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ECBC-TR-580

AMBIENT VOLATILITY
OF BIS-(2-CHLOROETHYL) SULFIDE

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14. ABSTRACT

The volatility of bis-(2-chloroethyl) sulfide (HD) has been measured in the presence of water vapor using methodology recently developed at the U.S. Army Edgewood Chemical Biological Center. Contrary to predictions based on ideal behavior as described by Raoult's Law, the volatility of HD is virtually independent of ambient humidity. This result suggests that the re-evaporation of HD after deposition into the environment is a function of temperature, wind speed, and interactions with materials on which deposition takes place, but it is not influenced by ambient humidity.

15. SUBJECT TERMS

Vapor pressure	Antoine constants	Mustard	Bis-(2-chloroethyl) sulfide
Volatility	Gas chromatography	HD	Two-component vapor-liquid equilibrium
Gas saturation	Water	Mixture	TCVLE

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PREFACE

The work described in this report was authorized under Project No. 6RAWX2. The work was started in November 2003 and completed in November 2004.

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AMBIENT VOLATILITY OF BIS-(2-CHLOROETHYL) SULFIDE

1.   INTRODUCTION

The single-component volatility (vapor pressure) of liquid phase HD has been well documented in the literature[1-10] and recently extended to sub-freezing temperatures[11] using vapor saturation methodology, which has also been employed to measure the vapor pressure of other chemical warfare agents.[12, 13, 14] Recent work performed at the U.S. Army Edgewood Chemical Biological Center (ECBC) promulgated methodology to measure two-component vapor-liquid equilibrium data by mixing vapors of interest downstream of their respective saturation generators and measuring the resulting condensation temperature. That work demonstrated that the volatility of dimethyl methylphosphonate (DMMP) is significantly suppressed by the presence of water vapor.[15] In fact, the suppression of DMMP volatility by water vapor exceeds what would be expected based on Raoult's Law by as much as 40% and was shown to approach two orders of magnitude compared to single-component vapor pressure of DMMP at high relative humidity values. Theoretical and experimental studies completed recently[16] suggest that the observed volatility suppression for DMMP is attributable to a strong hydrogen bonding interaction with water vapor. The current work extends the earlier investigations to study the effect of ambient humidity on the volatility of HD.

2.   EXPERIMENTAL PROCEDURES

Separate streams containing saturated water and HD vapors were generated using materials and methodology previously described in detail elsewhere.[15] Chemicals used in the present work were water and bis-(2-chloroethyl) sulfide (HD). Distilled water was obtained from a Barnstead Mega-Pure® Distillation System (Barnstead International, Dubuque, IA). The liquid HD sample, obtained from the Chemical Agent Standard Analytical Reference Material (CASARM) Program, was purged overnight using dry nitrogen at 100 standard cubic centimeters per minute (sccm) to remove volatile impurities and then analyzed by gas chromatography (GC) using a Thermal Conductivity Detector (TCD). Integration of the area under the HD peak resulted in an estimated sample purity of 98.6%. A similar analysis for the eluting vapor stream resulted in an estimated sample purity of 98.3% by GC using a flame ionization detector. The remaining liquid HD sample used in this study was also characterized immediately after the experimental data were collected with no observable change in purity. Dry nitrogen (Ultrapure carrier grade) was used as the HD carrier gas to preclude hydrolysis in the carrier stream. The PSA-dried air was used as the diluent and as the carrier for the water saturator. The respective streams were generated at 100 sccm each and mixed downstream to prevent cross contamination of the liquid saturators. The streams were combined upstream of a chilled mirror dew-point hygrometer (EdgeTech Model 2002 DewPrime II, Milford, MA) to measure the dew point of the mixture.

A schematic of the experimental setup used in the present work can be found in our previous report.[15] Two vapor saturators were used in parallel, and their effluent streams were combined in a heat-traced Nalgene 890 pTFE FEP 1/4-in. tubing (3/16-in. i.d.) transfer line. The combined vapors were then passed through a series of 1/4-in., heat-traced Swagelok® elbow

connectors and into the EdgeTech DewPrime II's temperature-controlled, chilled-mirror, dew point unit sensor compartment where the dew point was measured and recorded. Prior to entering the dew point sensor, a portion of the mixed flow stream was drawn into a 1-cc gas loop and analyzed using a Hewlett-Packard model 5890 GC equipped with a flame ionization detector (FID). A heat-traced Restek (Bellefonte, PA) Silicosteel 316 grade stainless steel 1/8-in. tube (0.085-in. i.d.) was used to transport the vapor sample to the heated GC loop. The GC column (Restek Corporation., Bellefonte, PA), a 30-m x 0.53-mm i.d. fused silica column with 1.0-μm RTx-1701 (14% cyanopropylphenyl - 86% dimethyl polysiloxane) film, was heated from 50 to 170 °C at a rate of 20 °C/min. Helium was used as the GC carrier gas at a flow rate of 8 sccm and as detector make-up gas at a flow rate of 22 sccm. Combustion gases used to support the FID were air at 400 sccm and hydrogen at 30 sccm. Using the instrumentation and operating conditions described, HD eluted at 4.25 min, which represents a GC column temperature of 135 °C. No evidence of HD decomposition was observed throughout this study as identical chromatograms were obtained for the HD vapor stream.

Data acquisition was controlled and recorded using National Instruments LabView® software and interfaces (SCXI 1001 chassis equipped with various 1320-series modules). Controlled temperatures included the water and HD saturator baths, flow path from the saturators to the vapor mixing area, the vapor mixing volume, the flow path from the mixing volume to the GC sample loop, the EdgeTech DewPrime II dew point unit's sensor compartment, and the flow path from the dew point sensor to the carbon filter. Other controlled variables included the water and HD saturator flow rates. Measured data included dew point temperature, saturator bath temperatures, temperature of the flow path from the saturators to the vapor mixing volume, the temperature of the vapor mixing volume, the temperature at the flow path inlet from the mixing area to the EdgeTech DewPrime II sensor compartment, the temperature of the circulating liquid used as the primary means to control the EdgeTech DewPrime II sensor compartment, and GC-FID traces with integrated HD area. Ambient pressure was monitored, but not reported here because it did not figure into any of the calculations. All of the data were captured and stored by the LabView® control program. This afforded the opportunity to change operating parameters on the fly and conduct unattended operations.

3.   RESULTS AND DISCUSSION

The saturators were set up so that the carrier gas could be directed through or bypass them. That being the case, four experimental configurations are possible (i.e., bypassing both saturators, bypassing one or the other, and bypassing neither). Bypassing both is not of interest. The other three combinations were investigated; of those, the most informative were bypassing HD and bypassing neither to get the measured dew point of the mixture. The majority of control experiments were performed by bypassing the HD saturator. In those cases, the saturated water vapor stream was diluted with the bypassed ultra-dry air and the dew point measured. Additional control experiments were performed by bypassing the water saturator. In those cases, the saturated HD vapor stream was diluted with the bypassed ultra-dry air and the dew point measured. Comparisons of the resulting dew points to those predicted by the

respective vapor pressures indicated that the system performance was predictable and well behaved as seen in the lowest trace of Figure 1.

The HD experiments were performed with both saturators held at the same temperature and flow rate. The HD was alternately excluded (bypassed), included, and again excluded from the mixture. During the two phases of this experiment when the HD was excluded, dry air from the HD-bypass stream was mixed with humidified air, and the measured condensation temperature was compared to the calculated value. The bath temperatures used in those experiments were 15.3, 20.3, 23.3, 25.3, 27.3, 29.3, 30.3, 35.3, and 40.3 °C, and the dew points of the resulting mixtures were recorded every 10 min. For the first interval of each experiment, dry air was mixed with humidified air, and dew point data were collected for 7 hr. During the second interval, HD vapor was mixed with humidified air, and dew point data were collected for an additional 7 hr. For the third interval, dry air was mixed with humidified air, and dew point data were collected for an additional 7-hr interval. Four similar experiments were performed by alternately bypassing the water saturator with both sources held at 25.3, 30.3, 35.3, or 40.3 °C, and those dew points were recorded. The resulting dew points observed in these experiments are shown in Figure 1, which also shows the condensation temperature of each of the diluted (by a factor of 2) pure components and that expected based on ideal behavior (i.e., Raoult's Law).

The measured dew points (or frost points in two cases) are shown in Figure 1 for the experiments described above along with lines showing the dew points calculated for water alone, dew points expected for HD alone, and (below its melting point, 14.5 °C) the frost point of HD alone. These values were calculated based on the known vapor pressures of the components following a two-fold dilution. For example, the vapor pressure for HD at 35 °C is 31.8 Pascal. Diluting by a factor of two (i.e., 15.9 Pa) and calculating the expected dew point using the Antoine equation,

$$T = \{b/[a - \ln(P)]\} - c \qquad \text{Antoine equation}$$

where,

a, b, and c are the Antoine constants taken from Penski[10] for liquid state HD; or

$$T = b/[a - \ln(P)] \qquad \text{Clausius-Clapeyron equation}$$

where, a and b are the Clausius-Clapeyron constants taken from Buchanan et al.[11] for solid HD, T is the condensation temperature, and P is the partial pressure of HD. The value was 15.9 Pa in this example, as compared to an HD-only calculated condensation (dew) point of 26.4 °C. A change in the slope of the predicted HD condensation temperature occurs at lower temperature, as shown in Figure 1. The expected slope change is caused by the phase transition of HD at 14.5 °C (i.e., when HD is evaporated as a liquid and condensed as a solid). As shown at the lower left of Figure 1, the slope returns to approximately the same as that seen for evaporation and condensation as liquid as the generation temperature falls below the freezing point of HD.

The data in Figure 1 appear as pairs of data points displaced vertically. These pairs of points represent the data measured at the same generation temperature, with or without bypassing the HD generator. As shown in Figure 1, two-fold dilution results in a larger depression (difference between generation and condensation temperature) of the dew point for water than for HD. This is a direct result of the fact that HD has a ca. 50% higher heat of evaporation than does water (i.e., 63.1 versus 44.2 kj/mol at 20 °C). Because the higher heat of evaporation corresponds to a higher slope of the vapor pressure curve, it is clear that the same reduction in partial pressure should have a larger effect on condensation temperature for the vapor with the lower heat of evaporation, as seen in Figure 1.

Table 1 lists the calculated and observed HD dew/frost points. The most interesting and informative aspect of Table 1 is the agreement between the measured mixture condensation points and the calculated dew/frost points of HD as a pure component, diluted by the water vapor stream. In fact, the measured single-component HD dew/frost points are on average 0.2 °C higher than calculated for single-component (dry) HD, which is very similar to the difference between calculated and measured dew points for diluted water vapor streams in the bypass experiments, 0.2 °C. These results suggest that the condensate is pure HD, although the current work cannot definitively come to that conclusion since chemical analysis was not performed on the condensate.

The result, demonstrated clearly in Figure 1, is that the measured dew point of HD is independent of the presence of water vapor as might have been anticipated based on the known very low solubility of HD. The implications are simply that the evaporation of HD following deposition into the ambient environment will not be significantly affected by diurnal changes in relative humidity.

Figure 2 shows a plot of HD volatility during a 24-hr cycle in which the dew point is fixed at 15 °C, while the temperature varies between 18 and 30 °C, as shown in Table 2. Also shown for comparison in Figure 2 is a similar plot of DMMP, derived from the data presented by Tevault, et al.[15] under the conditions shown in Table 2. Figure 2 shows a plot of ambient volatility of DMMP and HD versus time of day from data illustrated in Table 2. Because DMMP volatility is affected by temperature and ambient relative humidity, its volatility is suppressed by both as the temperature cools at night and actually falls below that of HD even though the vapor pressure of DMMP is nearly an order of magnitude higher than HD at 20 °C.

4.   CONCLUSIONS

The effect of ambient humidity on the volatility of chemical warfare agents will have a direct impact on their rates of re-evaporation following deposition into the environment. The present work shows that the volatility of HD is only weakly affected by ambient relative humidity, if at all. This result is not overly surprising in view of its very low water solubility. As demonstrated, the weak dependence on relative humidity can cause its ambient volatility to be higher than compounds, such as dimethyl methylphosphonate, whose vapor pressure is ca. one order of magnitude higher than HD under dry conditions.
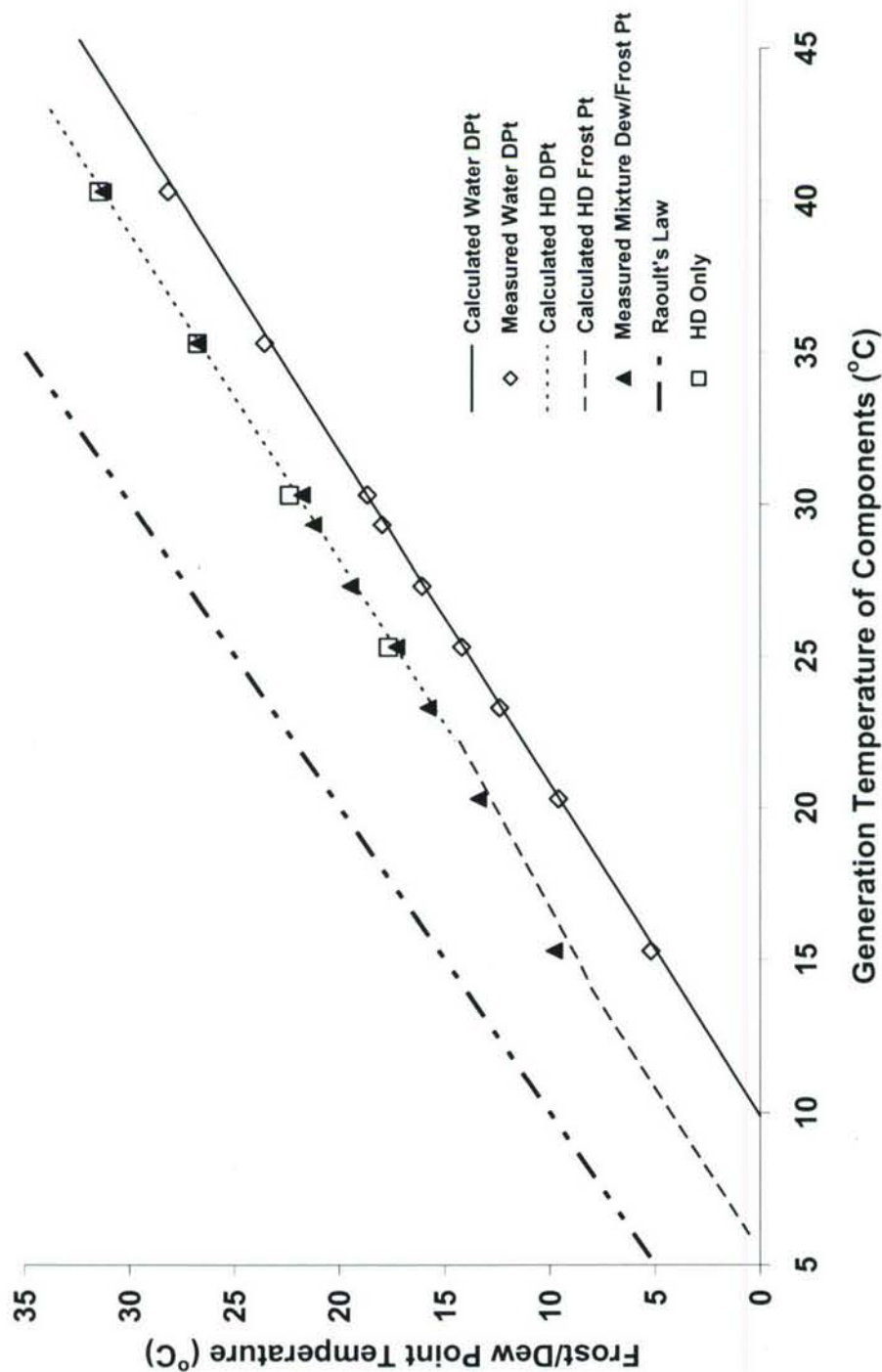
Figure 1. Condensation Points for Water-HD Mixtures. (Triangles) Measured Condensation Points for Mixtures of Water and HD Vapor. (Squares) Measured Dew Points for Saturated HD Vapor Streams Diluted by a Factor of Two with Dry Air. Dashed Line is the Calculated Single-Component Frost Point for HD Vapor Generated at the Values Shown on the Abscissa and Diluted by a Factor of Two. Dotted Line Shows the Calculated Single-Component Dew Point for HD Generated at the Values Shown on the Abscissa and Diluted by a Factor of Two. (Diamonds) Measured Dew Points for Saturated Water Vapor Streams Diluted by a Factor of Two with Dry Air; Solid Line is the Calculated Water Dew Point for Streams Generated at the Abscissa Temperature and Diluted by a Factor of Two. Dash-Dot Line is Raoult's Law.

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Table 1. Temperatures at which Saturated Streams of HD and Water Vapor were Generated, Each at 100 sccm, Observed Mixture Dew/Frost Points, and Calculated Dew/Frost Points for HD without Water Vapor (i.e., Diluted by a Factor of Two). Frost Points for HD are shown in bold font.

Generation Temperature (°C)	Measured Dew/Frost Point (°C)	Calculated HD Dew/Frost Point (°C)
40.3	31.3	31.3
35.3	26.8	26.7
30.3	21.8	22.0
29.3	21.3	21.1
27.3	19.5	19.2
25.3	17.3	17.4
23.3	15.8	15.5
20.3	**13.4**	**12.8**
15.3	**9.8**	**8.9**

Table 2. Calculated Volatility of HD and DMMP during the Course of a Day with Dew Point Fixed at 15 °C and Temperature Varying between 18 and 30 °C.

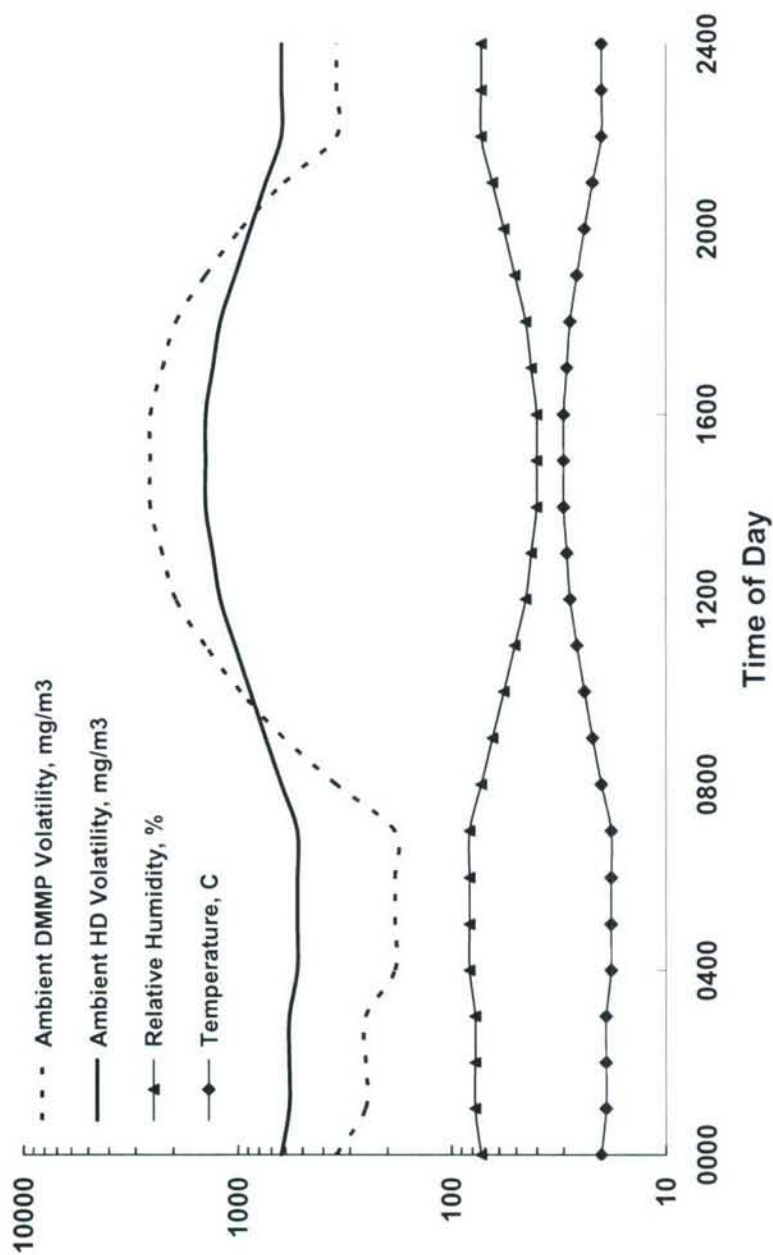| Time of Day	Temp (°C)	RH (%)	HD Volatility (mg/m³)	DMMP Volatility (mg/m³)
0000	20	72.9	628	347
0100	19	77.6	577	253
0200	19	77.6	577	253
0300	19	77.6	577	253
0400	18	82.6	529	185
0500	18	82.6	529	185
0600	18	82.6	529	185
0700	18	82.6	529	185
0800	20	72.9	628	347
0900	22	64.5	743	611
1000	24	57.1	877	971
1100	26	50.7	1032	1421
1200	28	45.1	1211	1954
1300	29	42.5	1311	2251
1400	30	40.1	1417	2567
1500	30	40.1	1417	2567
1600	30	40.1	1417	2567
1700	29	42.5	1311	2251
1800	28	45.1	1211	1954
1900	26	50.7	1032	1421
2000	24	57.1	877	971
2100	22	64.5	743	611
2200	20	72.9	628	347
2300	20	72.9	628	347

Figure 2. Diurnal Volatility of DMMP and HD. Graph of Ambient Temperature, Relative Humidity, and Volatility of HD and DMMP Over the Course of a Day Using Environmental Conditions Defined in Table 2.

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