke and Chang [1955] correlation using the original solvent association factor. Diffusivities calculated using the Hayduk and Laudie [1974] expression, which are commonly used in the gas exchange literature, were lower than the experimental results by 7–28%, depending on the temperature. Using the measured diffusivities results in an increase in the global DMS sea-to-air flux estimate of approximately 5%. The diffusivities are used to derive a set of Schmidt numbers for DMS in seawater which are recommended for use in gas exchange calculations.

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