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Diffusivity of methyl bromide in water

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Abstract

The oceans are important in the geochemical cycle of methyl bromide, as both a source of natural methyl bromide and a sink for anthropogenic methyl bromide. Air–sea exchange rate calculations are based on measured concentration differences across the air–sea surface, on various gas exchange–wind speed relationships, and on the diffusivity of methyl bromide in seawater. In this study, the diffusivity of methyl bromide in pure water has been experimentally determined over the temperature range 5–20°C. The diffusivity varied from 9.85×10^{-6} cm^2 s^{-1} at 5°C to 1.50×10^{-5} cm^2 s^{-1} at 19.4°C. The values obtained in this study are ~ 8–35% higher than those derived from semi-empirical estimates. The diffusivity of methyl bromide in 3.5% NaCl solution was also measured at 13°C and found to be the same as the diffusivity measured in pure water. This is a surprising result given the viscosity differences between these two media. Schmidt numbers (Sc) for seawater have been calculated as a function of temperature from the pure water diffusivities. Schmidt numbers varied from 1585 at 5°C to 700 at 20°C.

Keywords: methyl bromide; diffusion; air–sea exchange; geochemical cycle

1. Introduction

The transport of tropospheric methyl bromide into the stratosphere and its subsequent photolysis is thought to have a significant impact on the concentration and lifetime of stratospheric ozone (Wofsy et al., 1975; Mellouki et al., 1992). The oceans are both a source of natural methyl bromide and a sink for anthropogenic methyl bromide and are believed to have a strong influence on tropospheric methyl bromide concentrations and lifetime (Butler, 1994; Lobert et al., 1995). Air–sea exchange rates are therefore important to our understanding of the cycling of methyl bromide through the atmosphere (Anbar et al., 1996; Pilinis et al., 1996; Yvon and Butler, 1996).

Air–sea exchange calculations are based on measured concentration gradients across the air–sea surface, various gas exchange–wind speed relationships, and liquid-phase diffusivities in seawater. For low-solubility gases the gas–liquid flux can be expressed as (Liss and Slater, 1974):

$$F = k_l(C_l - C_g \alpha) \tag{1}$$

where k_l is the gas transfer velocity; C_l is the concentration of the species in the liquid phase; C_g is the concentration in the gas phase; and α is the Ostwald solubility (Reid et al., 1987) of the species. The gas transfer velocity is a strong, but poorly

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understood, function of the physical state of the interface (sea state, wind speed, etc.) and a function of the liquid-phase diffusion coefficient to a power n, where n is usually between $\frac{1}{2}$ and $\frac{2}{3}$ (Liss and Merlivat, 1986; Jähne et al., 1987b; Wanninkhof, 1992).

Air–sea exchange calculations have generally relied on semi-empirical estimates of liquid-phase diffusivity because there have been relatively few recent experimental measurements of the diffusivity of atmospheric gases. Jähne et al. (1987a) found that for all species previously measured (except CO_2) differences between various experimental measurements far exceeded the individual quoted errors. They believed unknown systematic errors in the earlier techniques to be responsible and remeasured a number of low-solubility gases using a modified Barrer (1941) method. Methyl bromide was not included in their study. In this paper we present the experimental determination of the diffusivity of methyl bromide in pure water over the temperature range 5–20°C. Experiments were not carried out above room temperature to avoid the problem of water condensing out in sample lines and the detector. Experiments were also carried out in 35‰ NaCl solution in order to determine the salt effects for extrapolation of the data to seawater.

2. Experimental

Diffusion coefficients were measured in a continuous flow diffusion cell in which the gas of interest is allowed to diffuse across an agar gel membrane. The experimental apparatus and procedure, and the solutions to the differential equations which describe the diffusion process have been discussed in detail before (Saltzman et al., 1993; King and Saltzman, 1995) and will only be described here in brief. The basic experiment involves flowing methyl bromide and helium across opposite sides of a gel membrane. The flux of methyl bromide through the gel gradually approaches a constant, steady-state value given by:

$$(\text{flux}) = D \cdot \Delta C / l \qquad (2)$$

where D is the diffusivity of methyl bromide; ΔC is the concentration difference across the gel; and l is the thickness of the gel (cm). In terms of experimental parameters the flux of gas through the gel is given by fC_{2g}/A, where C_{2g} and f are the gas-phase concentration of methyl bromide and the gas flow rate (cm^3 min^{-1}) on the low-concentration side of the gel, respectively, and A is the gel surface area (cm^2). Assuming that the liquid-phase concentration on the low-concentration side of the gel is negligible compared to the liquid-phase concentration on the high-concentration side of the gel, the diffusivity can be expressed as:

$$D = C_{2g} f l / C_{1g} \alpha A \qquad (3)$$

where C_{1g} is the gas-phase concentration of methyl bromide on the high-concentration side of the gel; and α is the Ostwald solubility of methyl bromide in the gel. Diffusion coefficients can therefore be determined from measurements of the concentration ratio (C_{2g}/C_{1g}) and the gas flow rate f if the gel dimensions and gas solubility are known.

The gels used in this study were 0.7% agar in water, 38 cm in diameter and 0.3–0.31 cm thick. Methyl bromide solubilities in both pure water and NaCl were measured in this laboratory (De Bruyn and Saltzman, 1997).

Methyl bromide was detected using gas chromatography with photo-ionization detection (PID; HNU Systems, Inc.). Gas samples were analyzed on a 0.32-cm-OD stainless-steel 0.5-m-long column packed with Porasil B 100/150 mesh (Alltech). The carrier gas flow rate was 20 cm^3 min^{-1} and the column was kept at 150°C. The PID was used with a 10.2-eV lamp, which gave a detection limit of 0.01 ng of methyl bromide injected on the column. Calibrations were constructed from successive dilutions of pure methyl bromide gas and were run before and after each experiment

Experiments were carried out with pure methyl bromide and mixtures of 20–30% methyl bromide in helium flowing at ~ 5 cm^3 min^{-1} on the high-concentration side of the gel. The diluted methyl bromide was necessary at 5°C to prevent methyl bromide from condensing out in the cell. Gas flow rates were mass flow controlled and measured by an electronic bubble meter. Helium gas flows on the low-concentration side of the gel were varied between 20 and 50 cm^3 min^{-1}. In this range the measured diffusivity was independent of flow rate.

Diffusion coefficients were corrected by 1.9% to account for the decreased solubility of methyl bromide in the agar gel and the hindrance of the three-dimensional agar structure (Langdon and Thomas, 1971). Diffusion coefficients determined from pure methyl bromide experiments were also corrected by 2.5% to take into account the non-ideality of the gas.

3. Results and discussion

3.1. *Diffusivity of methyl bromide in pure water*

The diffusivities measured in pure water gels are plotted as a function of temperature in Fig. 1. A non-linear fit to the data yields the equation:

$$D\ (\mathrm{cm^2\ s^{-1}}) = 0.035\exp(-18.9/RT)\quad (278\text{–}293\ \mathrm{K}) \tag{4}$$

where $R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}; and T is the temperature in kelvins. This equation is shown as the solid line in Fig. 1. The average relative residual in the fit is 4.1% ($1\sigma = 4.2\%$). The relative uncertainty in a single experimental determination of the diffusion coefficient is estimated to be 3–6% (1σ) over the temperature range studied, with the largest contributions from the solubility and the concentration ratio. The relative uncertainty in the solubility (α) is 2.5% (1σ) (De Bruyn and Saltzman, 1997) and the observed variance in the concentration ratio ranged from 1% to 4.3% (1σ). As shown in Fig. 1, the observed variance in the measured diffusion coefficients is consistent with the estimated uncertainty. The precision of replicate analyses ranged from ±3.6% (1σ) at 9° and 13°C to ±5.4% (1σ) and ±10% (1σ) at 20° and 5°C, respectively.

There are a number of semi-empirical methods for estimating diffusivities. The most commonly used are those of Wilke and Chang (1955) and Hayduk and Laudie (1974):

$$D_{\mathrm{W\text{-}C}} = 7.4 \times 10^{-8}(\Phi M_{\mathrm{b}})^{1/2}T/\eta_{\mathrm{b}}V_{\mathrm{a}}^{0.6} \tag{5}$$

$$D_{\mathrm{H\text{-}L}} = 13.26 \times 10^{-5}/\eta_{\mathrm{b}}^{1.4}V_{\mathrm{a}}^{0.589} \tag{6}$$

where Φ is a dimensionless association factor equal to 2.6 for water; M_{b} is the molecular weight of water; T is the temperature in kelvins: η_{b} is the viscosity of water in centipoises; and V_{a} is the molar volume of the solute at its boiling point (cm^3 mol^{-1}). The only significant difference between the two estimates is in their treatment of temperature dependence.

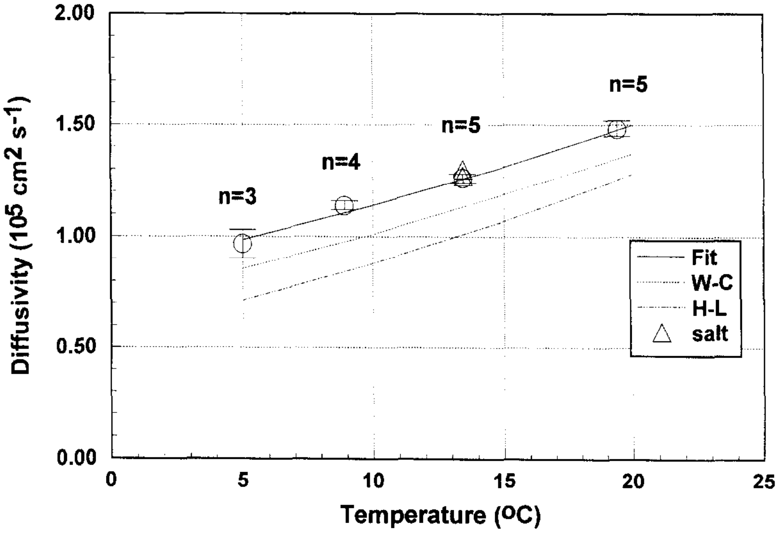

Fig. 1. Diffusion coefficients for methyl bromide measured in this study. Also shown are the semi-empirical estimates of Wilke and Chang (1955) and Hayduk and Laudie (1974). *Circles* are pure water average values. *Triangles* are measurements in 3.5% NaCl solution. *Error bars* are standard errors of the mean.

Also plotted in Fig. 1 are both of these semi-empirical estimates. The viscosity of pure water was taken from Korsen et al. (1969) and a value of 52.9 cm^3 mol^{-1} was used for the molar volume of methyl bromide. This value was calculated using the additive methods of Le Bas (Reid et al., 1987). Our measurements are ~ 12% higher than the estimates of Wilke and Chang (1955) at all temperatures and 17–38% higher than the Hayduk and Laudie (1974) estimates. The overall temperature dependence agrees well with that of Wilke and Chang (1955).

The only previous measurements of the diffusivity of methyl bromide in water are those of Maharajh and Walkey (1972). Maharajh and Walkey (1972) used an inverted tube-moving boundary technique and measured diffusivities 20–30% lower than the measurements discussed here. They quote an uncertainty of ±2% in their measurements. Their solubility source is not given. However, if we assume they used the solubilities of Wilhelm et al. (1977) (uncertainty of ±4.7%), the uncertainty in their diffusivities would be ~ ±5%. While we have no explanation for the discrepancy it should be noted that Maharajh and Walkey (1972) also measured CH_4 diffusivities which were 10–20% lower than recent measurements made by both Jähne et al. (1987a) and Saltzman et al. (1993). It is likely that the differences reflect a systematic bias between the techniques which is not currently understood.

3.2. Diffusivities of methyl bromide in 3.5% NaCl

Two measurements of the diffusivity of methyl bromide in 3.5% NaCl were carried out at 13°C and also plotted in Fig. 1. Measurements were made in 3.5% NaCl rather than seawater for comparison with the work of others. According to the *t* test, the diffusivity of methyl bromide in 3.5% NaCl does not differ significantly from that in pure water at the 99% confidence level. This is surprising when one considers that the diffusivity of a species should decrease as the viscosity of the liquid medium increases. The viscosity of seawater is ~ 6–7% higher than the viscosity of pure water at 15°C. According to the semi-empirical estimates given above this should have resulted in at least a 6–7% decrease in diffusivity. This anomalous behavior has also recently been observed for SF_6 (King and Saltzman, 1995) and CFC-11 (Zheng et al., 1996).

We do not believe the lack of a salt effect is a technique dependent artifact, as the expected effect has been observed for other gases using gel membranes. Jähne et al. (1987a) measured the diffusivities of He and H_2 in the temperature range 5–35°C. Their measurements were 5–8% lower in 3.5% NaCl than in pure water. Saltzman et al. (1993) measured the diffusivity of CH_4 at 15°C in pure water and in 3.5% NaCl. They found a 4% decrease in the diffusivity in the NaCl solution. Recently Zheng et al. (1996) observed a 7% decrease in the diffusivity of Freon-12 in seawater relative to that in pure water. The reason for not observing a salt effect is not known.

3.3. Schmidt numbers (Sc)

Diffusivities are used in air–sea exchange calculations in the form of their corresponding Schmidt numbers for seawater, where the Schmidt number is the kinematic viscosity (ν) of seawater divided by the diffusivity (D) of the species. Using pure water diffusivities generated from Eq. (4) and kinematic viscosities calculated from the viscosities of Millero (1974) and the densities of Millero and Poisson (1981), Schmidt numbers were calculated for seawater (Table 1). The uncertainty in each Schmidt number is dominated by the uncertainty in the diffusivity and is therefore estimated to be ~ 3–6% (1σ). A least-squares second-order polynomial fit to the

Table 1
Schmidt numbers ($Sc = \nu / D$) for methyl bromide in seawater

Temperature (°C)	Schmidt number
5	1585
10	1186
15	906
20	700
25	549 [a]
30	435 [a]

The uncertainty in each Schmidt number is estimated to be ~ 3–6% (1σ) (see text).

[a] Calculated by extrapolation of Eq. (4).

Schmidt numbers over the temperature range 5–30°C yields the equation:

$$\mathrm{Sc} = 2004 - 93.5t + 1.39t^2 \quad (278\text{–}303\ \mathrm{K}) \qquad (7)$$

where t is the temperature in degrees Celsius. The average relative residual in the fit is 1.80% ($1\sigma = 0.9\%$).

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