608 J. Chem. Eng. Data 1994, 39, 608-610

Physicochemical Properties of Dimethyl Selenide and Dimethyl Diselenide

U. Karlson

Department of Marine Ecology and Microbiology, National Environmental Research Institute,
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

W. T. Frankenberger, Jr.*

Department of Soil and Environmental Sciences, University of California, Riverside, California 92521

W. F. Spencer

USDA-ARS-USSL, Department of Soil and Environmental Sciences, University of California,
Riverside, California 92521

Volatilization of selenium (Se) is a dissipation mechanism by which gaseous Se is redistributed in the environment. The vapor pressures of dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) were determined using the isoteniscope method, and the solubility of DMSe in H_2O was determined in a closed system by headspace analysis. The vapor pressures at 25 °C were 32.03 and 0.38 kPa for DMSe and DMDSe, respectively. The enthalpies of vaporization were calculated as 31.90 and 74.92 kJ mol^{-1}, respectively. The solubility of DMSe was 0.0244 g/g of H_2O. The Henry's law constant for DMSe was calculated as 143 kPa kg mol^{-1} (0.144 kPa m^3 mol^{-1}).

1. Introduction

Volatilization is a significant mechanism for Se loss from soil and water (*1*). It is defined as the loss of chemicals from a surface in the vapor phase, that is, vaporization followed by diffusion into the atmosphere (*2*). Volatilization rates of chemicals from surface deposits are directly proportional to their relative vapor pressures (*2*). Therefore, vapor pressure is a key parameter controlling the behavior of methylated Se in the environment, along with water solubility, soil adsorption, stability, wind speed, and air turbulence. Vapor pressures often increase 3-4-fold for each 10 °C rise in temperature. For dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) the vapor pressure has not been determined to date.

Environmental partitioning of methylated Se among soil, water, and air depends on several factors, including Se solubility in water (*3*). The solubility of methylated Se species has not been reported. Confusion exists in the literature about this important physicochemical property. Characterizations range from "insoluble" in the case of DMSe (*4*), to "relatively insoluble" for methylated Se compounds (*3*), to "soluble" for methylated Se species (*5*). There is a need to quantitate the solubility of DMSe.

Recently, microbial volatilization of Se has been considered as an alternative means to detoxify Se-contaminated sediments (*6-8*). Application of certain soil amendments was found to strongly stimulate soil Se volatilization (*9*). The major volatile product was identified as DMSe, along with a small amount of DMDSe (*10*). The dissipation of soil Se by microbial volatilization is highly dependent on the rate of microbial production of alkyl selenides, their solubility in water, their adsorption to soil sufaces, and their diffusion into air. The latter is dependent on the vapor pressure of the Se compounds and its change with temperature. To predict volatile Se emissions, the physicochemical parameters for the major Se species released into the atmosphere need to be known. This study was undertaken to determine the vapor pressure of DMSe and DMDSe, and the solubility of DMSe.

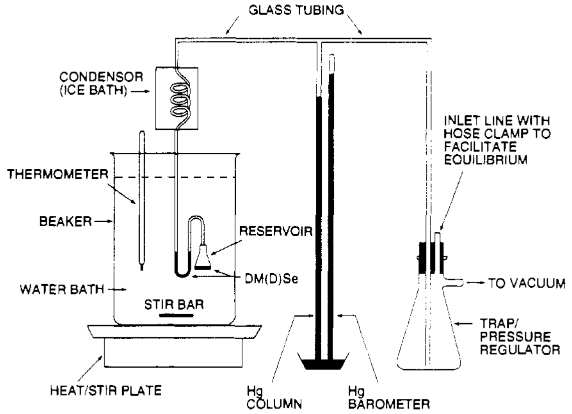

Figure 1. Experimental apparatus used for vapor pressure determinations of DMSe and DMDSe.

2. Experimental Methods

2.1. ***Vapor Pressure.*** Analytical grade DMSe and DMDSe were obtained from Strem Chemicals (Newburyport, MA). The vapor pressure of DMSe and DMDSe was determined by the isoteniscope method (*11*) with a calibrated thermometer (certified by Fisher Scientific, Pittsburgh, PA). The experimental apparatus is illustrated in Figure 1. Approximately 5 cm^3 of DM(D)Se was placed in the reservoir, and a small amount in the U-tube attached to it. Under a slight vacuum, the sample was heated to vigorous boiling to expel all air between the reservoir and the U-tube. Then the temperature in the water bath was lowered to the desired level by adding ice. The thermometer bulb was placed close to the reservoir with the liquid DM(D)Se. Measurements were performed at temperatures ranging from 5 to 40 °C. Using a hose clamp on the air intake line, the pressure of the system

0021-9568/94/1739-0608$04.50/0

was adjusted until equilibration between the reservoir and mercury (Hg) column was achieved, i.e., the DM(D)Se levels in the U-tube were equal. Vapor pressure was calculated as the difference between the height of the Hg column at equilibrium and that of a Hg barometer column. Precision of the measurements was estimated by calculating the 95% confidence limits for the regression equations of temperature on vapor pressure at 25 °C.

2.2. Solubility. The solubility of DMSe in water was determined in closed systems consisting of a silanized 125 cm^3 screw-top Erlenmeyer glass flask (approximate interior volume 141 cm^3) and a Mininert valve septum (Dynatech, Baton Rouge, LA). The exact interior volume of each flask had been determined by the mass of H_2O. Each flask was filled with 100 g of purified (Millipore, Milford, MA) water and closed with the valve septum. Using a syringe, DMSe was added to the system. Its quantity was determined by mass increase. Proper seal of the septum was confirmed by repeated weighing after 24 h. The systems were maintained at 25 ± 0.1°C in a water bath. Equilibration of DMSe among the undissolved, the dissolved, and the gas phases was facilitated by shaking. After 48 h, equilibration was assumed and vapor density was determined in the headspace. This was repeated 12 h later to confirm equilibration.

The vapor density of DMSe in the headspace was determined by taking a 0.5 cm^3 aliquot in a gas-tight syringe, diluting it with air in a silanized 125 cm^3 glass flask (holding a few glass beads and stoppered with a Mininert valve septum), and injecting a 0.25 cm^3 aliquot of the dilution directly into a gas chromatograph (model 5890, Hewlett-Packard, Avondale, PA). The instrument parameters were as follows: 3-m packed stainless steel column with liquid phase, 10% Carbowax 1000, and solid support, Chrom W-AW, mesh 60/80; flame ionization detector; column temperature, 58 °C rising to 80 °C after 2 min at 70 °C min^{-1}; injector/detector temperature, 105 °C; carrier gas (He), 10 $cm^3\ min^{-1}$; N_2, 30 $cm^3\ min^{-1}$; H_2, 40 $cm^3\ min^{-1}$; air flow, 370 $cm^3\ min^{-1}$. The signal was recorded with a Hewlett-Packard Model 3393A integrator. Standards were prepared by making gas dilutions, as above, from the equilibrated headspace over liquid DMSe at 20 °C, and assuming

$$P_a = P \tag{1}$$

where P is the vapor pressure at 25 °C, as determined by the isoteniscope method, and P_a is the apparent vapor pressure. Since

$$P_a = \frac{w}{V}\frac{RT}{M} \tag{2}$$

with w/V being the vapor density and M the molecular weight of DMSe, we were able to use

$$\frac{w}{V} = P\frac{M}{RT} \tag{3}$$

for calibration. The peak area was linear from 0 to 5 μg of Se injected. The solubility of DMSe in water at 25 °C was calculated from the intercept between the sloped and the horizontal segments of a plot fitted to the headspace vapor density data.

Precision of the gas chromatographic measurements was calculated at 5.2%, derived as the relative standard deviation of the analytical results in the horizontal segment of the plot. The precision of the solubility estimate was calculated as a 90% confidence interval outlined by the extremes of two overlapping 95% confidence bands around the horizontal and the sloped segments of the plot (Figure 3).

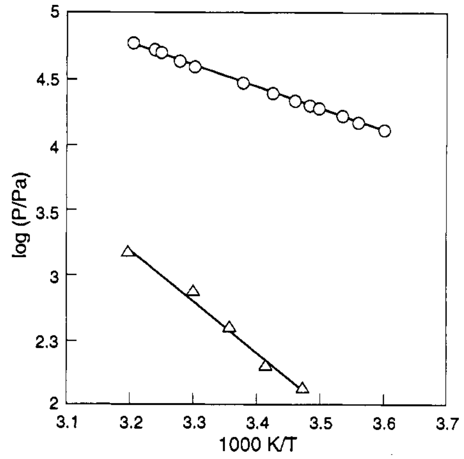

Figure 2. log P against $1/T$ for DMSe (○) and DMDSe (△).

Table 1. Experimental Data from Vapor Pressure Measurements

$(CH_3)_2Se$		$(CH_3)_2Se_2$	
t/°C	P/mmHg	t/°C	P/mmHg
39	428.5	40	11.0
36	379.0	30	5.5
35	364.0	25	3.0
32	320.5	20	1.5
30	288.0	15	1.0
23	219.0		
19	184.0		
16	159.0		
14	146.0		
13	139.5		
10	121.5		
8	109.0		
5	94.5		

The solubility of DMDSe was not determined. During attempts to do so, equilibration was not achieved even after 5 days. At the same time there was some evidence that a chemical reaction of DMDSe with H_2O was occurring with the appearance of a yellow color.

3. Results

3.1. Vapor Pressure. The dependence of the vapor pressure of DM(D)Se on temperature is illustrated in Figure 2. The simple regression equation for DMSe is

$$\log(P/\text{Pa}) = 10.093 - 1665.9/(T/\text{K}) \tag{4}$$

and for DMDSe

$$\log(P/\text{Pa}) = 15.709 - 3912.8/(T/\text{K}) \tag{5}$$

where T is the temperature and P is the vapor pressure. The correlation coefficients were $r = 0.999$ ($P < 0.001$) and $r = 0.993$ ($P < 0.001$), respectively. Experimental results are listed in Table 1. The vapor pressures for DMSe and DMDSe at 25 °C were calculated as 32.03 ± 1.99 and 0.38 ± 0.28 kPa, respectively.

3.2. Solubility. For determination of solubility, the linear regression equations for Figure 3 were derived as

$$C_1 = -0.093 + 0.586(w/\text{mg}) \qquad (r = 0.997; P < 0.0001) \tag{6}$$

$$C_2 = 1.340\ \text{mg L}^{-1} \qquad (s^2_{cw} = 0.005) \tag{7}$$

where w is the quantity of DMSe (mg) added to the system minus the quantity of DMSe in the headspace, C_1 and C_2 are the headspace alkylselenium concentrations (mg mL^{-1}) in the sloped and in the horizontal segments of the graph,

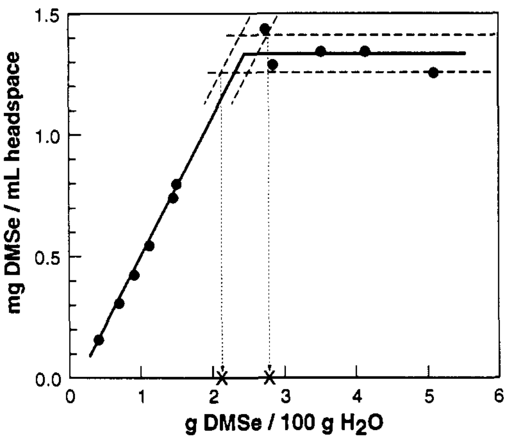

Figure 3. Vapor density, C, of DMSe in the headspace over H_2O versus w, the amount of DMSe in H_2O (=total quantity introduced into the system minus the quantity in the headspace). The temperature of the system was 25 °C. Dashed lines show 95% confidence limits for regression equations. Dotted lines illustrate determination of a 90% confidence interval for the solubility of DMSe.

respectively, and r and s^2_{cw} are the linear correlation coefficients and the variance of regression, respectively. The intercept between the two regression lines, where

$$C_1 = C_2 \qquad (8)$$

denotes the solubility of DMSe. By combining eqs 6–8, the solubility of DMSe was calculated to be 24.4 (+3.5; −3.0) g/1000 g of H_2O at 25 °C or 0.2238 mol/1000 g of H_2O.

3.3. Enthalpy of Vaporization. From one form of the Clausius–Clapeyron equation, the slope of the graph of log P versus $1/T$ is related to the heat of vaporization by the equation

$$\Delta_{vap}H = -2.303R(m) \qquad (9)$$

where $\Delta_{vap}H$ is the enthalpy of vaporization and R is the gas constant. For DMSe and DMDSe the enthalpies of vaporization were calculated to be 31.90 and 74.92 kJ mol^{-1}, respectively.

4. Discussion

Combining the results from the vapor pressure determinations and the solubility measurements allows calculation of the Henry's law constant. It is defined by

$$P = kX \qquad (10)$$

where P is the headspace vapor pressure at a defined temperature and X is the concentration in the underlying solution. Using the solubility of DMSe in water at 25 °C (0.2238 mol/1000 g of water), and the calculated vapor pressure for 25 °C, we arrive at

$$k = 143 \text{ kPa kg mol}^{-1} \ (0.144 \text{ kPa m}^3 \text{ mol}^{-1})$$

for DMSe. The dimensionless Henry's law constant (Kd) defined as the ratio of the saturated vapor density to solubility (calculated from Figure 3) is 0.058. This means that at equilibrium the water concentration is about 17 times greater than the air concentration.

With 32.03 kPa at 25 °C, the vapor pressure of DMSe is approximately 5 times that of ethanol and half that of ether. The vapor pressure of DMDSe (0.38 kPa at 25 °C) is approximately 1/10 that of water. Because of the exponential relationship between temperature and vapor pressure, DM(D)Se is expected to become overproportionally volatile with increasing temperature. This agrees with earlier findings that Se field emission rates are highly dependent on soil and air temperature and increase dramatically with the onset of the warm summer season (*7*). On the basis of earlier measurements over a temperature range between 7 and 64 °C, the vapor pressure of DMSe at 25 °C was calculated as 28.75 kPa (*12*). This value is 10% lower than our result 32.03 ± 1.99 kPa, but only 1.29 kPa outside of its confidence limits. For all calculations presented here, we have used our own data.

Some of the literature suggests a low solubility of DMSe in water. However, water was found to be an effective eluant for DMSe adsorbed to activated charcoal (*10, 13*). The data presented here confirm a high solubility for DMSe in H_2O and confirm our previous observations. With regards to our goal to dissipate soil Se through volatilization, a high solubility of DMSe in water can cause microbially produced alkylselenium to dissolve in soil water films, which would increase its probability of being adsorbed to soil surfaces or being scavenged by other microorganisms, thereby decreasing its rate of dissipation into the atmosphere. This obstacle could possibly be overcome by raising the soil temperature, thereby increasing the vapor pressure, and by promoting wetting and drying cycles.

Acknowledgment

We thank M. Cliath and W. Farmer for their valuable suggestions, and D. Olson for assistance in the laboratory.

Registry Numbers Supplied by Author. DMSe, 593-79-3; DMDSe, 75736-17-3.

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Received for review December 21, 1993. Accepted April 6, 1994.® Funding from the U.S. Department of the Interior, Bureau of Reclamation, made this research possible.

® Abstract published in *Advance ACS Abstracts*, May 15, 1994.