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AMBIENT VOLATILITY OF TRIETHYL PHOSPHATE

James H. Buchanan
John J. Mahle

RESEARCH AND TECHNOLOGY DIRECTORATE

David E. Tevault

JOINT RESEARCH AND DEVELOPMENT, INC.
Belcamp, MD 21017-1552

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14. ABSTRACT: Although deviations are common, the effect of humidity on the volatility of materials is predictable using Raoult's law. This report details the measurement of the effect of water vapor partial pressure on the volatility of triethyl phosphate (TEPO), which has been used as a testing surrogate for G-type nerve agents. The results are compared to similar work for dimethyl methylphosphonate, in which its volatility was suppressed beyond what was predicted by Raoult's law. The current work shows that the effect of humidity on TEPO volatility is nearly as predicted by Raoult's law, that is, vapor pressure suppression is proportional to ambient relative humidity. An empirical correlation taking into account nonideal behavior was developed to enable estimation of TEPO volatility at any combination of ambient temperature and humidity and compared to predications based on Raoult's law. These predictions may be used to support testing using TEPO with a variety of applications, including weapons effects and protective equipment.					
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PREFACE

The work described in this report was commissioned by the Defense Threat Reduction Agency (DTRA) and conducted between October 2016 and January 2017.

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Data reported herein are documented in the U.S. Army Edgewood Chemical Biological Center (ECBC) notebook number 07-0072.

This report has been approved for public release.

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AMBIENT VOLATILITY OF TRIETHYL PHOSPHATE

1. INTRODUCTION

Vapor pressure is a physical property that is required to predict the behavior of chemicals in the laboratory as well as in the environment. Knowledge of vapor pressure is important for a number of applications that are related to chemical warfare defense, including prediction of downwind time–concentration profiles after a release of chemical warfare agents (CWAs), generation of precisely controlled challenge concentrations for quantitative inhalation toxicology evaluations, detector testing, and prediction of chemical removal efficiency using air-filtration systems. Vapor pressure data can also be useful for estimating the concentration of solutions by quantitative analysis of the vapor composition that is in equilibrium with those solutions. This work explores the effect of ambient humidity on the volatility of triethyl phosphate (TEPO; Chemical Abstracts Service [CAS] no. 78-40-0). TEPO has been used to simulate CWAs (e.g., soman [GD or pinacolyl methyl phosphonofluoridate]; CAS no. 96-64-0) in laboratory and field testing due to the similarities in their vapor pressures and chemical structures. The chemical structure of TEPO is shown in Figure 1.

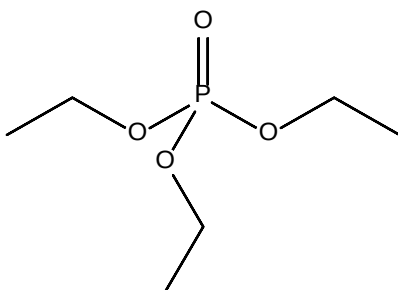


Figure 1. Chemical structure of TEPO.

The vapor pressure of pure TEPO has been reported in the literature.¹ To describe a mixture of TEPO and water, a mixture model is needed. Raoult's law states that the partial pressure of each component above an ideal solution equals the pure component vapor pressure of each component multiplied by its mole fraction in the solution, as shown in eq 1

$$P_i = x_i P_i^{\text{sat}} \quad (1)$$

where P_i is the partial pressure (Pa), x_i is the liquid-phase mole fraction, and P_i^{sat} is the saturation vapor pressure of component i .

The implication of Raoult's law for a two-component condensable mixture involving water vapor is that the volatility of the second component will be suppressed in proportion to the ambient relative humidity (RH). For example, at a water vapor relative pressure (i.e., partial pressure divided by pure component vapor pressure), which is also known as RH for

water, of 0.5 (50% RH), the volatility of the second component is expected to be one-half as much as in the absence of water vapor. Similarly, the measured volatility of the second component is expected to be one-fourth that of the pure component at 75% RH.

Earlier work from our laboratory demonstrated that the suppression of dimethyl methylphosphonate (DMMP; CAS no. 756-79-6) vapor pressure by humidity was greater than expected on the basis of Raoult's law.² In contrast, no volatility suppression was observed for bis-(2-chloroethyl) sulfide (HD; CAS no. 505-60-2).³ The current report explores the effect of humidity on the volatility of TEPO at conditions that simulate what might be anticipated in the environment at wide ranges of temperature and relative humidity.

2. EXPERIMENTAL DETAILS

The TEPO used in this study was obtained from the Sigma-Aldrich Company (St. Louis, MO), was certified by the supplier to be 99.8% pure, and was used as received. Our analysis determined the purity to be >99.9% by gas chromatography (GC), and the chemical structure was verified by GC/mass spectrometry. Deionized house water (40 M Ω) was used in the current work. The experimental method used was similar to that used in an earlier work² and will be described briefly here.

Parallel vapor streams of TEPO and water vapor were produced by separately flowing nitrogen carrier gas (Earlbeck Gases and Technologies; Baltimore, MD) through two specially fabricated vapor generators that each contained one of the pure components. The generators, hereafter referred to in this report as *saturators*, have been described in detail elsewhere in the literature.⁴ The saturators were submerged in Neslab model RTE-140 temperature-controlled, circulating ethylene glycol–water baths (Neslab Instruments; Portsmouth, NH). The flow rate of each carrier gas stream was independently controlled at flow rates between 50 and 153 standard cubic centimeters per minute (sccm) using calibrated Brooks Instrument (Hatfield, PA) flow controllers.

After the streams were combined, the dew point of the resulting stream was measured at a wide range of vapor-phase concentrations for each component using an EdgeTech DewPrime II dew point meter (West Wareham, MA). The temperatures of the baths were measured using calibrated thermometers (Miller and Weber, Inc.; Ridgewood, NY and Ertco; Dubuque, IA), which were accurate to within 0.05 °C. The vapor-phase concentrations of the water and TEPO components were controlled by adjusting the flow rates and bath temperatures of the component streams. Dew point meter calibration was performed by setting the TEPO stream flow rate to zero to determine how the measured water dew point matched the temperature of the water bath. The differences observed at water bath temperatures between 5 and 25 °C were less than 1 °C, and those results were used to correct the dew point meter data.

Saturation of the vapor stream exiting the TEPO saturator was verified by doubling the flow rate of the dry nitrogen carrier gas from 100 to 200 sccm and confirming that no change was observed in the measured dew point. All experimental data ranges and the uncertainty of each measurement are summarized in Table 1.

Table 1. Experimental Data Ranges and Uncertainties

Measurement	Range	Uncertainty
Water vapor carrier gas flow rate (sccm)	50 to 150	1.0
TEPO vapor carrier gas flow rate (sccm)	50 to 153	1.0
Water saturator temperature (°C)	2 to 37	0.05
TEPO saturator temperature (°C)	−25 to 40	0.05
Dew point temperature (°C)	−35 to 35	0.5

Because the vapor pressures of pure TEPO¹ and water⁵ are known, the partial pressures of these substances in the combined vapor phase may be calculated as well as their relative pressures at the experimentally measured condensation temperatures. In the current work, the concentration of water vapor was fixed by maintaining the flow rates of the two gas streams and the temperature of the water bath, while varying the temperature of the TEPO bath between −25 and 40 °C. Water bath temperatures were held between 2 and 37 °C. We assumed that the condensate contained both components and that it represented the saturation point for the TEPO and water vapors. The experimentally measured dew point temperatures are used to determine the TEPO–water, binary vapor–liquid equilibrium (VLE) partial pressures at each experimental condition. The VLE values for TEPO are referred to in this report as the *ambient volatilities* to distinguish them from vapor pressures, which refer exclusively to the property of pure materials. Ambient volatility may also be thought of as the equilibrium partial pressure of TEPO in the presence of water vapor.

3. RESULTS

The ambient volatilities of TEPO were measured at 12 different values of water partial pressure. Those results are tabulated in Tables 2–13 and plotted using the same temperature range for ease of comparison in Figures 2–13. A standard vapor pressure plot ($\ln[P]$ vs $10000/T$, where T is absolute temperature in Kelvin) was used for each figure. Each plot was compared to the vapor pressure of pure TEPO to demonstrate the effect of water partial pressure on TEPO volatility. Also shown in each figure is the predicted volatility of TEPO based on Raoult's law and the water-only dew point (i.e., the expected water dew point in the absence of TEPO).

Table 2. Experimental Dew Point Temperatures
at a Water Partial Pressure of 176 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-25	0.06	-15.1	0.216	190	0.930	1.145
-20	0.11	-13.2	0.328	222	0.796	1.124
-10	0.36	-5.3	0.444	412	0.428	0.872
0	1.06	1.5	0.642	681	0.259	0.901
10	2.86	9.0	0.824	1149	0.154	0.977
20	7.13	17.9	0.901	2052	0.086	0.987
30	16.54	27.0	0.955	3574	0.049	1.005
37	28.67	33.2	1.005	5100	0.035	1.039

Notes: Water saturator flow rate was 51 sccm at 2.0 °C. TEPO saturator flow rate was 153 sccm. The water-only dew point of this mixture was -16.0 °C.

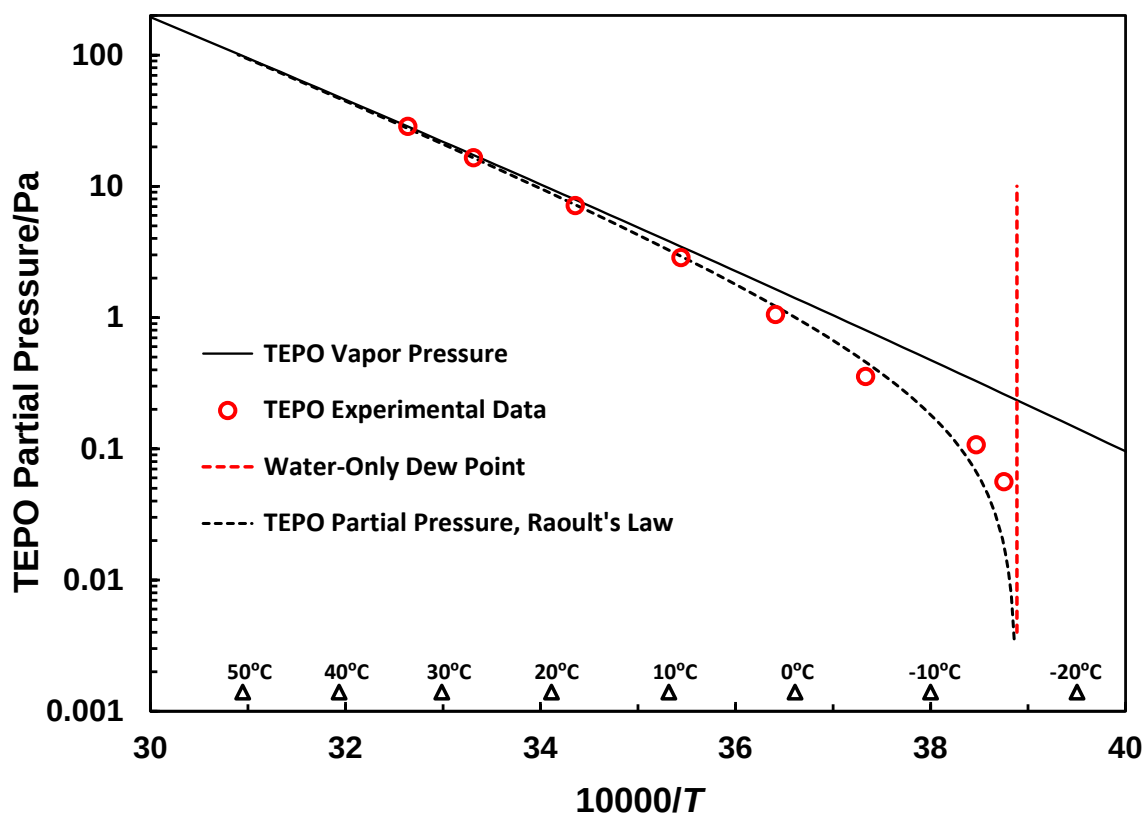


Figure 2. Experimental ambient volatility of TEPO at 176 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 3. Experimental Dew Point Temperatures
at a Water Partial Pressure of 307 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-25	0.06	-9.0	0.106	310	0.990	1.096
-15	0.20	-5.2	0.245	415	0.738	0.984
-5	0.62	0.6	0.416	636	0.482	0.898
5	1.76	7.0	0.613	1005	0.305	0.918
15	4.56	14.7	0.773	1668	0.184	0.957
25	10.95	23.0	0.892	2802	0.109	1.001
37	28.67	33.5	0.981	5186	0.059	1.041

Notes: Water saturator flow rate was 51 sccm at 10.0 °C. TEPO saturator flow rate was 153 sccm. The water-only dew point of this mixture was -9.1 °C.

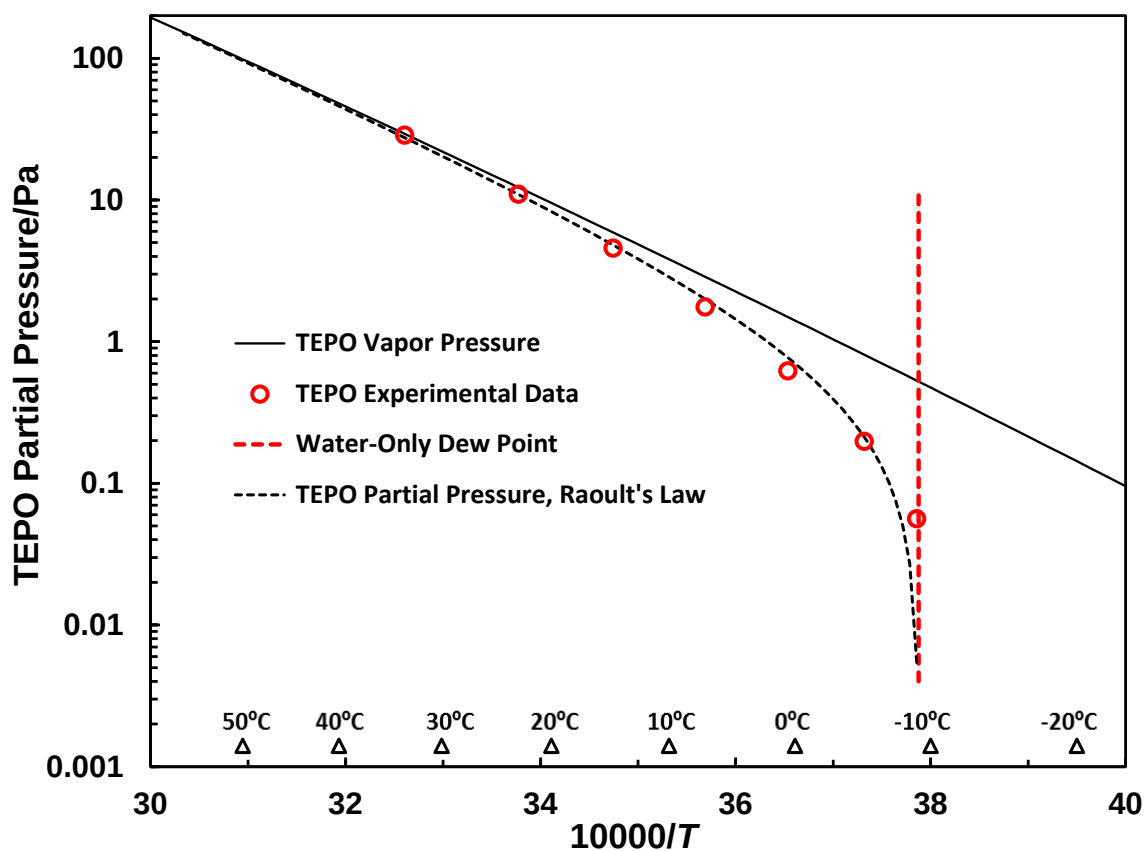


Figure 3. Experimental ambient volatility of TEPO at 307 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 4. Experimental Dew Point Temperatures
at a Water Partial Pressure of 353 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-16	0.12	-5.0	0.141	422	0.837	0.978
-5	0.41	-2.3	0.374	516	0.684	1.058
5	1.17	3.5	0.581	785	0.449	1.031
15	3.04	10.4	0.770	1257	0.281	1.051
25	7.30	18.7	0.859	2159	0.163	1.022

Notes: Water saturator flow rate was 100 sccm at 2.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was -7.33 °C.

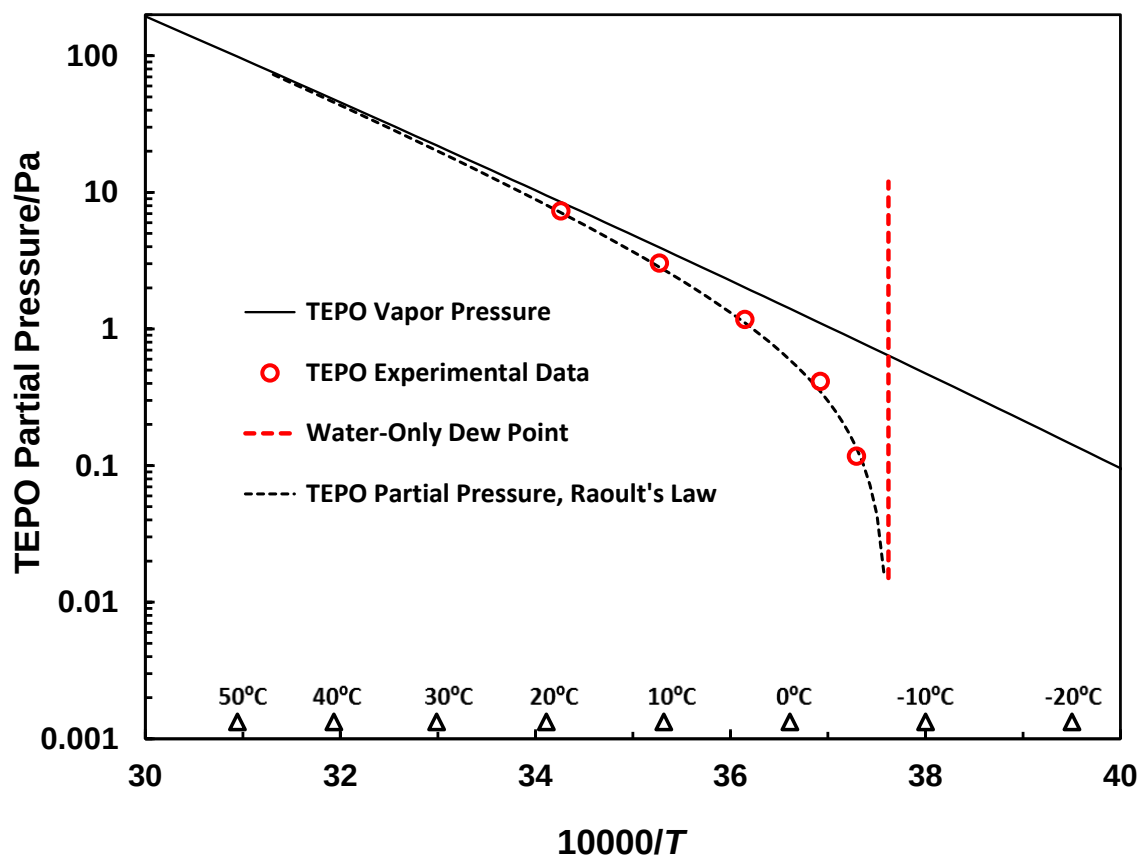


Figure 4. Experimental ambient volatility of TEPO at 353 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 5. Experimental Dew Point Temperatures
at a Water Partial Pressure of 436 Pa.

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-20	0.07	-3.2	0.071	484	0.900	0.971
-10	0.24	-2.3	0.214	516	0.845	1.060
0	0.70	3.2	0.361	767	0.568	0.929
10	1.91	8.1	0.601	1079	0.404	1.005
20	4.75	15.4	0.755	1747	0.250	1.004
30	11.03	22.8	0.913	2768	0.158	1.071

Notes: Water saturator flow rate was 100 sccm at 5.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was -4.6 °C.

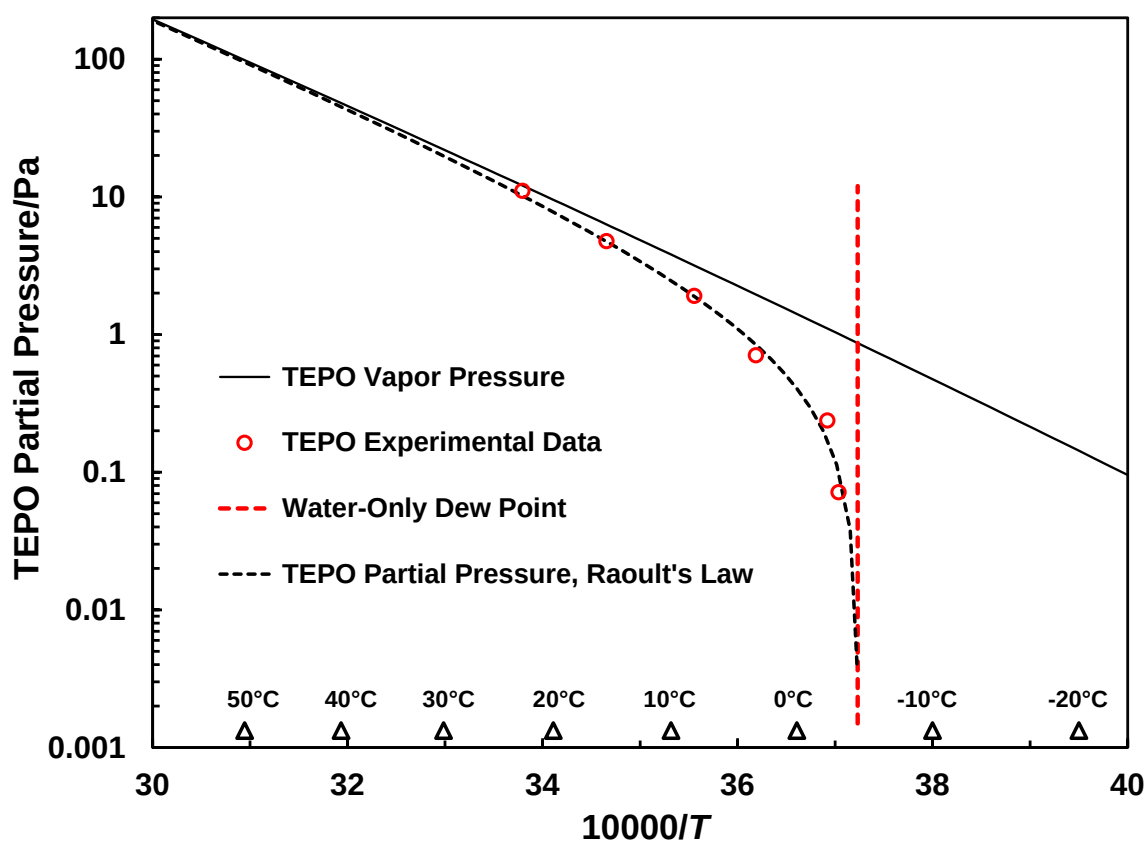


Figure 5. Experimental ambient volatility of TEPO at 436 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 6. Experimental Dew Point Temperatures
at a Water Partial Pressure of 584 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-25.0	0.06	-0.4	0.042	594	0.984	1.026
-15.0	0.20	0.8	0.130	646	0.905	1.035
-5.0	0.62	4.6	0.274	851	0.687	0.961
5.0	1.76	9.4	0.487	1181	0.495	0.981
15.0	4.56	16.0	0.685	1817	0.322	1.006
25.0	10.95	23.8	0.833	2940	0.199	1.032

Notes: Water saturator flow rate was 51 sccm at 20.0 °C. TEPO saturator flow rate was 153 sccm. The water-only dew point of this mixture was -0.6 °C.

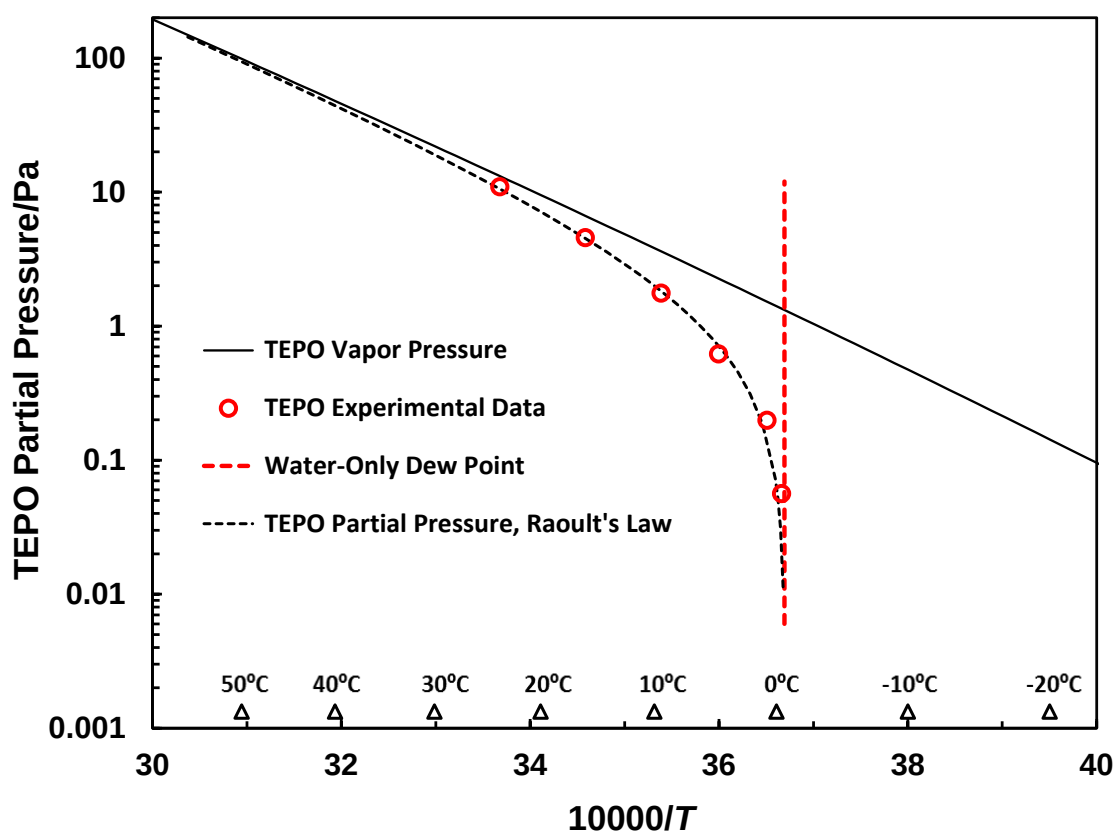


Figure 6. Experimental ambient volatility of TEPO at 584 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 7. Experimental Dew Point Temperatures
at a Water Partial Pressure of 614 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-20.0	0.07	0.1	0.050	617	0.995	1.045
-10.0	0.24	1.3	0.147	671	0.915	1.062
0.0	0.70	4.2	0.325	826	0.743	1.067
10.0	1.91	9.5	0.525	1186	0.517	1.042
20.0	4.75	16.2	0.701	1840	0.333	1.035
30.0	11.03	24.2	0.811	3010	0.204	1.015

Notes: Water saturator flow rate was 100 sccm at 10.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was 0.1 °C.

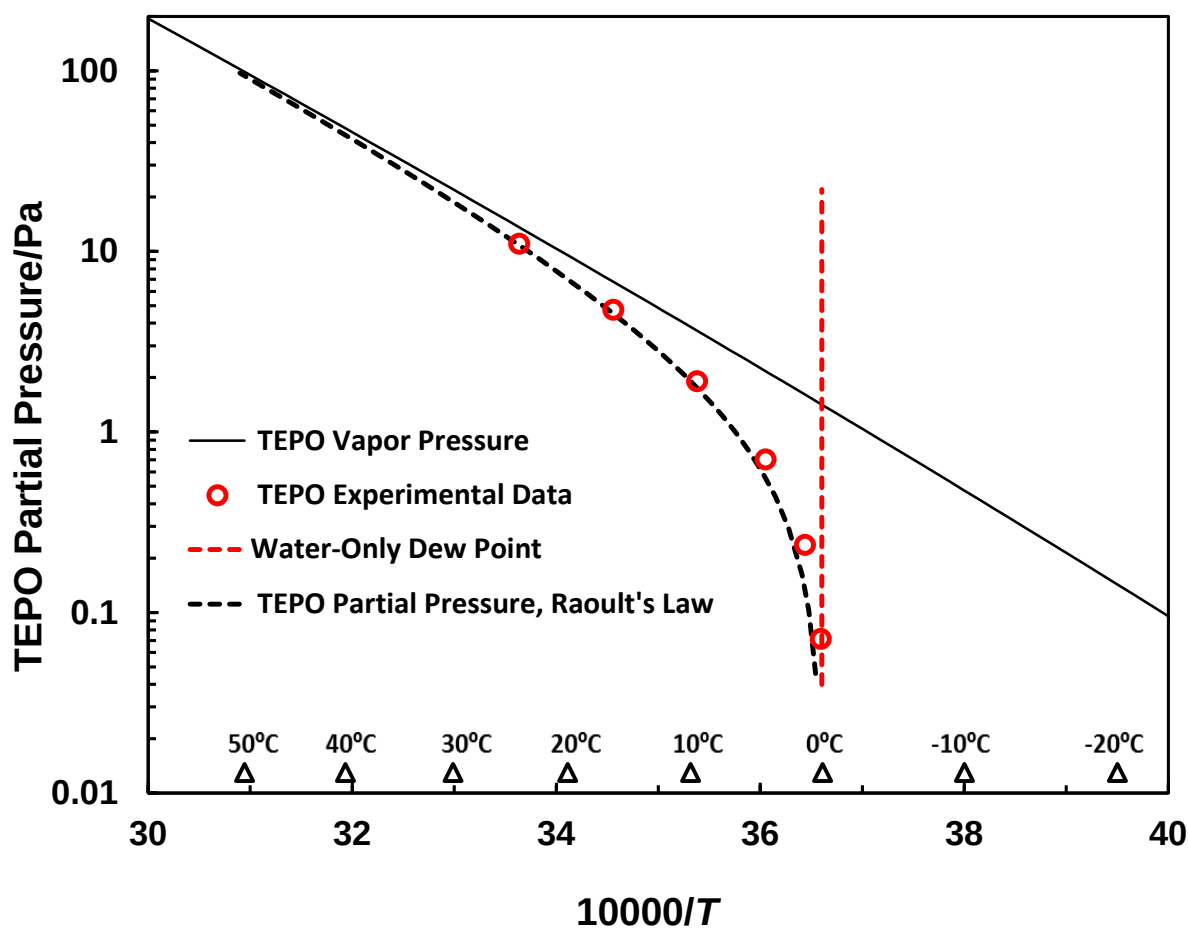


Figure 7. Experimental ambient volatility of TEPO at 614 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 8. Experimental Dew Point Temperatures
at a Water Partial Pressure of 852 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-15.0	0.13	5.3	0.055	889	0.958	1.013
-5.0	0.41	6.6	0.150	976	0.873	1.023
5.0	1.17	9.4	0.324	1181	0.721	1.046
10.0	1.91	13.3	0.365	1530	0.557	0.922
15.0	3.04	15.3	0.487	1735	0.491	0.978
20.0	4.75	18.8	0.554	2173	0.392	0.946
30.0	11.03	25.8	0.709	3312	0.257	0.966
40.0	23.98	32.9	0.860	5017	0.170	1.030

Notes: Water saturator flow rate was 100 sccm at 15.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was 4.67 °C.

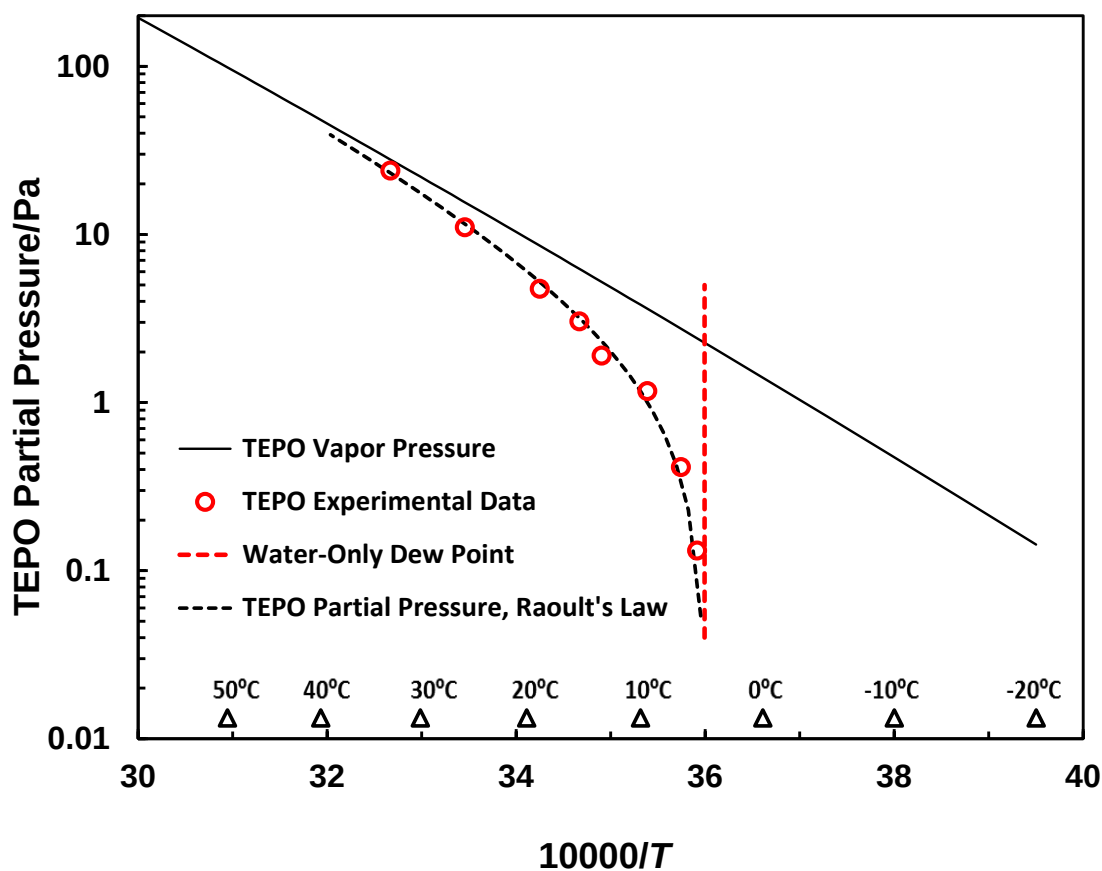


Figure 8. Experimental ambient volatility of TEPO at 852 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 9. Experimental Dew Point Temperatures
at a Water Partial Pressure of 1061 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-25.0	0.06	8.5	0.017	1109	0.957	0.974
-15.0	0.20	8.5	0.060	1109	0.957	1.017
-5.0	0.62	10.0	0.163	1223	0.868	1.031
5.0	1.76	13.8	0.324	1572	0.675	0.999
15.0	4.56	19.1	0.517	2215	0.479	0.996
25.0	10.95	25.8	0.704	3312	0.320	1.025
37.0	28.67	35.0	0.876	5626	0.189	1.064

Notes: Water saturator flow rate was 51 sccm at 30.0 °C. TEPO saturator flow rate was 153 sccm. The water-only dew point of this mixture was 7.85 °C.

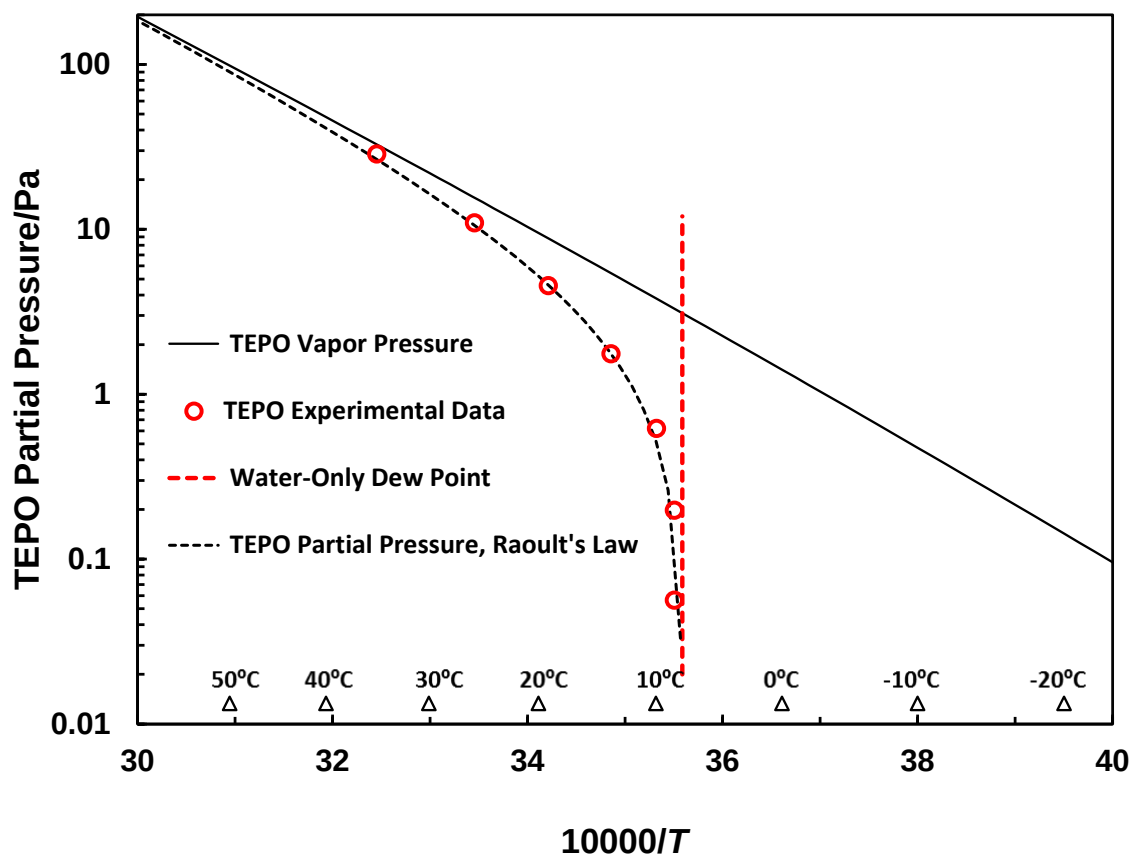


Figure 9. Experimental ambient volatility of TEPO at 1061 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 10. Experimental Dew Point Temperatures
at a Water Partial Pressure of 1169 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-10.0	0.24	9.6	0.064	1198	0.975	1.040
0.3	0.73	11.9	0.159	1393	0.839	0.998
5.0	1.17	13.6	0.220	1551	0.753	0.973
15.0	3.04	17.1	0.413	1950	0.599	1.012
21.2	5.28	20.4	0.538	2388	0.489	1.028
30.0	11.03	26.3	0.675	3430	0.341	1.016
37.0	19.11	31.0	0.801	4490	0.260	1.061

Notes: Water saturator flow rate was 100 sccm at 20.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was 9.3 °C.

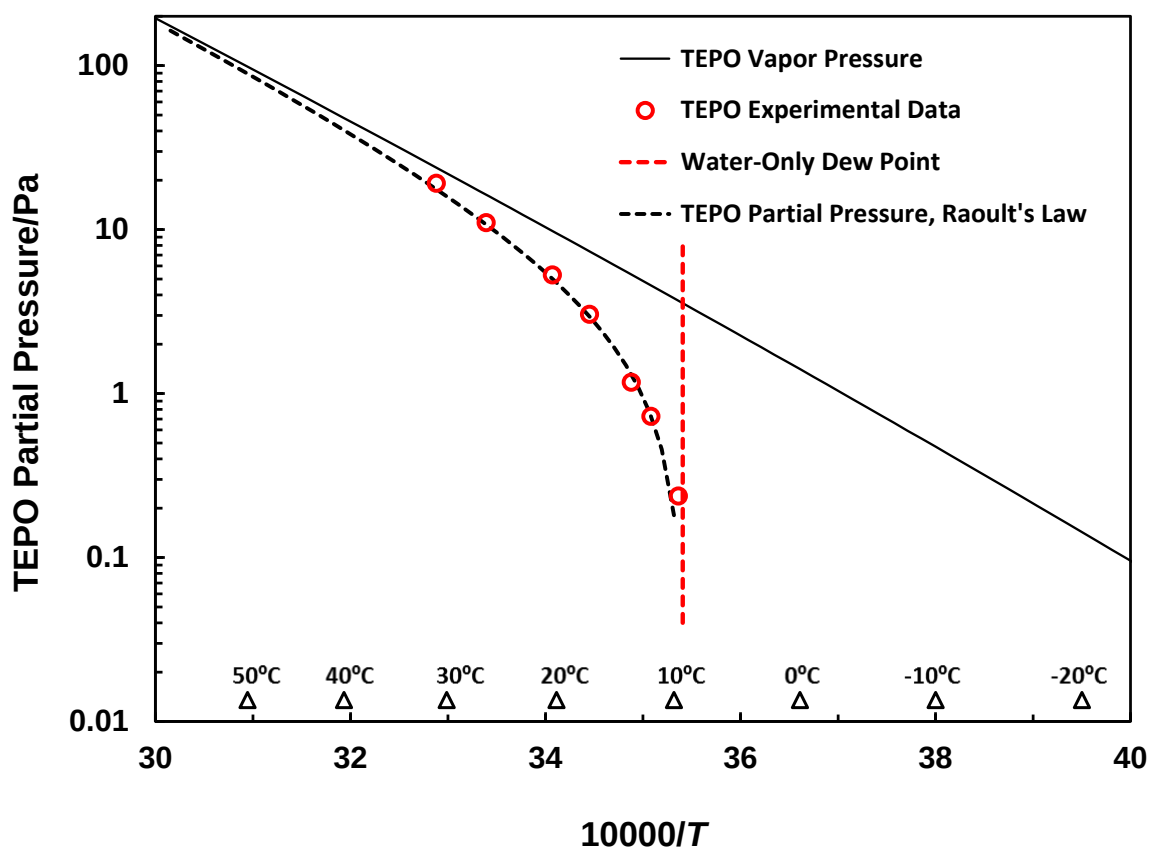


Figure 10. Experimental ambient volatility of TEPO at 1169 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 11. Experimental Dew Point Temperatures
at a Water Partial Pressure of 1584 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
0.0	0.70	14.7	0.121	1668	0.961	1.082
5.0	1.17	16.0	0.176	1817	0.870	1.046
10.0	1.91	17.5	0.246	2001	0.782	1.028
20.0	4.76	21.2	0.449	2509	0.628	1.077
30.0	11.03	27.2	0.618	3616	0.434	1.052
37.0	19.11	32.0	0.727	4747	0.329	1.056

Notes: Water saturator flow rate was 100 sccm at 25.0 °C. TEPO saturator flow rate was 100 sccm. The water-only dew point of this mixture was 13.9 °C.

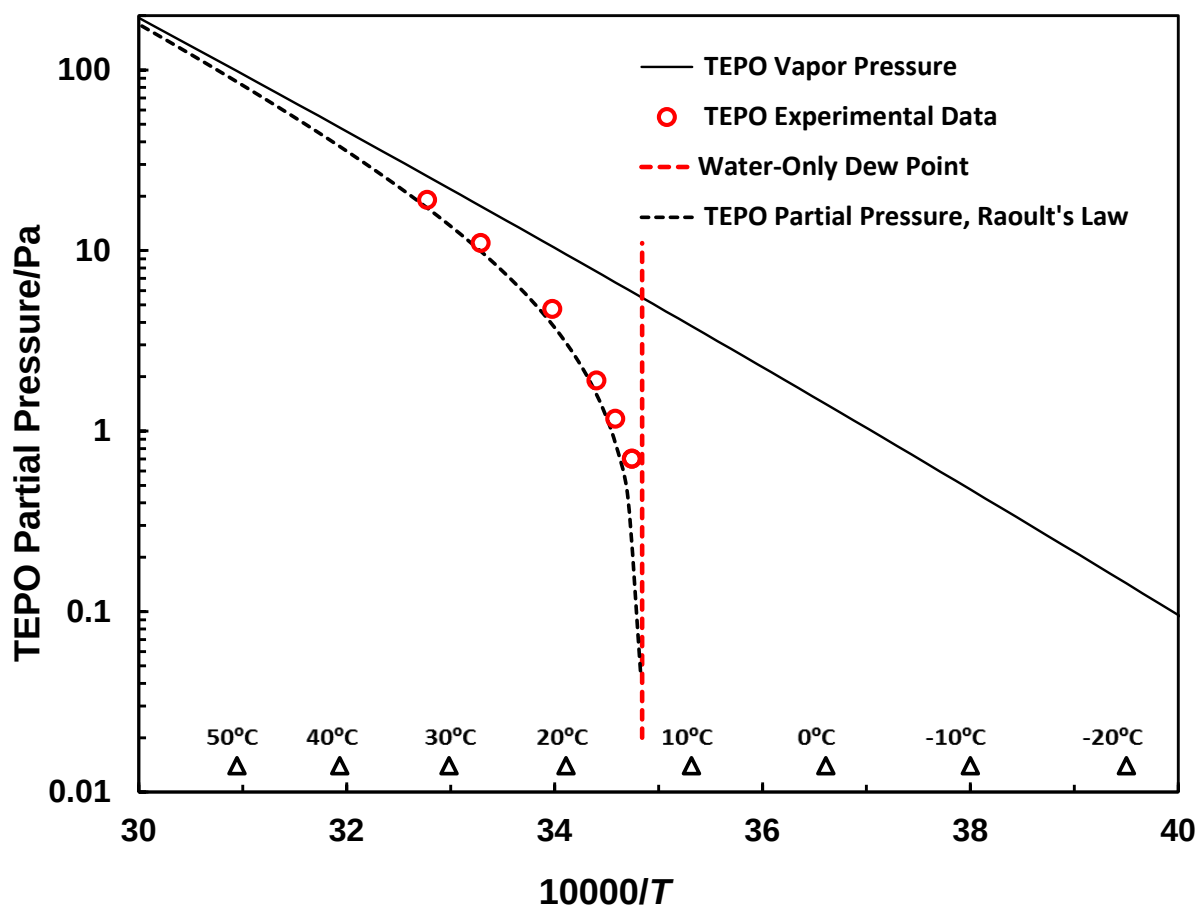


Figure 11. Experimental ambient volatility of TEPO at 1584 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 12. Experimental Dew Point Temperatures
at a Water Partial Pressure of 1754 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
0.0	0.35	15.8	0.054	1793	0.978	1.032
10.0	0.95	16.2	0.140	1840	0.953	1.093
20.0	2.37	18.7	0.279	2160	0.812	1.091
30.0	5.50	23.1	0.444	2818	0.622	1.067
35.0	8.18	25.6	0.530	3292	0.533	1.063

Notes: Water saturator flow rate was 150.4 sccm at 20.0 °C. TEPO saturator flow rate was 50 sccm. The water-only dew point of this mixture was 15.5 °C.

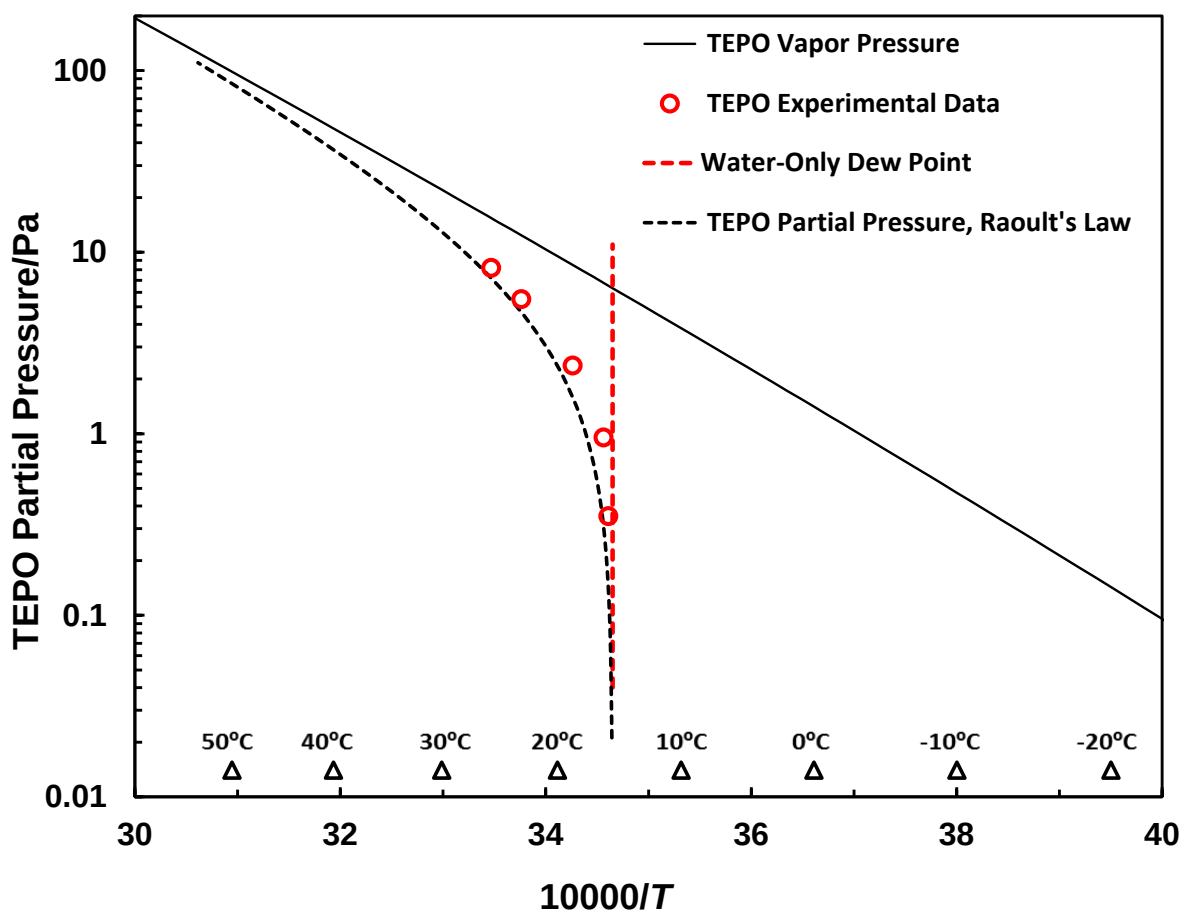
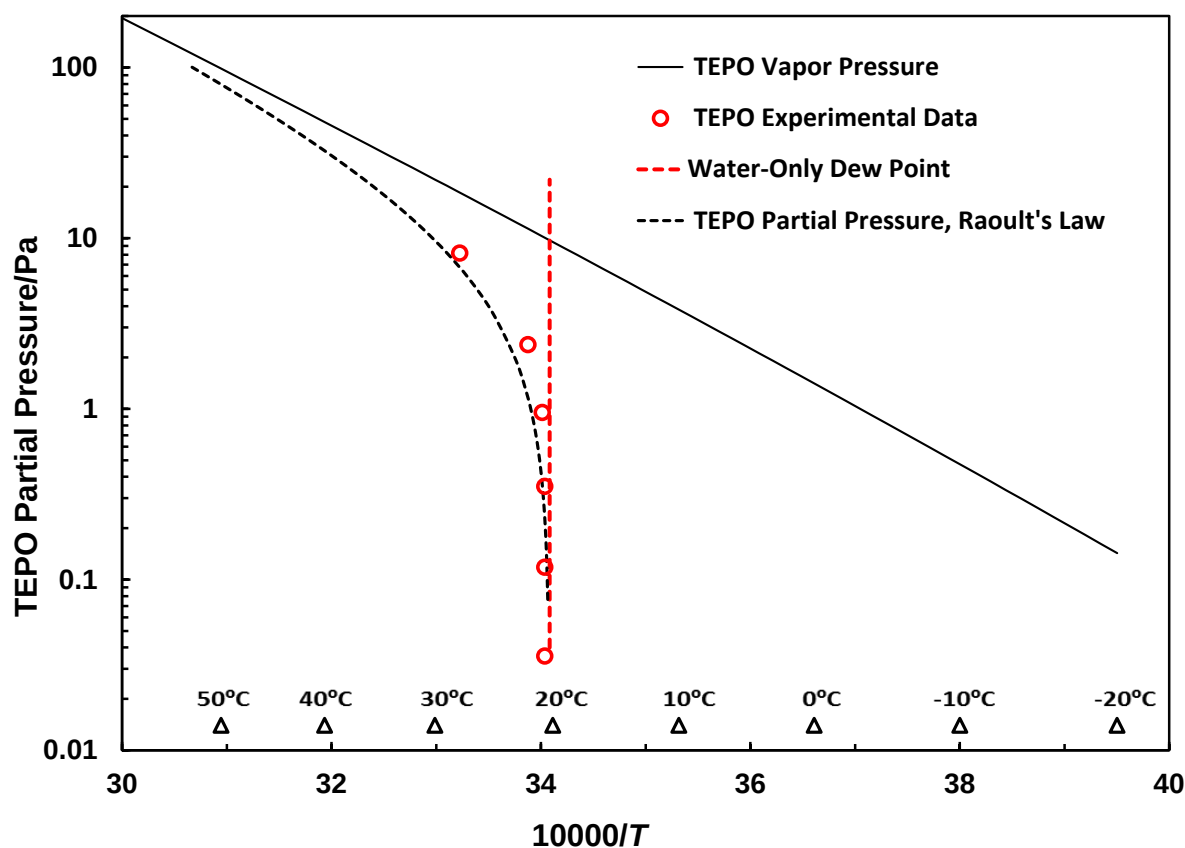


Figure 12. Experimental ambient volatility of TEPO at 1754 Pa water partial pressure, water-only dew point, and Raoult's law curve.

Table 13. Experimental Dew Point Temperatures
at a Water Partial Pressure of 2377 Pa

TEPO Saturator Temperature (°C)	TEPO Ambient Volatility (Pa)	Experimental Dew Point (°C)	TEPO Relative Pressure	Water Vapor Pressure at Dew Point (Pa)	Water Relative Pressure	Total Relative Pressure
-20.0	0.04	20.6	0.0035	2433	0.977	0.981
-10.0	0.12	20.6	0.0117	2433	0.977	0.989
0.0	0.35	20.6	0.0349	2433	0.977	1.012
10.0	0.95	20.8	0.0929	2463	0.965	1.058
20.0	2.37	22.0	0.2088	2651	0.897	1.105
35.0	8.18	27.8	0.4424	3743	0.635	1.077

Notes: Water saturator flow rate was 150.4 sccm at 25.0 °C. TEPO saturator flow rate was 50 sccm. The water-only dew point of this mixture was 20.3 °C.



As discussed herein, the TEPO–water data agreed well with the predictions that were based on Raoult’s law. Deviations from Raoult’s law, otherwise known as nonideal behavior in the VLE data, are often described through the use of activity coefficients. However, a model that can capture any nonideal behavior may provide a better fit to the experimental data. Equation 2, known as the modified Raoult’s law, assumes ideal gas phase behavior; it is written for each condensable component, where the activity coefficient, γ_i , is used to describe nonideal liquid behavior

$$P_i = \gamma_i x_i P_i^{\text{sat}} \quad (2)$$

Activity coefficients are a function of the vapor composition and temperature. In the saturation limit (i.e., as x_i approaches unity), the activity coefficient approaches unity.

One VLE model for binary systems is the two-suffix Margules equation, eqs 3 and 4, with one adjustable parameter, A .

$$R T \ln \gamma_1 = (A) x_2^2 \quad (3)$$

$$R T \ln \gamma_2 = (A) x_1^2 \quad (4)$$

where R is the ideal gas constant and T is temperature (Kelvin).

A more widely used VLE model for binary systems is the three-suffix Margules equation, eqs 5–6, with two adjustable parameters, A and B .

$$R T \ln \gamma_1 = (A + 3B) x_2^2 - 4B x_2^3 \quad (5)$$

$$R T \ln \gamma_2 = (A - 3B) x_1^2 + 4B x_1^3 \quad (6)$$

If $A = B = 0$, both γ values revert to unity, and these equations simplify to Raoult’s law.

The latter two models are only strictly correct for isothermal systems; however, the temperature dependence of the parameters is known to be small. A more accurate model, which does account for a temperature dependence of the model parameters, is the nonrandom two-liquid (NRTL) model described by eqs 7–10.⁶

$$\tau_1 = \left(\frac{A}{RT} \right) \quad ; \quad \tau_2 = \left(\frac{B}{RT} \right) \quad (7)$$

$$\ln G_1 = -\alpha \tau_1 \quad ; \quad \ln G_2 = -\alpha \tau_2 \quad (8)$$

$$R T \ln \gamma_1 = x_2^2 \left[\tau_2 \left(\frac{G_2}{x_1 + x_2 G_2} \right)^2 + \left(\frac{\tau_1 G_1}{(x_2 + x_1 G_1)^2} \right) \right] \quad (9)$$

$$R T \ln \gamma_2 = x_1^2 \left[\tau_1 \left(\frac{G_1}{x_2 + x_1 G_1} \right)^2 + \left(\frac{\tau_2 G_2}{(x_1 + x_2 G_2)^2} \right) \right] \quad (10)$$

where α is a fit parameter, τ is defined in eq 7, and G is the system free energy.

The TEPO–water ambient volatility data can be fit to these models, where the dew point temperature is used to calculate the saturation partial pressures. The computation would start with an initial estimate for A and B ; then using the identity in eq 11,

$$x_{\text{TEPO}} + x_{\text{H}_2\text{O}} = 1 \quad (11)$$

a set of liquid-phase mole fractions that satisfy eqs 3 and 4, 5 and 6, or 7–10 can be determined in an inner-computation loop. Using these mole fractions, another nonlinear minimization is performed in an outer loop on the residual of data and predicted partial pressures to optimize the parameters. A linear residual (eq 12) weights the higher partial pressures more, and a logarithmic residual (eq 13) weights all of the partial pressures more equally.

$$\text{Residual} = \sum (P_{\text{TEPO,data}} - P_{\text{TEPO,model}})^2 \quad (12)$$

$$\text{Residual} = \sum \text{abs} \left[\ln \left(\frac{P_{\text{TEPO,data}}}{P_{\text{TEPO,model}}} \right) \right] \quad (13)$$

where abs denotes absolute value. The logarithmic residual in eq 13 was selected for our computations.

A global optimization for all the data using the activity coefficient models described herein yields the residual errors for the 77 data points and the parameters as listed in Table 14. There is only a modest reduction in the residual with either form of the Margules model relative to Raoult’s law. The addition of a third parameter in the NRTL model improves the fit by about 20% as compared with Raoult’s law. Given that the data does not dramatically improve the fit versus Raoult’s law, the fact that the data exhibits ideal mixing behavior is confirmed, which is consistent with reported observation that TEPO and water are miscible.

Table 14. TEPO and Water VLE Correlation Parameters from the Data in this Report

Model	A/R	B/R	α	Residual (eq 13)
Raoult’s law	0	0	NA	7.94
Two-Suffix Margules	46.9	NA	NA	7.69
Three-Suffix Margules	22	–81	NA	7.27
NRTL	18.4	–4.1	–52.9	6.14

A/R and B/R are the parameters A and B from eqs 3–7 divided by the gas constant R ; α is the adjustable parameter in eq 8; and NA is not applicable.

4. DISCUSSION

The vapor pressures of water and TEPO are known, and their partial pressures in the mixtures studied here may be accurately determined, along with their relative pressures at the experimentally measured condensation temperatures. In the current work, the concentration of water vapor was fixed by maintaining a constant flow rate for each stream at water bath temperatures between 2 and 37 °C, while the temperature of the TEPO bath was varied between –25 and 40 °C. In doing so, we were able to vary the water partial pressure between 176 and 2377 Pa, which corresponded to water dew points between –15.98 and 20.85 °C. We assumed that the condensate contained both components and represented the condensation point for both. This assumption is reasonable, based on the high solubility of TEPO in water.⁷

The error corresponding to uncertainty in flowmeter measurements was ±3%. This relative error was linearly related to the error in the partial pressure of the chemical delivered to the system. The inverse of the dew point measurement was linearly related to the log of the measured partial pressure, as represented in the Antoine equation. These relationships are presented in eqs 14–15

$$\frac{dP}{P} = d \ln P = 0.03 = d \left[Ant_A - \frac{Ant_B}{Ant_C + T} \right] \quad (14)$$

$$d \left[Ant_A - \frac{Ant_B}{Ant_C + T} \right] = \frac{Ant_B}{(Ant_C + T)^2} dT = 0.03 \quad (15)$$

where Ant_A , Ant_B , and Ant_C are Antoine correlation equation coefficients.

Assuming a temperature of 298 K and using the Antoine parameters for water, the uncertainty in the dew point temperature measurement can be calculated to be ±0.5 °C.

The experimental data were plotted on standard vapor pressure plots with the limiting values. Specifically, the TEPO vapor pressure was plotted as a pure component at high temperatures, and the water-only dew point was plotted at low temperatures to demonstrate the effect of water at various partial pressures in the ambient range on TEPO volatility. In addition, we attempted to correlate the experimental ambient volatility of TEPO at the respective condensation temperature to an Antoine equation at each water partial pressure. The result of that effort was not as good as that obtained using the activity coefficient approach, which was largely due to the extreme curvature of the experimental data.

Figure 14 shows a plot of the TEPO ambient volatility data measured in this work at a water partial pressure of 584 Pa as compared with the TEPO vapor pressure, predicted ambient volatility of TEPO at a water vapor partial pressure of 584 Pa using the NRTL activity coefficient model, and the water-only dew point at 584 Pa water partial pressure (–0.62 °C). The NRTL activity coefficient curve in Figure 14 was indistinguishable from the Raoult's law curve in Figure 6. This was expected because of the small differences between activity coefficients and unity for TEPO and water vapor, as was observed in this work.

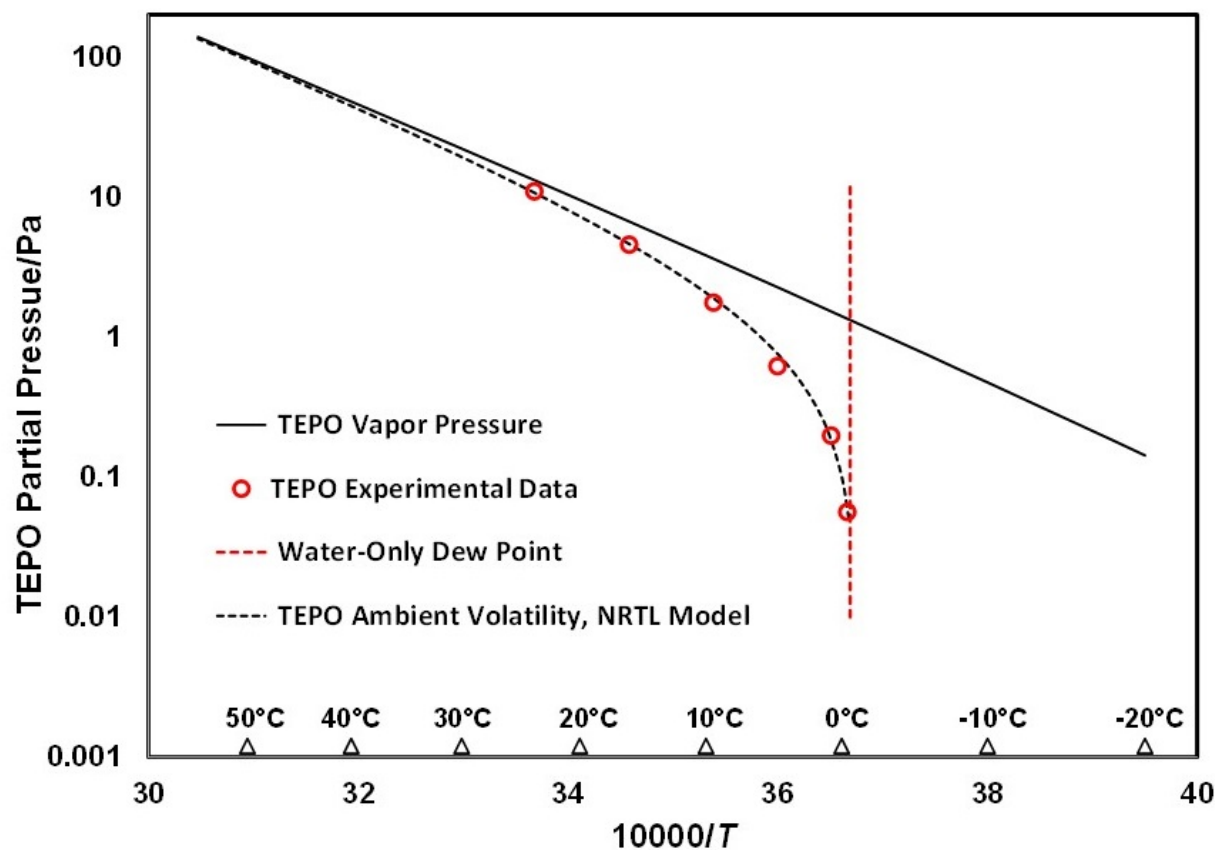


Figure 14. TEPO vapor pressure (—), experimental TEPO volatility at 584 Pa water partial pressure (○), water-only dew point at 584 Pa (- - -), and predicted volatility using the NRTL activity coefficient model (- - -).

Application of any of the models discussed in the report is limited by the fact that there are four independent variables and two equations to be solved. Therefore, two variables must be satisfied to find a solution. For example, if the partial pressure of water and the saturation temperature are specified, then the saturation pressures of water and TEPO would be calculated from the Antoine equation using the given temperature. If the Raoult's law model is used, the liquid-phase water mole fraction can then be calculated using eq 2, and the partial pressure of TEPO can be subsequently determined from that result.

If a model other than Raoult's law was chosen, one of the equations for activity coefficient would be solved using the parameters from Table 14, together with eq 2 for the liquid-phase mole fraction of water. This requires the solution of a nonlinear equation, which is best performed using a spreadsheet or programming algorithm. Using this resulting value of the water mole fraction, the TEPO mole fraction and activity coefficient can then be calculated and applied to eq 2 to yield the TEPO ambient volatility.

The model parameters and analyses discussed herein can be extended to other chemicals that have miscibility with water, such as DMMP⁸ or GD. However, GD may undergo hydrolysis, and therefore, may not have a strictly equilibrium relationship; only limited data exists for this system. The three nonideal models discussed herein, with activity coefficients written in terms of mole fractions, are limited to constant pressures, but all of the data reported herein were measured at atmospheric pressure. Systems that consider data over a range of liquid-phase pressures may be better described by a multicomponent equation of state. Extension of this approach to immiscible and partially miscible systems must be described by separate liquid–liquid equilibria models.

5. CONCLUSIONS

The ambient volatility of TEPO was determined in the presence of a wide range of water vapor partial pressures. The agreement between these experimental data and the predictions, which were based on Raoult's law and the activity coefficient calculations, was good for all cases tested, although some variation was observed. Water vapor suppression of TEPO volatility approached 2 orders of magnitude at the highest RH values investigated in this work.

Downwind CWA time–concentration profile estimates, which were based on the vapor pressure of a particular agent without regard for suppression by ambient water vapor, may over-estimate the rate of evaporation due to volatility suppression by ambient water vapor. Data such as those presented in this report for actual CWAs have the potential to improve those predictions significantly for agents that are subject to the limitations imposed by the presence of ambient humidity. The volatility suppression caused by the presence of ambient water vapor will depend on the chemical material under evaluation, and in some cases, may significantly retard secondary evaporation.

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ACRONYMS AND ABBREVIATIONS

<i>Ant_A</i> , <i>Ant_B</i> , and <i>Ant_C</i>	Antoine correlation equation coefficients
CAS	Chemical Abstracts Service
CWA	chemical warfare agent
DMMP	dimethyl methylphosphonate; CAS no. 756-79-6
GC	gas chromatography
GD	soman, pinacolyl methyl phosphonofluoridate; CAS no. 96-64-0
HD	bis-(2-chloroethyl) sulfide; CAS no. 505-60-2
NRTL model	nonrandom two-liquid model
<i>P</i>	vapor pressure, Pa
RH	relative humidity
<i>T</i>	temperature, Kelvin
TEPO	triethyl phosphate
VLE	vapor–liquid equilibrium

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