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U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
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VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED ORGANOPHOSPHORUS COMPOUNDS: DIBMP, DCMP, IMMP, IMPA, EMPA, AND MPFA

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14. ABSTRACT:

Recent work from our laboratory has focused on chemical warfare agents (CWAs), simulants, precursors, and degradation products. This report documents the vapor pressure data for three organophosphonate ester compounds and three phosphonic acids, all of which are related to CWAs. Due to structural similarities, these materials may also be considered to be CWA simulants and can be used to evaluate the performance of defensive equipment, which requires accurate knowledge of the thermophysical properties of these materials. Vapor pressure data were measured using two ASTM International methods that are based on differential scanning calorimetry (DSC) and vapor saturation. The data presented herein have been used to determine temperature–pressure correlations, and the fit constants have been used to determine temperature-dependent thermodynamic properties and to enable interpolation and limited extrapolation of the data. The criteria for assessing vapor pressure data quality are presented herein.

15. SUBJECT TERMS

Vapor pressure	Antoine equation	Clausius–Clapeyron equation
Enthalpy of vaporization	Volatility	Differential scanning calorimetry (DSC)
Vapor saturation	Boiling point	

Diisobutyl methylphosphonate (DIBMP), Chemical Abstracts Service (CAS) no. 7242-56-0
Dicyclohexyl methylphosphonate (DCMP), CAS no. 7040-53-1
Isopropyl methyl methylphosphonate (IMMP), CAS no. 690-64-2
Isopropyl methylphosphonic acid (IMPA), CAS no. 1832-54-8
Ethyl methylphosphonic acid (EMPA), CAS no. 1832-53-7
Methyl phosphonofluoridic acid (MPFA), CAS no. 1511-67-7

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PREFACE

The work described in this report was authorized under the Chemical and Biological Technology Base Program. This work was started in December 2015 and completed in October 2016. The data reported herein are contained in U.S. Army Edgewood Chemical Biological Center (ECBC) notebooks 97-0108, 99-0095, 11-0066, 02-0091, 07-0072, and 08-0085.

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This report has been approved for public release.

Acknowledgments

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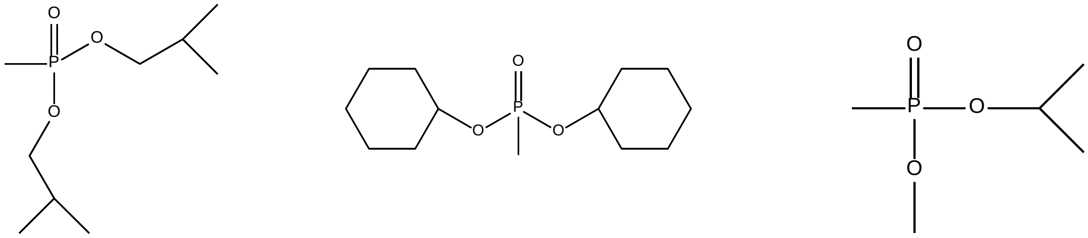
VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED ORGANOPHOSPHORUS COMPOUNDS: DIBMP, DCMP, IMMP, IMPA, EMPA, AND MPFA

1. INTRODUCTION

Knowledge of the physical properties of materials is critical for understanding 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 estimation of persistence, prediction of downwind time–concentration profiles after dissemination, generation of controlled challenge concentrations for detector testing, evaluation of toxicological properties, and assessment of the efficiency of air filtration systems.

The U.S. Army Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD) has a long history of interest in quantification of the physical properties of chemical warfare agents (CWAs) and related materials,[1–10] including the development of correlations to enable the accurate prediction of values at untested temperatures. Recent efforts have focused on investigation and documentation of vapor pressure and properties that were derived from such data, including temperature correlations, volatility, and temperature-dependent enthalpy of volatilization (vaporization for liquids and sublimation for solids) for CWAs and related compounds.[11–19]

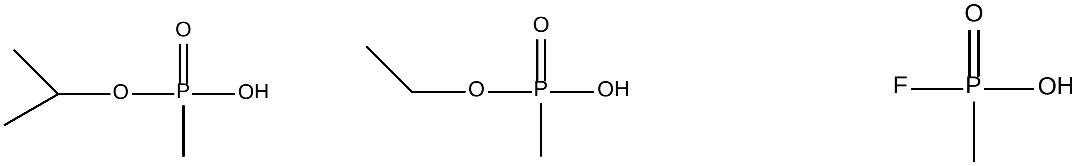
In addition to agents, recent work has focused on determination of the vapor pressure of agent precursors, degradation products, and simulants using two different ASTM International methods that are based on the differential scanning calorimetry (DSC) “pinhole” technique[20,21] and vapor saturation (or transpiration).[22] This report documents vapor pressure measurements, correlations, and derived properties for the organophosphorus G- and V-agent-related degradation products and simulants, whose structures, chemical names, Chemical Abstract Services (CAS) Registry Numbers, chemical formulas, and molecular weights are shown in Figure 1.



Diisobutyl Methyl-
phosphonate (DIBMP)
CAS No. 7242-56-0
$C_9H_{21}O_3P$, MW = 208.23 g/mol

Dicyclohexyl Methyl-
phosphonate (DCMP)
CAS No. 7040-53-1
$C_{13}H_{25}O_3P$, MW = 260.31 g/mol

Isopropyl Methyl Methyl-
phosphonate (IMMP)
CAS No. 690-64-2
$C_5H_{13}O_3P$, MW = 152.13 g/mol



Isopropyl Methyl-
phosphonic Acid (IMPA)
CAS No. 1832-54-8
$C_4H_{11}O_3P$, MW = 138.10 g/mol

Ethyl Methyl-
phosphonic Acid (EMPA)
CAS No. 1832-53-7
$C_3H_9O_3P$, MW = 124.08 g/mol

Methyl Phosphonofluoridic
Acid (MPFA)
CAS No. 1511-67-7
CH_4O_2PF, MW = 98.01 g/mol

Figure 1. Structures and chemical names of title compounds.

2. EXPERIMENTAL PROCEDURES

Table 1 lists the sources and mole fraction purities of the materials studied and the experimental vapor pressure method(s) used in this work. Not all samples were investigated using both methods.

The two different methods used in this work closely follow ASTM International standards and have been described in detail in previous publications.[12,15]

Table 1. Sample Information for Title Compounds

Compound	Vapor Pressure Method	Source	Purity (%)
DIBMP	DSC	In-house	99
	Saturator	Alfa Aesar (Ward Hill, MA)	97
DCMP	DSC	In-house	98
	Saturator	Hestia Laboratories (Milwaukee, WI)	99
IMMP	DSC	In-house	95
	Saturator	In-house	95
IMPA	DSC	Sigma-Aldrich (Milwaukee, WI)	98
EMPA	DSC	In-house	98
MFPA	DSC	In-house	98

Vapor pressure data were correlated using eq 1, the Antoine equation,[23] or eq 2, the Clausius–Clapeyron equation, by minimizing the sum of the squares of the differences between the logarithms of each measured and calculated vapor pressure value. The appropriate equation for this correlation was selected on the basis of data quality, breadth of the experimental temperature range and, in some cases, curvature of the data on a standard vapor pressure plot. Both of these equations are widely used, and the solution of either equation is more easily determined than those of other higher-term equations that might have higher fidelity. For data covering a wide temperature range, the Antoine equation is preferred over the Clausius–Clapeyron equation because it accurately describes the negative curvature characteristic of vapor pressure data that are plotted as a standard vapor pressure curve (ln[P] vs reciprocal temperature) over extended temperature ranges. The Clausius–Clapeyron equation was used in cases where the experimental temperature range was limited or the correlation indicated positive curvature (i.e., Antoine equation c constant was greater than 0).

$$\ln(P) = a - b/(c + T_K) \tag{1}$$

$$\ln(P) = a - b/(T_K) \tag{2}$$

where P is pressure (Pascal); T_K is absolute temperature (K); and a, b, and c are fit constants.

These equations may be converted to Torr–Celsius units using eqs 3–5.

$$A = [a - \ln(101325/760)]/\ln(10) \tag{3}$$

$$B = b/\ln(10) \tag{4}$$

$$C = c + 273.15 \tag{5}$$

Using these substitutions, the correlations in Torr–Celsius units are converted to eqs 6 and 7.

$$\mathrm{Log}(p) = A - B/(C + t) \tag{6}$$

$$\mathrm{Log}(p) = A - B/(273.15 + t) \tag{7}$$

where p is pressure (Torr); t is Celsius temperature; and A, B, and C are fit constants.

Equation 8 is used to calculate enthalpy of vaporization, ΔH_{vap}, in joules per mole.

$$\Delta H_{\text{vap}} = b \times R \times [T_K/(c + T)]^2 \tag{8}$$

where b and c are eq 1 coefficients, and R is the gas constant (8.3144 J/mol K).

The saturation concentration, C_{sat}, which is often referred to as volatility, at each temperature in milligrams per cubic meter is calculated from the vapor pressure, molecular weight, gas constant, and temperature according to eq 9

$$C_{sat} = P \times MW/R \times T_K \tag{9}$$

where MW is molecular weight.

3. RESULTS

The vapor pressure data, pressure–temperature correlation, comparison to literature data (where available), and calculated properties for each of the title compounds are detailed in this section. Data were measured over extended pressure ranges using the DSC and vapor saturator methods for the three organophosphorus esters: DIBMP, DCMP, and IMMP.

For comparison, measurements on the three phosphonic acids: IMPA, EMPA, and MPFA were carried out using DSC only and covered limited temperature ranges because of the thermal instability of these compounds. Literature data that were obtained in the ambient temperature range for IMPA using the Knudsen effusion method were combined and correlated with the DSC data. For EMPA and MPFA, literature data consists of limited, reduced-pressure boiling points that resulted from distillation, which we have typically found to be unreliable, especially at pressures below 1 Torr. It has been our experience that data resulting from the use of methodologies that are not specifically designed to measure vapor pressure are less accurate than data measured using standard vapor pressure methods. None of the reduced boiling points cited in the literature have been correlated with our measurements described herein.

3.1 DIBMP

Our experimental data for DIBMP consist of 14 points that were measured using DSC at 115.69 to 237.58 °C, and five points that were measured using the vapor saturation method at –20.0 to 20.0 °C. These DIBMP vapor pressure data extend over more than 6 orders of magnitude and are listed in Table 2 and shown graphically in Figure 2. Analysis of the data produced an Antoine equation that is also shown in Table 2 and plotted in Figure 2. Calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures within the range of measured data are provided in Table 3. The calculated normal boiling point for DIBMP is 235.98 °C.

Three reduced boiling-point values from the literature were located for DIBMP: 119 to 120 °C at 15 Torr,[24] 115 to 116 °C at 10 to 12 Torr,[25] and 72 °C at 3 Torr.[26] These values are also plotted in Figure 2 but were not used for calculation of the Antoine equation.

For comparison, an Antoine fit and a Clausius–Clapeyron fit, both based on the DSC data only, are also shown in Figure 2 to illustrate the difficulties associated with the extrapolation of high-temperature data to ambient temperatures. As expected with extrapolations over a wide temperature range, the Antoine fit introduces excessive curvature and underestimates the vapor pressure at ambient temperature. In contrast, the Clausius–Clapeyron fit, which assumes a constant enthalpy of vaporization, overestimates ambient-temperature vapor pressure. In addition, due to a small systematic error in the DSC calibration at the time these measurements were performed, the low ends of those data sets were often skewed to lower pressures.[16] This error exacerbated the excessive Antoine curvature and resulted in extrapolations that were even lower than was indicated by complementary data. As seen in Figure 2, the extrapolated value at 0 °C is approximately 1 order of magnitude lower than the value calculated using the fit based on both data sets. The uncertainties associated with the extrapolations demonstrate the value of generating data by complementary methods to minimize extrapolation beyond the experimental range.

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

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%)[b]
	(Torr)	(Pa)[a]	(Torr)	(Pa)	
Vapor Saturation					
–20.0	2.36×10^{-4}	3.15×10^{-2}	2.289×10^{-4}	3.052×10^{-2}	3.09
–10.0	8.34×10^{-4}	1.11×10^{-1}	8.379×10^{-4}	1.117×10^{-1}	–0.47
0.0	2.69×10^{-3}	3.58×10^{-1}	2.715×10^{-3}	3.620×10^{-1}	–0.99
10.0	7.72×10^{-3}	1.03×10^{0}	7.917×10^{-3}	1.055×10^{0}	–2.46
20.0	2.09×10^{-2}	2.79×10^{0}	2.106×10^{-2}	2.808×10^{0}	–0.64
DSC					
115.69	11.5	1533	12.07	1609	–4.70
120.92	14.8	1973	15.37	2050	–3.73
124.07	18.1	2413	17.72	2363	2.12
132.04	25.0	3333	25.11	3348	–0.44
139.82	35.1	4680	34.75	4632	1.02
145.38	45.1	6013	43.45	5792	3.80
153.17	60.2	8026	58.75	7832	2.47
158.94	75.1	10010	72.86	9714	3.07
166.64	98.8	13170	96.14	12820	2.77
179.77	150.0	20000	150.4	20050	–0.27
189.48	209.0	27860	205.5	27400	1.70
194.80	250.3	33370	242.3	32310	3.30
237.48	755.7	100800	789.2	105200	–4.25
237.58	755.7	100800	791.2	105500	–4.49
$\log(p) = 7.796595 - 2206.905/(t + 212.9636)$ $\ln(P) = 22.84509 - 5081.587/(T_K - 60.1864)$					

[a] Experimental DSC values were calculated from Torr values.

[b] $100 \times (P_{expt} - P_{calc})/P_{calc}$, where P_{expt} is the experimental vapor pressure, and P_{calc} is the calculated vapor pressure.

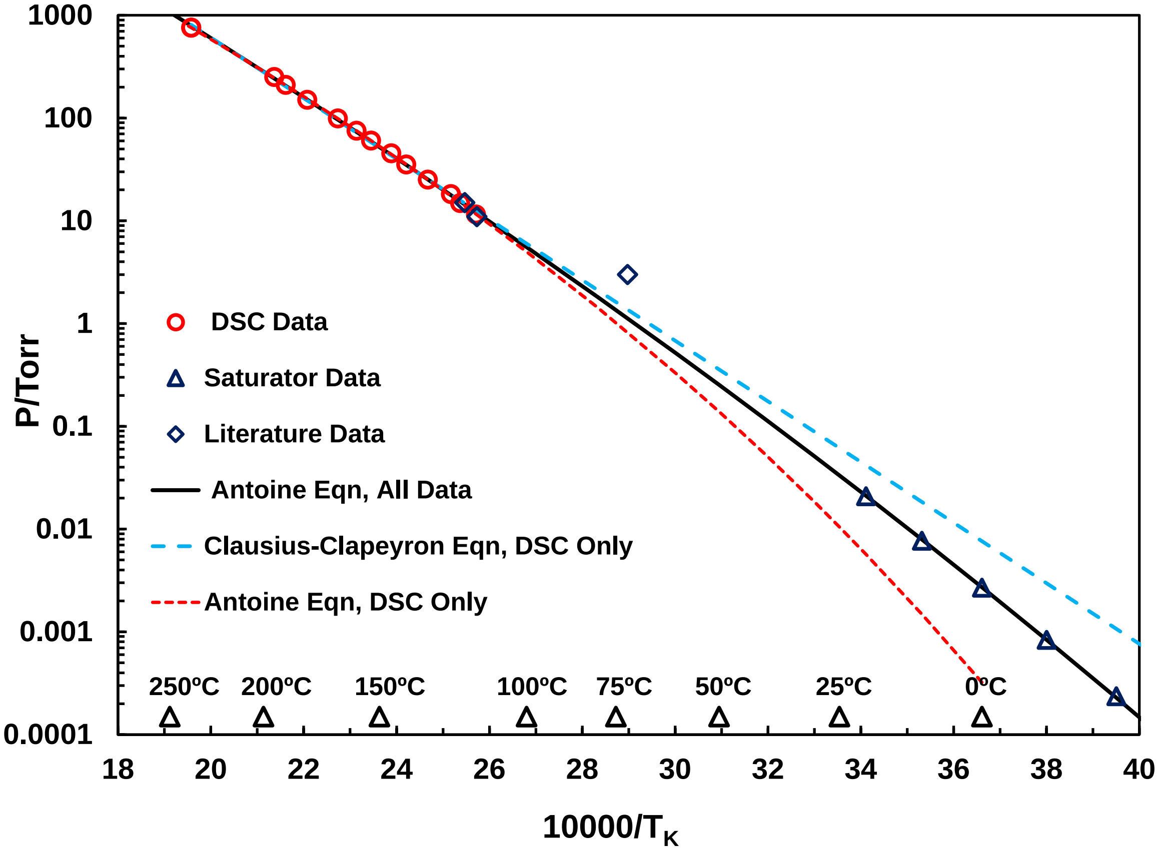


Figure 2. DIBMP vapor pressure data and Antoine equations based on all data and DSC data only, and the Clausius–Clapeyron equation based on DSC data only.

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

Temperature (°C)	Vapor Pressure (Torr)	Vapor Pressure (Pa)	Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
–20	2.289×10^{-4}	3.052×10^{-2}	3.020×10^{0}	72.72
–10	8.379×10^{-4}	1.117×10^{-1}	1.063×10^{1}	71.02
0	2.715×10^{-3}	3.620×10^{-1}	3.319×10^{1}	69.51
10	7.917×10^{-3}	1.055×10^{0}	9.336×10^{1}	68.14
20	2.106×10^{-2}	2.808×10^{0}	2.399×10^{2}	66.90
25	3.330×10^{-2}	4.440×10^{0}	3.730×10^{2}	66.33
30	5.168×10^{-2}	6.890×10^{0}	5.692×10^{2}	65.78
40	1.181×10^{-1}	1.575×10^{1}	1.260×10^{3}	64.75
50	2.536×10^{-1}	3.381×10^{1}	2.620×10^{3}	63.80
60	5.148×10^{-1}	6.863×10^{1}	5.159×10^{3}	62.94
80	1.835×10^{0}	2.446×10^{2}	1.735×10^{4}	61.39
100	5.559×10^{0}	7.411×10^{2}	4.974×10^{4}	60.06
120	1.474×10^{1}	1.965×10^{3}	1.252×10^{5}	58.91
140	3.500×10^{1}	4.667×10^{3}	2.829×10^{5}	57.89
160	7.575×10^{1}	1.010×10^{4}	5.839×10^{5}	56.99
180	1.515×10^{2}	2.020×10^{4}	1.117×10^{6}	56.18
200	2.835×10^{2}	3.780×10^{4}	2.001×10^{6}	55.46
220	5.005×10^{2}	6.672×10^{4}	3.389×10^{6}	54.81
235.98	7.600×10^{2}	1.013×10^{5}	4.984×10^{6}	54.34

3.2 DCMP

In this work, 12 data points were measured for DCMP using DSC at 180.50 to 237.10 °C, including pressures from 10 to 95 Torr. Measurements were attempted up to atmospheric pressure; however, the DSC endotherms became broad and erratic, indicating thermal instability of the compound. An additional seven data points were measured at –10.0 to 50.0 °C using the vapor saturation method. All data for DCMP are listed in Table 4 and shown graphically in Figure 3. Analysis of the data produced an Antoine equation that is also listed in Table 4 and shown in Figure 3. Calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures are provided in Table 5. Although the DSC data were limited by decomposition at higher temperatures, the saturator data extend the range to ambient temperatures, and the entire data set covers more than 7 orders of magnitude in pressure. The extrapolated, normal boiling-point temperature for DCMP is 314.46 °C; however, this value should be used with caution due to the instability of DCMP at high temperatures.

Three reduced boiling-point values from the literature were located for DCMP: 82 °C at 4 Torr,[26] 127 to 128 °C at 1 Torr,[27] and 123 °C at 0.15 Torr.[28] These values are plotted in Figure 3 but were not used for calculation of the Antoine equation.

An Antoine fit and a Clausius–Clapeyron fit, both based on the DSC data only, are also shown in Figure 3. Extrapolating the Antoine fit resulted in estimated values at 25 and 0 °C that are more than 4 and 8 orders of magnitude, respectively, lower than the values calculated using the fit based on both data sets. This difference increased as temperature decreased. This effect is due to the narrow temperature range of the DCMP DSC data and its lengthy extrapolation to ambient temperatures. In contrast, the Clausius–Clapeyron fit of the DSC data alone approximates the ambient temperature data more accurately than does the Antoine equation.

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

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%)[b]
	(Torr)	(Pa)[a]	(Torr)	(Pa)	
Vapor Saturation Method					
–10.0	2.25×10^{-6}	3.00×10^{-4}	2.392×10^{-6}	3.188×10^{-4}	–5.88
0.0	1.06×10^{-5}	1.41×10^{-3}	1.063×10^{-5}	1.418×10^{-3}	–0.49
10.0	4.35×10^{-5}	5.80×10^{-3}	4.136×10^{-5}	5.515×10^{-3}	5.14
20.0	1.52×10^{-4}	2.03×10^{-2}	1.432×10^{-4}	1.910×10^{-2}	6.12
30.0	4.47×10^{-4}	5.96×10^{-2}	4.479×10^{-4}	5.972×10^{-2}	–0.14
40.0	1.27×10^{-3}	1.70×10^{-1}	1.280×10^{-3}	1.707×10^{-1}	–0.48
50.0	3.38×10^{-3}	4.50×10^{-1}	3.379×10^{-3}	4.505×10^{-1}	–0.05
DSC					
180.50	10.4	1387	11.69	1558	–11.00
187.51	14.4	1920	15.58	2077	–7.58
194.19	19.5	2600	20.31	2707	–3.97
195.08	20.2	2693	21.02	2803	–3.91
198.40	25.2	3360	23.89	3185	5.49
204.40	30.3	4040	29.95	3992	1.18
211.35	40.1	5346	38.60	5146	3.90
216.15	49.8	6639	45.77	6102	8.80
223.62	60.3	8039	59.23	7897	1.80
230.64	75.4	10050	74.88	9983	0.69
230.85	75.1	10010	75.40	10050	–0.40
237.10	95.1	12680	92.31	12310	3.02
$\log(p) = 8.213878 - 2815.767/(t + 213.5220)$ $\ln(P) = 23.80592 - 6483.544/(T_K - 59.6280)$					

[a] Experimental DSC values were calculated from Torr values.

[b] 100 × ($P_{\text{expt}} - P_{\text{calc}}$)/$P_{\text{calc}}$, where P_{expt} is the experimental vapor pressure, and P_{calc} is the calculated vapor pressure.

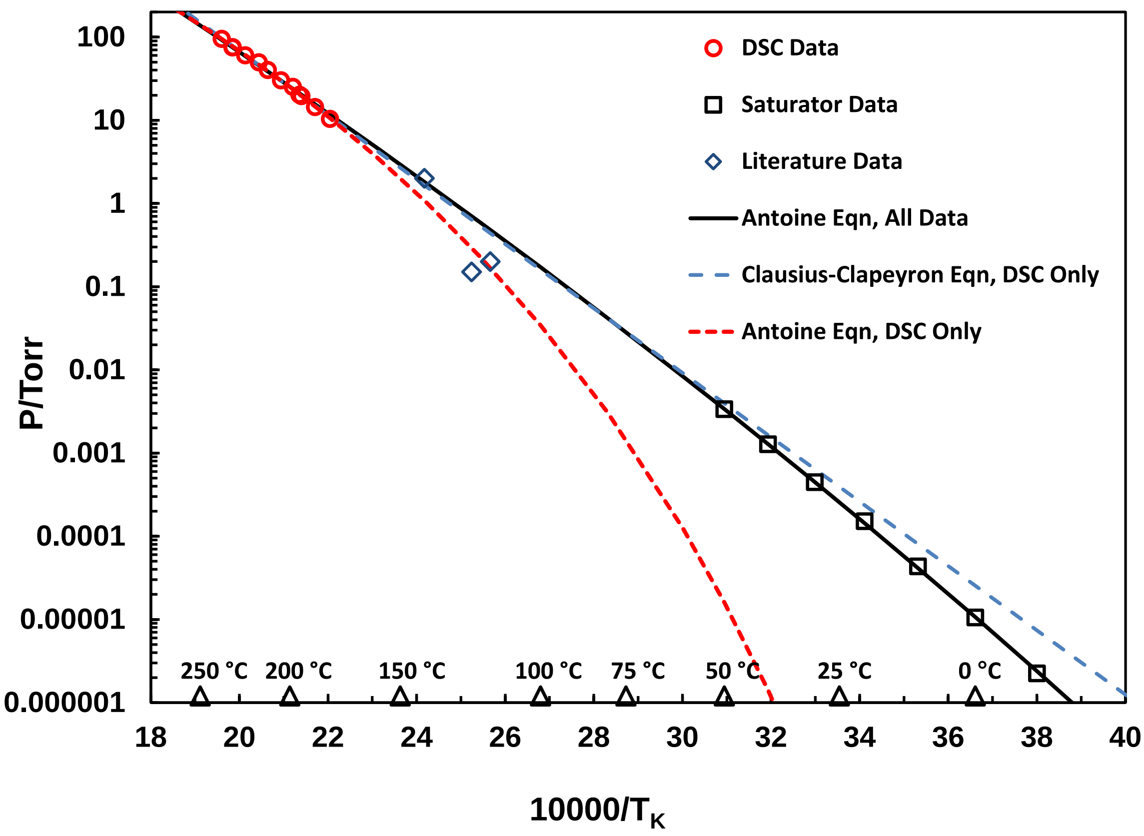


Figure 3. DCMP vapor pressure data and Antoine correlations based on all data and DSC data only, and the Clausius–Clapeyron equation based on DSC data only.

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

Temperature (°C)	Vapor Pressure (Torr)	Vapor Pressure (Pa)	Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
–20*	4.611×10^{-7}	6.147×10^{-5}	7.602×10^{-3}	92.24
–10	2.392×10^{-6}	3.188×10^{-4}	3.793×10^{-2}	90.12
0	1.063×10^{-5}	1.418×10^{-3}	1.625×10^{-1}	88.22
10	4.136×10^{-5}	5.515×10^{-3}	6.097×10^{-1}	86.50
20	1.432×10^{-4}	1.910×10^{-2}	2.039×10^{0}	84.95
25	2.563×10^{-4}	3.418×10^{-2}	3.589×10^{0}	84.23
30	4.479×10^{-4}	5.972×10^{-2}	6.167×10^{0}	83.54
40	1.280×10^{-3}	1.707×10^{-1}	1.706×10^{1}	82.25
50	3.379×10^{-3}	4.504×10^{-1}	4.364×10^{1}	81.06
60	8.306×10^{-3}	1.107×10^{0}	1.041×10^{2}	79.97
80	4.177×10^{-2}	5.569×10^{0}	4.937×10^{2}	78.03
100	1.709×10^{-1}	2.279×10^{1}	1.912×10^{3}	76.36
120	5.907×10^{-1}	7.875×10^{1}	6.271×10^{3}	74.91
140	1.774×10^{0}	2.365×10^{2}	1.792×10^{4}	73.63
160	4.736×10^{0}	6.315×10^{2}	4.564×10^{4}	72.49
180	1.144×10^{1}	1.526×10^{3}	1.054×10^{5}	71.48
200*	2.539×10^{1}	3.385×10^{3}	2.240×10^{5}	70.57
220*	5.233×10^{1}	6.977×10^{3}	4.430×10^{5}	69.76
240*	1.012×10^{2}	1.349×10^{4}	8.232×10^{5}	69.01
260*	1.851×10^{2}	2.468×10^{4}	1.449×10^{6}	68.34
280*	3.224×10^{2}	4.299×10^{4}	2.433×10^{6}	67.72
300*	5.378×10^{2}	7.170×10^{4}	3.917×10^{6}	67.15
314.46*	7.600×10^{2}	1.013×10^{5}	5.399×10^{6}	66.77

*Extrapolated.

3.3 IMMP

In this work, 13 IMMP data points were measured using DSC at 77.33 to 188.43 °C. These data were measured over a comparatively broad range of temperatures, and no evidence of decomposition was observed in the thermal curves over the full range of the measurements up to 1 atm. Data have also been measured at 5 to 23 °C using the vapor saturation method. The experimental data for IMMP are listed in Table 6 and shown graphically in Figure 4.

Analysis of the data produced an Antoine equation fit that is listed in Table 6 and plotted in Figure 4. Calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures are provided in Table 7. The calculated normal boiling point temperature for IMMP is 186.62 °C.

The single literature data point for IMMP, a reduced-pressure boiling point (69 °C at 13 Torr)[29] shown in Figure 4, is in poor agreement with the value extrapolated using the current correlation.

Figure 4 includes Antoine and Clausius–Clapeyron fits based on the DSC data only. The DSC-only Antoine fit resulted in an estimated value at 25 °C that is nearly an order of magnitude lower than the value calculated using the Antoine fit based on both data sets; however, the Clausius–Clapeyron correlation closely matches the Antoine fit based on both data sets.

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

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%)[b]
	(Torr)	(Pa)[a]	(Torr)	(Pa)	
Vapor Saturation					
5.0	0.120	16.0	0.1259	16.78	–4.67
11.0	0.202	26.9	0.2027	27.02	–0.34
17.0	0.331	44.1	0.3196	42.61	3.56
23.0	0.533	71.1	0.4943	65.90	7.84
DSC					
77.33	11.4	1519	12.54	1672	–9.12
82.08	14.5	1933	15.84	2112	–8.48
85.28	17.5	2333	18.47	2463	–5.27
88.96	22.2	2960	21.96	2928	1.07
96.66	29.6	3946	31.19	4158	–5.09
100.52	40.1	5346	36.97	4929	8.47
106.70	49.0	6533	48.17	6422	1.72
113.43	69.8	9306	63.62	8482	9.71
123.19	99.6	13280	93.59	12480	6.42
134.67	147.8	19700	143.8	19170	2.79
148.03	224.9	29980	229.8	30640	–2.14
155.72	300.0	40000	296.9	39590	1.04
188.43	761.7	101600	799.7	106600	–4.75
$\log(p) = 8.326556 - 2413.702/(t + 256.6031)$ $\ln(P) = 24.06537 - 5557.754/(T_K - 16.5469)$					

[a] Experimental DSC values were calculated from Torr values.

[b] $100 \times (P_{\text{expt}} - P_{\text{calc}})/P_{\text{calc}}$, where P_{expt} is the experimental vapor pressure, and P_{calc} is the calculated vapor pressure.

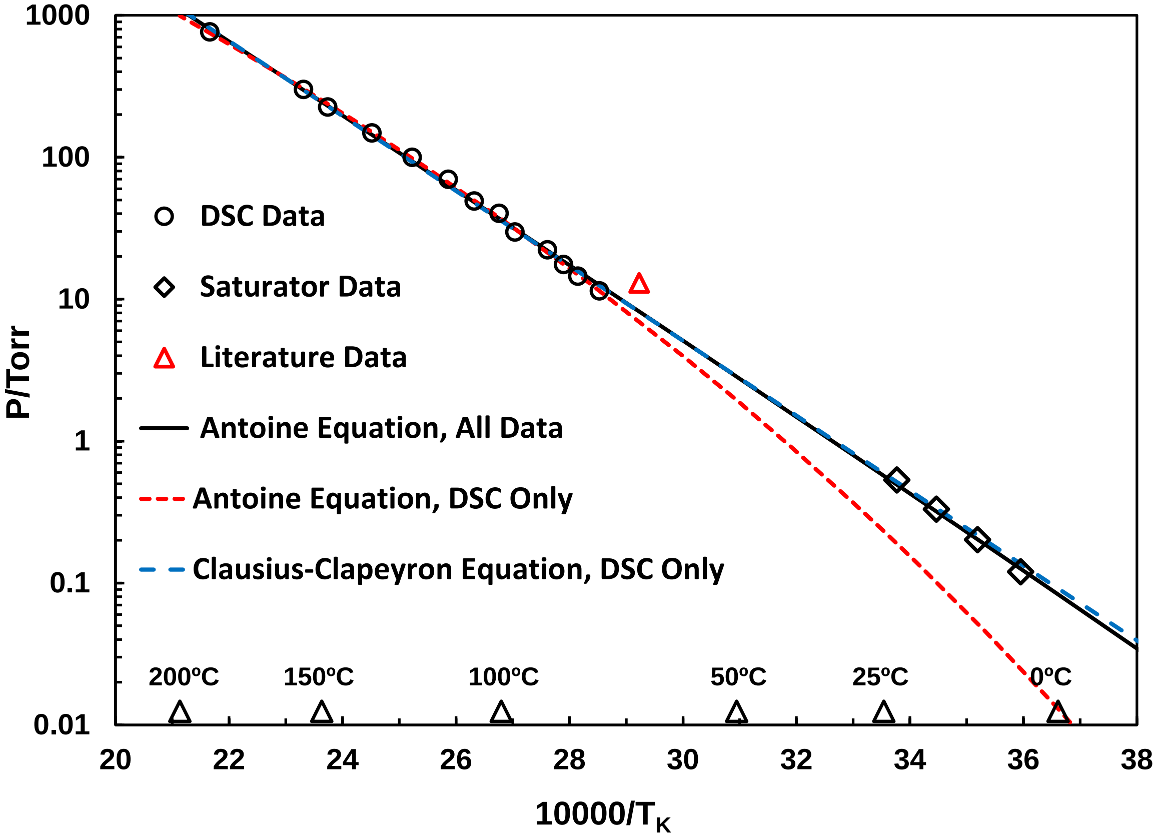


Figure 4. IMMP vapor pressure data and Antoine correlations based on all data and DSC data only, and the Clausius–Clapeyron correlation based on DSC data only.

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

Temperature (°C)	Vapor Pressure		Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
	(Torr)	(Pa)		
–20*	1.334×10^{-2}	1.778×10^{0}	1.285×10^{2}	52.90
–10*	3.457×10^{-2}	4.610×10^{0}	3.205×10^{2}	52.62
0*	8.321×10^{-2}	1.109×10^{1}	7.431×10^{2}	52.36
10	1.875×10^{-1}	2.500×10^{1}	1.615×10^{2}	52.12
20	3.984×10^{-1}	5.312×10^{1}	3.315×10^{3}	51.90
25	5.692×10^{-1}	7.589×10^{1}	4.657×10^{3}	51.80
30	8.032×10^{-1}	1.071×10^{2}	6.463×10^{3}	51.70
40	1.545×10^{0}	2.059×10^{2}	1.203×10^{4}	51.51
50	2.845×10^{0}	3.794×10^{2}	2.148×10^{4}	51.33
60	5.044×10^{0}	6.725×10^{2}	3.694×10^{4}	51.17
80	1.431×10^{1}	1.909×10^{3}	9.888×10^{4}	50.86
100	3.614×10^{1}	4.818×10^{3}	2.362×10^{5}	50.60
120	8.268×10^{1}	1.102×10^{4}	5.130×10^{5}	50.36
140	1.740×10^{2}	2.320×10^{4}	1.028×10^{6}	50.15
160	3.410×10^{2}	4.547×10^{4}	1.921×10^{6}	49.95
180	6.283×10^{2}	8.377×10^{4}	3.382×10^{6}	49.78
186.62	7.600×10^{2}	1.013×10^{5}	4.032×10^{6}	49.72

*Extrapolated.

3.4 IMPA

In this work, six data points were measured for IMPA using DSC at 115.8 to 156.9 °C and are listed in Table 8. The experimental range was severely limited by decomposition at higher pressures. We were unable to measure IMPA data in the ambient range due to its low vapor pressure, which precludes measurement by mass loss, and thermal instability, which makes measurement using thermal desorption methods impossible.

Fortunately, IMPA vapor pressure data, measured using the Knudsen effusion method in the ambient temperature range, have been reported by Neale,[30] who did not include a table of measured data but did provide four values calculated from the experimental data. Also included in Neale's report was a plot that appears to be the experimental data. We have inferred those five values for Neale's experimental data points by superimposing estimated values directly onto a photocopy of Neale's plot and adjusting our values until they overlapped as shown in Figure 5. The inferred values are listed in Table 8 and plotted in Figure 6 with Neale's correlation. Our DSC data and the new correlation, based on the inferred values and the DSC data, are also shown in Figure 6. Table 8 also lists the four calculated points that were reported by Neale.

The new correlation determined using the DSC data and Neale's inferred values has an unconventional positive curvature ($C > 273.15$). This suggests that the data sets are not in good agreement, which is likely due to a problem with one or both data sets. As a result, the fit was constrained to a Clausius–Clapeyron equation (no curvature, $C = 273.15$) that is provided in Table 8.

Table 9 provides the calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures that are based on our Clausius–Clapeyron equation. The calculated normal boiling point temperature for IMPA is 277.25 °C. This value should be used with caution due to the instability of IMPA at high temperature and the modest agreement between DSC and effusion data.

Neale's Figure 3 deserves special attention. A rather obvious typographical error was discovered when we attempted to superimpose inferred values onto Neale's figure. It appears to us that $10^3/T = 3.5$ was mislabeled and should actually be 3.6. When corrected, it was found that the values inferred from Neale's figure closely matched the values calculated using the correlation in Neale's report.

Four distillation values from the literature, 103 to 104 °C at 0.1 Torr,[31] 54 to 55 °C at 0.001 Torr,[32] 97 to 98 °C at 0.08 Torr, [33] and 123 to 125 °C at 0.2 Torr,[34] and a value extrapolated to 25 °C using reduced boiling points[35] cited by Rosenblatt et al. [36] are shown in Figure 6. None of these values were used for the calculation of the Clausius–Clapeyron correlation.

Table 8. Experimental and Calculated Vapor Pressure Values for IMPA

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%)[b]
	(Torr)	(Pa)[a]	(Torr)	(Pa)	
	(Calculated) Values in Neale's Table 1[c]		Calculated from Clausius–Clapeyron Equation in this Report		
15.0	7.0×10^{-4}	9.33×10^{-2}	6.951×10^{-4}	9.267×10^{-2}	0.71
20.0	1.09×10^{-3}	1.45×10^{-1}	1.143×10^{-3}	1.524×10^{-1}	–4.68
25.0	1.67×10^{-3}	2.23×10^{-1}	1.850×10^{-3}	2.466×10^{-1}	–9.23
30.0	2.52×10^{-3}	3.36×10^{-1}	2.946×10^{-3}	3.927×10^{-1}	–14.46
Values Inferred From Neale's Figure 3					
9.90	4.436×10^{-4}	5.914×10^{-2}	4.108×10^{-4}	5.477×10^{-2}	7.98
12.32	5.495×10^{-4}	7.326×10^{-2}	5.285×10^{-4}	7.046×10^{-2}	3.98
14.21	6.622×10^{-4}	8.829×10^{-2}	6.415×10^{-4}	8.552×10^{-2}	3.23
18.06	9.226×10^{-4}	1.230×10^{-1}	9.445×10^{-4}	1.259×10^{-1}	–2.32
20.11	1.079×10^{-3}	1.439×10^{-1}	1.156×10^{-3}	1.541×10^{-1}	–6.65
DSC					
115.8	1.0	133.3	1.339	178.6	–25.34
123.8	1.9	253.3	2.071	276.1	–8.26
138.9	4.9	653.3	4.502	600.2	8.85
148.2	7.4	986.6	7.063	941.7	4.76
152.5	9.8	1307	8.641	1152	13.41
156.9	11.3	1507	10.58	1410	6.83
$\log(p) = 9.517280 - 3652.373/(t + 273.15)$ $\ln(P) = 26.80712 - 8409.900/T_K$					

[a] Calculated from Torr values.

[b] $100 \times (P_{\text{expt}} - P_{\text{calc}})/P_{\text{calc}}$, where P_{expt} is the experimental vapor pressure, and P_{calc} is the calculated vapor pressure.

[c] Values calculated by Neale were not used for calculation of new correlation equation.

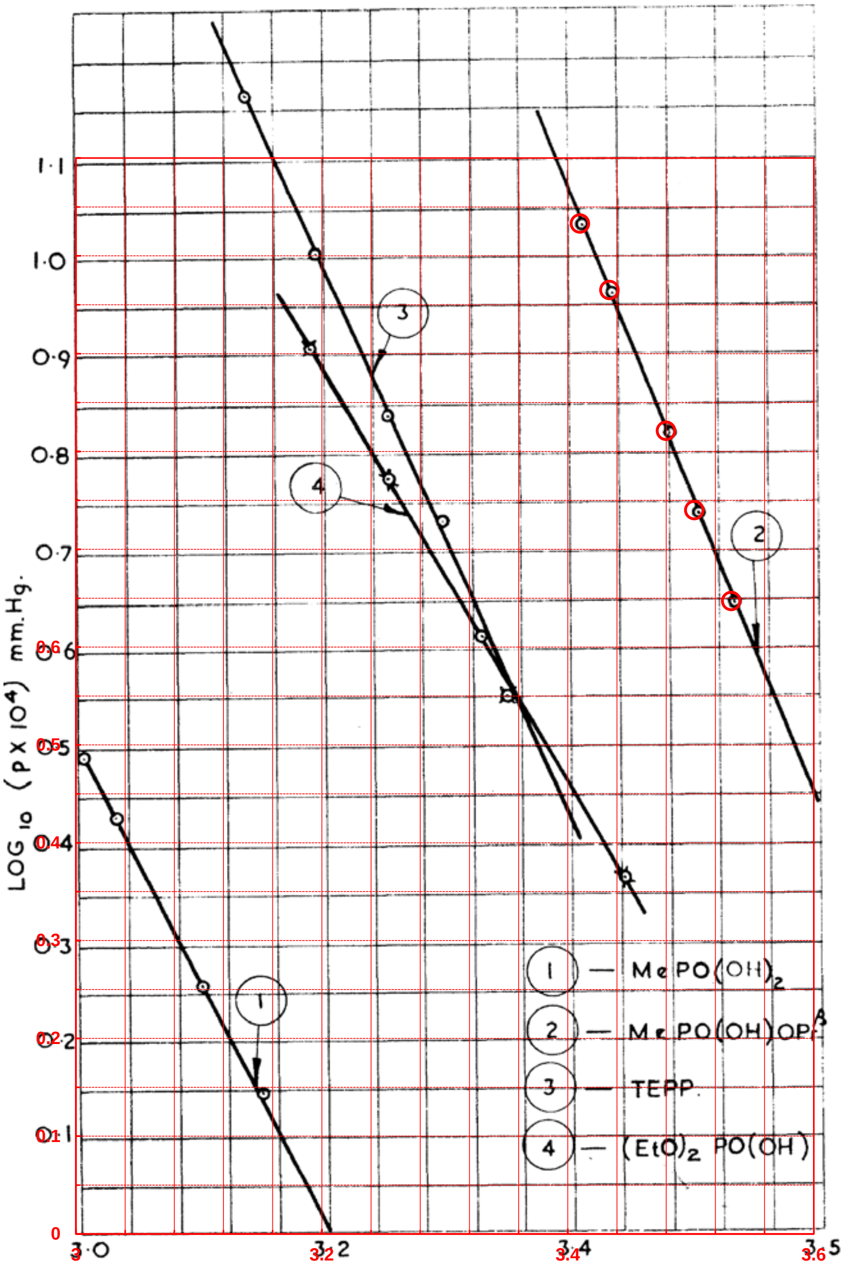


Figure 5. Superposition of inferred IMPA data (shown in red, IMPA data in upper right) onto a photocopy of Neale's Figure 3 (shown in black, IMPA data identified as ②).

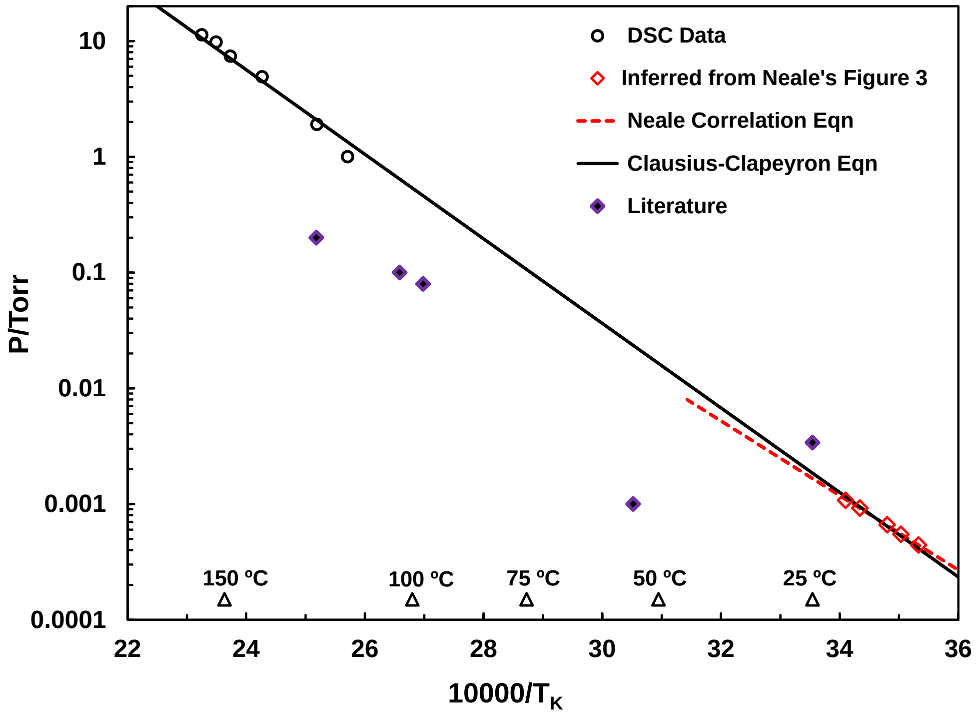


Figure 6. IMPA vapor pressure data and Clausius–Clapeyron correlations.

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

Temperature (°C)	Vapor Pressure (Torr)	Vapor Pressure (Pa)	Volatility (mg/m^3)	ΔH_{vap} (kJ/mol)
–20*	1.229×10^{-5}	1.639×10^{-3}	1.075×10^{-1}	69.92
–10*	4.344×10^{-5}	5.791×10^{-3}	3.655×10^{-1}	
0*	1.399×10^{-4}	1.866×10^{-2}	1.135×10^{0}	
10*	4.152×10^{-4}	5.535×10^{-2}	3.247×10^{0}	
20	1.143×10^{-3}	1.524×10^{-1}	8.638×10^{0}	
25	1.850×10^{-3}	2.466×10^{-1}	1.374×10^{1}	
30	2.946×10^{-3}	3.927×10^{-1}	2.152×10^{1}	
40	7.144×10^{-3}	9.525×10^{-1}	5.052×10^{1}	
50	1.640×10^{-2}	2.187×10^{0}	1.124×10^{2}	
60	3.582×10^{-2}	4.776×10^{0}	2.381×10^{2}	
80	1.496×10^{-1}	1.995×10^{1}	9.382×10^{2}	
100	5.362×10^{-1}	7.149×10^{1}	3.182×10^{3}	
120	1.688×10^{0}	2.250×10^{2}	9.505×10^{3}	
140	4.753×10^{0}	6.337×10^{2}	2.548×10^{4}	
160*	1.217×10^{1}	1.622×10^{3}	6.220×10^{4}	
180*	2.866×10^{1}	3.821×10^{3}	1.400×10^{5}	
200*	6.281×10^{1}	8.374×10^{3}	2.940×10^{5}	
220*	1.291×10^{2}	1.722×10^{4}	5.799×10^{5}	
240*	2.510×10^{2}	3.347×10^{4}	1.083×10^{6}	
260*	4.642×10^{2}	6.189×10^{4}	1.928×10^{6}	
277.25*	7.600×10^{2}	1.013×10^{5}	3.058×10^{6}	

*Extrapolated.

3.5 EMPA

Attempts to determine the vapor pressure of EMPA using DSC resulted in a single data point of 152.7 °C at 11.5 Torr. The DSC experiments were completed at temperatures from ambient to 215 °C and at pressures from 11 Torr to atmospheric pressure. Above 11.5 Torr, the thermal curves consisted of broad endothermic and exothermic peaks that were consistent with thermal degradation. At atmospheric pressure, a broad exotherm was detected with an onset point around 125 °C. No saturator data are available in the ambient temperature range for EMPA due to its low vapor pressure and thermal instability.

Literature values for EMPA consist of 105 to 110 °C at 0.2 Torr,[37] 108 to 110 °C at 0.1 Torr,[31] 53 to 54 °C at 0.001 Torr,[32] and 106 to 107 °C at 0.1 Torr.[33] Munro et al.[35] reported a calculated value at 25 °C of 0.00036 Torr, which was based on the value reported by Petrov et al.[31] These literature values are plotted with the DSC point in Figure 7. It is not appropriate to correlate the EMPA data because it is limited data of unknown accuracy.

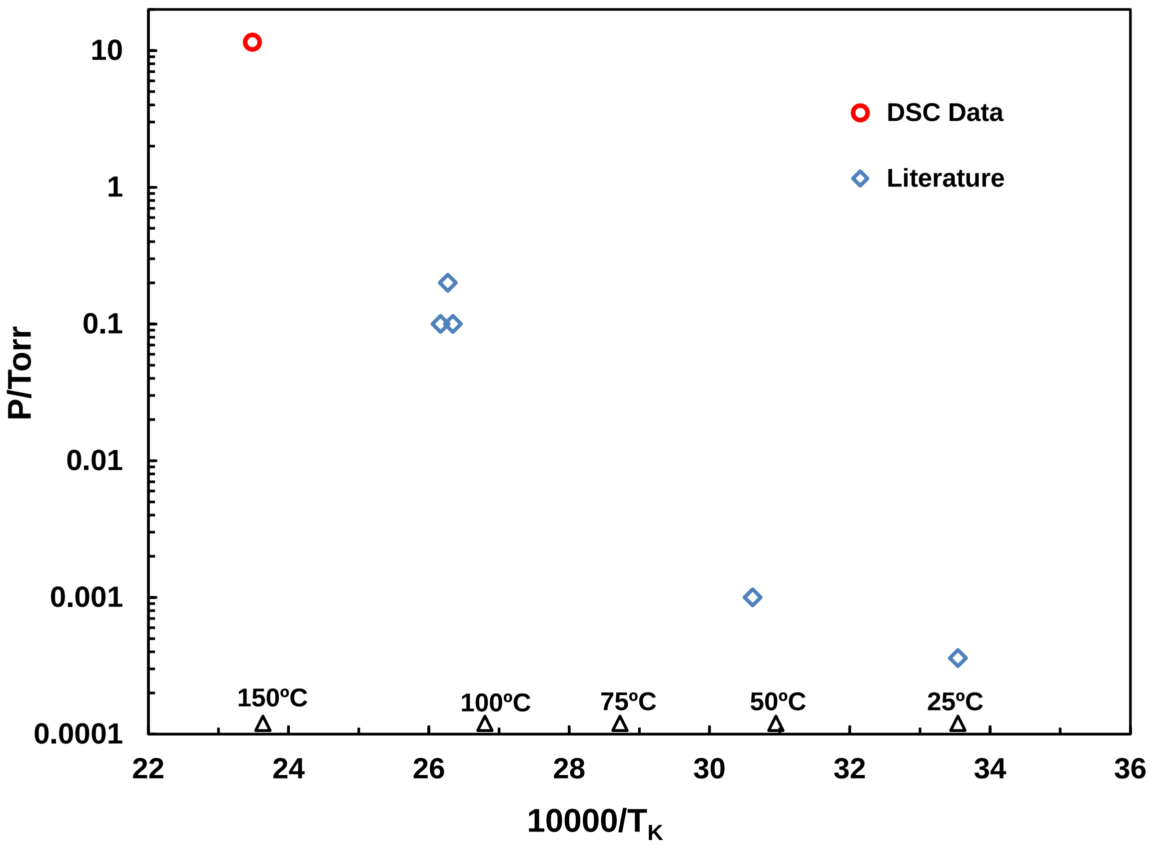


Figure 7. EMPA experimental vapor pressure data and literature values.

3.6 MPFA

Attempts to determine the vapor pressure of MPFA using DSC were unsuccessful. The DSC experiments were completed at pressures from 10 Torr to atmospheric pressure and covered temperatures from ambient to 240 °C. The thermal curves consisted of erratic endothermic and exothermic peaks, which indicated that the material was undergoing thermal degradation over the entire range studied. Literature values for MPFA include 70 to 72 °C at 2.5 Torr,[38] 69 to 72 °C at 2 Torr,[39] and 60 to 61 °C at 0.5 Torr.[32]

4. DISCUSSION

The primary purpose of this report was to document vapor pressure measurements for the six title compounds. Complementary data were measured at high temperatures using DSC and in the ambient temperature range using the vapor saturation method for DIBMP, DCMP, and IMMP. These data provide the basis for correlations that were used to estimate values within and beyond the experimental range. The data analysis method used in this report[40] enables a detailed assessment of data quality for compounds, even though there may be varying degrees of confidence in those data.

Although low volatility and thermal instability hindered our measurements using both DSC and vapor saturation methods for IMPA, EMPA, and MPFA, literature data were reported on IMPA by Neale, who used Knudsen effusion at ambient temperatures. We combined Neale's results with our limited-range DSC data for IMPA, but we were unable to measure meaningful data for EMPA and MPFA. Our unsuccessful efforts with those two compounds are documented herein to inform future efforts, possibly with other methods, in the event they are pursued.

A fundamental principle that guides our vapor pressure work is to measure data over as wide a range as possible using complementary methods to enhance confidence in the experimental data and to minimize extrapolation beyond the experimental range due to unknown errors associated with predicted values. The data reported herein document valuable examples of three distinct degrees of agreement between experimental data sets. The data also illustrate several common challenges that are associated with handling vapor pressure data including, interpolation within and extrapolation beyond the experimental range, correlation of data as a function of temperature using different equations, correlation of single or complementary data sets, and assessment of literature values.

The vapor pressure of DIBMP was measured over a wide range using complementary methods. All of the differences between the experimental data and calculated values for DIBMP are less than 5%, which makes the data for this compound among the most precise measured in our laboratory. The Antoine equation *C* constant for DIBMP of 212.96 indicates that the two data sets align well and produce the expected negative curvature that is characteristic of a wide range of compounds that were studied over the past 3 decades in our laboratory (*C* = 180 to 230). We feel that interpolation and limited extrapolation of the data, using the correlation presented herein, will produce highly accurate estimates.

The Antoine *C* constant for DCMP of 213.52 was comparable to that for DIBMP, which also reflects the expected negative curvature and the good agreement between data measured using complementary methods. Although the DCMP and DIBMP data sets cover comparable ranges, the precision of the DCMP is not as high as that of DIBMP, as judged by the larger differences between the experimental and calculated values. As a result, our confidence in the DCMP data is not as great as that for DIBMP, and extrapolated values may have greater uncertainty.

The next category of data agreement is demonstrated by the correlation for IMMP. With an Antoine *C* constant of 256.63, which approaches that of a linear Clausius–Clapeyron equation (*C* = 273.15), the agreement between the IMMP data sets was judged to be not as good as those of DCMP or DIBMP. This result was unexpected for data covering such a wide pressure range, reflects a greater uncertainty in the IMMP data as compared with DCMP and DIBMP, and suggests that one or both of the IMMP data sets may contain minor errors. It is likely that the errors are systematic in nature because each data set is internally consistent. As a result, extrapolation for IMMP should be performed with caution. The precision of the IMMP data is comparable to that of DCMP, as seen in the percent differences between experimental data and calculated values in Tables 4 and 6.

Analysis of the IMPA data produced a correlation with positive curvature ($C > 273.15$), which represents a third case that is thermodynamically prohibited and suggests that the two data sets are not in good agreement. As a result, our fit was constrained to a Clausius–Clapeyron equation ($C = 273.15$). Due to thermal instability, we were unable to confidently expand the pressure range above 12 Torr for IMPA. It should be noted that the DSC data for IMPA were measured below the recommended low-pressure limit of the method at the time the work was completed. It should also be noted that Neale's Knudsen IMPA data appear to be in reasonable agreement with three of the reduced-pressure boiling points; agreement with the remaining two distillation points is poor. We assess that more data are needed to provide the basis for accurate estimations of IMPA vapor pressure. Future work may demonstrate that one or both of the existing data sets is flawed. Extrapolation or even interpolation between DSC and literature data should be done with caution for IMPA.

Recent work in our laboratory has significantly expanded the range and accuracy of the DSC method to lower pressures[41] and measurably reduced the uncertainty associated with the low end of the DSC data. However, this improvement does not eliminate the problems associated with data extrapolation. The best practice to minimize extrapolation uncertainty is to measure data over wide temperature ranges, using complementary methods to enhance confidence in both data sets. We recommend this approach for future work.

The thermal instability of EMPA limited DSC measurements to a single data point (152.7 °C at 11.5 Torr). That value is consistent with literature distillation data and may provide the basis for an order-of-magnitude estimate of vapor pressure in the ambient temperature range.

A compilation by Munro et al.[35] cites values at 25 °C for IMPA (0.0034 Torr) and EMPA (0.00036 Torr) that were extrapolated from higher temperature distillation data; however, no indication was provided that the cited values were extrapolated. The value for IMPA was extrapolated using reduced boiling points of 97 to 98 °C at 0.08 Torr[33] and 123 to 125 °C at 0.2 Torr,[34] and the value for EMPA was based on a single distillation point of 108 to 110 °C at 0.1 Torr.[31] These are significant extrapolations of data with unknown certainty. We believe that the interpolated value for IMPA at 25 °C, presented in this report (0.0018 Torr), is more reliable than the extrapolated value given by Munro et al. because the former is based on experimental methodology that was designed to measure vapor pressure, and the interpolated value is less than 5 °C from what we believe to be the experimental range provided by Neale. It is surprising that the vapor pressure value for the higher molecular weight IMPA (isopropyl moiety) that appears in the Munro document is about an order of magnitude higher than the vapor pressure value of the lower molecular weight EMPA (ethyl moiety). Extrapolated values, based on meager data that are not clearly identified as such, can be misleading if cited sources are not investigated or do not address their experimental uncertainty.

We were unable to measure any usable data for MPFA. The literature distillation data are reasonably consistent but only cover a very narrow range.

The principal advantage of measuring data in different temperature ranges using complementary methods is that agreement of the data provides strong evidence that both data sets are accurate. Measuring data over a wide range of temperatures may also eliminate the need to extrapolate to the temperature of interest. The correlations derived in this report for DIBMP, DCMP, and IMMP, with and without ambient temperature data, illustrate the problems associated with extrapolating single-method data beyond the experimental range. It is apparent from close examination of Figures 2, 3, and 4 that relatively small errors in the lower end of the DSC data may lead to significant differences in the extrapolated values when compared with extrapolations that were based on both data sets. This was especially evident when correlation of the DSC data alone was performed with an Antoine versus a Clausius–Clapeyron equation.

The temperature range over which an extrapolation is performed also affects the accuracy of the predicted value. The lower limit of the DSC data for DCMP is more than 150 °C above ambient, and the values extrapolated to ambient temperature on the basis of DSC data alone are several orders of magnitude lower than the estimate determined using a combination of DSC and saturator data. Although a similar deviation was observed for DIBMP, the extrapolation to ambient temperature is much shorter, and the estimated value is within a factor of 2 of the value estimated using data from both DSC and vapor saturation methods.

Vapor pressure values presented in the literature should be investigated to assess methodology, sample purity, adequacy of documentation, and data consistency to determine uncertainty. We deem the values presented in literature without identification of the source to be unreliable.

Selection of vapor pressure simulants for testing of developmental CWA detection and protection equipment relies on accurate knowledge of the vapor pressures of the proposed simulants. Figure 8 shows a plot of the vapor pressures of the compounds in this report compared with the vapor pressures of several standard CWAs. The vapor pressures of the title compounds span the range from the high-volatility G agents to below that of the low-volatility V agents.

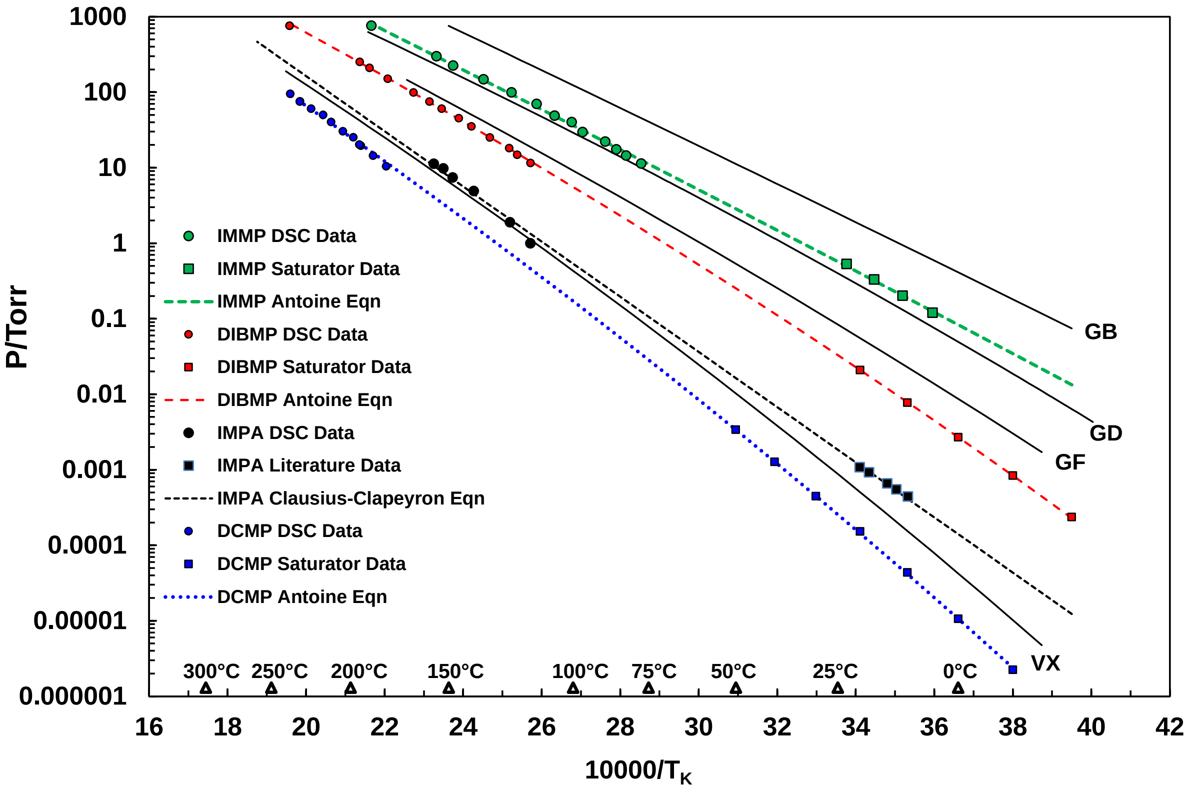


Figure 8. Vapor pressure comparison for title compounds
and selected CWAs.

5. CONCLUSIONS

This report documents vapor pressure information for DIBMP, DCMP, and IMMP using the DSC method at high temperatures and the vapor saturation method at ambient temperatures. DSC data, accompanied by literature data for IMPA, are also presented. The experimental data were used to determine correlations that enable interpolation, limited extrapolation, and estimation of thermodynamic properties, including the temperature-dependent enthalpy of vaporization and volatility. Agreement between the data, which were measured in different ranges by different methods, provides confidence in the data and suggests that the values extrapolated to untested conditions should be reasonably reliable. Data agreement, which was assessed using correlation methods that were developed in our laboratory, was used to determine data quality and the degree of confidence in extrapolation.

The thermal instability of EMPA limited DSC measurements to a single data point. DSC measurements for MFPA were unsuccessful.

The vapor pressures of the chemicals investigated in this report span the range of standard CWAs and may be considered as potential vapor pressure simulants, depending on testing criteria and operational requirements.

As clearly demonstrated by the data herein, lengthy extrapolations on the basis of high-temperature thermal data only may lead to large errors in estimates of values in the ambient temperature range. Although recent work in our laboratory has significantly expanded the range and improved the accuracy of the DSC method at lower pressures, we recommend that future work should include data measured by complementary methods in different temperature ranges whenever possible.

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ACRONYMS AND ABBREVIATIONS

ΔH_{vap}	enthalpy of vaporization
CAS	Chemical Abstracts Service
C_{sat}	saturation concentration or volatility
CWA	chemical warfare agent
DCMP	dicyclohexyl methylphosphonate
DIBMP	diisobutyl methylphosphonate
DSC	differential scanning calorimetry
EMPA	ethyl methylphosphonic acid
IMMP	isopropyl methyl methylphosphonate
IMPA	isopropyl methylphosphonic acid
MPFA	methyl phosphonofluoridic acid
MW	molecular weight
P	pressure (Pa)
p	pressure (Torr)
P_{calc}	calculated vapor pressure
P_{expt}	experimental vapor pressure
R	gas constant
T_K	temperature (Kelvin)
t	temperature (Celsius)

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