SELECTED THERMOPHYSICAL PROPERTIES OF 2,2-DIMETHYLCYCLOPENTYL METHYLPHOSPHONOFLUORIDATE (GP) AND 2,2-DIMETHYLCYCLOPENTANOL (DMCP)

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14. ABSTRACT:

Physical properties of chemical warfare agents are of interest to the chemical warfare defense community so that inhalation toxicity, performance of protective equipment, and environmental behavior may be accurately evaluated, and the most-appropriate surrogates may be selected for testing purposes. Thermophysical properties, including vapor pressure, density, viscosity, surface tension, and flash point, are reported for 2,2-dimethylcyclopentyl methylphosphonofluoridate (GP; Chemical Abstracts Service [CAS] no. 453574-97-5). Density data above the melting point, and vapor pressure of the liquid and solid phases are also reported for 2,2-dimethylcyclopentanol (DMCP; CAS no. 37617-33-7), which is the precursor of GP. Correlations were derived from the experimental vapor pressure data and were used to calculate the temperature-dependent enthalpy of vaporization, volatility, and entropy of vaporization for both compounds and the enthalpy of fusion and sublimation of DMCP below its melting point. Temperature correlations were determined for the liquid densities of both compounds and for the viscosity of GP.

15. SUBJECT TERMS

2,2-Dimethylcyclopentyl methylphosphonofluoridate (GP)
2,2-Dimethylcyclopentanol (DMCP)
Differential scanning calorimetry (DSC)
DMCP Chemical Abstracts Service (CAS) no. 37617-33-7
GP CAS no. 453574-97-5
Viscosity

Vapor pressure
Density
Flash point
Volatility
Transpiration

Antoine equation
Surface tension
Enthalpy of vaporization
Enthalpy of fusion
Enthalpy of sublimation

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PREFACE

The work described in this report was authorized under the Chemical and Biological Technology Base Program. The work was started in March 2015 and completed in April 2016. The data reported here is contained in the U.S. Army Edgewood Chemical Biological Center (ECBC) notebooks 02-0091 and 04-0045.

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This report has been approved for public release.

<u>Acknowledgments</u>

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SELECTED THERMOPHYSICAL PROPERTIES OF 2,2-DIMETHYLCYCLOPENTYL METHYLPHOSPHONOFLUORIDATE (GP) AND 2,2-DIMETHYLCYCLOPENTANOL (DMCP)

1.   INTRODUCTION

This report documents thermophysical property data, including density, viscosity, surface tension, flash point, and vapor pressure, measured by the Chemical Analysis and Physical Properties Branch and the CBR Filtration Branch at the U.S. Army Edgewood Chemical Biological Center for 2,2-dimethylcyclopentyl methylphosphonofluoridate (GP; Chemical Abstracts Service [CAS] no. 453574-97-5). We also report the density of the precursor of GP, 2,2-dimethylcyclopentanol (DMCP; CAS no. 37617-33-7), above its melting point and the vapor pressure of liquid and solid DMCP. Where possible, correlations of the data to temperature have been determined to enable interpolation and limited extrapolation. Vapor pressure correlations were used to infer thermodynamic properties including volatility, enthalpy and entropy of vaporization for GP and DMCP, and the enthalpies of sublimation and fusion of solid DMCP. The structures of GP and DMCP are shown in Figure 1.

a   **b**
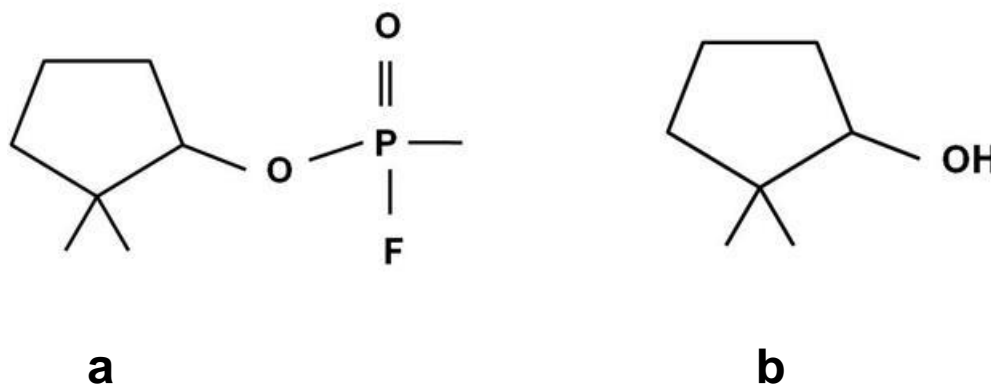
Figure 1. Structures of (a) GP and (b) DMCP.

GP is of particular interest to the chemical defense community because of its extreme toxicity and structural similarity to several G-type chemical warfare nerve agents. Knowledge of the physical properties and toxicology of materials such as GP is required to accurately assess the threat posed after their dissemination into the environment and to select their most-appropriate surrogates for use in testing detection, protection, and remediation equipment. Physical properties dictate practical considerations of interest such as how materials spread on surfaces, how they disperse when released, and their suitability for explosive dissemination. Physical property information facilitates an understanding of chemical behavior in the environment and how to generate and precisely control concentrations for testing purposes, such as evaluating the performance of air purification technologies.

Due, in part, to its extreme toxicity, very little experimental work has been conducted on and published for GP. A report by Cekovic et al.[1] documents GP toxicity, selected spectroscopic (nuclear magnetic resonance [NMR], infrared [IR], and mass spectrometry), and limited physical property (density, vapor pressure, and solubility) data. More recently, Williams et al.[2] investigated the NMR, IR, Raman, and mass spectroscopies of GP. Several reports on the reaction mechanisms of DMCP and closely related compounds contain limited ambient- and reduced-pressure vapor pressure data and a melting temperature range of $t = 28$ to 29 °C, where t is temperature in degrees Celsius.[3–8]

2.   EXPERIMENTAL DETAILS

Sample information for GP and DMCP used in this work is provided in Table 1. Both compounds used in the current work were synthesized in-house and were received as clear, colorless liquids. Sample purities were determined by gas chromatography using a thermal conductivity detector (GC-TCD).

Table 1. Sample Information for GP and DMCP

Chemical Name	Mole Fraction Purity	Purification Method	Analysis Method
GP	0.961	Distillation	GC-TCD
DMCP	0.975	Distillation	GC-TCD

Liquid density data were measured at $t = 25$ to 50 °C for GP and at $t = 30$ to 50 °C for DMCP, in accordance with ASTM D 4052, *Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter*, using an Anton Paar (Ashland, VA) model DMA 58 digital density meter.[9] Before measuring the data, the instrument was calibrated using air and distilled water at each experimental temperature. Proper instrument operation was validated by comparison of measured values to the National Institute of Standards and Technology standard, toluene.

Kinematic viscosity was determined at $t = 25$ to 50 °C for GP in accordance with ASTM D 445, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)*, using a Cannon-Manning semi-micro viscometer and Cannon CT-1000 constant temperature bath (Cannon Instrument Company; State College, PA).[10] The viscometer used for this work was calibrated by the manufacturer.

Surface tension measurements were done for GP at $t = 25$ °C using a Krüss (Hamburg, Germany) K12 tensiometer with an external Lauda RM-6 circulating bath (Lauda-Brinkman; Delran, NJ) in accordance with the Wilhelmy plate method.[11–13] Proper operation of the tensiometer was verified using diethyl oxalate.

The flash point was determined for GP in accordance with ASTM D 6450, *Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester*, using the Grabner FLPH MINIFLASH tester (Grabner Instruments; Vienna, Austria).[14] Before sample measurements were performed, instrument operation was validated using *n*-dodecane.

High-temperature vapor pressure data was measured in accordance with ASTM E 1782, *Standard Test Method for Determining Vapor Pressure by Thermal Analysis*.[15] A TA Instruments (New Castle, DE) 910 differential scanning calorimeter (DSC) and 2200 controller were used for this work. Before sample measurements were performed, the DSC was calibrated using ASTM E 967, *Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers*.[16] The temperature ranges for the DSC data were 100.23 to 156.66 °C for GP and 57.08 to 153.87 °C for DMCP.

A modified version of ASTM E 1194, *Standard Test Method for Vapor Pressure*, was used to measure the vapor pressure of GP and DMCP in the ambient temperature range.[17] Transpiration (vapor saturation) method measurements were conducted using a Hewlett-Packard (Palo Alto, CA) model 5890 series II gas chromatograph equipped with a flame ionization detector, as described in detail in earlier reports from our laboratory.[18,19] The temperature range for the transpiration data was –20 to +20 °C for each compound.

Experimental uncertainties for the GP and DCMP vapor pressure data were estimated as described in an earlier report.[19] Transpiration data are uncertain by about 3%, mainly due to uncertainties associated with temperature measurements and sampling flow rates. DSC experimental uncertainty is ascribed to accuracy in reading the manometer and temperature calibration and traditionally varies between 10% at the lowest temperatures to less than 1% at the normal boiling point. Recent work has extended the temperature range for the DSC method and substantially reduced the uncertainty at lower temperatures.[20]

3.   RESULTS

GP density data (ρ_{GP}) are summarized in Table 2, along with a linear correlation and comparisons between observed (ρ_{expt}) and calculated (ρ_{calc}) values for GP. Figure 2 illustrates the agreement between the correlation and the experimental GP density data. Liquid density data for DMCP (ρ_{DMCP}) are listed in Table 3, along with a linear correlation. Figure 3 compares the DMCP density data to the correlation. The experimental uncertainty of the DMCP density data was 0.0001 g/mL, based on comparison to the accepted values for toluene.

Table 2. Experimental and Correlated Density for GP

Temperature, t (°C)	Density, ρ (g/mL)		Difference[a] (%)
	Experimental	Calculated	
25	1.0795	1.07949	0.0009
35	1.0698	1.06981	−0.0009
50	1.0553	1.05530	0.0000
$\rho_{GP} = 1.10369 - 0.00096789 \times t$			

[a] $100 \times (\rho_{expt} - \rho_{calc})/\rho_{calc}$
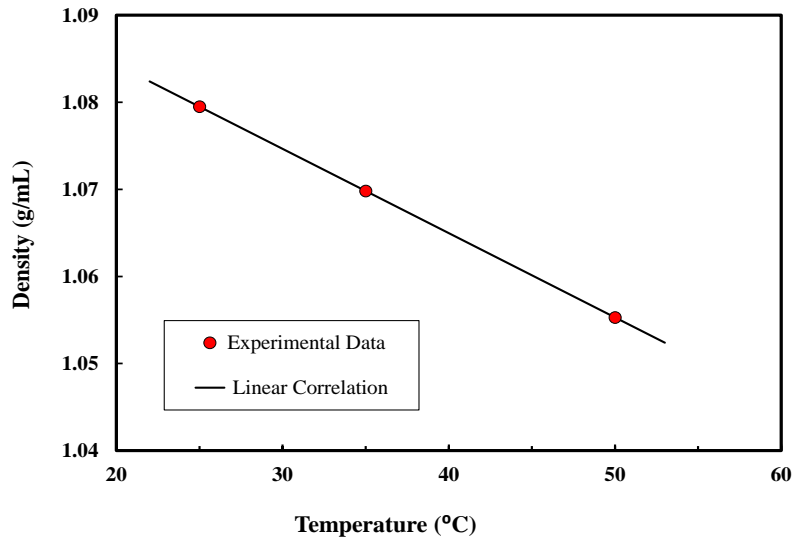
Figure 2. Liquid GP density data and linear correlation.

Table 3. Experimental and Correlated Density for DMCP

Temperature, t (°C)	Density, ρ (g/mL)		Difference[a] (%)
	Experimental	Calculated	
30	0.9278	0.92791	−0.012
35	0.9235	0.92336	0.015
50	0.9097	0.90974	−0.004
$\rho_{DMCP} = 0.95516 - 0.00090846 \times t$			

[a] $100 \times (\rho_{expt} - \rho_{calc})/\rho_{calc}$
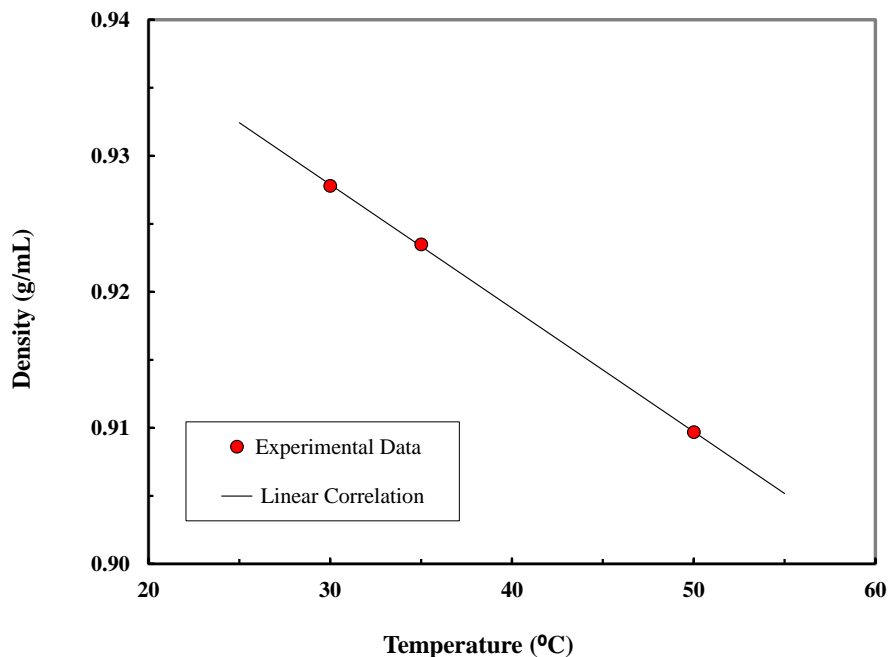
Figure 3. Liquid DMCP density data and linear correlation.

GP viscosity data are listed in Table 4 and plotted in Figure 4, which shows that the viscosity of GP depends nonlinearly on the temperature over the range investigated. The viscosity data are accurately described using an Antoine correlation[21] over the entire experimental temperature range. In the current work, the correlation shown in Table 4 was determined by minimizing the sum of the squares of the natural logarithms of experimental (v_{expt}) and calculated (v_{calc}) viscosity values for GP. As documented in earlier work from our laboratory,[18] the principal uncertainty associated with viscosity measurements involves measurement of the sample fall time, which was done manually. This uncertainty is estimated to be 0.2 s. The resulting viscosity data uncertainty was 0.003 centistokes (cSt).

Table 4. Experimental and Calculated Kinematic Viscosity for GP

Temperature, t (°C)	Viscosity, ν (cSt)				Difference[a] (%)
	Experimental	Mean	Standard Deviation	Calculated	
25	4.68099	4.687	0.005	4.6862	0.017
	4.68770				
	4.69083				
35	3.62315	3.621	0.003	3.6221	−0.030
	3.62287				
	3.61830				
50	2.59443	2.594	0.000	2.5941	−0.004
	2.59443				
	2.59443				
$\ln(\nu) = -2.804834 + 690.9985/(t + 133.8705)$					

[a]$100 \times (\nu_{expt} - \nu_{calc})/\nu_{calc}$

Due to limited sample availability, the amount of material required for each determination, and the destructive nature of the analysis, only two determinations of the flash point of GP were performed. These measurements resulted in values of $t = 99$ and 93 ºC.

The value measured for the surface tension of GP at 25 ºC was 22.9 dyn/cm, with a standard deviation of 0.6 dyn/cm. This value is the average of six separate measurements, each of which was the average of 10 separate determinations.

Table 5 lists the vapor pressure data measured for GP at $t = -20$ to 20 ºC using transpiration and at $t = 100.23$ to 156.66 ºC using the complementary DSC method. This table also shows the Antoine equation that represents the correlation of the combined experimental data sets and comparisons between experimental and correlated values. This correlation was determined by minimizing the sum of the squares of the difference of the natural logarithms of experimental (P_{exp}) and calculated (P_{calc}) vapor pressure values. DSC experiments were also run at pressures higher than those listed in Table 5, but the thermal curves exhibited characteristics of decomposition; therefore, those results were not included in Table 5. The experimental vapor pressure data and Antoine correlation for GP are shown in Figure 5.
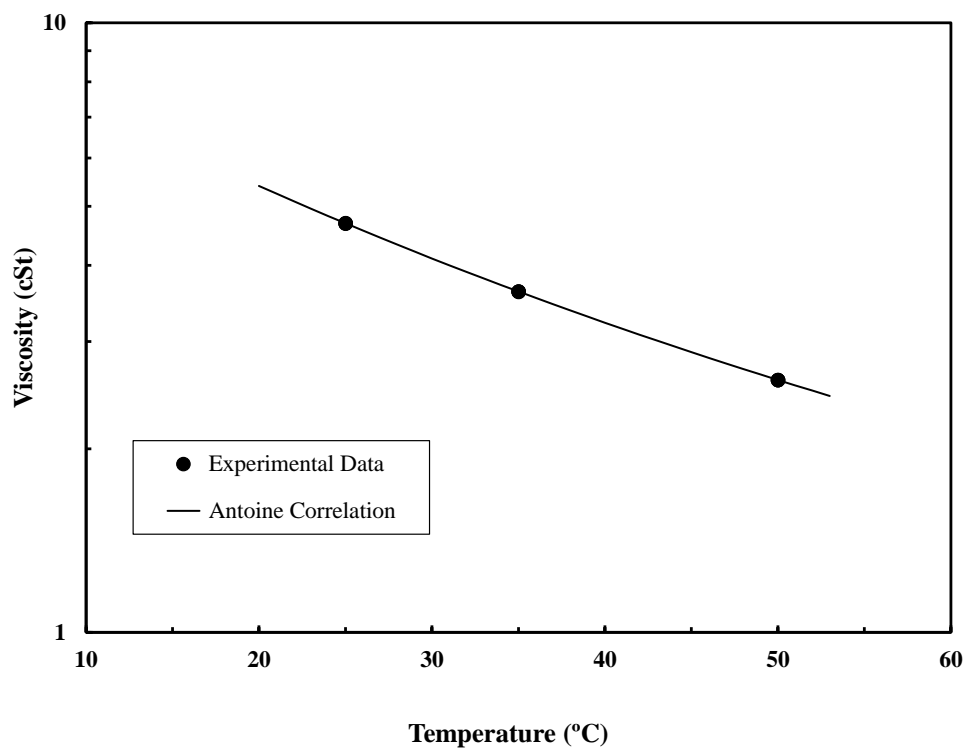
Figure 4. GP viscosity data and Antoine correlation.

Table 5. GP Vapor Pressure Data, Calculated Values, % Difference, % Uncertainty, and Antoine Equation

Temperature		$P_{experimental}$		$P_{calculated}$		Difference[a] (%)	Experimental Uncertainty (%)
t (ºC)	T (K)	P_{Torr} (Torr)	P_{Pa} (Pa)	P_{Torr} (Torr)	P_{Pa} (Pa)		
Transpiration							
−20.0	253.15	0.00102	0.136	0.001035	0.1380	−1.45	3.0
−10.0	263.15	0.00330	0.440	0.003328	0.4437	−0.83	3.0
0.0	273.15	0.00976	1.30	0.009633	1.284	1.25	3.0
10.0	283.15	0.0256	3.42	0.02544	3.392	0.83	3.0
20.0	293.15	0.0637	8.49	0.06200	8.267	2.70	3.0
DSC							
100.23	373.38	10.1	1350	10.64	1419	−4.86	9.66
107.57	380.72	15.3	2040	15.04	2005	1.75	7.64
113.75	386.90	19.9	2650	19.88	2651	−0.04	6.53
119.31	392.46	25.2	3360	25.34	3379	−0.56	5.67
128.26	401.41	35.2	4690	36.85	4913	−4.54	4.63
134.73	407.88	48.4	6450	47.74	6365	1.34	3.87
138.82	411.97	55.1	7350	55.96	7461	−1.49	3.57
142.94	416.09	65.4	8720	65.44	8725	−0.06	3.24
147.19	420.34	80.0	10670	76.62	10220	4.40	2.89
151.89	425.04	90.4	12050	90.84	12110	−0.50	2.67
156.66	429.81	110.2	14690	107.5	14330	2.51	2.38
Antoine Equation: $\ln(P_{Pa}) = 22.77351 - 4998.550/(T - 51.22156)$ $\text{Log}(P_{Torr}) = 7.765506 - 2170.843/(t + 221.9284)$							

[a] $100 \times (P_{expt} - P_{calc})/(P_{calc})$
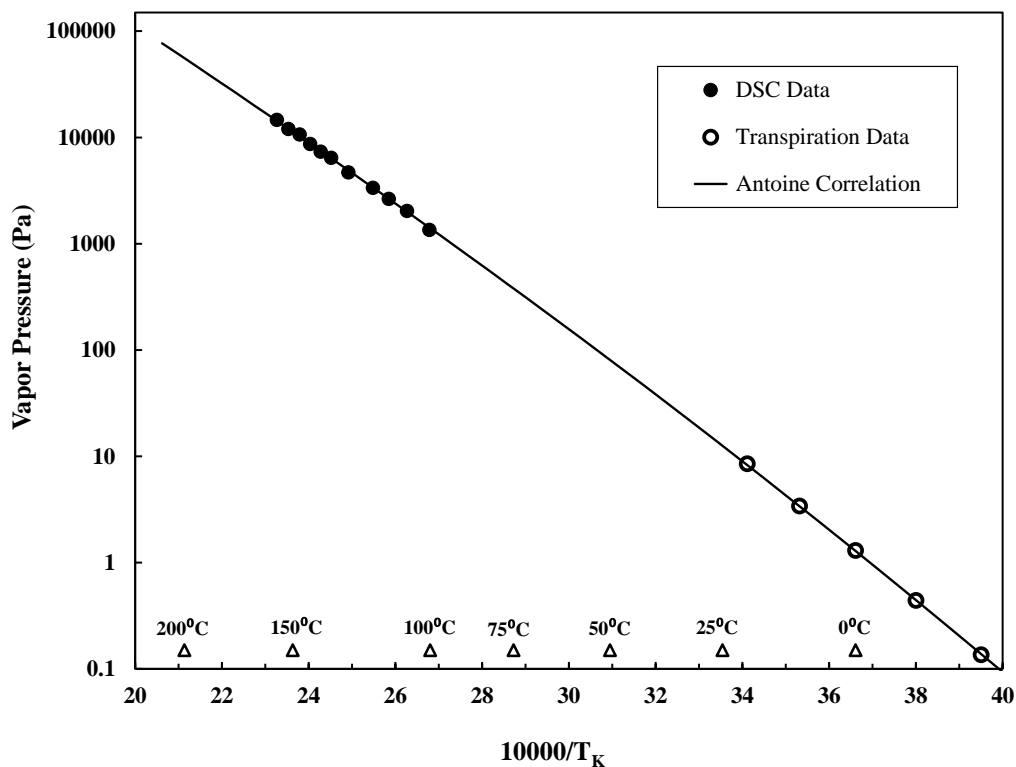
Figure 5. GP DSC and transpiration vapor pressure data and
Antoine correlation.

Vapor pressure, volatility (saturation concentration), and enthalpy of vaporization (ΔH_{vap}) values that were calculated using the correlation constants in Table 5 are listed at selected temperatures for GP in Table 6. The extrapolated normal boiling point of GP, based on the correlation, is $t = 222.49$ °C. The entropy of vaporization for GP was calculated on the basis of the current data to be $\Delta S_{vap} = 104.3$ J/mol·K, which is ~15% higher than expected, based on Trouton's rule. The reason for this deviation is unknown.

Table 6. Calculated Vapor Pressure, Volatility, and
Enthalpy of Vaporization for GP at Selected Temperatures

Temperature (ºC)	Pressure		Volatility (mg/m³)	ΔH_{vap} (kJ/mol)
	(Pa)	(Torr)		
−20	0.1380	0.001035	12.73	65.32
−10	0.4437	0.003328	39.38	64.08
0	1.284	0.009633	109.8	62.96
10	3.392	0.02544	279.8	61.94
20	8.267	0.06201	658.6	61.02
25	12.56	0.09422	983.9	60.59
30	18.77	0.1408	1446	60.18
40	40.04	0.3003	2986	59.40
50	80.77	0.6059	5838	58.69
60	155.0	1.163	10870	58.03
70	284.6	2.134	19370	57.42
80	501.7	3.763	33180	56.86
100	1403	10.53	87830	55.84
120	3480	26.10	206700	54.94
140	7806	58.55	441300	54.16
160[a]	16090	120.7	867500	53.46
180[a]	30860	231.4	1590000	52.83
200[a]	55640	417.3	2746000	52.26
220[a]	95110	713.3	4504000	51.75
222.49[a]	101325	760	4774000	51.69

[a]Extrapolated.

Vapor pressure data were measured at $t = -20$ to 20 ºC for solid DMCP by transpiration and at $t = 57.08$ to 153.87 ºC for liquid DMCP by DSC and are listed in Table 7. Although the highest temperature data point measured by transpiration was below the reported melting point,[6] there was some uncertainty regarding the phase at this temperature. As a result, this data point was not used in the correlation of either data set. The data listed in Table 7 were correlated as before, using separate Antoine equations for the data measured for solid and liquid phases under the boundary condition that the correlations intersect at the melting point with a value of $P = 290$ Pa, as determined by extrapolating both data sets.

Table 7. DMCP Vapor Pressure Data, Calculated Values, % Differences, % Uncertainty, and Antoine Equations for Liquid and Solid Phases

Temperature (°C)	$P_{experimental}$		$P_{calculated}$		Difference[a] (%)	Experimental Uncertainty (%)
	P_{Torr} (Torr)	P_{Pa} (Pa)	P_{calc} (Torr)	P_{calc} (Pa)		
Transpiration						
−20.0	0.0168	2.24	0.01686	2.248	−0.36	3.0
−10.0	0.0562	7.49	0.05632	7.509	−0.25	3.0
0.0	0.172	22.9	0.1667	22.22	3.06	3.0
10.0	0.431	57.4	0.4446	59.27	−3.15	3.0
20.0[b]	1.11	148	1.084	144.6	2.38	3.0
DSC						
57.08	11.7	1550	12.95	1726	−10.22	6.31
64.01	17.7	2360	18.96	2528	−6.64	5.92
70.33	26.1	3480	26.44	3525	−1.29	5.54
78.65	41.3	5520	40.14	5352	3.14	5.04
87.29	61.4	8190	60.54	8071	1.47	4.52
97.63	98.2	13100	96.24	12830	2.09	3.84
120.91	252.6	33680	247.70	33020	1.99	2.23
153.87	761.6	101530	778.5	103800	−2.17	0.49
Solid Phase	$\ln(P_{Pa}) = 23.61701 - 4084.925/(T - 74.04123)$ $\mathrm{Log}(P_{Torr}) = 8.131836 - 1774.060/(t + 199.1088)$					
Liquid Phase	$\ln(P_{Pa}) = 23.93258 - 4821.41/(T - 37.64682)$ $\mathrm{Log}(P_{Torr}) = 8.268883 - 2093.912/(t + 235.5032)$					

[a] $100 \times (P_{expt} - P_{calc})/(P_{calc})$

[b] Data not used due to phase uncertainty.

The data and resulting Antoine correlations for DMCP are illustrated in Figure 6. Table 8 provides a list of DMCP vapor pressures, volatilities, enthalpies of sublimation for the solid phase, and enthalpies of vaporization for the liquid phase at selected temperatures that were calculated using the correlations listed in Table 7. The extrapolated normal boiling point of DMCP, based on the liquid-phase correlation, is $t = 153.12$ °C. The enthalpy of fusion is the difference in the enthalpy of vaporization and sublimation values for the liquid and solid phases, respectively, at the melting point and was calculated to be $\Delta H_{fus} = 7.31$ kJ·mol^{-1}. The entropy of vaporization that was calculated using the current data for DMCP is $\Delta S_{vap} = 113.15$ J/mol·K, which is higher than that predicted by Trouton's rule, and is most likely associated with hydrogen bonding at the alcohol moiety. The methodology used to determine the experimental uncertainty of the vapor pressure data was described in an earlier report.[18] The available thermophysical property data for GP and DMCP are provided in Table 9.

Table 8. Calculated Vapor Pressure, Volatility, and Enthalpies of Sublimation and Vaporization for DMCP at Selected Temperatures

Temperature (ºC)	P_{calc} (Torr)	P_{calc} (Pa)	Volatility (mg/m³)	$\Delta H_{volatilization}$[a]
Solid Phase				
−20.0	0.01686	2.248	122.0	67.85
−10.0	0.05632	7.509	391.9	65.77
0.0	0.1667	22.22	1117	63.92
10.0	0.4446	59.27	2875	62.27
20.0	1.0840	144.60	6772	60.80
25.0	1.6430	219.10	10090	60.11
28.5	2.1750	290.0	13200	59.65
Liquid Phase				
28.5	2.175	290.0	13200	52.34
30.0	2.412	321.5	14570	52.26
40.0	4.662	621.5	27260	51.79
50.0	8.605	1147	48760	51.36
60.0	15.24	2032	83750	50.95
70.0	26.00	3466	138700	50.58
80.0	42.87	5715	222300	50.22
90.0	68.55	9140	345600	49.90
100.0	106.6	14210	523100	49.59
110.0	161.6	21540	772200	49.30
120.0	239.3	31900	1114000	49.03
130.0	346.8	46230	1575000	48.77
140.0	492.7	65690	2184000	48.53
150.0	687.5	91660	2975000	48.30
153.12	760.0	101325	3264000	48.23

[a]For the solid phase, the values are enthalpies of sublimation, and for the liquid phase, the values are enthalpies of vaporization.
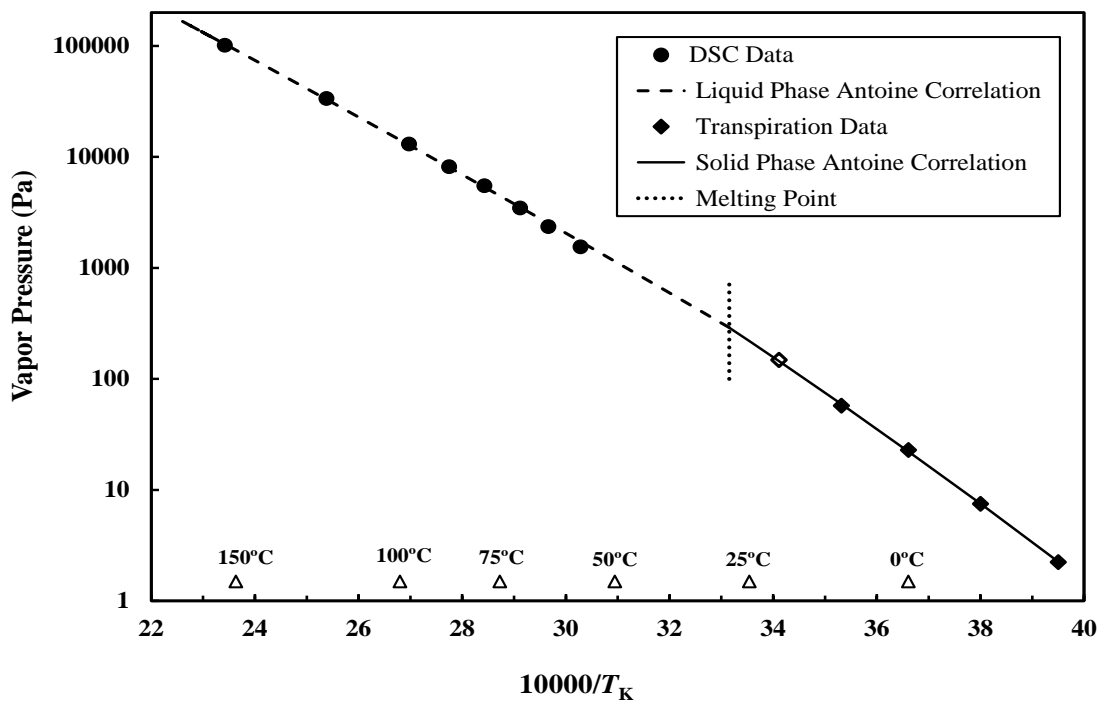
Figure 6. DMCP vapor pressure data. Liquid- and solid-phase Antoine correlations.
Open diamond data point was not used for Antoine equation derivation.

Table 9. Physical Properties of GP and DMCP at $t = 25$ °C

Property	Value	
	GP	DMCP
Density (g/mL)	1.0795	0.9279[a]
Kinematic viscosity (cSt)	4.6862	—
Surface tension (dyn/cm)	22.9	—
Flash point, closed cup (°C)	93	—
Vapor pressure (Pa)	12.56	219.1
Vapor pressure (Torr)	0.09422	1.643
Volatility (mg/m^3)	983.9	10090
Normal boiling point (°C)	222.49	153.12
Standard enthalpy of vaporization (kJ/mol)	60.59	—
Standard enthalpy of sublimation (kJ/mol)	—	60.11
Entropy of vaporization (J/mol·K)	104.3	113.15
Enthalpy of fusion (kJ/mol)	—	7.31
Melting point (°C)[6]	—	28.5

[a]$t = 30$ °C
—, no data

4.   DISCUSSION

The GP density data reported here are accurately described by a linear correlation as illustrated in Table 2 and Figure 2. The only GP density data comparable to that presented in Section 3 were published by Cekovic et al.[1] Our value of $\rho = 1.0795$ g/mL at $t = 25$ °C agrees with the single density value of 1.08 ± 0.05 g/mL at $t = 25$ °C reported by Cekovic et al. No previous density data are available for DMCP. It is noted that the density of DMCP is about 20% less than that of GP, as expected on the basis of comparisons to the closely related G-type nerve agents, isopropyl methylphosphonofluoridate (GB), pinacolyl methylphosphonofluoridate (GD), cyclohexyl methylphosphonofluoridate (GF),[21] and their alcoholic precursors.

No previous viscosity data are available for GP. The value reported herein for the viscosity of GP is 4.688 cSt at $t = 25$ °C, which is within 10% of the 4.816 cSt value that was reported previously for GF[22] (a structurally similiar G agent).

The value reported here for the surface tension of GP is 22.9 dyn/cm at 25 °C. This value is lower than that of GB (26.0 dyn/cm at 25 °C), GD (24.5 dyn/cm at 26.5 °C), or GF (32.3 dyn/cm at 25.5 °C).[22]

The two flash-point temperature measurements reported here for GP differ by 6 °C. Due to safety considerations, it is prudent to report the lower experimental value as the preferred flash-point temperature.

The normal boiling point reported here for GP of $t = 222.49$ °C is comparable to the value estimated by Cekovic et al.[1] of $T = 488.95$ K (215.8 °C). Cekovic et al.'s estimate was based on a single, reduced-pressure boiling point and on a predictive equation.[23] However, it appears that this estimated normal boiling point was based on an entropy of vaporization parameter at the experimental temperature of $t = 102.0$ °C, instead of the parameter at the normal boiling point as prescribed in the iterative procedure.[23] When the second step was performed, the resulting normal boiling point increased to $t = 219.25$ °C, which is in good agreement with our extrapolated value of $t = 222.49$ °C (495.64 K). Cekovic et al.'s experimental data point of $P = 2666$ Pa at $T = 375.15$ K (102.0 °C) is nearly twice that of our correlated value of $P = 1545$ Pa at $t = 102.0$ °C. Cekovic et al.'s correlation diverges further from ours as temperature decreases.

Because of the lack of detail provided in Cekovic et al.'s report concerning their measured data point, we are unable to comment on its accuracy. However, the consistency of the current GP vapor pressure data, measured using complementary methods, provides confidence in the data presented herein. The two DSC values that have marginally greater differences between experimental and correlated values and the experimental uncertainty suggest that small additional uncertainties, either unknown or known but underestimated, might exist.

The vapor pressure of GP is similar to that of GF over the experimental temperature range.[24] A potential low-toxicity surrogate for GP is triethyl phosphate,[25] whose vapor pressure is about 30% higher than that of GP in the ambient temperature range.

The vapor pressure data measured for DMCP span its reported melting temperature of $t = 28$ to 29 °C. As such, the fit to all of the vapor pressure data should include the change in slope at the melting point, which is characteristic of the enthalpy of fusion. A recent report by Tevault[26] details how such data may be correlated using the boundary condition that the vapor pressures of the liquid and solid states coincide at the melting temperature. In the present case, the vapor pressure at the melting point has been assigned a value of $P = 290$ Pa, which was determined using both data sets. The DMCP sample used in this work appeared to be liquid phase at 20 °C, but solid at all other temperatures below 20 °C. As a result, the data point at $t = 20$ °C was not used in the determination of either Antoine equation, even though it agrees well with the rest of the saturator data.

As can be seen in Figure 7, the values calculated using our liquid-phase correlation are in good agreement with the six literature[3–8] DMCP vapor pressure data points at $t = 60$ to 150 °C, with the exception of the lowest point at $P = 1333$ Pa.[8]
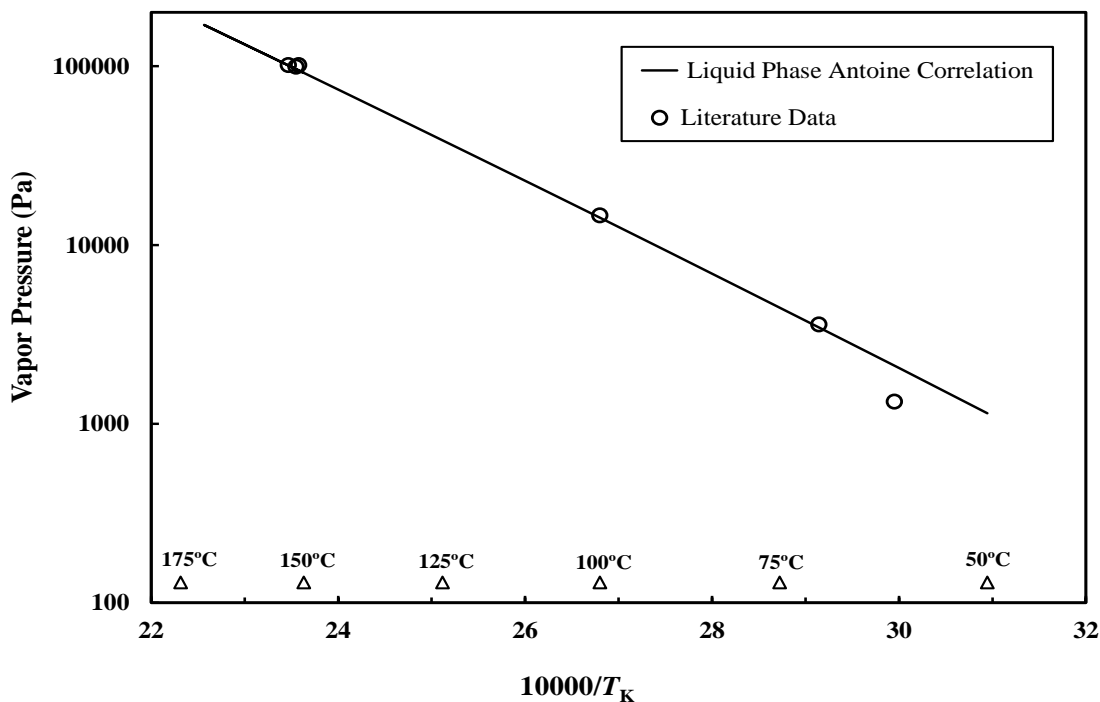
15

Figure 7. DMCP liquid-phase Antoine correlation and literature data.

Differences for several of the experimental vapor pressure values for DMCP marginally exceed their respective calculated values by more than can be attributed to experimental uncertainty. These deviations are likely to be the result of the imposed melting point value constraint and the accompanying uncertainty of the melting temperature of the sample used in our work.

5.   CONCLUSIONS

This report documents the thermophysical property data (density, viscosity, surface tension, flash point, and vapor pressure) measured in our laboratory for GP. We also report the liquid density and vapor pressure of liquid and solid DMCP.

Comparisons of the experimental data to that of related traditional G-type chemical warfare agent compounds are provided.

Temperature-dependent correlations have been developed for the density and vapor pressure of each compound and for the viscosity of GP to enable interpolation and limited extrapolation of the measured data. The density data reported here agree with and expand the temperature range available in the literature.

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Although the extrapolated normal boiling point agrees with ours, the single vapor pressure data point previously reported in the literature for GP appears to be inaccurate. The agreement of data generated using complementary techniques in our work provides confidence in the accuracy of the vapor pressure data presented in this report.

New data for liquid DMCP are in general agreement with previous reports. Data are presented for the first time for solid DMCP in this report and agree well with the expected values.

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ACRONYMS AND ABBREVIATIONS

ΔH_{fus}	enthalpy of fusion
ΔH_{vap}	enthalpy of vaporization
ΔS_{vap}	entropy of vaporization
ν	viscosity symbol
ρ	density symbol
CAS	Chemical Abstracts Service
cSt	centistokes
DMCP	2,2-dimethylcyclopentanol
DSC	differential scanning calorimeter
GB	isopropyl methylphosphonofluoridate
GC	gas chromatography
GD	pinacolyl methylphosphonofluoridate
GF	cyclohexyl methylphosphonofluoridate
GP	2,2-dimethylcyclopentyl methylphosphonofluoridate
IR	infrared
NMR	nuclear magnetic resonance
P	pressure
t	temperature, Celsius
T	temperature, Kelvin
TCD	thermal conductivity detector

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