Ambient Volatility of DMMP[1]

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A novel experimental apparatus and procedures have been developed and implemented to measure the volatility of a chemical warfare agent simulant as a function of ambient temperature and water vapor partial pressure. Initial data have been measured for dimethyl methylphosphonate (DMMP) to validate the methodology. The results presented herein reveal a significant volatility suppression for DMMP, increasing as the relative humidity increases. Deviation from ideal behavior as described by Raoult's law has been quantified. The maximum deviation from ideality occurs at water partial pressures near 500 Pa. An empirical model has been developed to enable interpolation and limited extrapolation of the data to higher water partial pressures as might be found in compressed-air regenerative filtration applications.

KEY WORDS: dimethyl methylphosphonate; mixture; two-component vapor-liquid equilibrium; water.

1. INTRODUCTION

The vapor pressures of dimethyl methylphosphonate (DMMP) [1] and a number of chemical warfare agents, e.g., O-ethyl-2-(isopropylaminoethyl) methyl phosphonothiolate (VX) [2,3] and cyclohexyl methylphosphono-fluoridate (GF) [4], have been measured in the ambient temperature range recently. So far, that work has not included effects of atmospheric water vapor. The objective of studying the volatility of toxic vapors in humid environments is to refine predictions of downwind time-concentration evolution following deposition of chemicals into the environment as well as to

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determine more realistic environmental evaporation rates, i.e., persistence. The work reported here establishes methodology to characterize materials of interest.

2. EXPERIMENTAL

Figure 1 shows schematically the experimental setup used in the present work. Two vapor saturators [1] were used in parallel, and their effluent streams were combined in a heat-traced Nalgene 890 FEP 6.35-mm tubing (4.8-mm i.d.) transfer line. The combined vapors were then passed through a passive mixing volume, ca. $25\,cm^3$, and a portion of the mixing cell effluent was drawn into a chilled mirror dew pointer (Model 911 Dew-All[TM] Digital Humidity Analyzer, EG&G Environmental Equipment, Burlington, Massachusetts), where the mixture dew point temperature was measured and recorded.

Data acquisition was performed using National Instruments LabView® software and interfaces (SCXI 1001 chassis equipped with various 1320-series modules). Controlled parameters included the temperatures of both saturator baths, mixing cell temperature, and saturator flow rates. Measured data included the mixture dew point temperature and ambient pressure. The methods and materials for measuring these parameters have been described in detail in previous reports [1,2]. Briefly, calibrated thermometers were used to measure bath temperatures and are
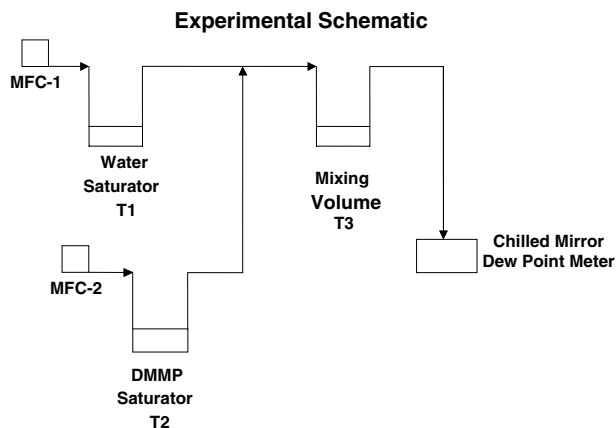

Fig. 1. Schematic of experimental apparatus showing mass flow controllers (MFC), flow path, and components described in the text.

believed to be accurate within 0.1°C, and flow rates were measured using factory-calibrated electronic mass-flow controllers (Tylan General, San Diego, California). In selected cases, we have also measured the flow rates in our laboratory by water displacement and believe these measurements to be accurate within 1%. A calibrated Princo Instruments Hg barometer was used to measure ambient pressure, which was corrected for temperature and latitude and is believed to be accurate to within 0.01%. The dew point meter was calibrated on-line by directing the flow of the water saturator only to the analytical system prior to data measurement to ensure that the dew point recorded corresponded to that of the water saturator bath. Data were not collected unless the agreement was within 0.2°C. The saturators were constructed by fusing a roughened ceramic thimble inside a 2-cm diameter glass tube such that the carrier stream must make three passes prior to exiting. A number of experiments have been performed to show that the concentration of the saturator effluent does not vary with carrier flow rate and, thus, the effluent stream is, in fact, saturated. As stated above, in the present work, the dew-point meter calibration was performed by directing the effluent of the water saturator only to the dew-point meter to ensure that the indicated dew-point temperature corresponds to the water saturator bath temperature, which also demonstrates that the system had attained equilibrium.

99% DMMP was obtained from Alfa Johnson Matthey (Ward Hill, Massachusetts) and used without purification. The principal organic impurities are trimethyl phosphate $(MeO)_3P(O)$ and dimethyl phosphite, $(MeO)_2 P(O)H$. Triply distilled water was used to generate water vapor. The carrier gas used in the present work was Matheson UHP nitrogen.

The first series of experiments used flow rates of 250 standard cm^3 per minute (sccm) for the water saturator and 50 sccm for the DMMP saturator to generate high-humidity conditions. The second series used flows of 100 and 200 sccm, respectively, to explore low-humidity conditions.

3. RESULTS

Table I shows the measured mixture dew points and the partial pressure of each component in the mixture from series 1 in this study, which consists of 71 data points, i.e., nine DMMP partial pressure measurements at eight water vapor partial pressure values, save the one data point at the highest partial pressure value for each. Table II lists 10 similar data points for three low water vapor partial pressure values under different saturator flow values for series 2 as detailed above. Figure 2 shows a plot of the measured volatility of DMMP as a function of temperature at 11 different water partial pressures investigated in the present work, as well as vapor

Table I. Measured Mixture Dew Points at Indicated DMMP and Water Vapor Partial Pressures (Series 1: Water Vapor Flow = 250 sccm and DMMP Flow = 50 sccm.)

P_{H2O} (Pa)	520	742	1040	1440	1970	2670	3580	4740
P_{DMMP} (Pa)	Mixture Dew Point (°C)							
2.6	4.0	7.55	11.2	15.05	19.2	23.5	27.95	32.55
3.9	5.6	8.9	12.4	16.05	20.3	24.05	28.4	32.9
5.9	7.4	10.5	13.8	17.2	21.1	24.8	28.95	33.3
8.7	9.4	12.25	15.4	18.6	22.3	25.8	29.7	33.9
12.7	11.5	14.2	17.1	20.1	23.6	27.1	30.8	34.6
18.3	13.9	16.3	19.0	21.9	25.1	28.45	31.95	35.5
25.8	16.4	18.6	21.1	23.8	26.85	30	33.25	36.6
36.0	19.0	21.1	23.4	25.8	28.7	31.7	34.7	37.8
49.6	21.4	23.6	25.7	27.8	30.75	33.5	36.7	––

Table II. Measured Mixture Dew Points at Indicated Component Partial Pressures (Series 2: Water Vapor Flow = 100 sccm and DMMP Flow = 200 sccm.)

P_{H2O} (Pa)	208	414	788
P_{DMMP} (Pa)	Mixture Dew Point (°C)		
23.8	9.6	14.5	18.7
51.1	––	21.0	24.6
103.6	––	28.2	30.9
198.8	35.9	36.6	37.9

pressure data previously measured for DMMP using ultra-dry conditions [1]. Also, calculations for two humidity values are shown.

Figure 3 shows a plot of the sum of the relative pressures of the components (DMMP plus water) versus the relative pressure of each component, i.e., two points for each table entry corresponding to the water and DMMP relative pressures, for all data listed in Tables I and II. These data reveal clear trends. Most importantly, the magnitude of the deviation from Raoult's law reaches a maximum near water relative pressures of 0.4 (40% RH). A more subtle trend is that the deviation appears to be a maximum at partial pressure values near 500 Pa (water dew point near 0°C).

4. DISCUSSION

Raoult's law states that the partial pressure of each component over an ideal liquid mixture is given by the product of the pure component vapor pressure and mole fraction (x) for that component:
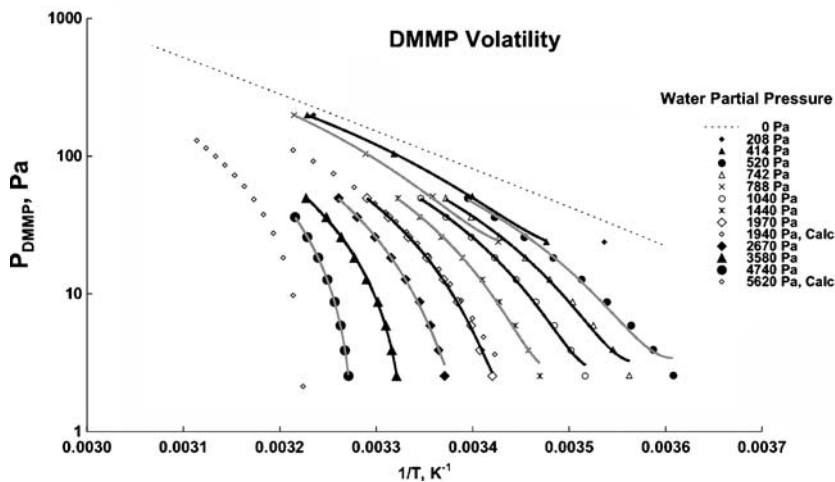
Fig. 2. Measured volatility of DMMP as a function of temperature at the several water partial pressures indicated in the legend. Lines indicate quadratic equation fits to data points as listed in Table III; small open diamonds are calculated values based on quadratic fits.
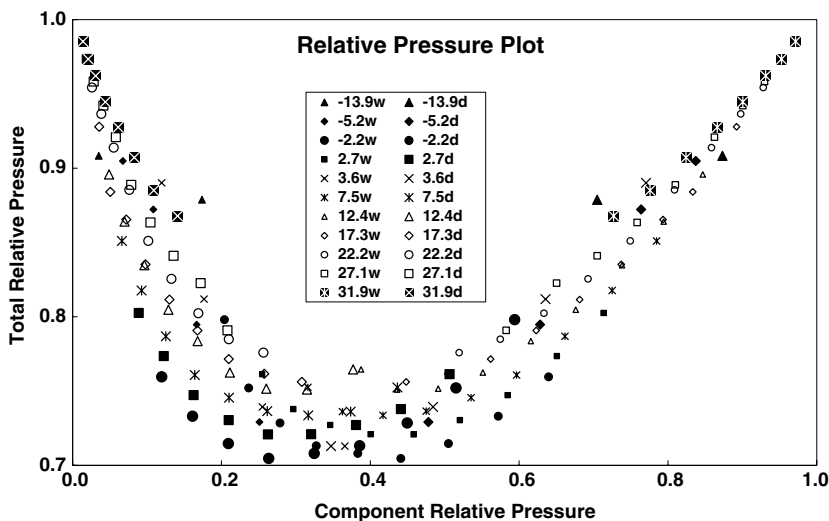

Fig. 3. Sum of relative pressures of DMMP and water versus component relative pressures. Small filled triangles labeled −13.9 w represent water relative pressure (RH) at a water dew point of −13.9°C, large filled triangles (−13.9d) represent DMMP relative pressure at a water dew point of −13.9°C, etc. The 11 data series at fixed water partial pressure shown here correspond to the 11 series listed in Tables I and II and shown in Fig. 2.

$$P_1 = x_1(P_1)^0$$
$$P_2 = x_2(P_2)^0$$
etc.

This expression is usually applied to the liquid phase in order to estimate the vapor-phase composition and is commonly used to model purification of liquids by distillation. An identical expression of Raoult's law for a two-component mixture is

$$x_1 = P_1/(P_1)^0$$
$$x_2 = P_2/(P_2)^0$$

where $P_1/(P_1)^0$ represents the relative pressure of component 1, and $P_2/(P_2)^0$ represents the relative pressure of component 2. (For water, the relative pressure is commonly referred to as the relative humidity.) By employing material balance, the sum of the relative pressures over an ideal solution will always equal unity. Conversely, the partial pressure of vapor component 2 at a particular condition is predictably altered (suppressed) by the presence of component 1. As shown in Fig. 3, the sum of the partial pressures is less than 1.0 for all data reported herein, and the deviation from ideal behavior reaches a maximum at RH values near 40%. The observed deviations from Raoult's law are largest at water partial pressures near 500 Pa. Recent theoretical calculations and infrared spectroscopy reported by Ault and co-workers [5] indicate that intermolecular hydrogen bonding between water and DMMP contributes significantly in explaining the phenomena reported herein.

5. MODELING

A quadratic equation correlation between the measured mixture dew point temperatures and DMMP partial pressure was developed for data measured at each water partial pressure with the exception of the data measured at a water partial pressure of 208 Pa. These equations are listed in Table III. This overly simplistic approach fits the data quite well as shown by the lines connecting the data points in Fig. 2, although the quality of the fits falls off at lower temperatures for several of the lower water partial pressure curves.

A more general predictive capability was derived by correlating the coefficients of these equations with the water dew point temperatures. Two predicted DMMP vapor pressure curves based on these correlations are shown in Fig. 2 for water partial pressures of 1940 and 5620 Pa. The former compares well with data measured for water partial pressures of

Table III. Quadratic Equations Describing the Vapor Pressure of DMMP at Various
Water Vapor Partial Pressures (T in K).

Water Partial Pressure (Pa)	DMMP Vapor Pressure Correlation (Pa)
414	$P_{DMMP} = 2.15 \times 10^9/T^2 - 1.51 \times 10^7/T + 2.66 \times 10^4$
520	$P_{DMMP} = 9.99 \times 10^8/T^2 - 7.20 \times 10^6/T + 1.30 \times 10^4$
742	$P_{DMMP} = 1.17 \times 10^9/T^2 - 8.38 \times 10^6/T + 1.50 \times 10^4$
788	$P_{DMMP} = 3.16 \times 10^9/T^2 - 2.18 \times 10^7/T + 3.77 \times 10^4$
1040	$P_{DMMP} = 1.38 \times 10^9/T^2 - 9.74 \times 10^7/T + 1.72 \times 10^4$
1440	$P_{DMMP} = 1.81 \times 10^9/T^2 - 1.26 \times 10^7/T + 2.20 \times 10^4$
1970	$P_{DMMP} = 2.07 \times 10^9/T^2 - 1.42 \times 10^7/T + 2.45 \times 10^4$
2670	$P_{DMMP} = 2.62 \times 10^9/T^2 - 1.78 \times 10^7/T + 3.02 \times 10^4$
3580	$P_{DMMP} = 2.69 \times 10^9/T^2 - 1.81 \times 10^7/T + 3.05 \times 10^4$
4740	$P_{DMMP} = 4.27 \times 10^9/T^2 - 2.83 \times 10^7/T + 4.69 \times 10^4$

1970 Pa; the points are slightly higher than the measured data as expected
by the trend of decreasing DMMP vapor pressure as the water partial
pressure increases. The latter (water partial pressure = 5620 Pa) also seems
to predict what might be expected for a water dew point of 35°C as well
as the trend of changing shapes of the lower water partial pressure data.

It is instructive to note that the present data, when plotted using stan-
dard vapor pressure format (Fig. 2), are very nonlinear. The deviation
from linearity increases as the water partial pressure increases. Two lim-
its dictate the observed nonlinearity. At low water relative pressures, each
two-component vapor pressure curve approaches the line representing the
dry DMMP vapor pressure line (upper left of Fig. 2). At low DMMP
partial pressures for each two-component vapor pressure curve, the lines
asymptotically approach the vertical line defined by the water dew point
of that series.

The heat of vaporization can be inferred from volatility data using
standard methods. Using the Antoine equation, $\ln(P) = a - b/(c + T)$,

$$\Delta H_{vap} = bRT^2/(c + T)^2$$

In this case, the *apparent* ΔH_{vap} varies from that of single-component
DMMP (ca. 50 kJ·mol^{-1}) at low RH values to unrealistically high values
(>350 kJ·mol^{-1}) at high humidity conditions.

6. CONCLUSIONS

The present data demonstrate clearly that the volatility of DMMP
is very sensitive to the presence of water vapor as well as temperature.

In addition to the expected suppression described by Raoult's law, a significant negative deviation from ideal behavior has been observed. The results of the present work enable accurate predictions of the evaporation of DMMP in the environment at a wide variety of temperature and dew point conditions. A simplistic model has been developed from the present data that would allow prediction of DMMP volatility at any atmospheric relative humidity condition. The model could be extended to higher humidity values characteristic of industrial processes or, of more immediate interest, feed conditions for air purification systems employing high temperature and pressure, such as pressure-swing adsorption, where influent water partial pressures may exceed 10^4 Pa, and ambient temperatures may exceed $50°$C.

ACKNOWLEDGMENTS

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