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The solubility of methyl bromide in pure water, 35‰ sodium chloride and seawater

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Abstract

A simple gas–liquid membrane equilibrator has been used to determine the solubility of methyl bromide in pure water, 35‰ NaCl, and seawater over the temperature range from 0° to 30°C. The measurements have an accuracy of ±2% and a relative precision of 4%. The data have been fit to a temperature- and salinity-dependent expression to provide solubilities for methyl bromide in pure water, seawater, and NaCl solutions.

Keywords: methyl bromide; solubility; salting out; seawater; air–sea exchange; geochemical cycle

1. Introduction

Methyl bromide is a major source of stratospheric bromine which is an efficient catalyst for ozone destruction (Wofsy et al., 1975; Mellouki et al., 1992). This has led to efforts to regulate the manufacturing and agricultural use of methyl bromide under the Montreal Protocol (Copenhagen Amendments to the Montreal Protocol, 1994) and Clean Air Act (USEPA, 1993). This in turn has stimulated research aimed at understanding the global methyl bromide budget and the fluxes and feedbacks that control atmospheric methyl bromide. 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 (Singh et al., 1983; Penkett et al., 1985; Khalil et al., 1993; Singh and Kanakidou, 1993; Butler, 1994; Lobert et al., 1995; Anbar et al., 1996; Pilinis et al., 1996; Yvon and Butler, 1996).

Estimates of the flux of methyl bromide across the air–sea boundary are strongly dependent on its solubility in seawater. The solubility of methyl bromide in pure water is well documented in the literature (Haight, 1951; Glew and Moelwyn-Hughes, 1953; Swain and Thornton, 1962; Wilhelm et al., 1977). However, there has been little experimental work on the solubility of methyl bromide in seawater. Singh et al. (1983) estimated the salting out of methyl bromide in seawater relative to pure water, based on data for similar compounds. Elliott and Rowland (1993) recently measured the solubility of methyl bromide in pure water, NaCl solution, and seawater at two temperatures.

In this study, the solubility of methyl bromide has

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been measured in pure water, 35‰ NaCl, and seawater over the temperature range from 0° to 30°C. The data are used to derive an expression for the solubility of methyl bromide in seawater and NaCl solutions as a function of salinity and temperature.

2. Experimental

The solubility of methyl bromide was measured using a simple gas–liquid membrane equilibrator (Fig. 1). The membrane consisted of a 90-cm length of 3-mm-I.D. Gore Tex® microporous Teflon tube. The tube is submerged in the solution of interest in a sealed 1-l glass container. The equilibrator was kept in a temperature-controlled bath and the liquid was stirred using a submerged pneumatic-driven magnetic stirrer. Mass flow-controlled helium was metered slowly through the microporous tube, in order to equilibrate with dissolved gases in the liquid. The microporous tubing has a porosity of 50% and allows gas to pass freely through its walls. It is also naturally hydrophobic and repels water. The tubing has a water breakthrough pressure of 12.8 psi (19.7 kPa), which was never exceeded under the conditions of this experiment.

At the start of an experiment, 2.5–5 ml of pure gaseous methyl bromide were injected with a gas-tight syringe into the liquid to produce liquid–phase concentrations varying from 1×10^{-4} to 2×10^{-4}

mol l^{-1}. These concentrations are approximately three orders of magnitude below the maximum concentration of methyl bromide that can be dissolved in the solution (Glew and Moelwyn-Hughes, 1953). Zero headspace in the glass vessel, vigorous stirring of the liquid, and a 10-min delay ensures that all the methyl bromide is dissolved in the liquid prior to data acquisition.

The gas stream emerging from the equilibrator flowed through the injection loop of a gas chromatography injection valve and was periodically injected onto a stainless-steel column (0.318-cm OD, 0.5-m long) packed with Porasil B 100/150 mesh, held isothermally at 80°C. The first injection in all experiments is a pure helium injection and is the system blank. Methyl bromide was detected with a photo-ionization (10.7-eV lamp energy) or thermal conductivity detector. Methyl bromide concentrations in the tube were determined from calibration curves prepared by serial dilution of pure methyl bromide with helium in a glass gas-tight syringe. Concentrations varied from 3×10^{-5} to 4×10^{-5} mol l^{-1}. For syringe injections the precision of replicate analysis is better than $\pm 1.4\%$ (1σ) and the accuracy of a single concentration measurement is estimated to be ± 0.6–2.0% (1σ). For each experiment, an average peak area was calculated from 5–10 injections after the peak areas had stabilized. Once stabilized, peak areas varied by less than $\pm 1.8\%$ (1σ). The estimated accuracy of a single
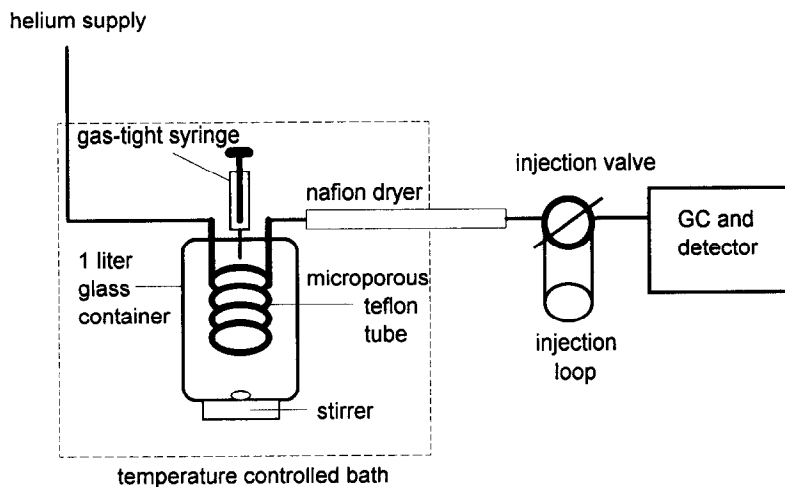

Fig. 1. Experimental apparatus for solubility determinations.

solubility measurement is better than $\pm 2.5\%$ (1σ). Calibration curves and experimental data were normalized for pressure and temperature changes.

During the experiment, the gas–liquid interaction time is controlled by the volume of the membrane tubing and the gas flow rate. To ensure that gas–liquid equilibrium was achieved, gas flow rates of < 3 ml min^{-1} were used, giving interaction times on the order of minutes. Equilibrium was verified by varying the gas flow rate during the course of individual experiments, and observing invariant gas-phase concentrations.

During experiments carried out at temperatures above that of the laboratory (22°C), the equilibrated gas stream was passed through a Nafion membrane dryer before leaving the bath to prevent water vapor condensing out in the gas lines before the detector. Methyl bromide loss in the dryer was checked by carrying out experiments at cooler temperatures with and without the dryer. No methyl bromide loss was observed. A small correction was applied to gas-phase concentrations determined in experiments with the dryer to account for the removal of water vapor from the gas stream ($\sim 3\%$ at 25°C and $\sim 4\%$ at 30°C).

Experiments were carried out in deionized water, 35‰ NaCl solution, and Biscayne Bay seawater. The seawater samples ranged in salinity from 34 to 36‰, as determined using a Guildline Portasal 8410 salinometer. Experiments carried out with filtered and autoclaved seawater indicated that solubility measurements were not affected by biological activity or particulates.

At helium flow rates of < 3 ml min^{-1}, the fraction of liquid-phase methyl bromide transferred to the gas phase during the course of an experiment is minimal. The loss is greatest at 30°C in seawater, where the change in the liquid-phase concentration is calculated to be $\sim 0.2\%$ per run at 3 ml min^{-1}. In this case, the initial peak area was used to calculate the solubility.

3. Non-ideality

Solubilities of methyl bromide (H') are expressed as the ratio of the liquid-phase concentration (mol l^{-1}) to the gas-phase fugacity (atm) at the tempera-

ture of the liquid. H' is proportional to the inverse of the Henry's law coefficient. Corrections have been made to gas volumes and partial pressures have been converted to fugacities to account for the non-ideality of the experiment. These corrections are based on the virial equation of state expanded up to the second virial coefficient and follow the approach of Weiss (1974). Second virial coefficients for the pure gas were obtained from a polynomial fit to the data of Dymond and Smith (1980):

$$B(T) = -6100 + 31.04T - 0.0416T^2 \qquad (1)$$

where B is in units of cm^3 mol^{-1}; and T is the temperature in kelvins.

Liquid-phase concentrations were calculated from the volume of pure methyl bromide injected into the liquid- and gas-phase concentrations were determined from a calibration curve prepared by serial dilution. The mole fraction of methyl bromide in the calibration syringe is calculated from the volume of pure methyl bromide injected into a syringe and the total volume of the syringe. The number of moles of methyl bromide injected in both cases was calculated using the equation (Guggenheim, 1967; Weiss, 1974):

$$V = RT/P + B(T) \qquad (2)$$

where V is the volume (l) of 1 mol of the real gas; P is the system pressure in atmospheres; T is the temperature in kelvins; R is the gas constant; and $B(T)$ is obtained from Eq. (1). Because the gas mixture in the calibration syringe after dilution is more than 99.5% helium the mixture can be treated as essentially ideal and the total number of moles in the gas phase can therefore be determined from the ideal gas law.

Fugacities of methyl bromide were calculated using the following equation (Guggenheim, 1967; Weiss, 1974):

$$f_1 = x_1 P \exp\left[\left\{B(T) + 2 x_2^2 \delta_{12}\right\} P/RT\right] \qquad (3)$$

where f_1 is the fugacity of methyl bromide in the mixture; x_1 and x_2 are the mole fractions of methyl bromide and helium, respectively; P is the total pressure; and δ_{12} is a function of the methyl bromide–helium mixed virial coefficients. Because there are no data available on mixed virial coefficients of methyl bromide it was assumed that δ_{12} is zero (Lewis and Randall rule; Guggenheim, 1967; Weiss,

1974). In all experiments the total pressure was 1 ± 0.01 atm. Correcting experimental volumes for non-ideality increased solubilities by $\sim 2.5\%$ at all temperatures. Expressing H' in terms of fugacities rather than partial pressures increased the solubilities by a further 2.3% (30°C) to 3.2% (1°C).

4. Results

Experimentally determined solubilities are given in Table 1 and shown in Fig. 2. Each point is the mean of 2–9 experiments carried out at a given temperature. Relative standard errors range from 0.5% to 2.5% for pure water runs, from 0.6% to 3.9% for seawater runs and from 0.7% to 3.2% for NaCl solution runs. The average relative precision and average relative standard error for all solutions and temperatures is 4% and 2%, respectively.

The temperature and salinity dependence of trace gas solubilities in aqueous solutions are usually expressed by functions based on van 't Hoff and Setchenow relationships. To provide expressions for the calculation of methyl bromide solubility as a function of temperature and salinity (or ‰ NaCl), the data have been fit to an expression analogous to that recommended by Weiss (1970, 1974)):

$$H' = \exp\left[a_1 + a_2(100/T) + a_3 \ln(T/100) \right.$$
$$\left. + S\{b_1 + b_2(T/100) + b_3(T/100)^2\}\right] \qquad (4)$$

where T is the temperature in kelvins; S is the salinity or NaCl concentration in ‰; and the a_i and b_i are constants.
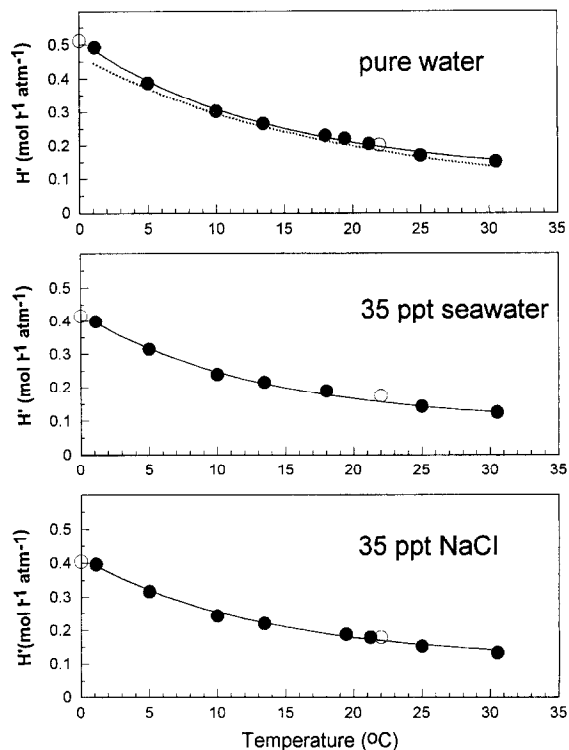

Fig. 2. Solubility of methyl bromide in pure water, seawater, and NaCl as a function of temperature. ● = experimental data from this study; ○ = experimental data from Elliott and Rowland (1993). The *solid lines* are the fits of Eq. (4) to the data from this study (coefficients given in Table 2). The *dotted line* is the pure water solubility function given by Wilhelm et al. (1977).

Eq. (4) was fit to two different data sets to provide two different sets of constants: (1) the pure water and seawater data to obtain constants for pure

Table 1
Solubility measurements for methyl bromide in pure water, seawater, and 35‰ NaCl solution

Temperature(°C)	Solubilities (H′)		
	pure water	seawater	35‰ NaCl
1.1	0.493 (0.0059, 4)	0.399 (0.0033, 5)	0.397 (0.0080, 4)
5.0	0.387 (0.0097, 9)	0.315 (0.0036, 3)	0.316 (0.0078, 6)
10.0	0.303 (0.0046, 9)	0.239 (0.0042, 5)	0.243 (0.0069, 3)
13.4	0.266 (0.0033, 5)	0.215 (0.0048, 4)	0.220 (0.0016, 2)
18.0	0.230 (0.0064, 4)	0.189 (0.0073, 2)	
19.4	0.221 (0.0052, 6)		0.188 (0.0061, 6)
21.2	0.205 (0.0046, 4)		0.179 (0.0013, 3)
25.0	0.170 (0.0008, 2)	0.143 (0.0016, 2)	0.152 (0.0018, 2)
30.5	0.152 (0.0023, 5)	0.125 (0.0008, 3)	0.133 (0.0033, 2)

The data listed are given as mean values, with the standard error and number of replicates given in parentheses.

Table 2
Constants for the calculation of methyl bromide solubility using Eq. 4

Constants	Seawater	NaCl solutions
a_1	−171.2	−171.1
a_2	254.3	254.1
a_3	77.04	76.99
b_1	0.2591	0.1521
b_2	−0.1828	−0.1192
b_3	0.03142	0.02244

water and seawater; and (2) the pure water and NaCl data to obtain constants for pure water and NaCl solutions. The resultant fits are shown as solid lines in Fig. 2, and the constants determined for each case are given in Table 2. The mean residual of the fits was $4 \pm 3.6\%$, and $4 \pm 3.3\%$ for seawater and NaCl solutions, respectively.

5. Discussion

Wilhelm et al. (1977) generated an expression for the solubility of methyl bromide in pure water as a function of temperature based on the measurements of Haight (1951), Glew and Moelwyn-Hughes (1953), and Swain and Thornton (1962). This function is in reasonable agreement with our data (Fig. 2). Their expression is based on data from 5–80°C, with a quoted uncertainty of $\pm 4.7\%$ (1σ). Our data lie within this uncertainty range at all temperatures except at 0° and 30°C where our data are ~ 10% higher. However, it should be noted that 0°C is outside the recommended temperature range for the Wilhelm et al. (1977) expression and the data in the Wilhelm et al. compilation have not been assessed for experimental deviations from ideality.

The only previous methyl bromide solubility measurements made in seawater and NaCl solutions are those of Elliott and Rowland (1993). They measured the solubility of methyl bromide in pure water, 33.34 $\pm 0.29‰$ salinity seawater and 0.5 M NaCl solution (29.22‰ NaCl) at 0° and 22°C. For the purposes of comparison to this work, their seawater and NaCl solution data have been corrected to 35‰ using Eq. (4) and are shown along with their pure water data in Fig. 2. The agreement between their data and our fits

is good at 0°C. Their solubilities are 0.9%, 2.3%, and 0.9% lower than our fits for pure water, seawater, and NaCl solutions, respectively. At 22°C, their solubilities are slightly higher than Eq. (4) for all solutions (2.8% for pure water, 11.9% for seawater, 8% for NaCl solutions). Their pure water data are also higher than the Wilhelm et al. (1977) expression at both 0° and 22°C.

There have been a number of recent attempts to measure and model the air–sea exchange of methyl bromide. All require the solubility of methyl bromide in seawater. Singh et al. (1983) analyzed seawater concentrations by equilibrating individual seawater samples with air at laboratory temperatures. To determine the saturation state of the ocean their data had to be corrected to the temperature of the sea surface using a temperature-dependent solubility function. The solubility of methyl bromide in seawater is also required to determine the air–sea flux of methyl bromide from their measured saturation states. Based on data for similar compounds, Singh et al. (1983) estimated that the solubility of methyl bromide in seawater would be 20% less than in pure water. They obtained seawater solubilities as a function of temperature by correcting the pure water data of Wilhelm et al. (1977). The salting out measured in this work agrees well with the Singh et al. (1983) estimate, varying from ~ 20% at 0°C to ~ 18% at 30°C. However, because our pure water measurements are 4–5% higher that the pure water data of Wilhelm et al. (1977) the resultant Singh et al. (1983) seawater solubilities are 4–5% lower than our seawater measurements. Net sea–air fluxes calculated in Singh et al. (1983) would be correspondingly 4–5% lower if calculated using the seawater solubilities measured in this study.

Lobert et al. (1995) used a flowing Weiss equilibrator (described by Butler et al., 1988) to directly determine the saturation state of methyl bromide in surface ocean waters. Because the equilibrator ran at near ambient temperatures, the saturation state can be obtained from their data with only a minor correction for solubility effects. However, as with Singh et al. (1983), the solubility of methyl bromide in seawater is needed to calculate an air–sea flux from their data. Lobert et al. (1995) used the solubility relationship of Elliott and Rowland (1993), which results in a higher air to sea flux (10–12%) than would be

calculated using the solubilities from this study, particularly at higher temperatures.

There have been several recent modeling studies of the air–sea exchange of methyl bromide (Butler, 1994; Lobert et al., 1995; Anbar et al., 1996; Pilinis et al., 1996). In these models, a constant or a chlorophyll-derived methyl bromide production rate is assumed and methyl bromide is lost from the water column via hydrolysis and chloride substitution, downward advection, and air–sea exchange. Anbar et al. (1996) used the Singh et al. (1983) solubility estimate which, as discussed above, underestimates the solubility by 4–5%. Pilinis et al. (1996) used a preliminary solubility relationship derived from our NaCl data which overestimates the solubility by ~ 6%. Using the correct seawater solubility would correspondingly increase the air to sea flux in the Anbar et al. (1996) study and decrease the air to sea flux in the Pilinis et al. (1996) study.

6. Summary

In summary, the solubility of methyl bromide in pure water, 35‰ NaCl, and seawater has been measured over the temperature range from 0° to 30°C. The measurements have an accuracy of $\pm 2\%$ and a relative precision of 4%. The data have been fit to a temperature- and salinity-dependent expression to provide solubilities for methyl bromide in pure water, seawater and NaCl solutions. The solubility of methyl bromide in seawater and NaCl solution is respectively given by:

$$H' \left(\mathrm{mol}\, l^{-1}\, \mathrm{atm}^{-1} \right)$$
$$= \exp\left[-171.2 + 254.3(100/T) \right.$$
$$+ 77.04\ln(T/100) + S\{0.2591$$
$$\left. - 0.1828(T/100) + 0.03142(T/100)^2\} \right]$$

and

$$H' \left(\mathrm{mol}\, l^{-1}\, \mathrm{atm}^{-1} \right)$$
$$= \exp\left[-171.1 + 254.1(100/T) \right.$$
$$+ 76.99\ln(T/100) + S[0.1521$$
$$\left. - 0.1192(T/100) + 0.02244(T/100)^2\} \right]$$

where T is the temperature in kelvins; and S is the

salinity or NaCl concentration in ‰. The solubility of methyl bromide in pure water is given by either expression with $S = 0$.

Acknowledgements

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