Vapor Pressure of Solid Bis(2-chloroethyl) Sulfide

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The vapor pressure of the vesicant chemical warfare agent, bis(2-chloroethyl) sulfide (also known as sulfur mustard or HD), has been measured at $T = (-25\text{ to }+20)$ °C using a modified ASTM vapor saturation methodology. This work represents the initial report of the measured vapor pressure of HD below its melting point, +14.45 °C. The data measured for solid-phase HD are consistent with the previously reported enthalpy of fusion and liquid-phase vapor pressure of HD.

Introduction

Numerous investigators have reported the vapor pressure of liquid bis(2-chloroethyl) sulfide (HD) using a variety of methods,[1−6] including $T = (80\text{ to }217)$ °C using a boiling point method,[2] (15 to 76) °C using dynamic gas saturation,[2−6] and (18 to 82) °C using a static method.[4] The early work of Mumford et al.[6] contains data from well below the melting point up to 60 °C; however, the agreement with subsequent data is poor below 30 °C and gets worse as temperature decreases. At least one attempt to infer the vapor pressure of solid HD from its vapor pressure at the melting point and enthalpy of fusion has been reported.[2] Buckles has summarized the physical properties of HD.[7] The literature data reported for liquid HD are internally consistent and have been described by an Antoine equation correlation by Penski.[8,9] To the best of our knowledge, accurate experimental data for the vapor pressure of solid HD have not been reported in the literature. It is not suitable to extrapolate liquid-phase HD vapor pressure data below its melting point, 14.45 °C,[10] as shown in this report.

We have measured solid HD vapor pressure using a modified ASTM vapor saturation method[11] developed recently in our laboratory and exploited to measure the vapor pressure of numerous liquid chemical warfare (CW) agents and their simulants in the ambient temperature range.[12−14] Our modifications of the vapor saturation method include the use of a vapor concentrator and flame ionization detection gas chromatography to allow precise measurement of volatile components of direct interest. These measurements, which are often made in the presence of both higher and lower volatility impurities, eliminate errors associated with approaches such as direct mass loss, which cannot discriminate between the target species and its impurities. A similar methodology has recently been exploited to measure adsorption equilibrium data for HD[15] and isopropyl phosphonofluoridate[16] (nerve agent GB) at vapor-phase concentrations some 4 orders of magnitude below what had previously been the state of the art (i.e., relative pressures in the 10^{-10} range).

The vapor saturation method has been further modified recently to facilitate measurement of volatility as a function of both temperature and humidity.[17−19] The latter body of work demonstrated proof of principle using the nerve agent simulant, dimethyl methylphosphonate (DMMP), whose vapor pressure is suppressed beyond what is predicted by Raoult's law.[17,18] We have recently investigated HD volatility as a function of ambient humidity,[19] where no measurable suppression has been observed. In our efforts to do so, it came to our attention that accurate fundamental data for the solid-phase vapor pressure of HD were not available in the literature.

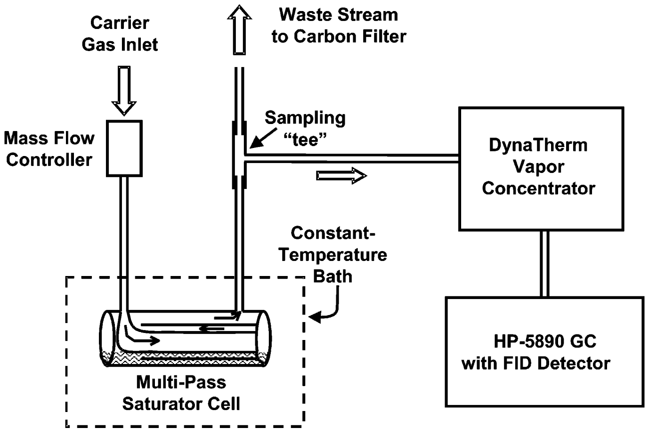

Figure 1. Schematic of data acquisition system used to measure solid HD vapor pressure.

Experimental Section

Bis(2-chloroethyl) sulfide, more commonly known as distilled mustard or HD, is a strong vesicant. Its only known use is as a chemical warfare agent. It is highly toxic and should only be used in facilities specially equipped and permitted to handle materials of this nature.

Saturated HD vapor streams were generated by flowing dry nitrogen carrier gas (Matheson, UHP) at 25 standard cubic centimeters per minute (sccm) through a glass vessel (i.e., saturator) containing solid HD, shown schematically in Figure 1. The vapor saturator used in the present work has been described in detail in previous reports from this laboratory.[12−14]

In this work, the saturator was loaded with approximately 5 g of neat liquid HD, Chemical Agent Standard Analytical Reference Material (CASARM), Lot No. HD-U-9040-CTF-N. The HD sample was purged using dry nitrogen for 70 h at room temperature to remove volatile impurities. After this initial purge, the liquid phase was analyzed using gas chromatography (GC) with a thermal conductivity detector (TCD). Integration of the HD peak resulted in an area amounting to 98.5 % of the

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total, corresponding to the liquid phase mole fraction. This value was used in subsequent data analyses. The HD sample used in this work was also analyzed immediately after the data were collected by the same method with no observable change in purity.

The saturated HD stream, generated by flowing dry nitrogen carrier gas through the saturator at 25 sccm, was sampled by drawing 5 to 10 sccm of the saturator effluent to the Dynatherm concentrator, a modified ACEM model 900 (Dynatherm Analytical Instruments Inc., Kelton, PA) system containing a Tenax adsorbent tube. The sampling flow rate was controlled using a calibrated 10 sccm mass flow controller (Tylan Model FC-280, Austin, TX), which was connected to a vacuum pump and allowed to sample for 2 to 50 min, depending on the HD concentration (i.e., the flow rate and temperature). The saturator effluent was sampled at a “tee” connection 3 cm downstream of the saturator, whose temperature was maintained by immersion in a model RTE-140 Neslab constant-temperature bath (Neslab Instruments, Portsmouth, NH). The sampling line was constructed of 1.6 mm o.d., 1.0 mm i.d. Sulfinert tubing (Restek Corp., Bellefonte, PA). All connectors between the saturator effluent line “tee” and the concentrator were fabricated from 316 stainless steel. The concentrator sampling line between the “tee” and the ACEM was heated to approximately 80 °C to reduce sample line holdup and thus reduce the time needed to achieve steady-state conditions following sample temperature changes. The ACEM 900 valve box, external six-port valve, and transfer line to the GC were maintained at 100 °C. The sample was concentrated by the ACEM 900 using the following operating parameters. The temperature of the 10 mm o.d. Tenax collection tube was maintained at 40 °C during the 2 to 50 min sample collection time. A 1-min sampling line purge using dry nitrogen was employed as the next step of the sampling process as a precaution to flush any residual HD in the sampling line onto the trap. The sample was then rapidly heated to 275 °C under a flow rate of 20 sccm dry nitrogen for 5 min and transferred to the ACEM 900 Tenax focusing trap, which was maintained at 40 °C. Transfer continued for an additional minute as the 10 mm o.d. Tenax collection tube cooled. The Tenax focusing trap was then rapidly heated to 300 °C under a flow of 8 sccm dry nitrogen for 5 min to effect sample transfer to the GC column. The saturator flow rate was increased to as high as 50 sccm with no observable change in the FID response to demonstrate that the concentration of HD is independent of saturator flow rate and, thus, that the system had attained vapor−liquid or vapor−solid equilibrium. Ambient atmospheric pressure and saturator temperature were measured using a calibrated liquid mercury barometer and thermometers, respectively, as described in an earlier report.[13]

The GC column (Restek Corp., Bellefonte, PA), a 30 m × 0.53 mm i.d. fused silica column with a 1.0 μm RTx-1701 (14 % cyanopropylphenyl + 86 % dimethyl polysiloxane) film was programmed to go from 40 to 225 °C at a rate of 10 °C/min after a 1.5 min post-injection delay. A Hewlett-Packard (HP) model 5890 series II GC equipped with a flame ionization detector (FID) was used to quantify the mass of HD collected in each cycle. Nitrogen was used as the GC carrier (8 sccm) and detector makeup (22 sccm) gas. Combustion gases were air (400 sccm) and hydrogen (30 sccm). Using the instrumentation and operating conditions described, HD eluted at 12.5 min with a corresponding GC column temperature of 150 °C.

Two stock solutions were prepared for calibration of the ACEM 900-5890 FID system by adding an accurately measured volume of analyte to the appropriate solvent and correlating the resulting GC integrated peak areas to analyte mass; 25 μL of neat CASARM HD (98.5 % molar purity, sampled from the saturator) was added to about 8 mL of hexane (Capillary GC Grade, Aldrich Chemical Co., Milwaukee, WI) using a 25 μL Drummond model 525 digital microdispenser (Drummond Scientific Co., Broomall, PA). The resulting solution was diluted to 10.0 mL using additional hexane. Converting this volume of HD to mass using the liquid density at room temperature (1.2712 g/mL at 22.5 °C) and correcting for HD purity (98.5 %) resulted in a solution with a concentration of 3.13 μg of HD/μL. The second calibration standard was prepared in a similar manner by adding 10 μL of the 98.5 % molar purity CASARM HD to about 8 mL of hexane using a 10 μL Hamilton model 701 MICROLITER syringe (Hamilton Co., Reno, NV) and diluting to 10.0 mL with hexane. Converting this volume of HD to mass using the liquid density at room temperature and correcting for HD purity resulted in a solution with a concentration of 1.25 μg of HD/μL.

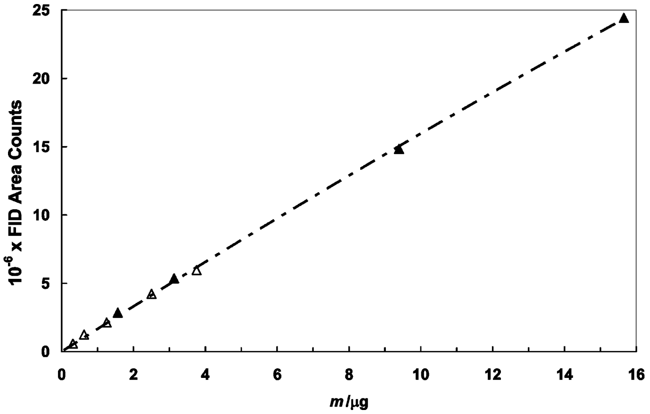

Figure 2. HD calibration curve. Filled triangles show data measured using 3.13 μg/μL standard, and open triangles show data measured using 1.25 μg/μL standard. m_{HD} = mass of HD (μg) injected and A = GC area (in millions of area counts). The standard deviation for this regression fit equals 0.191159 million area units. Clausius−Clapeyron equation: $\ln(P/\text{Pa}) = 35.383 - 9732/(T/\text{K})$.

All calibrations were performed on the same day that the standards were prepared. The ACEM 900-5890 FID system was calibrated by making 1- to 5-μL injections of HD + hexane standards into the 80 °C 1.6 mm o.d., 1.0 mm i.d. Sulfinert tubing in close proximity to where the saturator effluent is situated during data collection and supplied with dry nitrogen carrier gas at a flow rate of 10 sccm to facilitate sample transfer. The ACEM 900 and GC operating parameters were identical to those used for experimental data acquisition with one exception. The ACEM 900 external sampling time for calibration data was held at 15 min to allow sufficient time for HD transfer to the Tenax sampling tube. The resulting HD calibration curve (, Figure 2) was generated by plotting observed FID area versus mass of HD injected for the combined high- and low-concentration standard calibration samples. Equation 1 describes the combined calibration data set most accurately given the constraints that the calibration curve go through the origin and is limited to a quadratic equation for ease of analysis:

$$A = -0.007198 m_{HD}^{2} + 1.668432 m_{HD} \qquad (1)$$

where m_{HD} = mass of HD (in μg) injected and A = GC area (in millions of area counts). Vapor pressure values are calculated from the measured data using eq 2:

$$\text{VP}_{HD} = P_{\text{ambient}} \cdot n_{HD}/(n_{HD} + n_{\text{carrier}}) \qquad (2)$$

Table 1. HD Vapor Pressure Data Measured in This Work[a]

	P/Pa		
t/°C	measured	calculated	$100(P - P_{calc})/P$
20.0*	9.12	9.16	−0.44
15.0*	6.04	5.82	3.7
13.0	4.81	4.83	−0.47
10.0	3.34	3.37	−0.76
5.0	1.86	1.82	2.3
0.0	0.984	0.957	2.7
−5.0	0.490	0.493	−0.43
−10.0	0.241	0.247	−2.4
−15.0	0.118	0.121	−2.6
−20.0	0.0560	0.0573	−2.4
−25.0	0.0277	0.0264	4.6

[a] Calculated vapor pressures using literature Antoine coefficients for temperatures above 14.5 °C and Clausius−Clapeyron coefficients from this work for temperatures below 14.5 °C and difference. An asterisk (*) indicates liquid-phase data measured in this work.

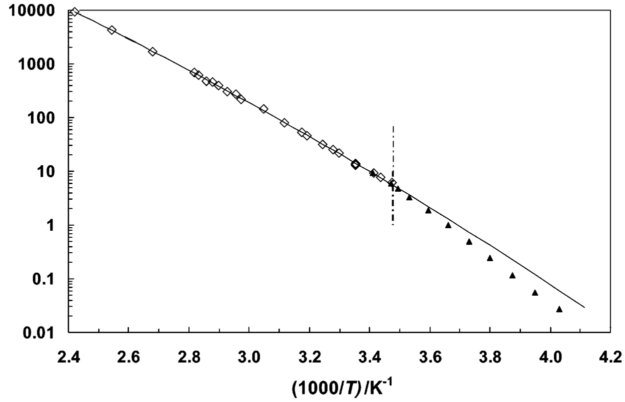

Figure 3. Literature (diamonds) and saturator (triangles) vapor pressure data for HD and liquid-phase Antoine equation (line). Melting point of HD is indicated by the broken vertical line.

where VP_{HD} = vapor pressure of HD calculated from measured data; $P_{ambient}$ = ambient atmospheric pressure; n_{HD} = number of moles of HD, measured by GC-FID; and $n_{carrier}$ = number of moles of nitrogen carrier, measured as described above.

Ambient pressure was measured using a calibrated Princo Instruments Nova model mercury barometer (Princo Instruments, Incorporated, Southampton, PA), which was corrected for temperature and latitude and accurate to 13 Pa (0.013 %). Saturator temperature was controlled by submersion in a temperature-controlled bath, as described above, filled with 50 % ethylene glycol aqueous solution, and the bath temperature was measured using calibrated thermometers accurate to within 0.1 °C.

Results and Discussion

Table 1 lists the HD vapor pressures measured in the present work at temperatures between −25 and +20 °C. Data reported in this work along with literature data are depicted in Figure 3, which also shows Penski's Antoine equation fit to the literature data and the melting point of HD. Two data points shown in Figure 3 and Table 1 were measured in the current work above the melting point to demonstrate agreement between our measurements and accepted literature values. The differences between measured and calculated values, based on Penski's Antoine equation, for those data were 0.4 % and 3.7 %, which is considered to be excellent agreement. Deviations from Penski's Antoine equation predictions increase monotonically as temperature decreases below the melting point as seen in Figure 3.

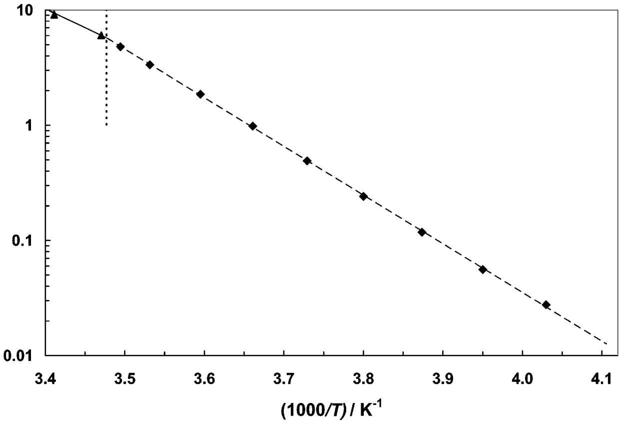

Figure 4. Vapor pressure data measured for solid (diamonds) and liquid (triangles) HD and Clausius−Clapeyron fit (dashed line). Solid line indicates Antoine fit to literature data after Penski, and dotted line indicates HD melting temperature.

An Antoine fit to the solid-phase data was performed; however it was found that the agreement between measured and calculated data does not warrant a three-parameter fit since the two-parameter Clausius−Clapeyron fit shown in Figure 4 described the data equally well. This observation is principally attributable to the narrow temperature range of the solid-state data. The Clausius−Clapeyron equation is $\ln(P/\text{Pa}) = 35.585 - 9732/(T/\text{K})$. It should be noted that the average difference between calculated and observed data points for solid HD is 2.1 %, which demonstrates the excellent experimental precision of the current data.

A comparison of the data reported here to values estimated by Pecorella and Macy[2] reveals that the discrepancy between those values and the data reported here is significant. For example, the value reported in their work for −10 °C is 15 % higher than our measured value, and the projected discrepancy increases further to 25 % at the lowest temperature reported here, −25 °C.

The enthalpy of fusion can be determined using the historical liquid-phase and the new solid-phase data. The liquid-state enthalpy of vaporization at the melting temperature, estimated using the Antoine B and C coefficients, is 64.0 $\text{kJ}\cdot\text{mol}^{-1}$. The indicated HD enthalpy of sublimation is 80.8 $\text{kJ}\cdot\text{mol}^{-1}$, indicating a enthalpy of fusion of 16.7 $\text{kJ}\cdot\text{mol}^{-1}$. This value compares favorably to the value of 17.6 $\text{kJ}\cdot\text{mol}^{-1}$ estimated by Pecorella and Macy.[2] Our lower value is also consistent with the discrepancy between the estimated and the measured solid-phase HD vapor pressure reported here.

Conclusions

Experimental vapor pressure data for solid HD are reported for the first time. The enthalpy of fusion has been estimated to be 16.7 $\text{kJ}\cdot\text{mol}^{-1}$ based on the change in slope of the liquid- and solid-phase vapor pressure plots at the melting point. The high precision of the present data, agreement with previous liquid-phase data, and consistency between the currently observed data and that expected based on prior work provide significant confidence in the accuracy of the present data.

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