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Vapor Pressure of Organophosphorus Nerve Agent Simulant Compounds

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The vapor pressures of four lower alkyl phosphonate compounds, dimethyl phosphonate (DMHP, CAS 868-85-9), dimethyl methylphosphonate (DMMP, CAS 756-79-6), diethyl methylphosphonate (DEMP, CAS 683-08-9), and diisopropyl methylphosphonate (DIMP, CAS 1445-75-6), have been measured by complementary methods that allow data collection at ambient and high temperatures by use of gas saturation and differential scanning calorimetry, respectively. Kosolapoff (*J. Chem. Soc.* **1955**, 2964−2965) reported vapor pressure data above 200 Pa for several of these compounds measured by use of isoteniscope, although the lowest data points were deemed to be "not trustworthy" by the author. Our report extends the low end of the measured data range by 2 to 3 orders of magnitude in pressure. Antoine correlations, normal boiling temperatures, temperature-dependent enthalpies of vaporization, and volatility have been derived based on the measured data reported herein. The advantages of using complementary methodology and measuring, as opposed to extrapolating, data have been demonstrated in this work.

Introduction

Vapor pressure is a critical physical property for understanding the behavior of chemicals in the environment. Knowledge of vapor pressure, or volatility, is important for a number of applications related to chemical warfare defense, including generation of precisely controlled challenge concentrations for quantitative toxicology evaluations and detector testing as well as their removal by air filtration systems. Small alkyl phosphonate compounds are of significant interest to the chemical defense community. These compounds are used to simulate the behavior of more toxic chemical warfare agents (CWA), both in the laboratory to develop correlations to chemical warfare agent behavior and in outdoor testing where it is virtually impossible to perform CWA testing. Over 5 decades ago, Kosolapoff[1] reported vapor pressure and density data for several lower alkyl phosphonate compounds, including several of the ones reported herein.

Selection of less toxic materials to simulate the properties of chemical warfare agents for performance evaluation of defensive equipment requires detailed knowledge of the properties of each and depends heavily on the property being simulated. For example, methyl salicylate is often used to simulate the blister agent bis(2-chloroethyl)sulfide (HD) since its vapor pressure is similar; however, it would not be a useful simulant for decontamination testing or for stand-off detection employing spectroscopic methods. Similarly, the compounds under investigation are somewhat similar in structure to organophosphorus nerve agents and represent a range of vapor pressures that could be of interest to future testing applications. It is of considerable interest to understand quantitatively how simulant properties compare to the compounds of principal interest.

Over the past decade, we have modified and extensively exploited two ASTM methods[2,3] for measuring vapor pressure of supertoxic chemical warfare nerve and blister agents. In related work,[4] we have reported data in the 10^{-6} Pa range, giving us confidence in the methodology used in this work. Vapor pressures have been measured for *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX),[5] *O*-isobutyl-*S*-(2-diethylaminoethyl) methyl phosphonothiolate (Russian V agent),[6] isopropyl methylphosphonofluoridate (sarin, GB),[7] pinacolyl methylphosphonofluoridate (soman, GD),[8] cyclohexyl methylphosphonofluoridate (cyclosarin, GF),[9] and bis(2-chloroethyl)sulfide (HD).[10] Our results for VX and Russian V compare favorably with those of Rittfeldt.[11] The first method[2] involves vapor saturation. We have modified that method to include use of a sample concentrator and gas chromatograph (GC) equipped with flame photometric or flame ionization detection in order to extend the measurable range to less than 10^{-6} Pa, which covers the ambient temperature down to below −40 °C for the low-volatility CWA of interest, including VX and Russian V agent, which have normal boiling points in the range of 300 °C. This approach has the distinct advantage of enabling measurements for somewhat impure low-volatility materials with high-volatility impurities, such as VX.[5] The second method,[3] involving the differential scanning calorimetry (DSC) pinhole technique, has been used with modifications in an attempt to extend the measurable range to lower pressure by using larger pinholes. Those efforts have been moderately successful and will be discussed below.

Experimental Section

Ambient-temperature vapor pressure measurement for DMHP, DEMP, and DIMP generally follows ASTM saturator methodology but has been modified in the present work as described in detail in a recent report from our laboratory.[7] Ambient-temperature DMMP vapor pressure data were obtained by measuring mass loss of DMMP from a glass saturator. For the lower temperatures investigated in the latter work, individual data points were obtained after 1 or more days of purging. Minimum acceptable mass loss was 50 mg in all cases. These data were the first vapor pressures measured at our laboratory by saturator methodology, and it was quickly determined that a more sensitive method would be required to obtain data for

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lower-volatility species of interest in a reasonable amount of time. Therefore, development of the GC methodology was required. The GC method is performed by isolating a sample in a gas loop of known temperature, pressure, and volume[8,9] for GC analysis or concentrating a fixed mass of carrier and sample on an adsorbent followed by thermal desorption onto a column for GC quantification.[5−8] This approach has the distinct advantage of being able to work with impure materials, which was a particular advantage in working with VX and Russian V agent owing to the presence of many higher-volatility impurities in those materials. Flame ionization detection (FID) was used for all of the present work, except for DMMP, which was done gravimetrically. The dynamic range extends to as low as the 10^{-6} Pa range for the FID-based method.

DEMP, stated purity of 97 %, was purchased from Alfa Aesar (Pelham, NH). DIMP, stated purity of 98 %, was purchased from Johnson Matthey (Ward Hill, MA). DMMP, stated purity of 99 %, and DMHP, stated purity of 98 %, were purchased from Aldrich Chemical Co. (Milwaukee, WI). All chemicals were used as received.

The glass saturators used in this effort were designed in our laboratory and have been described previously.[7] Each was purged with ultradry nitrogen (dew temperature < −70 °C) at a flow rate of 20 $\text{cm}^3\cdot\text{min}^{-1}$ at STP for 3 days prior to loading with the test material.

The equipment and procedures used to generate the saturated vapor steam are identical to those used previously[5−9] to measure vapor pressure data in our laboratory and are briefly described here. Vapor streams saturated with simulant were generated by flowing dry nitrogen carrier gas at 25 $\text{cm}^3\cdot\text{min}^{-1}$ at STP through the saturator containing liquid simulant of high purity. In this work, each saturator was loaded with approximately 4 g of liquid simulant, which was analyzed by gas chromatography (GC) before and after each set of vapor pressure data was measured. The GC was calibrated by injecting known quantities of the respective simulants and measuring instrument response. Those data were plotted, and the resulting data were linear with R^2 values greater than 0.997 in all cases. For all compounds, analyses indicated no change in simulant sample purity and composition after 2 to 3 weeks of vapor pressure measurements; 99.87 ± 0.17 area % by GC by use of a thermal conductivity detector (TCD) for DMHP, 97.56 ± 0.07 area % by GC-TCD for DEMP, and 98.67 ± 0.15 area % by GC-TCD for DIMP.

The saturator was fabricated of 25 mm Pyrex tubing, 100 mm long. The inlet and outlet ends were closed and attached to 7 mm o.d. Pyrex tubing. A porous ceramic wick was located inside the Pyrex tube coaxially such that the carrier gas had to pass through the section loaded with liquid analyte three times before exiting. A precisely measured volume of saturator effluent was passed through the concentrator and deposited onto the calibrated gas chromatograph, as described below, to determine the mass of analyte in the sample. The vapor pressure was then determined by use of the ideal gas law (eq 1 below). The temperature of the saturator was controlled by immersing it in a water−ethylene glycol bath circulating in a Neslab RTE-140 (Newington, NH) temperature controller system.

The temperature of the bath was measured with calibrated ERTCO (West Paterson, NJ) thermometers, stated accuracy within ± 0.1 K. Ambient pressure was measured periodically during each run with a Princo Instruments Nova Model mercury barometer (Princo Instruments Inc., Southampton, PA). All barometer readings were corrected for temperature and latitude according to the manufacturer's instructions and are accurate to ∼ 13 Pa (0.1 Torr). These readings were used in the vapor pressure calculation as described below.[5−7] No corrections were included for pressure drop between the sampling location and ambient. This correction was determined to be less than 1 Pa in earlier work.[7]

The saturator effluent was sampled by drawing (5 to 10) $\text{cm}^3\cdot\text{min}^{-1}$ at STP to a modified ACEM Model 900 (Dynatherm Analytical Instruments Inc., Kelton, PA) adsorbent (20/35 mesh tenax TA) concentrator collection tube maintained at 313 K for between (1 and 15) min. The total volume of simulant vapor collected ranged from (5 to 150) cm^3, measured at STP. A Tylan (Austin, TX) model FC-280S calibrated mass flow controller, accurate to 1 % of full scale and operated at 50 % or 100 % of capacity, was used to determine the total volume of simulant vapor collected and the total carrier gas flow.

After sample collection, the tenax collection tube was rapidly heated to 558 K under a flow rate of 20 $\text{cm}^3\cdot\text{min}^{-1}$ at STP of UHP-grade helium for 5 min and transferred to the ACEM 900 tenax focusing trap maintained at 313 K. Transfer continued for an additional 1 min to allow the 10 mm o.d. tenax collection tube to cool. Then the focusing trap was rapidly heated to 673 K under a flow rate of 8.0 $\text{cm}^3\cdot\text{min}^{-1}$ at STP UHP-grade helium for 5 min to effect sample transfer to the gas chromatographic column. The 15 m × 0.53 mm i.d. fused silica GC column (Restek Corp., Bellefonte, PA), with a 1.0 μm $RT_x - 1$ (polydimethylsiloxane) stationary phase, was maintained at 313 K for 2 min following sample introduction and then heated at a rate of 10 $\text{K}\cdot\text{min}^{-1}$ to 393 K for DMHP. For DIMP, the $RT_x - 1$ megabore column was maintained at 313 K for 4 min following sample introduction and then heated at a rate of 15 $\text{K}\cdot\text{min}^{-1}$ to 493 K. The same oven temperature profile was used for DEMP.

A Hewlett-Packard model 5890 series II GC equipped with FID was used for the saturator-chromatographic work. Nitrogen was used as the GC carrier gas at a flow rate of 8.0 $\text{cm}^3\cdot\text{min}^{-1}$ and as detector makeup gas at a flow rate of 22.0 $\text{cm}^3\cdot\text{min}^{-1}$. Combustion gases were air at 400 $\text{cm}^3\cdot\text{min}^{-1}$ and hydrogen at 30 $\text{cm}^3\cdot\text{min}^{-1}$.

Under the instrumentation and operating conditions described, DMHP eluted at 4.7 min, which corresponds to a GC column temperature of 340 K; DEMP eluted at 7.3 min, which corresponds to a GC column temperature of 366.2 K; and DIMP eluted at 10.7 min, which corresponds to a GC column temperature of 414 K. Saturator GC vapor analyses revealed that each simulant compound sample was of very high purity and that the peaks of interest were symmetrical with baseline resolution, with neither interfering nor coeluting peaks present.

Calibration of the ACEM 900 HP 5890 FID system was accomplished by preparing a calibration standard solution for each simulant compound. Each was prepared by adding an accurately measured amount of simulant analyte to the appropriate solvent and correlating the resulting GC integrated peak areas to analyte mass as previously described.[5−7] All calibrations were performed during the same day that the standard was prepared. The ACEM 900 HP 5890 FID system was calibrated by making (0.5 to 5) μL injections of the simulant−solvent standard into the distal end of the heated (100 °C) 1.5 mm o.d., 0.015 mm i.d. Sulfinert tubing, which was supplied with dry nitrogen carrier gas at a flow rate of 10 $\text{cm}^3\cdot\text{min}^{-1}$ at STP. ACEM 900 and GC operating parameters were identical to those used for experimental data acquisition with one exception. The ACEM 900 external sampling time for calibration data was always maintained at 15 min to allow sufficient time for analyte transfer to the tenax sampling tube.

For work involving saturator methodology, vapor pressure data points were determined at each temperature by use of eq 1, derived by taking the ratio of the ideal gas law expressions for total pressure and partial pressure of analyte

$$\mathrm{VP} = P_{\mathrm{amb}}[n_{\mathrm{a}}/(n_{\mathrm{carrier}} + n_{\mathrm{a}})] \tag{1}$$

where VP = vapor pressure of analyte, $P_{\mathrm{amb}} = P_{\mathrm{analyte}} + P_{\mathrm{carrier}}$ = ambient atmospheric pressure, n_{a} = moles of analyte measured by gas chromatographic analysis, and n_{carrier} = moles of carrier gas.

Each saturator-determined vapor pressure data point represents the average of between 5 and 25 individual vapor pressure measurements. Saturator carrier gas was quantified with calibrated Tylan General model FC-280 mass-flow controllers. Mole fraction of analyte was measured by directly analyzing the samples by gas chromatography before and after vapor pressure data were collected. Confirmation that the vapor stream was saturated was demonstrated by doubling the flow rate through the saturator and observing no measurable change in the analyte output concentration.

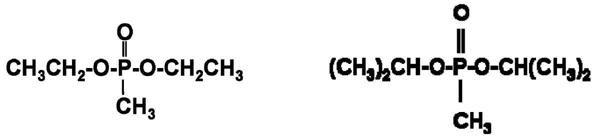
Vapor pressures at higher temperatures were measured on a TA Instruments (New Castle, DE) 910 differential scanning calorimeter (DSC) with a 2200 controller according to a second ASTM method.[3] The measurement consists of heating a small specimen (4 μL) of test material in the DSC cell through the boiling temperature at a controlled rate (5 K·min^{-1}) while the pressure in the cell is held constant. At the boiling temperature, the vaporized specimen escapes from the sample pan through a small orifice ("pinhole") in the lid. The energy associated with the transition from liquid to vapor is recorded as a sharp boiling endotherm. The boiling point is taken at the intersection of tangents to the curve at the onset of boiling. The experimental pressure, measured with a mercury manometer, is the pressure in the cell as the specimen boils. This process is repeated with new specimens at different pressures to obtain a series of points to be fitted to the vapor pressure curve. The DSC was calibrated in accordance with ASTM Practice E967; observed endotherm onset temperatures for water and indium were well within the method uncertainty of ± 1 K.

The DSC method, using hermetic-type sealable pans with a pinhole in the lid ≤ 125 μm diameter, is recommended for use down to 5 kPa. At lower pressures, boiling endotherms broaden, complicating accurate determination of extrapolated onset temperature from the intersection of tangents to the curve. Peak broadening reflects loss of equilibrium and self-pressurization as the rate of specimen vaporization inside the pan exceeds the rate at which molecules exit through the pinhole. In 2003, we investigated use of pinholes up to 375 μm diameter to extend the useful range of the DSC technique to pressures below the recommended 5 kPa limit.[21] Use of larger pinholes at lower pressures restored peak sharpness consistent with a return to equilibrium boiling conditions and appeared to ameliorate the peak broadening problems at low pressures to some extent.

Subsequent unpublished quantitative studies with octanol have shown that while use of larger pinholes retains peak sharpness at lower pressures, method accuracy degrades. With the method-recommended ≤ 125 μm pinhole at 133 Pa, the lowest pressure that could be achieved with this instrument, the observed boiling point for octanol was almost 17 K below the literature value; with larger pinholes, that difference was reduced to around 8 K. Given the improvement in peak shape, this uncertainty remains surprisingly high and suggests that variables other than those investigated to date influence the accuracy with which equilibrium boiling through the pinhole is represented by DSC; slower heating rates have been identified as an area for further study. At 1330 Pa, literature agreement improved significantly compared with the 133 Pa data. With the recommended ≤ 125 μm pinholes, the observed octanol boiling point was 2.5 K below the literature value at 1330 Pa; the larger pinholes yielded boiling points within 2 K.


a. Structure of DMHP

b. Structure of DMMP


c. Structure of DEMP

d. Structure of DIMP

Figure 1. Structures of (a) DMHP, (b) DMMP, (c) DEMP, and (d) DIMP.

Table 1. Measured Vapor Pressure for DMHP

T / K	P / Pa	P_{calcd} / Pa	difference[a] / %
243.2	3.18	3.18	0.0
253.2	7.91	8.13	−2.6
263.2	19.9	19.2	3.5
273.2	47.2	42.6	10.7
283.2	100.6	88.8	13.4
303.3[b]	226.6		
309.3[b]	346.6		
316.4[b]	533.3		
320.1	706.6	872.4	−19.0
321.8	839.9	956.3	−12.2
324.7	1027	1116	−8.0
328.4	1293	1353	−4.4
337.2	2040	2100	−2.9
341.8	2626	2618	0.3
350.8	3960	3959	0.0
361.4	6399	6266	2.1
379.7	13320	12990	2.6
412.4	39960	40330	−0.9
443.2	99930	99910	0.0

[a] Percent difference was calculated as $100(P_{\mathrm{meas}} - P_{\mathrm{calcd}})/P_{\mathrm{calcd}}$. [b] DSC data not used for Antoine equation.

The octanol results indicate that sharp boiling endotherms, albeit of lower accuracy, can still be generated at pressures below the recommended method limit. While accuracy decreases as pressure is reduced, the improvement in both peak shape and literature agreement supports use of larger pinholes at lower pressures. For applications where this increased uncertainty can be tolerated, such as in combination with data generated at even lower pressures by another method, DSC pinhole measurements below the recommended 5 kPa limit may be appropriate. However, use of low-end DSC data and extrapolation of DSC data generated in this range should be done with caution. We have measured and list data down to 146.7 Pa using DSC. Due to the residual deviations, we have elected to include data only down to 640 Pa for the Antoine equation calculations.

Results

DMHP. The structure of DMHP is shown in Figure 1a. Data were measured at T = (243.2 to 283.2) K by the saturator method in combination with GC-FID analysis and at T = (303.3 to 443.2) K by DSC. Table 1 lists the vapor pressure data measured for DMHP determined in the present work along with

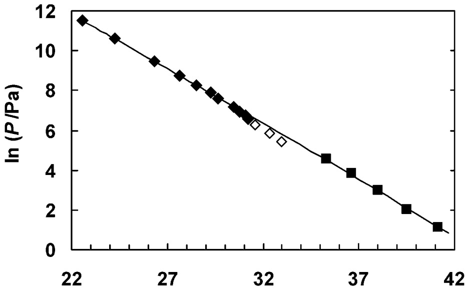


Figure 2. DMHP vapor pressure: ◆, data generated via DSC methodology; ◇, DSC data below 640 Pa that were not used in the Antoine correlation; ■, data generated via saturator methodology; —, Antoine correlation equation.

Table 2. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DMHP Based on Antoine Coefficients Listed in Table 9

T / K	P / Pa	volatility / $\mathrm{mg \cdot m^{-3}}$	$\Delta_{\mathrm{vap}}H$ / $\mathrm{kJ \cdot mol^{-1}}$
243.2	3.175	172.8	48.3
253.2	8.127	424.9	47.9
263.2	19.25	968.4	47.6
273.2	42.61	2065	47.3
283.2	88.77	4150	47.1
293.2	175.3	7913	46.8
298.2	241.8	10 730	46.7
303.2	329.8	14 400	46.6
313.2	594.4	25 120	46.4
333.2	1725	68 530	46.0
353.2	4404	165 100	45.7
373.2	10 110	358 700	45.4
393.2	21 240	715 100	45.1
413.2	41 370	1 325 000	44.9
433.2	75 540	2 308 000	44.7
443.66	101 325	3 023 000	44.6

a comparison to the values calculated by use of the Antoine coefficients. These values are plotted in Figure 2. Calculated vapor pressure, volatility, and enthalpy of vaporization based on the Antoine coefficients for DMHP at $T = (243.2 \text{ to } 443.66)$ K are listed in Table 2. The normal boiling point calculated for DMHP on the basis of the present data is 443.66 K.

DMMP. The structure of DMMP is shown in Figure 1b. Saturator data were measured at $T = (258.2 \text{ to } 293.2)$ K by measuring mass loss directly. DSC data were measured at $T = (326.4 \text{ to } 454.4)$ K. Table 3 lists the vapor pressure data measured for DMMP determined in the present work along with a comparison to the values calculated by use of the Antoine coefficients. These values are plotted in Figure 3. Calculated vapor pressure, volatility, and enthalpy of vaporization based on the Antoine coefficients for DMMP at $T = (263.2 \text{ to } 453.8)$ K are listed in Table 4. The normal boiling point calculated for DMMP on the basis of the present data is 453.80 K.

DEMP. The structure of DEMP is shown in Figure 1c. Data were measured at $T = (253.2 \text{ to } 293.2)$ K by the saturator method in combination with GC-FID analysis and at $T = (316.8 \text{ to } 465.9)$ K by DSC. Table 5 lists the vapor pressure data measured for DEMP determined in the present work along with a comparison to the values calculated by use of the Antoine coefficients. These values are plotted in Figure 4. Calculated vapor pressure, volatility, and enthalpy of vaporization for DEMP at $T = (253.2 \text{ to } 465.36)$ K are listed in Table 6. The normal boiling point calculated for DEMP on the basis of the present data is 465.36 K.

Table 3. Measured Vapor Pressures for DMMP, Calculated Values Based on Antoine Coefficients listed in Table 9, and Percent Difference

T / K	P / Pa	P_{calcd} / Pa	difference[a] / %
258.2	3.73	3.67	1.8
263.4	5.67	6.20	−8.6
273.2	15.2	15.2	−0.1
278.2	24.5	23.5	4.4
283.2	35.0	35.5	−1.4
285.0	41.7	41.0	1.7
288.2	52.8	52.8	0.1
293.2	78.5	77.2	1.8
326.4	653.3	677.3	−3.8
330.2	799.9	840.3	−4.8
332.4	933.3	949.5	−1.7
335.2	1067	1112	−4.1
337.6	1200	1265	−5.1
339.2	1387	1376	1.0
345.8	1973	1921	2.7
356.8	3346	3271	2.3
376.8	7999	7880	1.5
389.8	13 350	13 160	1.4
402.0	21 280	20 580	3.4
421.8	39 930	39 920	0.0
454.4	102 200	102 800	−0.6

[a] Percent difference was calculated as $100(P_{\mathrm{meas}} - P_{\mathrm{calcd}})/P_{\mathrm{calcd}}$.

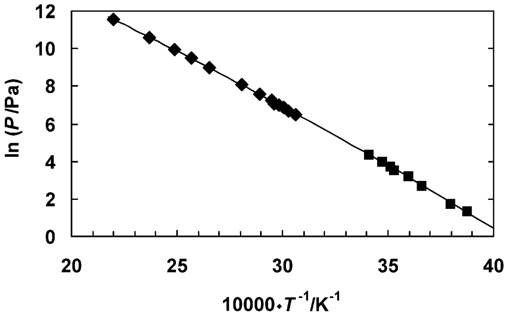


Figure 3. DMMP vapor pressure: ◆, data generated by DSC methodology; ■, data generated by saturator methodology; —, Antoine correlation equation.

Table 4. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DMMP Based on Antoine Coefficients Listed in Table 9

T / K	P / Pa	volatility / $\mathrm{mg \cdot m^{-3}}$	$\Delta_{\mathrm{vap}}H$ / $\mathrm{kJ \cdot mol^{-1}}$
263.2	6.025	341.8	55.9
273.2	15.22	831.8	54.9
283.2	35.49	1871	54.0
293.2	77.15	3928	53.2
298.2	111.1	5562	52.8
303.2	157.7	7763	52.4
313.2	305.1	14 540	51.8
333.2	992.2	44 450	50.6
353.2	2760	116 600	49.5
373.2	6758	270 300	48.6
393.2	14 900	565 700	47.8
413.2	30 100	1 088 000	47.1
433.2	56 490	1 947 000	46.5
453.8	101 325	3 333 000	46.0

DIMP. The structure of DIMP is shown in Figure 1d. Data were measured at $T = (253.2 \text{ to } 293.2)$ K by the saturator method in combination with GC-FID analysis and by DSC at $T = (338.9 \text{ to } 468.0)$ K. Table 7 lists the vapor pressure data measured for DIMP determined in the present work along with a comparison to the values calculated by use of the Antoine coefficients. These values are plotted in Figure 5. Calculated vapor pressure, volatility, and enthalpy of vaporization based on the Antoine coefficients for DIMP at $T = (253.2 \text{ to } 468.0)$

Table 5. Measured Vapor Pressures for DEMP, Calculated Values Based on Antoine Coefficients Listed in Table 9, and Percent Difference

T / K	P / Pa	P_{calcd} / Pa	difference[a] / %
253.2	0.862	0.862	0.0
263.2	2.56	2.54	0.7
273.2	6.88	6.81	1.1
283.2	16.5	16.7	−1.4
293.2	37.4	38.0	−1.7
316.8[b]	146.7		
318.9[b]	186.7		
321.1[b]	226.6		
322.2[b]	246.6		
324.7[b]	280.0		
327.3[b]	360.0		
331.1[b]	466.6		
335.2	639.9	634.9	0.8
339.8	799.9	821.8	−2.7
343.3	959.9	994.6	−3.5
346.4	1173	1173	0.0
353.3	1660	1674	−0.8
359.4	2360	2261	4.4
370.3	4000	3761	6.4
382.6	6639	6411	3.6
397.3	12 012	11 530	4.2
411.0	20 030	19 090	4.9
433.3	40 050	40 090	−0.1
465.9	101 400	102 600	−1.2

[a] Percent difference was calculated as $100(P_{\text{meas}} - P_{\text{calcd}})/P_{\text{calcd}}$. [b] DSC data not used for Antoine equation derivation.

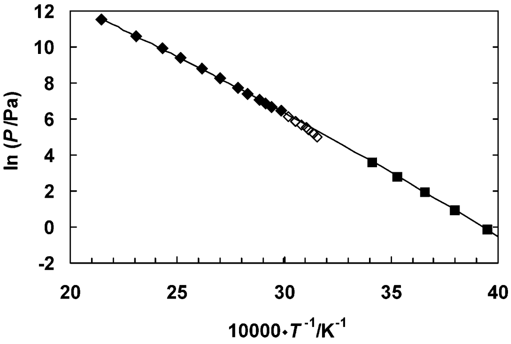


Figure 4. DEMP vapor pressure: ◆, data generated by DSC methodology; ◇, data below 640 Pa that were not used in the Antoine equation correlation; ■, data generated by saturator methodology; —, Antoine correlation equation.

K are listed in Table 8. The normal boiling point calculated for DIMP on the basis of the present data is 462.83 K.

Table 9 presents a compilation of the Antoine equations determined from the present work for all four compounds. The form of the Antoine equation[12] is provided in eq 2

$$\ln (p/p^0) = a - b/(c + T) \tag{2}$$

where $p^0 = 1$ Pa; a, b, and c are empirical coefficients; and T = temperature (in kelvins).

A composite plot showing a comparison of the Antoine equations based on the data presented above to that of nerve agents isopropyl methylphosphonofluoridate (GB, sarin) and pinacolyl methylphosphonofluoridate (GD, soman) is presented in Figure 6.

Discussion

Antoine equations were derived for the each of the four compounds of interest by minimizing the sum of the absolute percentage differences between measured and calculated values for selected data points as described above. The ASTM method used to measure DSC data recommends using data only above 5 kPa. We have chosen to include data down to 640 Pa by virtue of recent work in our laboratory indicating that larger pinholes

Table 6. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DEMP Based on Antoine Coefficients Listed in Table 9

T / K	P / Pa	volatility / mg·m^{-3}	$\Delta_{\text{vap}}H$ / kJ·mol^{-1}
253.2	0.8620	62.30	60.6
263.2	2.545	176.9	59.3
273.2	6.806	455.9	58.2
283.2	16.70	1079	57.2
293.2	38.02	2373	56.3
298.2	55.93	3432	55.9
303.2	81.01	4889	55.5
313.2	162.8	9513	54.7
333.2	566.0	31 090	53.4
353.2	1666	86 290	52.2
373.2	4280	209 900	51.2
393.2	9841	458 000	50.3
413.2	20 620	913 200	49.6
433.2	39 960	1 688 000	48.9
453.2	72 480	2 926 000	48.3
465.36	101 325	3 983 000	47.9

Table 7. Measured Vapor Pressures for DIMP, Calculated Values Based on Antoine Coefficients Listed in Table 9, and Percent Difference

T / K	P / Pa	P_{calcd} / Pa	difference[a] / %
253.2	0.619	0.6194	0.0
263.2	1.88	1.88	0.0
273.2	5.02	5.16	−2.8
283.2	12.6	13.0	−3.3
293.2	28.0	30.3	−7.7
338.9	653.3	690.4	−5.4
339.8	666.6	726.9	−8.3
341.6	813.3	805.2	1.0
342.1	813.3	828.3	−1.8
346.2	1040	1040	0.0
347.0	1080	1086	−0.6
350.9	1347	1340	0.5
358.0	2013	1935	4.0
367.4	3200	3071	4.2
376.0	4680	4576	2.3
388.6	7986	7915	0.9
396.1	10 650	10 760	−1.0
412.1	19 870	19 860	0.1
434.4	39 960	42 840	−6.7
468.0	100 300	116 800	−14.1

[a] Percent difference was calculated as $100(P_{\text{meas}} - P_{\text{calcd}})/P_{\text{calcd}}$.

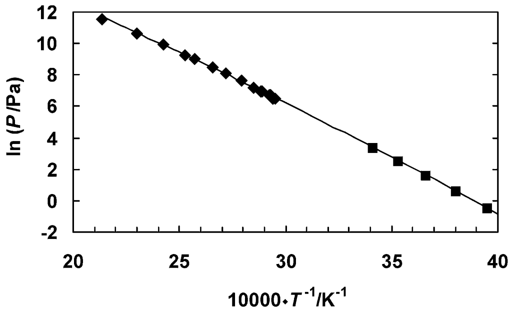


Figure 5. DIMP vapor pressure: ◆, data generated by DSC methodology; ■, data generated by saturator methodology; —, Antoine correlation equation.

Table 8. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DIMP Based on Antoine Coefficients Listed in Table 9

T / K	P / Pa	volatility / $\mathrm{mg \cdot m^{-3}}$	$\Delta_{\mathrm{vap}}H$ / $\mathrm{kJ \cdot mol^{-1}}$
253.2	0.6194	53.02	62.1
263.2	1.880	154.8	60.9
273.2	5.163	409.6	59.9
283.2	13.00	995.0	58.9
293.2	30.34	2243	58.0
298.2	45.17	3283	57.6
303.2	66.21	4733	57.3
313.2	136.2	9422	56.5
333.2	494.0	32 140	55.2
353.2	1512	92 780	54.2
373.2	4028	23 390	53.2
393.2	9571	527 600	52.4
413.2	20 670	1 084 000	51.6
433.2	41 200	2 061 000	51.0
453.2	76 660	3 666 000	50.4
462.83	101 325	4 742 000	50.1

can be used to extend the pressure range of the method and the agreement between the latter and fits developed by use of DSC and saturator data. Enthalpy of vaporization was calculated as a function of temperature by use of eq 3

$$\Delta_{\mathrm{vap}}H = bRT^2/(c + T)^2 \qquad (3)$$

where $\Delta_{\mathrm{vap}}H$ = enthalpy of vaporization (in joules per mole) and R = gas constant [8.314 $\mathrm{J \cdot (K \cdot mol)^{-1}}$].

As used here, volatility is defined as the vapor density of the saturated vapor in units of milligrams per cubic meter at a given temperature and is used extensively by the toxicology community, especially in reference to inhalation hazard determination. Volatility is defined by eq 4

$$D = PM/RT \qquad (4)$$

where D = vapor density or volatility (milligrams per cubic meter), M = molecular mass (grams per mole), and R = gas constant [8.314 $\mathrm{Pa \cdot m^3 \cdot (mol \cdot K)^{-1}}$].

DMHP. The DMHP results had the highest average percent difference between observed and calculated vapor pressures of any of the compounds reported here and likely contain a greater unknown systematic error than the others. The data are described nearly as well by a two-parameter Clausius−Clapeyron equation as by a three-parameter Antoine equation. These observations might be related, although it is unclear at this time if the shape of the curve is a result of experimental uncertainty or the differences in structure between DMHP and the other species investigated in this work. The average difference between the pressures calculated by the Clausius−Clapeyron equation and experimental values was 5.9 % compared to 5.2 % for the Antoine correlation, and the main discrepancy was at low temperatures of the combined data set where the Clausius−Clapeyron equation calculates values nearly 10 % higher than does the Antoine equation. For DMHP, the two lowest DSC data points included in the calculation exhibit significantly higher deviation than do any of the other data points used to calculate Antoine equation coefficients but less than the deviations observed for the lowest three DSC points, which were not used to develop the correlation due to their obvious and significant error when combined with the saturator data. Exclusion of selected high-discrepancy data points did not significantly alter the correlation constants. A consequence of the near-linear dependence of ln P versus $1/T$ plot shown in Figure 2 in comparison to the other compounds of interest here is that the enthalpy of vaporization for DMHP varies by only 3.7 $\mathrm{kJ \cdot mol^{-1}}$ over the temperature range shown in Table 2. This is by far the least variation of any of the compounds under study here.

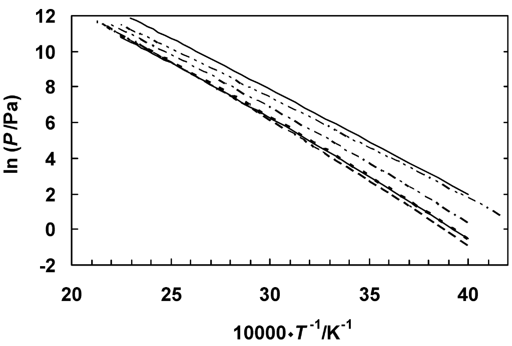


Figure 6. Composite Antoine equation plot of simulants and CW agents. Isopropyl methylphosphonofluoridate (nerve agent sarin) is shown by the upper solid line. Next lower line, — • • —, is DMHP; and then — • — is DMMP. Three overlapping lines are pinacolyl methylphosphonofluoridate (nerve agent soman), lower solid line; DEMP, ••• (mostly obscured by the lower solid line); and DIMP, — — —.

DMMP. The average difference between DMMP data and Antoine equation was 2.2 %, and the data were described significantly better by the Antoine equation than by a two-parameter fit, whose average error was greater than 5.4 %. The measured data for the lowest four DSC temperatures, all above 1200 Pa, range from (2.5 to 5.5) % below the calculated values, which is an indication that the systematic error for DSC method is beginning to take effect.

Several recent literature citations[13−17] indicate values between (100 and 164) Pa for the vapor pressure of DMMP at 25 °C in comparison to our value of 111 Pa. We have not been able to clearly discern the source of those values even after contacting a number of those authors. One source of the errant DMMP data in recent literature appears to be Table 2 in Singer et al.,[18] in which those authors cite Meylan and Howard,[19] who extrapolated the Antoine equation of Boublik et al.[20] to values below the experimental range. Meylan and Howard reported a value of 0.962 Torr (128 Pa) at 25 °C, although the value indicated by Boublik's equation is 12.8 Pa. Boublik et al.[20] derived an Antoine correlation based on Kosolapoff's entire data set,[1] which is inappropriate since, as Kosolapoff recognizes, the "last values in Table 1 are not trustworthy". Nonetheless, the resulting equation suggests a value of 12.8 Pa at 25 °C. It appears that the latter value was errantly transcribed to 128 Pa in Singer's paper.[18] Other discrepancies are present for DEMP.[19,20]

DEMP. The average difference between DEMP data and Antoine equation predictions was less than 2.2 %. Like DMMP, the DSC data suggest a negative deviation toward the lower end of the range. Seven of the low-pressure DSC data points were excluded from the Antoine fit. The Antoine correlation of Boublik et al.[20] for DEMP appears to have been derived in a manner similar to that used for DMMP and is unreliable below 343 K.

DIMP. The average difference between DIMP data and Antoine equation predictions was less than 3.2 %. Only the two lowest DTA data points suggested evidence for the same low-end falloff as observed for DEMP and DMMP, although it was less severe in this case. The Antoine correlation of Boublik et al.[20] for DIMP appears to have been derived in a manner similar to that used for DMMP and is unreliable below 350 K.

The overall vapor pressure trend shown in Figure 6 for the compounds under study here follows the order that might have been expected on the basis of their respective molecular weights;

that is, the lightest molecules have the highest vapor pressure. This trend is followed except where DIMP crosses DEMP near their respective normal boiling points, as seen in Figure 6. The crossover is unexpected, and no explanation is obvious.

The cause of the low-temperature deviation in the DSC data remains a concern. Sample containers used in the present work employed larger orifices to minimize self-pressurization effects.[21] The origin of the residual error is under further evaluation and will be the subject of a future publication. Interestingly, a similar falloff was observed for the isoteniscope data,[1] which is a static as opposed to dynamic measurement, and the reason for the bias in those data is unknown.

The experimental uncertainty for the DMMP data reported here is identical to that in a recent publication from our laboratory,[22] and our analysis of the uncertainty in the present data is quite similar. The difference for the other compounds investigated in the present work is that all of the saturator measurements were made by injecting known volume samples from the concentrator into a calibrated gas chromatograph. The resulting uncertainty in those measurements is dominated by the calibration procedure in which standard solutions were prepared by use of pipettes with manufacturer's stated accuracy of 1 % ($U_{\mathrm{pip}} = 1$ %). In addition, a series of injections were made with known volumes of the standard solutions in microsyringes. We estimate that the volume of those injections is uncertain by as much as 1 % ($U_{\mathrm{inj}} = 1$ %). Other parameters measured in our saturator work, with anticipated uncertainty in parentheses, include ambient pressure ($U_{\mathrm{p}} = 0.02$ %), flow rate to the concentrator ($U_{\mathrm{c}} = 1.0$ or 2.0 %), and bath temperature ($U_t = 0.1$ K). U_{t} was evaluated in terms of its effect on the resulting vapor pressure and found to depend on temperature, from about 1.1 % at 253 K to 0.7 % at 298 K. The flow rate uncertainty stems from the manufacturer's stated 1 % full-scale accuracy for calibrated mass flow meters, which were operated at either 50 % or 100 % of capacity. Fortuitously, the higher sampler flow rates are normally used at lower temperatures, offsetting the associated uncertainty to some extent.

Aggregate uncertainty was estimated by the method described by Currell and Dowman,[23] as shown in eq 5, and varies from 1.9 % under low-temperature, low-flow conditions to 2.7 % for the high-temperature, high-flow scenarios in this temperature range.

$$U_{\mathrm{aggregate}} = [(U_{\mathrm{pip}})^2 + (U_{\mathrm{inj}})^2 + (U_{\mathrm{p}})^2 + (U_{\mathrm{c}})^2 + (U_{\mathrm{t}})^2]^{0.5} \tag{5}$$

The DSC method infers boiling temperatures at a variety of controlled pressures, measured to within 13 Pa. The temperature accuracy of the instrumentation is determined by measuring the melting point of two standard materials in the range of interest for each chemical and validated by measuring the vapor pressure of a standard. The acceptance criterion for the latter is a maximum error of 1 K. Curve broadening due to improper selection of pinhole size, impurity, thermal decomposition, etc., may degrade the data in some cases but not significantly in the work reported here. Our assessment, based on comparison to standard octanol data,[24] is that the results are accurate to within 0.3 K near the normal boiling point, 1 K at the ASTM-recommended limit of the method, and 3 K at 640 Pa. The resulting pressure uncertainties are 0.8 %, 4.5 %, and 18.6 %, respectively. As noted earlier, the importance of the lower values is greatly diminished by the addition of saturator data, and our assessment is that this combination of data sets gathered usingby complementary methodologies greatly reduces the uncertainty attached to either data set alone.

Table 9. Antoine Equation[a] Coefficients for DMHP, DMMP, DEMP, and DIMP Based on Fits to Data in This Report

compound	*a*	*b*	*c*
DMHP	23.068	4890.0	−20.0
DMMP	22.319	4340.0	−51.7
DEMP	22.471	4500.0	−54.2
DIMP	23.130	4785.0	−50.5

[a] Antoine equation: $\ln P = a - b/(c + T)$.

Conclusions

This report extends the range of measured vapor pressure data for four lower alkyl phosphonate compounds by 2 to 3 orders of magnitude to lower pressures in the ambient temperature range.

The current vapor pressure data for DMMP conflict with values quoted in recent literature.[13−17] We think that the reasons for the DMMP discrepancies are the inappropriate correlation of Kosolapoff's data[1] by Boublik et al.,[20] followed by the transcription error by Meylan and Howard.[19] Boublik et al.[20] also inappropriately correlated DEMP and DIMP vapor pressures using data at the low end of the respective isoteniscope data sets, which were acknowledged to be untrustworthy by Kosolapoff[1] and would underpredict vapor pressure for those compounds in the ambient temperature range as well. The present results increase considerably the vapor pressure values projected by the previous data and analysis.

The combination of high-temperature DSC and ambient-temperature saturator data increases the confidence in the data overall and in the ability to interpolate and extrapolate to untested conditions. It also provides insight relative to data quality.

The vapor pressure for DMHP, DMMP, DEMP, and DIMP at 298.2 K are (241.8, 111.1, 55.9, and 45.2) Pa, respectively. Normal boiling temperatures for DMHP, DMMP, DEMP, and DIMP are (443.6, 453.8, 465.36, and 462.83) K, respectively.

Acknowledgment

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