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Vapor Pressure Data and Analysis for Selected V-Agent Decomposition Products: TEPTO, OSDEEP, DEMPS, OSDIBMP, OSDEMP, and OSDMMP

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14. ABSTRACT:
Recent work from our laboratory has focused on measurement of the physical properties of chemical warfare agents and their surrogates, precursors, and degradation products. This report documents vapor pressure data for six V-agent decomposition products that were measured using an ASTM International method based on differential scanning calorimetry. The data presented herein were used to determine temperature–pressure correlations to enable interpolation and limited extrapolation of the data, and the fit constants were used to calculate temperature-dependent thermodynamic properties. The new data are compared to previous literature for the title compounds and two standard chemical warfare agents.

15. SUBJECT TERMS
Clausius–Clapeyron equation
Chemical Abstracts Service (CAS)
Triethyl phosphorothionate (TEPTO) CAS no. 126-68-1
O,S-Diethyl ethylphosphonothiolate (OSDEEP) CAS no. 2511-11-7
O,O'-Diethyl methylphosphonothionate (DEMPS) CAS no. 6996-81-2
O,S-Diisobutyl methylphosphonothiolate (OSDIBMP) CAS no. 100860-55-7
O,S-Diethyl methylphosphonothiolate (OSDEMP) CAS no. 2511-10-6
O,S-Dimethyl methylphosphonothiolate (OSDMMP) CAS no. 58259-60-2
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Entropy of vaporization
Vapor pressure
Antoine equation
Volatility
V-agent
Differential scanning calorimetry (DSC)

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PREFACE

The work described in this report was funded by the Defense Threat Reduction Agency, Joint Science and Technology Office (Fort Belvoir, VA), project number CB3662. The work was performed between March 2015 and January 2018.

At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC Chemical Biological Center) was known as the U.S. Army Edgewood Chemical Biological Center (ECBC). The data reported herein are documented in ECBC notebooks 99-0095 and 02-0091.

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This report has been approved for public release.

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VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED V-AGENT DECOMPOSITION PRODUCTS: TEPTO, OSDEEP, DEMPS, OSDIBMP, OSDEMP, AND OSDMMP

1. INTRODUCTION

The U.S. Army Combat Capabilities Development Command Chemical Biological Center (formerly U.S. Army Edgewood Chemical Biological Center [ECBC]; Aberdeen Proving Ground, MD) has a long history of interest in the thermophysical properties of chemical warfare agents (CWAs) and related compounds.[1–8] Knowledge of the physical properties of materials is necessary to understand their behavior in the environment as well as in the laboratory. Vapor pressure is an important physical property for a wide variety of chemical defense-related applications, including evaluating toxicological properties, estimating persistence, assessing the efficiency of air filtration systems, predicting downwind time–concentration profiles after dissemination, and generating controlled challenge concentrations for detector testing.

Recently, our laboratory investigated and documented the experimental vapor pressure and properties derived from such data, which included temperature-dependent enthalpy of volatilization (vaporization for liquids and sublimation for solids) of selected CWAs and related precursors, degradation products, and simulants.[9–21] A recent report focused on exploring correlations to enable extrapolation of high-temperature data to ambient to facilitate accurate prediction of vapor pressure and related properties at untested (ambient) conditions that are of the most practical interest.[20]

This report documents vapor pressure measurements, correlations, and thermodynamic properties that are derived from vapor pressure data for six V-agent degradation products of interest to the chemical defense community as potential signature compounds. The structures, full and common names, formulas, Chemical Abstracts Service (CAS) registry numbers, and molecular weights for the subject compounds are provided in Figure 1. The measurements were performed using differential scanning calorimetry (DSC). Literature data for the title compounds primarily comprise reduced-pressure boiling points. We have found such data to be generally unreliable, especially at low pressures and, as a result, those data were not used to determine the correlations.

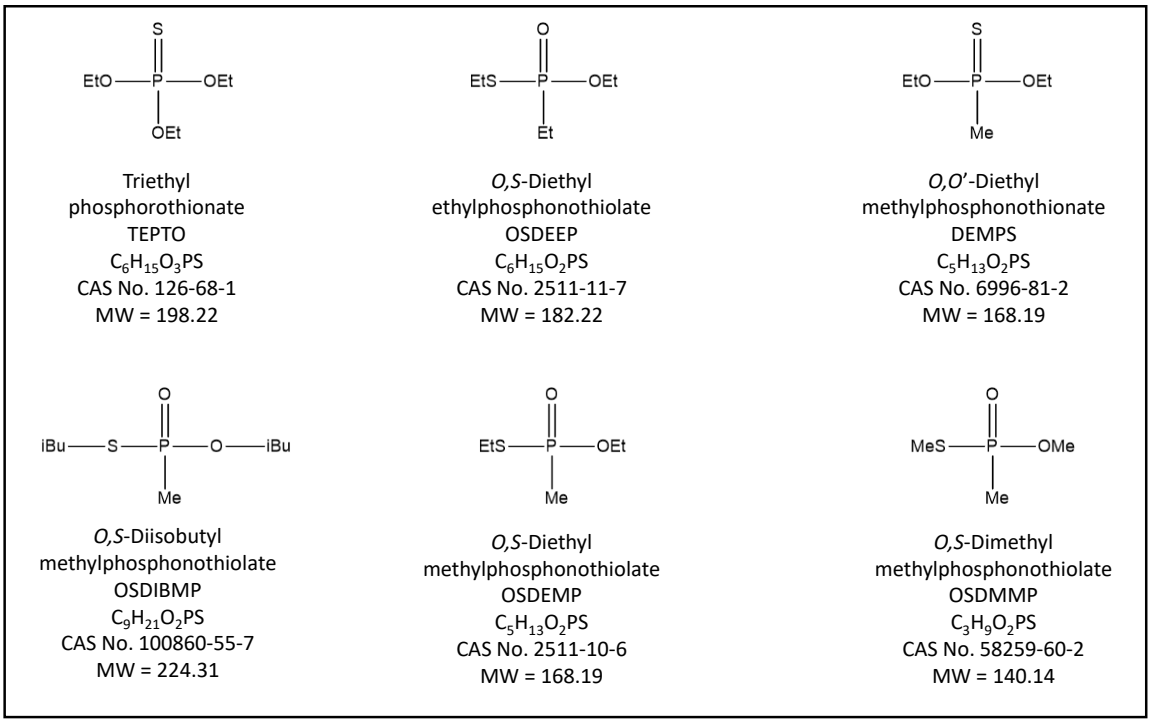

Figure 1. Structures, identifications, CAS numbers, and molecular weights (MWs) of title compounds.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and Method

The sources and purities of the materials used in the current work are listed in Table 1.

Table 1. Sample Information for Title Compounds

Compound	Purity (%)	Source
TEPTO	99.5	Chem Service, Inc. (West Chester, PA)
OSDEEP	98.0	Radian Chemicals (Kingwood, TX)
DEMPS	97.0	Aldrich Chemical Company (Milwaukee, WI)
OSDIBMP	96.1	Agent Chemistry Branch, ECBC
OSDEMP	95.0	
OSDMMP	98.0	

A TA Instruments (New Castle, DE) model 910 differential scanning calorimeter with a 2200 controller was used in this work, and the measurements were carried out in accordance with ASTM International method E1782 (*Standard Test Method for Determining Vapor Pressure by Thermal Analysis*; ASTM International: West Conshohocken, PA, 2017). The method and instrumentation have been described in detail in a previous publication.[12]

2.2 Data Analysis

Accurately correlating vapor pressure data as a function of temperature to permit interpolation within the experimental range and extrapolation beyond that range was the subject of an earlier report from our laboratory.[21] These correlations can be challenging due to the number of equations available for this purpose, inadequately documented experimental work, poor data quality, or limited experimental range. High-quality vapor pressure data measured over a wide range typically exhibit negative curvature on a standard vapor pressure plot (ln P versus reciprocal temperature) that corresponds to decreasing enthalpy of vaporization with increasing temperature. The commonly used Clausius–Clapeyron correlation (eq 1) has no curvature due to the assumption of a constant enthalpy of vaporization as a function of temperature. It is usually used to correlate data over narrow temperature ranges and may be useful for limited extrapolation. An Antoine fit (eq 2) accommodates curvature of the experimental data, but depending on range and data quality, its use may produce thermodynamically prohibited positive curvature rather than the expected negative curvature that is characteristic of high-quality data. However, an Antoine fit may also produce excessive negative curvature, depending on data quality and range. Consequently, correlations can result in improper estimation of vapor pressure at untested conditions outside the experimental temperature range.

$$\ln(P) = a - b/T \tag{1}$$

$$\ln(P) = a - b/(c + T) \tag{2}$$

where P is vapor pressure in pascal; T is absolute temperature; and a, b, and c are fit constants.

A recent publication describes methodology to correlate vapor pressure data using the Antoine equation, which is optimized using a least-squares method.[22] This method also applies to the Clausius–Clapeyron equation, where the c constant is assigned a value of 0.

The ability to accurately predict vapor pressure at ambient temperatures is of particular concern when only high-temperature data are available. We have found that assigning a c value of –43, as suggested by Thomson,[23] produces better estimates of ambient-temperature vapor pressure than does applying a Clausius–Clapeyron or unconstrained Antoine fit to the experimental data.[20] This approach was used in the current report because none of the title compounds have reliable ambient-temperature vapor pressure data available. Although the amount of previously reported vapor pressure data varies from more than 40 points for TEPTO to none for OSDMMP, these data are primarily based on measurement of reduced-pressure boiling points. In our experience, this type of data is unreliable, especially at pressures below 500 Pa. These values are shown in the figures herein but were not used to determine the correlations.

Thermodynamic properties can be calculated from the vapor pressure correlation. The enthalpy of vaporization, ΔH_{vap}, in joules per mole, is calculated by multiplying the slope of the standard vapor pressure plot by $R \times T^2$, as shown in eq 3.

$$\Delta H_{vap} = b \times R \times [T/(c + T)]^2 \quad (3)$$

where b and c are eq 2 coefficients, and R is the gas constant (8.3144 J/mol K).

The saturation concentration, C_{sat}, often referred to as volatility, in milligrams per cubic meter, is calculated as a function of temperature according to

$$C_{sat} = P \times \mathrm{MW}/R \times T \quad (4)$$

where MW is molecular weight, and R is 8.3144 Pa m^3/mol K.

The entropy of vaporization, ΔS_{vap}, in joules per mole kelvin, is calculated by dividing the enthalpy of vaporization at the normal boiling point (NBPt) by the NBPt, as shown in eq 5. Trouton's rule states that this value should be near 21 cal/mol K (88 J/mol K).

$$\Delta S_{vap} = \Delta H_{vap}/\mathrm{NBPt} \quad (5)$$

Vapor pressure correlations in the literature are given using a variety of units. Most commonly in the older literature, pressure is reported in torr (mmHg; abbreviated herein as *p),* and temperature is in Celsius. Currently, most journals require that authors provide pressure in pascal and temperature in kelvin. In previous publications from our laboratory,[13,21] equations were included to convert Antoine correlation constants from torr–Celsius to pascal–kelvin units.

3. RESULTS

The experimental data, pressure–temperature correlations, comparisons to literature data, and calculated properties for each of the title compounds are provided in the following sections.

3.1 TEPTO

The 13 TEPTO data points listed in Table 2 were measured using DSC from t = 88.62 to 218.36 °C (where t is temperature in Celsius). The measurements covered a wide pressure range that included atmospheric pressure. The boiling endotherms were sharp and exhibited no indication of specimen degradation with the exception of the atmospheric pressure peak. This peak had a small, reproducible shoulder preceding the boiling endotherm that did not interfere with determination of the boiling onset temperature. The experimental data were correlated using an Antoine equation with the c constant constrained to –43. The resulting Antoine equation is given in Table 2 with the experimental data, calculated values, and the percent difference at each experimental temperature. Figure 2 shows the current experimental

data, the Antoine correlation, and literature data, including an NBPt and 40 reduced-pressure boiling points.[24–52] Table 3 lists the calculated values for TEPTO vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for TEPTO is 216.86 °C. The entropy of vaporization calculated for TEPTO using the DSC data, 101.7 J/mol K, is higher than expected on the basis of Trouton's rule.

Table 2. Experimental Data and Calculated Vapor Pressure Values for TEPTO

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
88.62	8.0×10^{0}	1.067×10^{3}	8.539×10^{0}	1.138×10^{3}	–6.31
89.56	9.3×10^{0}	1.240×10^{3}	8.941×10^{0}	1.192×10^{3}	4.02
91.53	1.00×10^{1}	1.333×10^{3}	9.837×10^{0}	1.311×10^{3}	1.66
95.21	1.13×10^{1}	1.507×10^{3}	1.172×10^{1}	1.563×10^{3}	–3.60
103.32	1.72×10^{1}	2.293×10^{3}	1.702×10^{1}	2.269×10^{3}	1.06
112.63	2.62×10^{1}	3.493×10^{3}	2.555×10^{1}	3.406×10^{3}	2.55
123.46	4.01×10^{1}	5.346×10^{3}	3.989×10^{1}	5.319×10^{3}	0.52
135.56	6.40×10^{1}	8.533×10^{3}	6.362×10^{1}	8.481×10^{3}	0.60
147.83	9.92×10^{1}	1.323×10^{4}	9.904×10^{1}	1.320×10^{4}	0.16
159.48	1.486×10^{2}	1.981×10^{4}	1.470×10^{2}	1.959×10^{4}	1.12
171.60	2.192×10^{2}	2.922×10^{4}	2.162×10^{2}	2.883×10^{4}	1.38
182.51	3.013×10^{2}	4.017×10^{4}	3.002×10^{2}	4.003×10^{4}	0.36
218.36	7.648×10^{2}	1.020×10^{5}	7.889×10^{2}	1.052×10^{5}	–3.05
$\log(p) = 7.726473 - 2166.068/(t + 230.15)$ $\ln(P) = 22.68363 - 4987.555/(T - 43.000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

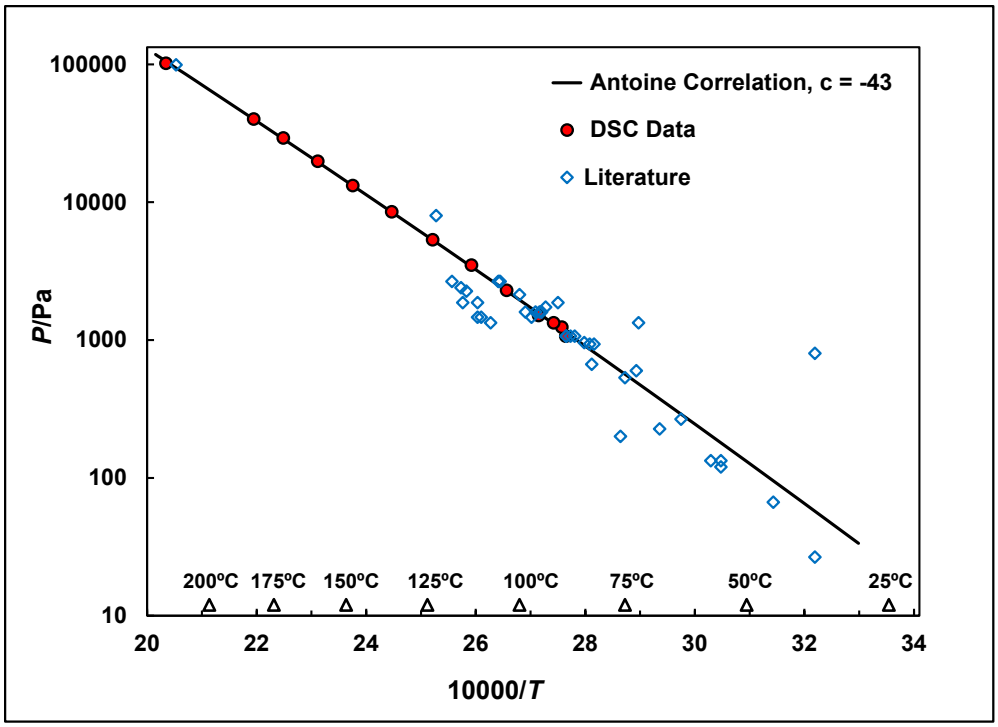

Figure 2. Vapor pressure data and Antoine equation correlation for TEPTO.

Table 3. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for TEPTO at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	2.626×10^{-3}	3.500×10^{-1}	3.297×10^{1}	60.18
–10*	7.716×10^{-3}	1.029×10^{0}	9.320×10^{1}	59.25
0*	2.065×10^{-2}	2.753×10^{0}	2.403×10^{2}	58.41
10*	5.091×10^{-2}	6.788×10^{0}	5.715×10^{2}	57.65
20*	1.168×10^{-1}	1.557×10^{1}	1.266×10^{3}	56.95
25*	1.726×10^{-1}	2.301×10^{1}	1.840×10^{3}	56.62
30*	2.513×10^{-1}	3.351×10^{1}	2.635×10^{3}	56.31
40*	5.110×10^{-1}	6.813×10^{1}	5.187×10^{3}	55.72
50*	9.878×10^{-1}	1.317×10^{2}	9.716×10^{3}	55.18
60*	1.824×10^{0}	2.432×10^{2}	1.741×10^{4}	54.67
80*	5.528×10^{0}	7.370×10^{2}	4.975×10^{4}	53.76
100	1.464×10^{1}	1.952×10^{3}	1.247×10^{5}	52.97
120	3.470×10^{1}	4.627×10^{3}	2.806×10^{5}	52.28
140	7.492×10^{1}	9.989×10^{3}	5.764×10^{5}	51.66
160	1.495×10^{2}	1.993×10^{4}	1.097×10^{6}	51.11
180	2.788×10^{2}	3.717×10^{4}	1.956×10^{6}	50.62
200	4.908×10^{2}	6.543×10^{4}	3.297×10^{6}	50.17
216.86	7.600×10^{2}	1.013×10^{5}	4.930×10^{6}	49.83

*Extrapolated.

3.2 OSDEEP

The 13 OSDEEP data points listed in Table 4 were measured using DSC from $t = 98.75$ to 233.16 °C. The measurements covered nearly 2 orders of magnitude up to atmospheric pressure. The boiling endotherms were sharp and exhibited no indication of specimen degradation. The experimental data were correlated using an Antoine equation with the c constant constrained to –43. The resulting Antoine equation is given in Table 4, along with calculated values and the percent difference at each experimental temperature. Figure 3 shows the current experimental data, the Antoine correlation, and literature data, including an NBPt and 11 reduced pressure boiling points.[53–60] Table 5 lists the calculated values for OSDEEP vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for OSDEEP is 231.70 °C. The entropy of vaporization calculated for OSDEEP using the DSC data, 103.2 J/mol K, is higher than expected on the basis of Trouton's rule.

Table 4. Experimental Data and Calculated Vapor Pressure Values for OSDEEP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
98.75	7.9×10^{0}	1.053×10^{3}	7.703×10^{0}	1.027×10^{3}	2.55
101.30	8.2×10^{0}	1.093×10^{3}	8.709×10^{0}	1.161×10^{3}	–5.85
104.36	1.03×10^{1}	1.373×10^{3}	1.007×10^{1}	1.342×10^{3}	2.33
111.02	1.34×10^{1}	1.786×10^{3}	1.367×10^{1}	1.823×10^{3}	–1.99
113.75	1.53×10^{1}	2.040×10^{3}	1.545×10^{1}	2.059×10^{3}	–0.95
121.55	2.21×10^{1}	2.946×10^{3}	2.167×10^{1}	2.888×10^{3}	2.01
132.61	3.42×10^{1}	4.560×10^{3}	3.414×10^{1}	4.552×10^{3}	0.17
143.90	5.32×10^{1}	7.093×10^{3}	5.283×10^{1}	7.043×10^{3}	0.71
155.40	8.04×10^{1}	1.072×10^{4}	8.026×10^{1}	1.070×10^{4}	0.17
168.78	1.299×10^{2}	1.732×10^{4}	1.267×10^{2}	1.689×10^{4}	2.54
183.44	2.007×10^{2}	2.676×10^{4}	2.019×10^{2}	2.692×10^{4}	–0.60
197.53	3.185×10^{2}	4.246×10^{4}	3.067×10^{2}	4.088×10^{4}	3.86
233.16	7.525×10^{2}	1.003×10^{5}	7.877×10^{2}	1.050×10^{5}	–4.46
$\log(p) = 7.813979 - 2278.390/(t + 230.15)$ $\ln(P) = 22.88512 - 5246.186/(T - 43.0000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

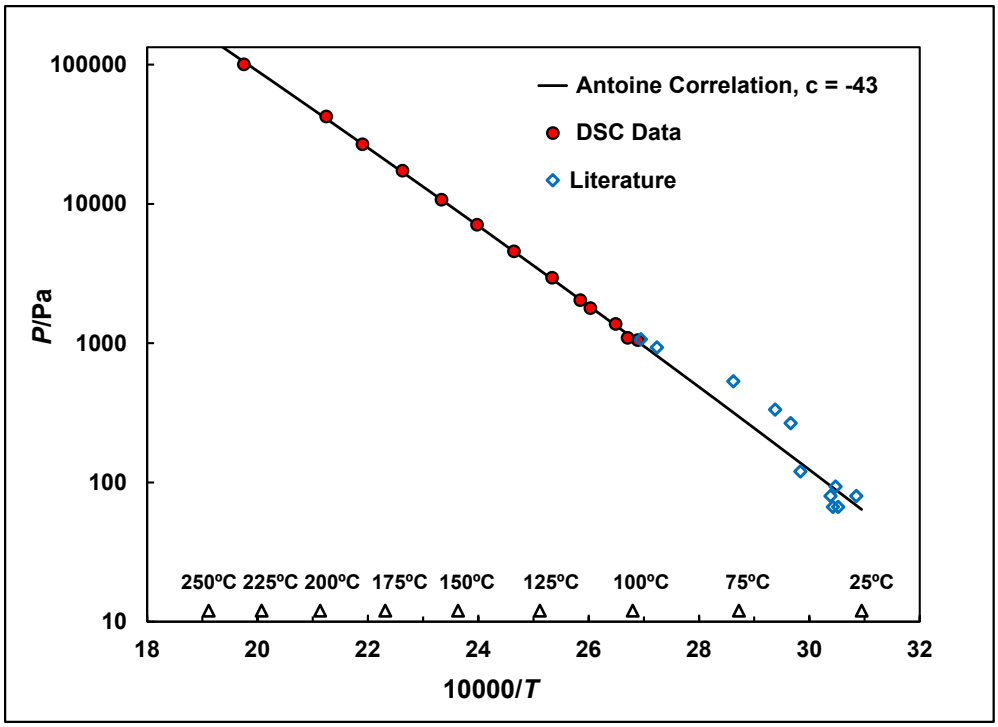

Figure 3. Vapor pressure data and Antoine equation correlation for OSDEEP.

Table 5. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for OSDEEP at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	9.381×10^{-4}	1.251×10^{-1}	1.083×10^{1}	63.30
–10*	2.916×10^{-3}	3.887×10^{-1}	3.237×10^{1}	62.32
0*	8.211×10^{-3}	1.095×10^{0}	8.783×10^{1}	61.44
10*	2.121×10^{-2}	2.828×10^{0}	2.189×10^{2}	60.64
20*	5.080×10^{-2}	6.773×10^{0}	5.064×10^{2}	59.90
25*	7.662×10^{-2}	1.022×10^{1}	7.509×10^{2}	59.56
30*	1.138×10^{-1}	1.517×10^{1}	1.096×10^{3}	59.23
40*	2.400×10^{-1}	3.200×10^{1}	2.239×10^{3}	58.61
50*	4.800×10^{-1}	6.399×10^{1}	4.340×10^{3}	58.04
60*	9.152×10^{-1}	1.220×10^{2}	8.027×10^{3}	57.51
80*	2.937×10^{0}	3.916×10^{2}	2.430×10^{4}	56.55
100	8.183×10^{0}	1.091×10^{3}	6.407×10^{4}	55.72
120	2.028×10^{1}	2.704×10^{3}	1.507×10^{5}	54.99
140	4.557×10^{1}	6.075×10^{3}	3.223×10^{5}	54.34
160	9.423×10^{1}	1.256×10^{4}	6.357×10^{5}	53.76
180	1.815×10^{2}	2.420×10^{4}	1.171×10^{6}	53.24
200	3.290×10^{2}	4.387×10^{4}	2.032×10^{6}	52.78
220	5.657×10^{2}	7.542×10^{4}	3.352×10^{6}	52.35
231.70	7.600×10^{2}	1.013×10^{5}	4.399×10^{6}	52.12

*Extrapolated.

3.3 DEMPS

Six data points were measured by Belkin and Brown in the 1970s for DEMPS (reported to be 97.1% pure) using differential thermal analysis (DTA), which is a method similar to DSC. These data points range from 82.5 to 190.5 °C, corresponding to pressures from 2193 Pa to atmospheric pressure. A correlation was published,[61] and the data points were documented, but the thermal curves from which these points were derived are not available. As a result, DSC measurements were performed on DEMPS. Nineteen data points for DEMPS were successfully measured from 64.31 to 162.68 °C, corresponding to pressures from 853.3 to 43,160 Pa. Measurement of atmospheric pressure data was also attempted, but those results were not useable due to the presence of a nonreproducible shoulder on the boiling endotherm plot. The DSC and DTA data are listed in Table 6. The DTA and DSC data have a range of more than 2 orders of magnitude and were used to determine the Antoine equation correlation. The experimental data were correlated using an Antoine equation with the *c* constant constrained to –43. The resulting Antoine equation is given in Table 6, along with the calculated values and the percent difference at each experimental temperature. Figure 4 shows the Antoine correlation and six reduced-pressure boiling points from the literature.[53,62–66] Table 7 lists the calculated values for DEMPS vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for DEMPS is 191.21 °C. The entropy of vaporization calculated for DEMPS using the DSC data, 102.0 J/mol K, is higher than expected on the basis of Trouton's rule.

Table 6. Experimental Data and Calculated Vapor Pressure Values for DEMPS

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
DSC					
64.31	6.4×10^{0}	8.533×10^{2}	6.273×10^{0}	8.364×10^{2}	2.02
66.42	6.4×10^{0}	8.533×10^{2}	7.026×10^{0}	9.367×10^{2}	–8.91
68.23	7.2×10^{0}	9.599×10^{2}	7.734×10^{0}	1.031×10^{3}	–6.90
65.90	7.3×10^{0}	9.733×10^{2}	6.834×10^{0}	9.111×10^{2}	6.82
70.76	8.2×10^{0}	1.093×10^{3}	8.826×10^{0}	1.177×10^{3}	–7.09
75.14	1.04×10^{1}	1.387×10^{3}	1.104×10^{1}	1.472×10^{3}	–5.78
80.65	1.48×10^{1}	1.973×10^{3}	1.449×10^{1}	1.932×10^{3}	2.11
87.14	2.01×10^{1}	2.680×10^{3}	1.973×10^{1}	2.631×10^{3}	1.85
90.41	2.49×10^{1}	3.320×10^{3}	2.295×10^{1}	3.059×10^{3}	8.51
95.65	2.97×10^{1}	3.960×10^{3}	2.903×10^{1}	3.871×10^{3}	2.29
98.70	3.34×10^{1}	4.453×10^{3}	3.318×10^{1}	4.424×10^{3}	0.66
101.89	3.80×10^{1}	5.066×10^{3}	3.806×10^{1}	5.074×10^{3}	–0.15
104.70	4.36×10^{1}	5.813×10^{3}	4.284×10^{1}	5.712×10^{3}	1.76
108.23	5.00×10^{1}	6.666×10^{3}	4.959×10^{1}	6.611×10^{3}	0.84
116.88	6.99×10^{1}	9.319×10^{3}	7.005×10^{1}	9.339×10^{3}	–0.21
126.42	1.001×10^{2}	1.335×10^{4}	1.006×10^{2}	1.341×10^{4}	–0.46
137.87	1.501×10^{2}	2.001×10^{4}	1.514×10^{2}	2.019×10^{4}	–0.87
153.94	2.496×10^{2}	3.328×10^{4}	2.581×10^{2}	3.441×10^{4}	–3.28
162.68	3.237×10^{2}	4.316×10^{4}	3.386×10^{2}	4.515×10^{4}	–4.41
DTA					
82.5	1.645×10^{1}	2.193×10^{3}	1.585×10^{1}	2.113×10^{3}	3.80
104.5	4.700×10^{1}	6.266×10^{3}	4.249×10^{1}	5.665×10^{3}	10.62
129.0	1.135×10^{2}	1.513×10^{4}	1.105×10^{2}	1.474×10^{4}	2.69
149.0	2.144×10^{2}	2.859×10^{4}	2.201×10^{2}	2.935×10^{4}	–2.57
169.0	3.997×10^{2}	5.330×10^{4}	4.091×10^{2}	5.454×10^{4}	–2.29
190.5	7.578×10^{2}	1.010×10^{5}	7.459×10^{2}	9.944×10^{4}	1.60
$\log(p) = 7.714995 - 2036.926/(t + 230.15)$ $\ln(P) = 22.65720 - 4690.195/(T - 43.000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

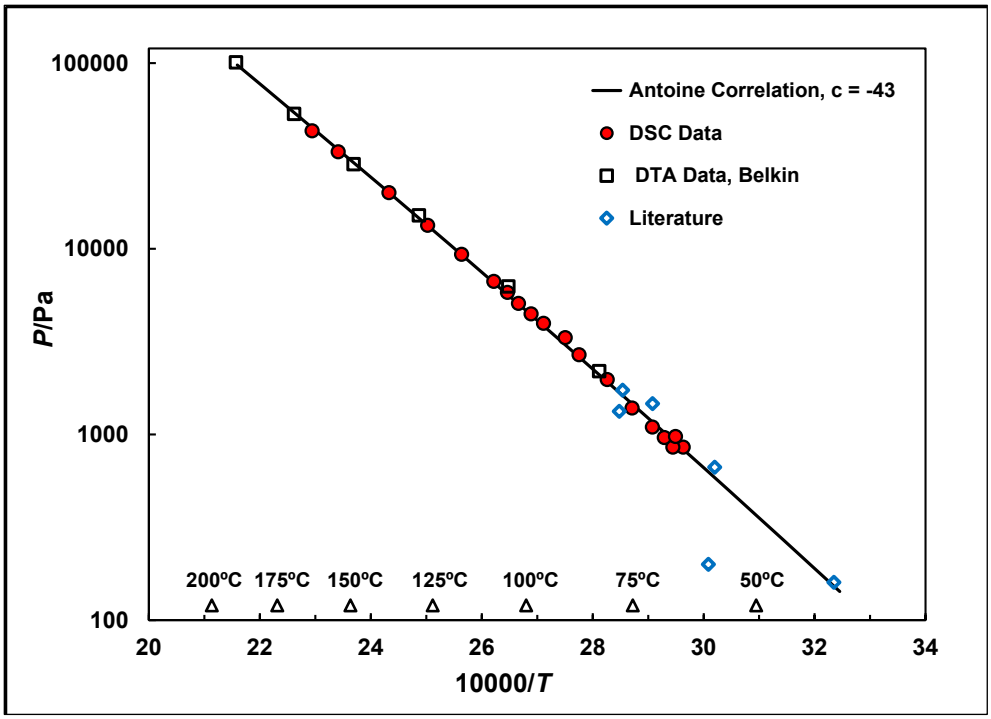

Figure 4. Vapor pressure data and Antoine equation correlation for DEMPS.

Table 7. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DEMPS at Selected Temperatures

Temp. (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	1.053×10^{-2}	1.403×10^{0}	1.121×10^{2}	56.59
–10*	2.901×10^{-2}	3.868×10^{0}	2.973×10^{2}	55.72
0*	7.321×10^{-2}	9.760×10^{0}	7.228×10^{2}	54.93
10*	1.710×10^{-1}	2.280×10^{1}	1.629×10^{3}	54.21
20*	3.734×10^{-1}	4.978×10^{1}	3.435×10^{3}	53.56
25*	5.392×10^{-1}	7.189×10^{1}	4.877×10^{3}	53.25
30*	7.677×10^{-1}	1.023×10^{2}	6.830×10^{3}	52.95
40*	1.496×10^{0}	1.995×10^{2}	1.289×10^{4}	52.40
50*	2.781×10^{0}	3.707×10^{2}	2.321×10^{4}	51.89
60*	4.952×10^{0}	6.602×10^{2}	4.008×10^{4}	51.41
70	8.485×10^{0}	1.131×10^{3}	6.668×10^{4}	50.97
80	1.404×10^{1}	1.872×10^{3}	1.072×10^{5}	50.56
100	3.510×10^{1}	4.679×10^{3}	2.537×10^{5}	49.82
120	7.901×10^{1}	1.053×10^{4}	5.420×10^{5}	49.16
140	1.629×10^{2}	2.172×10^{4}	1.064×10^{6}	48.58
160	3.120×10^{2}	4.159×10^{4}	1.942×10^{6}	48.07
180	5.607×10^{2}	7.475×10^{4}	3.337×10^{6}	47.60
191.21	7.600×10^{2}	1.013×10^{5}	4.414×10^{6}	47.36

*Extrapolated.

3.4 OSDIBMP

The 12 OSDIBMP data points listed in Table 8 were measured up to 1 atm using DSC from t = 134.52 to 256.73 °C. The DSC measurements covered fewer than 2 orders of magnitude. The DSC boiling endotherms were acceptably sharp over the entire temperature range. The experimental data were correlated using an Antoine equation with the c constant constrained to –43. The resulting Antoine equation is given in Table 8, along with calculated values and percent differences at each experimental temperature. Figure 5 shows the Antoine correlation, a point found in a manufacturer's safety data sheet,[67] and one reduced-pressure boiling point found in the literature.[68] Table 9 lists the calculated values for OSDIBMP vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for OSDIBMP is 257.73 °C. The entropy of vaporization calculated for OSDIBMP using the DSC data, 115.1 J/mol K, is higher than expected on the basis of Trouton's rule.

Table 8. Experimental Data and Calculated Vapor Pressure Values for OSDIBMP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
134.52	1.04×10^{1}	1.387×10^{3}	1.033×10^{1}	1.378×10^{3}	0.65
142.74	1.54×10^{1}	2.053×10^{3}	1.504×10^{1}	2.005×10^{3}	2.42
150.66	2.14×10^{1}	2.853×10^{3}	2.126×10^{1}	2.834×10^{3}	0.68
165.94	4.03×10^{1}	5.373×10^{3}	3.986×10^{1}	5.314×10^{3}	1.10
176.75	6.01×10^{1}	8.013×10^{3}	6.044×10^{1}	8.058×10^{3}	–0.56
176.49	6.03×10^{1}	8.039×10^{3}	5.985×10^{1}	7.980×10^{3}	0.75
188.14	9.02×10^{1}	1.203×10^{4}	9.156×10^{1}	1.221×10^{4}	–1.49
203.60	1.503×10^{2}	2.004×10^{4}	1.554×10^{2}	2.072×10^{4}	–3.27
211.80	1.968×10^{2}	2.624×10^{4}	2.026×10^{2}	2.701×10^{4}	–2.87
227.31	3.013×10^{2}	4.017×10^{4}	3.262×10^{2}	4.349×10^{4}	–7.63
254.61	7.596×10^{2}	1.013×10^{5}	7.003×10^{2}	9.337×10^{4}	8.47
256.73	7.596×10^{2}	1.013×10^{5}	7.405×10^{2}	9.872×10^{4}	2.58
$\log(p) = 8.405625 - 2695.427/(t + 230.15)$ $\ln(P) = 24.24744 - 6206.451/(T - 43.000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

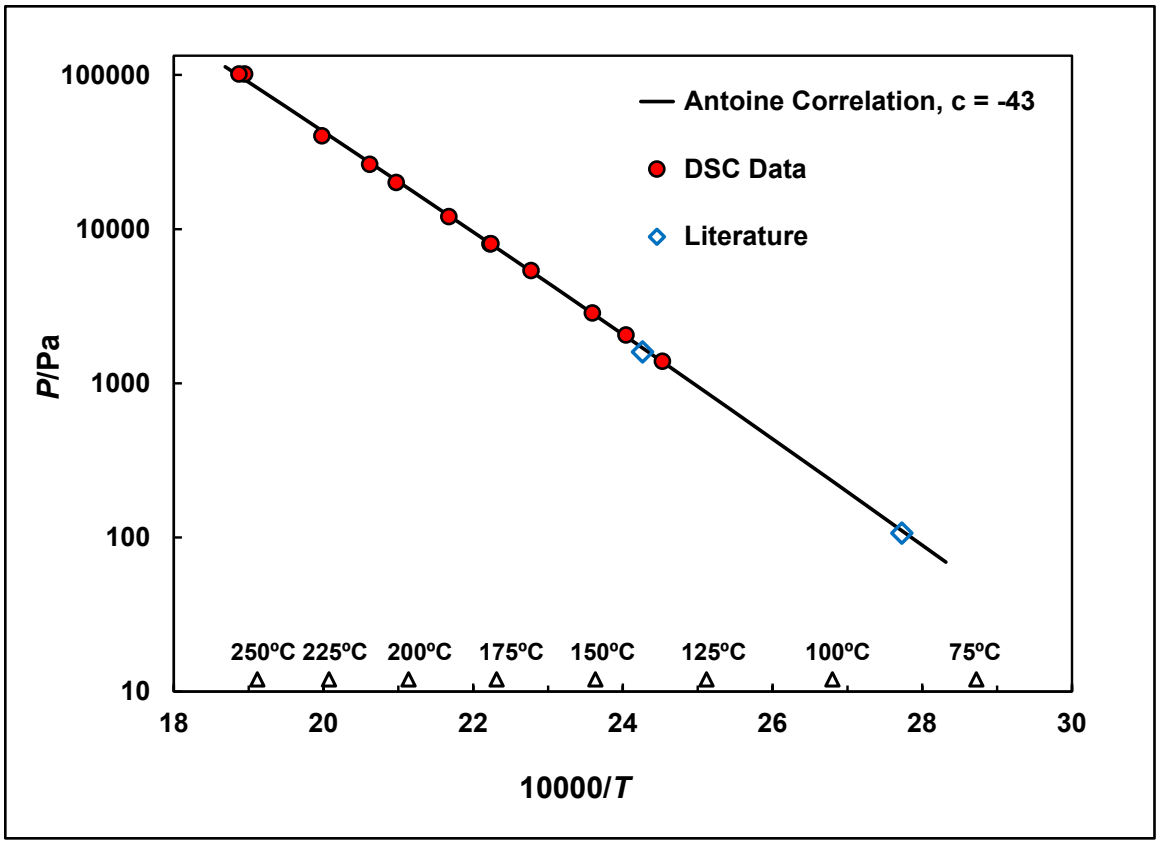

Figure 5. Vapor pressure data and Antoine equation correlation for OSDIBMP.

Table 9. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for OSDIBMP at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	3.797×10^{-5}	5.062×10^{-3}	5.395×10^{-1}	74.88
–10*	1.452×10^{-4}	1.936×10^{-2}	1.985×10^{0}	73.73
0*	4.943×10^{-4}	6.590×10^{-2}	6.509×10^{0}	72.69
10*	1.519×10^{-3}	2.026×10^{-1}	1.930×10^{1}	71.74
20*	4.270×10^{-3}	5.692×10^{-1}	5.239×10^{1}	70.87
25*	6.943×10^{-3}	9.256×10^{-1}	8.376×10^{1}	70.46
30*	1.108×10^{-2}	1.477×10^{0}	1.315×10^{2}	70.07
40*	2.680×10^{-2}	3.573×10^{0}	3.078×10^{2}	69.34
50*	6.085×10^{-2}	8.113×10^{0}	6.773×10^{2}	68.66
60*	1.306×10^{-1}	1.741×10^{1}	1.410×10^{3}	68.03
70*	2.663×10^{-1}	3.550×10^{1}	2.791×10^{3}	67.45
80*	5.187×10^{-1}	6.915×10^{1}	5.283×10^{3}	66.90
100*	1.743×10^{0}	2.324×10^{2}	1.680×10^{4}	65.92
120*	5.102×10^{0}	6.802×10^{2}	4.667×10^{4}	65.06
140	1.329×10^{1}	1.772×10^{3}	1.157×10^{5}	64.29
160	3.140×10^{1}	4.186×10^{3}	2.607×10^{5}	63.60
180	6.821×10^{1}	9.093×10^{3}	5.414×10^{5}	62.99
200	1.378×10^{2}	1.838×10^{4}	1.048×10^{5}	62.44
220	2.617×10^{2}	3.489×10^{4}	1.909×10^{6}	61.93
240	4.704×10^{2}	6.272×10^{4}	3.297×10^{6}	61.47
257.73	7.600×10^{2}	1.013×10^{5}	5.149×10^{6}	61.10

*Extrapolated.

3.5 OSDEMP

The 10 OSDEMP data points listed in Table 10 were measured up to 1 atm using DSC from $t = 98.25$ to 224.55 °C. The DSC measurements covered nearly 2 orders of magnitude. The boiling endotherms were sharp and showed no indication of specimen degradation. The experimental data were correlated using an Antoine equation with the c constant constrained to –43. The resulting Antoine equation is given in Table 10, along with calculated values and percent differences at each experimental temperature. Figure 6 shows the Antoine correlation and eight reduced-pressure boiling points found in the literature.[56,68–73] Table 11 lists the calculated values for OSDEMP vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for OSDEMP is 223.91 °C. The entropy of vaporization calculated for OSDEMP on the basis of the DSC data, 102.3 J/mol K, is higher than the value that was expected on the basis of Trouton's rule.

Table 10. Experimental Data and Calculated Vapor Pressure Values for OSDEMP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
98.25	1.01×10^1	1.346×10^3	1.032×10^1	1.376×10^3	–2.12
106.95	1.51×10^1	2.013×10^3	1.541×10^1	2.054×10^3	–2.00
112.84	2.00×10^1	2.666×10^3	1.998×10^1	2.664×10^3	0.09
121.86	2.99×10^1	3.986×10^3	2.925×10^1	3.900×10^3	2.21
132.40	4.49×10^1	5.986×10^3	4.458×10^1	5.944×10^3	0.72
143.92	6.99×10^1	9.319×10^3	6.876×10^1	9.168×10^3	1.65
153.88	9.93×10^1	1.324×10^4	9.795×10^1	1.306×10^4	1.38
175.30	2.001×10^2	2.668×10^4	1.976×10^2	2.635×10^4	1.26
195.06	3.506×10^2	4.674×10^4	3.546×10^2	4.728×10^4	–1.13
224.55	7.572×10^2	1.010×10^5	7.722×10^2	1.030×10^5	–1.94
$\log(p) = 7.760634 - 2215.718/(t + 230.15)$ $\ln(P) = 22.76229 - 5101.879/(T - 43.000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

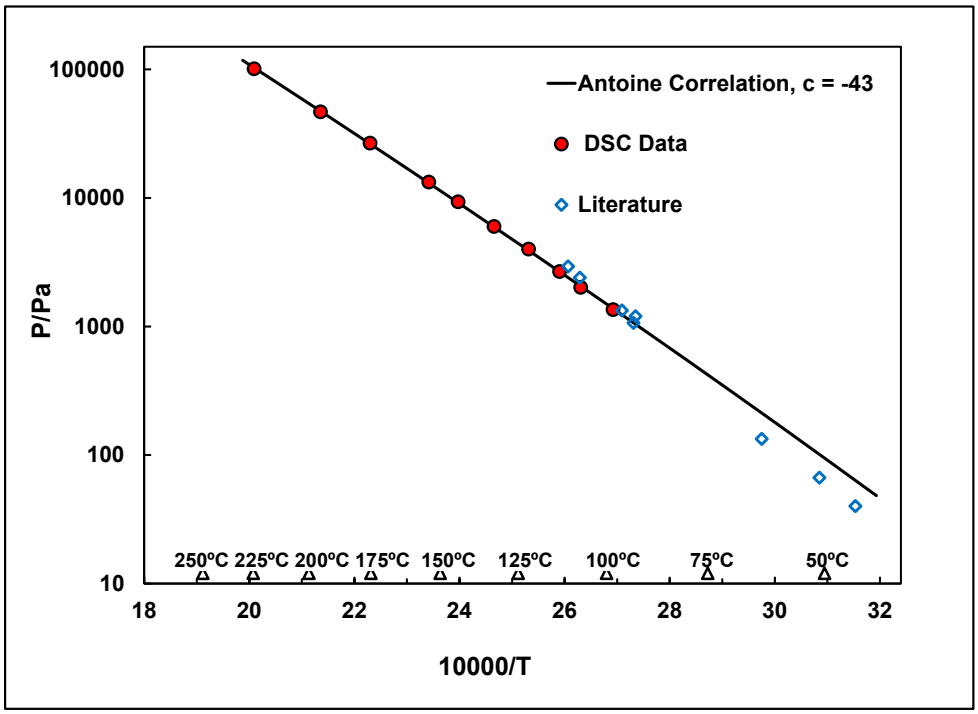

Figure 6. Vapor pressure data and Antoine equation correlation for OSDEMP.

Table 11. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for OSDEMP at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	1.649×10^{-3}	2.198×10^{-1}	1.756×10^{1}	61.55
–10*	4.967×10^{-3}	6.621×10^{-1}	5.090×10^{1}	60.61
0*	1.359×10^{-2}	1.812×10^{0}	1.342×10^{2}	59.75
10*	3.422×10^{-2}	4.562×10^{0}	3.259×10^{2}	58.97
20*	8.000×10^{-2}	1.067×10^{1}	7.360×10^{2}	58.26
25*	1.193×10^{-1}	1.591×10^{1}	1.079×10^{3}	57.92
30*	1.752×10^{-1}	2.336×10^{1}	1.559×10^{3}	57.60
40*	3.621×10^{-1}	4.828×10^{1}	3.118×10^{3}	57.00
50*	7.105×10^{-1}	9.473×10^{1}	5.930×10^{3}	56.44
60*	1.331×10^{0}	1.775×10^{2}	1.078×10^{4}	55.92
70*	2.391×10^{0}	3.188×10^{2}	1.879×10^{4}	55.44
80*	4.136×10^{0}	5.515×10^{2}	3.159×10^{4}	55.00
100*	1.120×10^{1}	1.494×10^{3}	8.098×10^{4}	54.19
120*	2.708×10^{1}	3.611×10^{3}	1.858×10^{5}	53.48
140	5.952×10^{1}	7.935×10^{3}	3.885×10^{5}	52.85
160	1.206×10^{2}	1.608×10^{4}	7.511×10^{5}	52.29
180	2.283×10^{2}	3.043×10^{4}	1.358×10^{6}	51.78
200	4.070×10^{2}	5.426×10^{4}	2.320×10^{6}	51.32
220	6.894×10^{2}	9.191×10^{4}	3.770×10^{6}	50.91
223.91	7.600×10^{2}	1.013×10^{5}	4.124×10^{6}	50.83

*Extrapolated.

3.6 OSDMMP

The 13 OSDMMP data points listed in Table 12 were measured up to 1 atm using DSC from t = 64.31 to 162.68 °C and were used to determine the Antoine equation correlation. The DSC measurements covered nearly 2 orders of magnitude up to atmospheric pressure. Except for the ambient pressure points, the boiling endotherms were sharp and exhibited no indication of specimen degradation. The ambient pressure points were broader, but they were consistent with the other points and deemed useable. The experimental data were correlated using an Antoine equation with the c constant constrained to –43. The resulting Antoine equation is given in Table 12, along with calculated values and percent differences at each experimental temperature. No vapor pressure data were found for OSDMMP in the literature. Figure 7 shows the DSC data and Antoine correlation. Table 13 lists the calculated values for OSDMMP vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated NBPt for OSDMMP is 211.50 °C. The entropy of vaporization calculated for OSDMMP using the DSC data, 104.7 J/mol K, is higher than expected on the basis of Trouton's rule.

Table 12. Experimental and Calculated Vapor Pressure Values for OSDMMP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference† (%)
	Torr	Pa*	Torr	Pa	
92.37	1.04×10^{1}	1.387×10^{3}	1.094×10^{1}	1.459×10^{3}	–4.96
98.64	1.53×10^{1}	2.040×10^{3}	1.477×10^{1}	1.969×10^{3}	3.60
105.00	1.99×10^{1}	2.653×10^{3}	1.979×10^{1}	2.638×10^{3}	0.56
113.94	3.01×10^{1}	4.013×10^{3}	2.932×10^{1}	3.909×10^{3}	2.67
124.01	4.51×10^{1}	6.013×10^{3}	4.457×10^{1}	5.943×10^{3}	1.18
131.46	5.98×10^{1}	7.972×10^{3}	5.987×10^{1}	7.981×10^{3}	–0.11
139.37	8.00×10^{1}	1.066×10^{4}	8.082×10^{1}	1.078×10^{4}	–1.02
145.10	1.001×10^{2}	1.335×10^{4}	9.966×10^{1}	1.329×10^{4}	0.44
156.88	1.499×10^{2}	1.999×10^{4}	1.504×10^{2}	2.005×10^{4}	–0.31
173.14	2.495×10^{2}	3.326×10^{4}	2.550×10^{2}	3.400×10^{4}	–2.15
184.50	3.510×10^{2}	4.680×10^{4}	3.598×10^{2}	4.797×10^{4}	–2.46
210.41	7.513×10^{2}	1.002×10^{5}	7.386×10^{2}	9.848×10^{4}	1.71
210.63	7.514×10^{2}	1.002×10^{5}	7.429×10^{2}	9.904×10^{4}	1.15
$\log(p) = 7.866642 - 2202.011/(t + 230.15)$ $\ln(P) = 23.00638 - 5070.319/(T - 43.000)$					

*Experimental Pa values were calculated from Torr values.

†$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

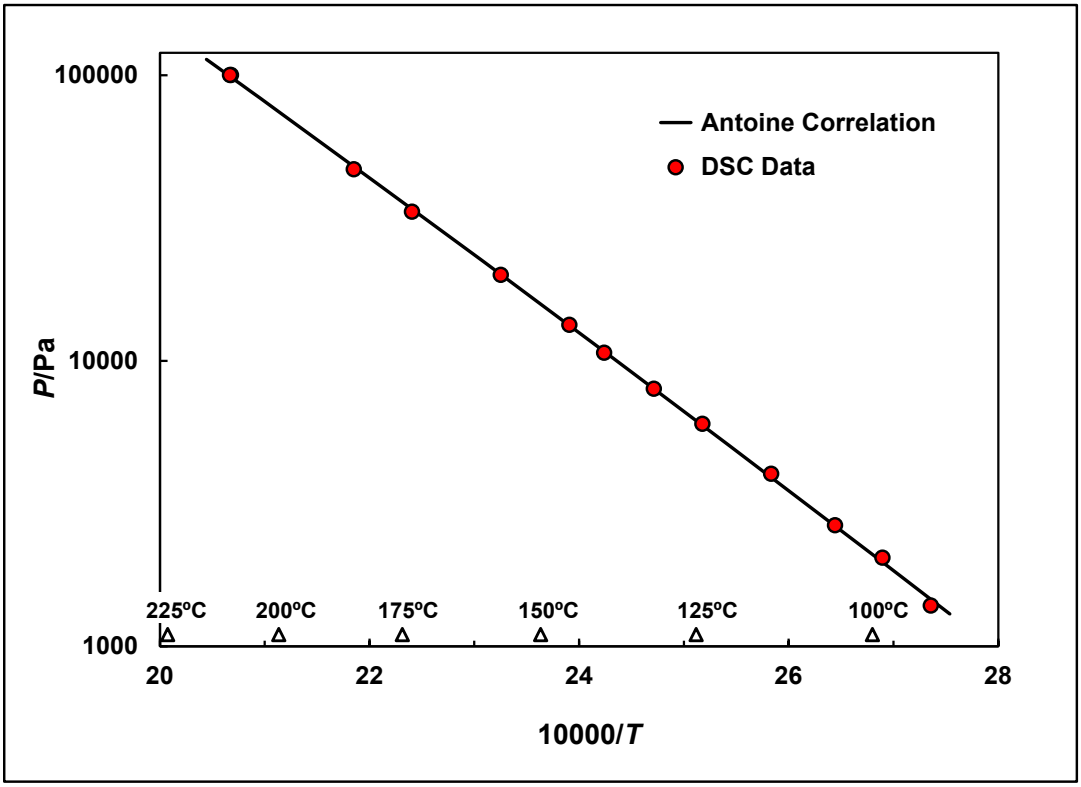

Figure 7. Vapor pressure data and Antoine equation correlation for OSDMMP.

Table 13. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for OSDMMP at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	Torr	Pa		
–20*	2.445×10^{-3}	3.260×10^{-1}	2.171×10^{1}	61.17
–10*	7.317×10^{-3}	9.755×10^{-1}	6.248×10^{1}	60.23
0*	1.990×10^{-2}	2.654×10^{0}	1.637×10^{2}	59.38
10*	4.981×10^{-2}	6.641×10^{0}	3.953×10^{2}	58.61
20*	1.158×10^{-1}	1.544×10^{1}	8.880×10^{2}	57.90
25*	1.723×10^{-1}	2.298×10^{1}	1.299×10^{3}	57.56
30*	2.525×10^{-1}	3.366×10^{1}	1.872×10^{3}	57.24
40*	5.195×10^{-1}	6.926×10^{1}	3.728×10^{3}	56.65
50*	1.015×10^{0}	1.353×10^{2}	7.059×10^{3}	56.09
60*	1.894×10^{0}	2.525×10^{2}	1.278×10^{4}	55.58
70*	3.391×10^{0}	4.520×10^{2}	2.220×10^{4}	55.10
80*	5.845×10^{0}	7.793×10^{2}	3.720×10^{4}	54.66
100	1.574×10^{1}	2.098×10^{3}	9.477×10^{4}	53.85
120	3.783×10^{1}	5.044×10^{3}	2.162×10^{5}	53.15
140	8.273×10^{1}	1.103×10^{4}	4.500×10^{5}	52.52
160	1.670×10^{2}	2.226×10^{4}	8.662×10^{5}	51.96
180	3.147×10^{2}	4.195×10^{4}	1.560×10^{6}	51.46
200	5.591×10^{2}	7.454×10^{4}	2.655×10^{6}	51.01
211.50	7.600×10^{2}	1.013×10^{5}	3.524×10^{6}	50.77

*Extrapolated.

4. DISCUSSION

Figure 8 shows that the vapor pressure curves of the title compounds generally fall between those of pinacolyl methyl phosphonofluoridate (GD) and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX), which are prototypical medium- and low-volatility CWAs, respectively. DEMPS has the highest vapor pressure among the title compounds; it is approximately 25% higher than that of GD at 25 °C. The vapor pressures of the other compounds decrease in the following order: DEMPS > OSDMMP ~ TEPTO > OSDEMP > OSDEEP > OSDIBMP. Data precision varies somewhat; the average percent differences between the calculated and experimental values range from 1.5% for OSDEMP to 3.5% for DEMPS, which covers the widest pressure range for compounds studied in this work. The average percent differences correlate roughly with the number of data points measured below 1330 Pa (10 Torr), which was the region known to exhibit increased experimental uncertainty for DSC data at the time these measurements were performed.

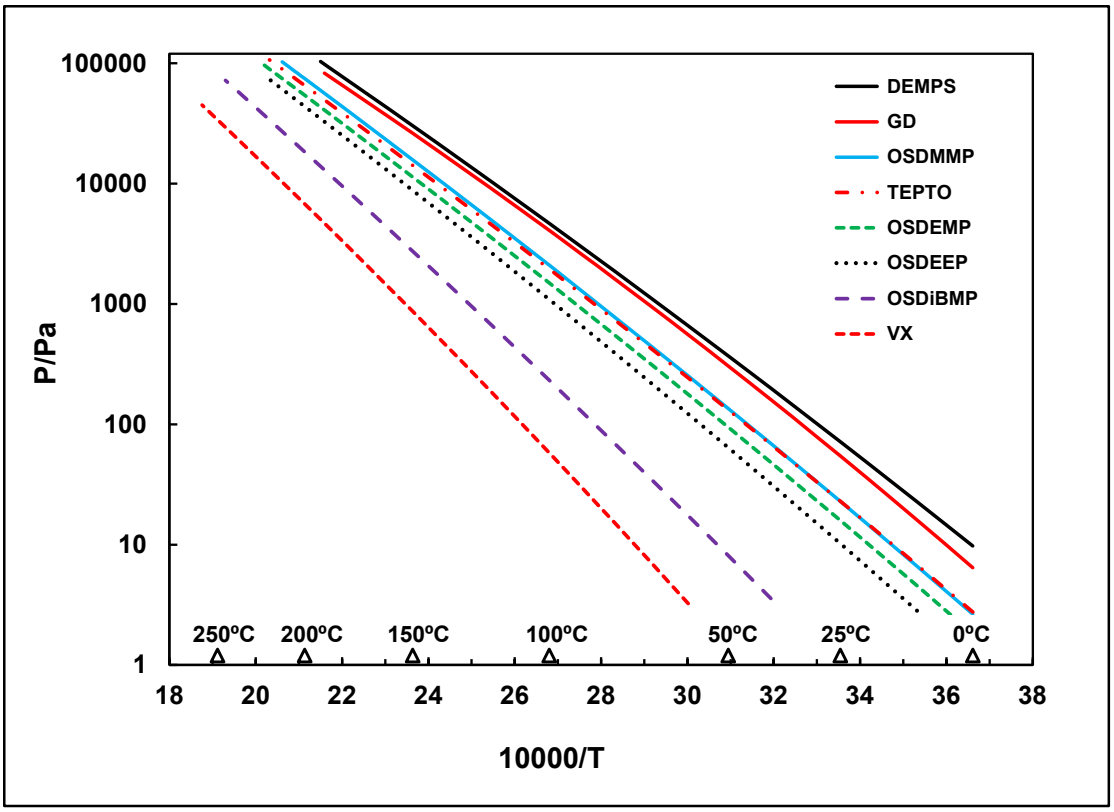

Figure 8. Antoine equation correlations for the title compounds compared to those of VX and GD.

With the exception of the DTA data from Belkin and Brown,[61] the literature data for these compounds consist primarily of reduced-pressure boiling points. These vary from more than 40 data points for TEPTO to none for OSDMMP; the agreement between our data and the literature data varies. Due to the earlier observations that reduced-pressure boiling point data are less reliable, especially at lower pressures, none of the literature data were used for the correlations.

The high values calculated for entropy of vaporization follow the trend reported earlier for a variety of compounds.[21] The discrepancy between the entropy of vaporization calculated on the basis of the experimental data and the value that is predicted using Trouton's rule is consistent with the trend first reported by Langmuir,[74] namely, that liquids with higher boiling points tend to have higher entropies of vaporization than predicted by Trouton's rule.

5. CONCLUSIONS

This report documents liquid-phase vapor pressure data measured using DSC for six V-agent degradation products. In the absence of ambient-temperature information, the data were correlated to an Antoine equation that was constrained by setting the *c* constant to –43 as suggested by Thomson.[23] This treatment has been shown to produce superior ambient-temperature vapor pressure estimates when only high-temperature data are available. Although

some of the literature data for the title compounds were consistent with ours, we have found that distillation data are generally less reliable than data produced by methods specifically designed to measure vapor pressure; therefore, these data were not used to generate the correlations.

Entropies of vaporization calculated on the basis of the current data result in values that are considerably higher than those predicted by Trouton's rule. Similar results have been reported for a variety of compounds in recent work from our laboratory. These results are consistent with Langmuir's observation that Trouton's constant is generally higher for substances having higher boiling points.[74]

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ACRONYMS AND ABBREVIATIONS

ΔH_{vap}	enthalpy of vaporization
ΔS_{vap}	entropy of vaporization
a, b, c	fit constants
CAS	Chemical Abstracts Service
C_{sat}	saturation concentration or volatility
CWA	chemical warfare agent
DEMPS	*O,O'*-diethyl methylphosphonothionate
DSC	differential scanning calorimetry
DTA	differential thermal analysis
ECBC	U.S. Army Edgewood Chemical Biological Center
GD	pinacolyl methyl phosphonofluoridate; soman
MW	molecular weight
NBPt	normal boiling point
OSDEEP	*O,S*-diethyl ethylphosphonothiolate
OSDEMP	*O,S*-diethyl methylphosphonothiolate
OSDIBMP	*O,S*-diisobutyl methylphosphonothiolate
OSDMMP	*O,S*-dimethyl methylphosphonothiolate
P	pressure (pascal)
p	pressure (torr)
P_{calc}	calculated vapor pressure
P_{exptl}	experimental vapor pressure
R	gas constant
T	temperature (kelvin)
t	temperature (Celsius)
TEPTO	triethyl phosphorothionate
VX	*O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate

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