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VAPOR PRESSURE OF BIS-(2-CHLOROETHYL)ETHYLAMINE (HN1)

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14. ABSTRACT

Previous laboratory measurements of the vapor pressure of *bis*-(2-chloroethyl)ethylamine (HN1) were done in the 1940s and were only measured down to a temperature of 10 °C. We have recently made additional measurements of the vapor pressure of the vesicant chemical agent using a saturator cell technique and recomputed the Antoine constants. The new data extends the measured range from 5 to 85 °C.

15. SUBJECT TERMS

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PREFACE

The work described in this report was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency, Joint Science and Technology Office (DTRA-JSTO). This work was started in April 2011 and completed in May 2011.

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Acknowledgments

The authors are grateful to Ann Brozena and Patrice Abercrombie, Chemical Sciences Division of the U.S. Army Edgewood Chemical Center (ECBC), for providing the historical data that was incorporated in this report. Their depth of knowledge of the measurement of physical properties of chemical warfare agents is unmatched. The authors also thank Ngai Wong, DTRA-JSTO, for his continuing support and encouragement of this work.

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CONTENTS

FIGURES

TABLES

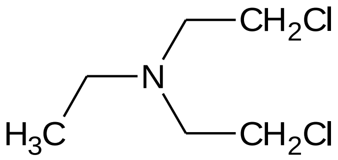
VAPOR PRESSURE OF BIS-(2-CHLOROETHYL)ETHYLAMINE (HN1)

1. ABSTRACT

Previous laboratory measurements of the vapor pressure of *bis*-(2-chloroethyl)ethylamine (HN1) were done in the 1940s and were only measured down to a temperature of 10 °C. We have recently made additional measurements of the vapor pressure of the vesicant chemical agent using a saturator cell technique and recomputed the Antoine constants. The new data extends the measured range from 5 to 85 °C.

2. INTRODUCTION

The nitrogen mustards (HN1, HN2, and HN3) are similar to sulfur mustard (HD) in their physical properties and physiological effects. All are delayed-casualty agents that produce conjunctivitis, laryngitis, bronchitis, hoarseness, coughing, elevated temperature, nausea, and vomiting on exposure.[1] Selected properties of the agent are presented in Figure 1.



Bis-(2-chloroethyl)ethylamine
CAS RN: 538-07-8
Symbol: HN1
Formula: $C_6H_{13}Cl_2N$
FW: 170.08
Density: 1.09 g/cm^3 at 25 °C
Purity: >99%

Figure 1. Selected properties of HN1.

Previous experimental measurements of the vapor pressure of the compound were reported in 1943 by Dawson and Witten[2] and in 1944 by Redemann et al.[3] The authors of those studies reported that they used dynamic vapor saturation techniques. A controlled flow of carrier gas was passed across or through the liquid-phase to achieve a saturated vapor-liquid equilibrium. The total volume of the carrier gas and the change in mass of the liquid were input into the ideal gas law to obtain the pressure of the compound. The reports encompassed a range of 10 to 85 °C, with a gap in the experimental data between 10 and 25 °C.

We recently obtained a highly purified sample of HN1 that we used in our laboratory to generate the vapor-phase absorptivity coefficient of the compound.[4] Analysis of an aliquot of the material by ^{13}C nuclear magnetic resonance (NMR) spectroscopy, gas chromatography (GC) with thermal conductivity detection (TCD), and GC with mass spectrometry (MS) yielded the results shown in Table 1.

Table 1. Results from Analysis of HN1 Sample Used for Vapor Pressure Studies in this Work

Analytical Technique	Purity (%)
NMR	>99
GC-TCD	99.5
GC-MS	99.2

The spectra that were obtained to compute the vapor-phase absorptivity coefficient showed traces of water vapor that purged during the first day of data acquisition. During the remaining seven days of experiments, the spectra showed little evidence of change.

3. EXPERIMENTAL APPARATUS AND METHODS

We used a system to generate vapor pressure data that is similar to one developed at the U.S. Army Edgewood Chemical Biological Center (ECBC) for measuring the vapor pressures and volatility of chemical warfare (CW) agent-related compounds.[5-8] The ECBC system has been adopted as an ASTM method.[9] The saturator cell method passed a stream of nitrogen carrier gas, obtained in our laboratory from the boil-off of a bulk liquid nitrogen tank, across an alumina wicking mechanism in a glass holder filled with the analyte (Figure 22). A saturated vapor-liquid equilibrium of the analyte was obtained on the downstream side of the saturator cell, with the concentration of the analyte governed by the temperature of the liquid phase.

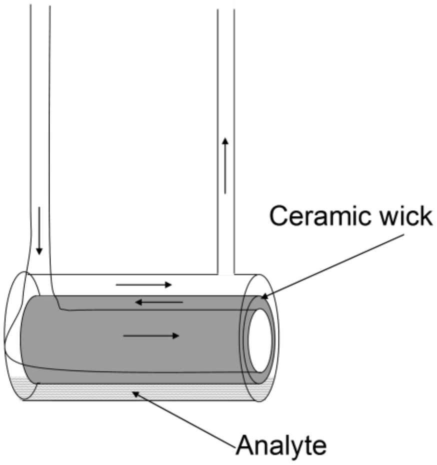


Figure 2. Schematic of saturator cell that was used to generate continuous vapor streams of compounds for determining vapor pressures. The arrows indicate the direction of flow of the nitrogen carrier gas.

The saturator cell (Glassblowers.com, Turnersville, NJ) was suspended in a Julabo (Allentown, PA) model F25 constant-temperature bath with a precision of 0.05 K. The bath temperature was verified using a National Institute of Standards and Technology (NIST)-traceable liquid-in-glass thermometer with an uncertainty of ±0.02 K. The carrier gas was controlled at a constant rate of 75 cm^3min^{-1} and referenced to 294.35 K and 101,325 Pa using a Brooks (Hatfield, PA) model 5850S mass flow controller. Linearity of the S-series mass flow controllers is adjusted using a second-order polynomial, resulting in uncertainties of approximately 1% or better of a flow rate of ≥25% of full scale. The mass loss of the compound from the saturator cell was determined by weighing the saturator cell at the beginning and end of the experiment using a Sartorius (Goettingen, Germany) BP211D analytical balance with a precision of ≤0.1 mg and a linearity of ≤0.2 mg. Before masses were recorded, the balance was checked at points above and below the mass of the saturator cell with weights traceable to NIST. After an experiment was finished, the saturator cell was dried with a lint-free paper towel and allowed to equilibrate to room temperature for a minimum of 2 h. Prior to placing the saturator cell in the weighing chamber, we passed it across a Haug (Mississauga, ON) model EN-C deionizing bar . This step has proven useful even at relative humidities as high as 40 to 50%, eliminating the slow drift in the measured mass before stabilization was achieved. We then recorded at least four readings and calculated the mean. Ambient pressure was recorded with an Omega Engineering (Stamford, CT) DPI 740 digital barometer. Bath temperature, gas flow rate, and ambient pressure were recorded at 4 s intervals using a National Instruments (Austin, TX) LabVIEW program. All flow, temperature, and mass devices and instruments were verified periodically in accordance with the U.S. Army calibration guidance.

The vapor pressure of the compound was calculated using eq 1:

$$P = P_{sat} \frac{n_{analyte}}{n_{carrier} + n_{analyte}} \qquad (1)$$

where P is the pure compound saturation pressure at the pressure of the saturator cell, P_{sat} is the pressure in the saturator cell, $n_{analyte}$ is the number of moles of analyte, and $n_{carrier}$ is the number of moles of carrier gas. The number of moles of nitrogen ($n_{carrier}$) was obtained from the carrier rate and time using the ideal gas law. The number of moles of the compound ($n_{analyte}$) for eq 2 was obtained from the mass loss of the compound and the formula weight of HN1, 170.08:

$$n_{analyte} = \frac{\Delta_{mass}}{170.08} \qquad (2)$$

4. RESULTS AND DATA TREATMENT

Two vapor pressure experiments were conducted at temperatures of 278.15 and 288.15 K. The first trial, at 288.15 K, was run for more than 21 h and yielded a Δ mass of 0.1025 g. The second experiment, at 278.15 K, was run for nearly 4 days and yielded a Δ mass of 0.1830 g. As stated previously, the carrier gas flow rate was maintained at 75 cm^3min^{-1} for both runs. The data from the trials are summarized in Table 2.[a] GC-MS and GC-TCD analyses

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[a] The National Institute of Standards and Technology (NIST) stipulates that torr is no longer acceptable as a unit of pressure under the International System of Units (SI), and open literature journals normally require the use of pascal. We have, nevertheless, provided graphs and tables with both units. This has been done for two reasons.

indicated that the impurities were probably much less volatile than the HN1, thus depressing the measured vapor pressure of the HN1 in our tests. For that reason, we divided our calculated vapor pressure values (from eq 1) by 0.995, the purity of the HN1 from GC-TCD. The results from the two measurements are shown in Table 22.

Table 2. Experimental Data from Vapor Pressure Measurements of HN1 in Our Laboratory

Temperature		Carrier rate[§] ($cm^3 min^{-1}$)	Time (min)	Δ Mass (g)	Vapor Pressure	
°C	K				Torr	Pa
5.0	278.15	75	5656	0.1830	0.0467	6.229
15.0	288.15	75	1274	0.1025	0.1140	15.20

[§] Referenced to 294.25 K and 101,325 Pa

Table 3. Measured Vapor Pressure of HN1, Including Literature Values

	Vapor Pressure in Torr (Pa)		
Temperature (K)	This Work	Literature Reference 2	Literature Reference 3
278.15	0.04612 (6.229)		
288.15	0.1140 (15.20)		
293.15			0.168 (22.4)
298.15		0.250 (33.3)	
308.15		0.493 (65.7) 0.483 (64.4) 0.496 (66.2)	
313.15			0.728 (97.1)
318.15		0.960 (128) 0.975 (130) 0.982 (131) 0.971 (129)	
333.15			2.59 (345)
358.15		10 (1330)	

The measured vapor pressure values in Table 3 were combined into matrix form and MathWork's (Natick, MA) Matlab computer language was used to compute the least-squares fit of the Antoine equation:

$$\ln(\mathrm{P}) = a - \frac{b}{\mathrm{T} + c} \tag{3}$$

where temperature (T) is in kelvin (K). Table 3 gives the values of the constants in the Antoine equation derived from the least-squares fit of the data in Table 2, as well as the parameters for

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First, the most recent edition of FM 3-11.9 has continued to present vapor pressure in torr. Second, the historical data points were given in torr, and the inclusion of the older unit correctly presents the precision of the earlier measurements.

calculating the vapor pressure in pascal (Pa). Figure 3 is a plot of the data points from Table 3, with the vapor pressure in torr. Figure 44 was generated from data points plotted in pascal.

Measured and calculated values of the vapor pressure of HN1, as well as the fractional deviations from the calculated values, are shown in Table 4. Table 55 shows the Antoine constants for calculating the vapor pressure in torr and pascal. Table 66 gives calculated values of the vapor pressure of HN1 from the Antoine constants derived in our work and as reported in the literature references.

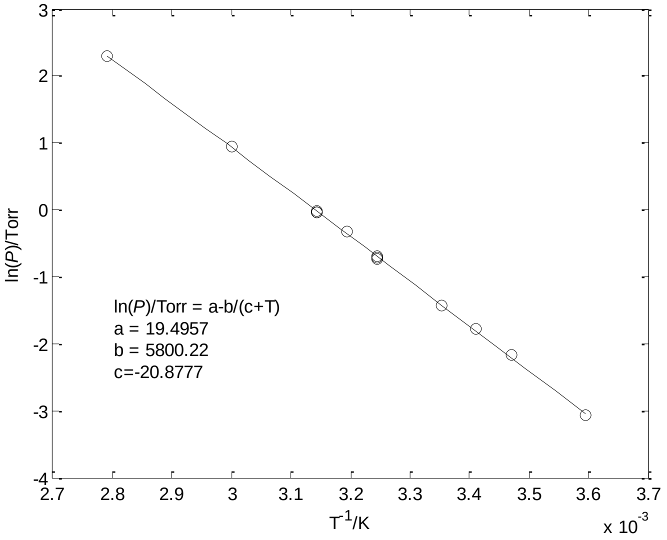

Figure 3. Vapor pressure of HN1 computed in torr. The line was generated from the best fit with the Antoine equation shown in the lower-left corner of the figure.

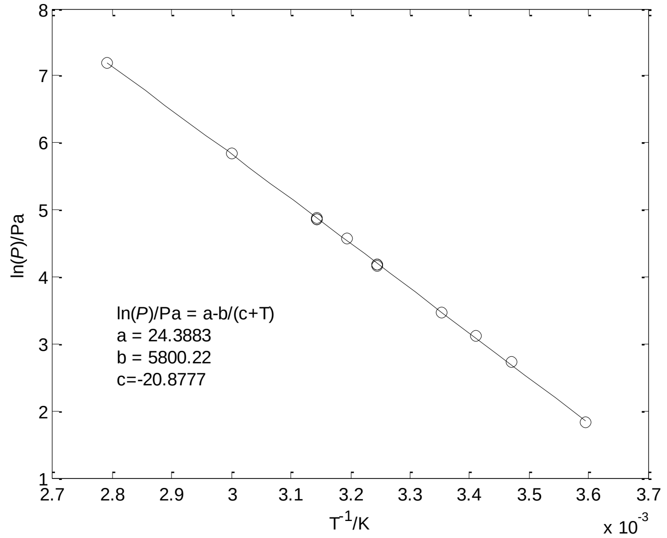

Figure 4. Vapor pressure of HN1 computed in pascal. The line was generated from the best fit with the Antoine equation shown in the lower-left corner of the figure.

Table 4. Measured and Calculated Values of the Vapor Pressure of HN1 and Fractional Deviations

Temperature (K)	Pressure (Torr)		$(P_{meas}-P_{calc})/P_{calc} \bullet 100$
	Measured	Calculated	
278.15	0.0467	0.0475	-1.406
288.15	0.114	0.110	3.489
293.15	0.168	0.164	2.381
298.15	0.239	0.241	-0.809
308.15	0.493	0.500	-1.219
308.15	0.483	0.500	-3.223
308.15	0.496	0.500	-0.618
313.15	0.728	0.706	3.264
318.15	0.960	0.985	-2.473
318.15	0.975	0.985	-0.949
318.15	0.982	0.985	-0.238
318.15	0.971	0.985	-1.355
333.15	2.59	2.51	3.027
358.15	10	9.94	0.435

Table 5. Values of the Constants in the Antoine Equation for Calculating the Pressure of HN1 in Torr and Pascal

Antoine Constant	Value of the Constant in the Indicated Pressure Units	
	Torr	Pa
a	19.4957	24.3883
b	5800.22	5800.22
c	–20.8777	–20.8777

Table 6. Calculated Values of the Vapor Pressure of HN1 at Several Temperatures.

Temperature (K)	Temperature (°C)	Pressure This Work (Pa)	Pressure This Work (Torr)	Pressure (Torr)	
				Literature Reference 2	Literature Reference 3
273.15	0	4.04	0.0303	0.0329	
293.15	20	21.88	0.1641	0.171	0.164
298.15	25	32.12	0.2410	0.250	0.239
385.15	85	1327	9.957	10.2	10.0

Note: The last two columns show the values of the vapor pressure reported in the indicated literature references.

5. CONCLUSIONS

Historical measurements of the vapor pressure of HN1 were made at a minimum temperature of 20 °C. We recently measured the vapor pressure of HN1 at 5 and 15 °C. By combining the historical data with our measurements, we have calculated new coefficients for the Antoine equation that will improve the accuracy of the predictions of the vapor pressure of the compound at sub-ambient temperatures.

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ACRONYMS AND ABBREVIATIONS

CW	chemical warfare
ECBC	U.S. Army Edgewood Chemical Biological Center
GC	gas chromatography
HN1	*bis*-(2-chloroethyl)ethylamine
HN2	b*is*-(2-chloroethyl)methylamine
HN3	*Tris*-(2-chloroethyl)amine
HD	sulfur mustard
K	kelvin
MS	mass spectrometry
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
Pa	pascal
T	temperature
TCD	thermal conductivity detection


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