Experimental Determination of the Diffusion Coefficient of Dimethylsulfide in Water

E. S. Saltzman and D. B. King

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida

K. Holmen and C. Leck

Department of Meteorology, Arrhenius Laboratory, Stockholm University, Stockholm

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 \( \nu_{\text{DMS}} \), 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% \( (1 \sigma) \) in each measurement. A best fit to all the experimental results yields the equation

\[
\nu_{\text{DMS}} = 0.020 \exp \left( \frac{-18.1}{RT} \right),
\]

where \( R = 8.314 \times 10^{-3} \text{ kJ mole}^{-1} \text{ K}^{-1} \) and \( T \) is temperature in kelvin.

The values of \( \nu_{\text{DMS}} \) 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

\[
\text{Flux} = K(C_l - C_a/a) = K_a(C_l - C_a) \tag{1}
\]

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 \( a \) 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:

\[
\frac{1}{K} = \frac{1}{k_l} + \frac{1}{ak_g} \tag{2}
\]

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

\[
k_l = f(Sc^{-n}) \propto f(D^n) \tag{3}
\]

where \( n \) may vary from 1/2-2/3 depending on the sea state [Liss and Merlivat, 1986; Jähne et al., 1987a]. The magnitude of the gas exchange coefficient has been deduced from a variety of artificial and natural tracer experiments utilizing \( ^{14}\text{C, Rn, SF}_6, \text{ and } ^{3}\text{He} \) [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.
The flux across the membrane is obtained by taking $-D\frac{\partial C}{\partial x}$, which yields

$$\Phi = -D \frac{\partial C}{\partial x} = -D \frac{(C_2 - C_1)}{l} - \frac{2D}{l}$$

$$\cdot \sum_{n=1}^{\infty} (C_2 \cos n\pi - C_1) \cos \frac{nx\pi}{l} \exp - \left(Dn^2\pi^2t/l^2\right)$$

$$- \frac{4DC_0}{l} \sum_{m=1}^{\infty} \cos \frac{(2m + 1)\pi x}{l} \exp - \left[D(2m + 1)^2\pi^2t/l^2\right]$$

At $x = l$ this expression reduces to

$$\Phi = -D \frac{\partial C}{\partial x} = -D \frac{(C_2 - C_1)}{l} - \frac{2D}{l}$$

$$\cdot \sum_{n=1}^{\infty} (C_2 \cos n\pi - C_1) \cos n\pi \exp - \left(Dn^2\pi^2t/l^2\right)$$

$$- \frac{4DC_0}{l} \sum_{m=1}^{\infty} \cos \frac{(2m + 1)\pi x}{l} \exp - \left[D(2m + 1)^2\pi^2t/l^2\right]$$

Assuming that $C_2$ and $C_0$ are both equal to zero gives

$$\Phi = -D \frac{\partial C}{\partial x} = -D \frac{C_1}{l} + \frac{2DC_1}{l}$$

$$\cdot \sum_{n=1}^{\infty} \cos n\pi \exp - \left(Dn^2\pi^2t/l^2\right)$$

In our experiments the concentration ratio of the diffusing gas in contact with either side of the diffusion membrane ($C_2/C_1$) 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:

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

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

$$\frac{\Phi}{C_1} = \frac{D}{l}$$

**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
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 perfluoralkoxy 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 ($C_{2g}$) and low-concentration ($C_{lg}$) 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 cm$^3$ 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

$$ \ln \alpha = -10.1794 + 3761.33(1/T) $$  \hspace{1cm} (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.
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 cm$^2$ 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 $I$ to vary [Marquardt, 1963]. The values of $D$ and $I$ 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].

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

$$D = A e^{-E_a/RT}$$  \hspace{1cm} (12)

where $E_a$ is the "activation energy" for diffusion in water (in kJ mole$^{-1}$), $R = 8.314 \times 10^{-3}$ kJ mole$^{-1}$ 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 cm$^2$ sec$^{-1}$ (1σ = 6.7%) and an $E_a$ of 18.3 kJ mole$^{-1}$ (1σ = 14.6%). The mean estimated uncertainty of this fit to the experimental data is

| Parameter                  | Range      | Absolute Uncertainty | Relative Uncertainty % |
|----------------------------|------------|----------------------|------------------------|
| Flow rate, $f_2$ (in cm$^3$ 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, $a$ | 9-28       | 0.15-0.38            | 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                |
factor recommended by Hayduk and Laudie. The curve is a plot of dimethylsulfide estimates using the Wilke-Chang relationship with the association and Hayduk and Laudie [1974] relationships. Also plotted are the stated uncertainty of both sets of measurements.  

\[ D = 0.020 \exp(-18.1/RT) \]

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 \( D_{\text{DMS}} \) 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 cm\(^2\) sec\(^{-1}\) (ltr = 1 cm\(^3\)) and a value of \( Ea \) of 18.1 kJ mole\(^{-1}\) (1σ = 6.5%). The mean estimated uncertainty of this fit is 14.68% (1σ).

Previous estimates of \( D_{\text{DMS}} \) 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 expected, the Wilke-Chang expression using the original association factor provides 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 \( D_{\text{CH4}} \) of 1.47 \( \times 10^{-5} \) (1σ = 0.02 \( \times 10^{-5} \)), and the four pure water 15°C runs (shown in Figure 3) gave a mean of 1.53 \( \times 10^{-5} \) (1σ = 0.02 \( \times 10^{-5} \)). These results suggest that \( D_{\text{CH4}} \) in seawater is 3.9 ± 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 \( D_{\text{DMS}} \) in seawater. We obtained the appropriate Schmidt numbers for diffusion of DMS in seawater using the kinematic viscosity, \( \nu \) (in cm\(^2\) sec\(^{-1}\)) 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°C-30°C. A least squares third-order polynomial fit to the data gave the equation

\[ Sc = 2674.0 - 147.12t + 3.726t^2 - 0.038t^3 \]

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, $Sc (v/D)$ |
|-----------------------------|--------------------------|
| 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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K. Holmen and C. Leck, Department of Meteorology, Arrhenius-laboratory, Stockholm University, Stockholm S-106 91, Sweden. D. B. King and E. S. Saltzman, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149.

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