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Vapor Pressure of Trimethyl Phosphite and Triethylamine

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Ebulliometric measurements on the vapor pressure of trimethyl phosphite (29.2–70.3 °C) and triethylamine (28.6–64.5 °C) are reported. Antoine equation and a series-type equation represent most of the experimental data on trimethyl phosphite and triethylamine with a percent average absolute deviation of about 2.5 and 1.1, respectively.

Values of pure-component vapor pressure are needed for the design of separation processes such as distillation. Data on the vapor pressure of trimethyl phosphite and triethylamine, in particular, are useful in the design of a distillation setup for the separation of trimethyl phosphite from a mixture of benzene and triethylamine. A literature survey revealed that vapor pressure measurements on these substances are confined to (*a*) those of Kobe and Mathews (*1*), from 149 to 221 °C on trimethyl phosphite, and (b) those of Thompson and Linnett (*2*) in the range 12.4–64.4 °C, Hoy (*3*) in the range 25–89.5 °C, and Handa and Fenby (*4*) at 10 °C for triethylamine besides some normal boiling point data. Hence, the present study of vapor pressure measurements of trimethyl phosphite (29.2–70.3 °C) and triethylamine (28.6–64.5 °C) is undertaken.

Experimental Section

A modified form of Swietoslawski's ebulliometer, in which the internal nichrome heater of the reboiler is replaced by an external heating coil, is used for the present study. Fine glass pieces fused inside the heated wall of the reboiler serve as nuclei for the boiling process. The use of the external heater makes the apparatus suitable for work on corrosive fluids as well. A mercury manometer connected to the system and a vacuum pump attached through a 25-L buffer vessel (to dampen any pressure fluctuations) enable the measurement of pressures to a precision of 1 mmHg. A mercury-in-glass thermometer (0–150 °C range) calibrated against the boiling points of pure (99.9%) samples of benzene and toluene is used to measure temperatures to a precision of 0.1 °C. The temperatures recorded are values after applying appropriate corrections. About 130-mL liquid samples are charged to the ebulliometer and the vacuum is set at the desired level. The heater is switched on and the potential difference across the heater is adjusted slowly till the intensity of heating is controlled at a value which results in a steady drop rate of 25–30 drops per minute in accordance with the suggestions of Hala et al. (*5*). Equilibrium values of the temperature at all the desired pressures are recorded.

Samples

Trimethyl phosphite and triethylamine (98% purity) supplied by Merck Co., Germany, are fractionated in an 18-mm i.d. and 1-m high column packed with Fenske helices at a reflux ratio of 1:20. The middle cuts showing a single peak on a gas–liquid chromatogram are used in the experiments. Refractive index and density measurements of the samples used are compared with literature data in Table I.

Table I. Comparison of Refractive Index and Density with Literature Data

	refractive index at 20 °C		density at 20 °C, g/mL	
substance	sample used	lit. value	sample used	lit. value
trimethyl phosphite	1.4084	1.40836[a]	1.049	
triethylamine	1.4008	1.401[b]	0.7275	0.728[b]

[a] Reference *1*. [b] Dreisbach, R. R. "Physical Properties of Chemical Compounds"; American Chemical Society: Washington, DC, 1961; Vol. III.

Table II. Vapor Pressure of Trimethyl Phosphite[a]

			% deviation in using	
temp, °C	vapor press., mmHg	ref	Antoine eq	Angus et al. eq
29.2	30.0	this work	+1.59	−0.86
34.9	40.0	this work	−2.72	−3.94
34.9	41.0	this work	−2.15	−1.40
39.6	55.0	this work	3.54	+3.12
42.0	57.0	this work	−5.46	+5.63
44.9	71.0	this work	+1.90	+2.11
45.2	72.0	this work	+1.90	+2.04
49.9	88.0	this work	−6.36	−0.19
50.1	93.0	this work	+3.88	+4.32
51.9	101.0	this work	+3.80	+4.32
53.9	107.0	this work	+5.88	+1.16
56.0	119.0	this work	+1.90	+2.51
58.6	130.0	this work	−4.65	+0.18
59.9	138.0	this work	+1.39	+0.65
61.2	148.0	this work	+1.58	+2.21
61.9	152.0	this work	+1.36	+1.99
66.4	169.0	this work	−6.27	−5.67
68.7	185.0	this work	−6.13	−5.58
70.3	200.0	this work	−4.32	−3.38
111.2	755.7	*1*	+7.47	+0.22
111.0	760.0	*10*	+7.43	+2.83
overall % deviation			2.5	2.6

[a] $A = 5.5434$, $B = 63.5817$, $C = 12.6886$, $D = -5.1903$, $E = 6.7277$, $F = -9.1844$.

Results and Discussion

Observations on trimethyl phosphite and triethylamine are given in Tables II and III, respectively. Observations of this work as well as literature values (*6*) for each substance are fitted to equations in the form

$$\log P^\circ = A - B/(t + C) \quad (1)$$

$$\ln (P^\circ/P_c) = D[1 - (T_c/T)]^{0.5} + E[1 - (T_c/T)] + F[1 - (T_c/T)]^{1.5} \quad (2)$$

with P_c = 34.48 atm and T_c = 576.2 K for trimethyl phosphite and P_c = 30 atm and T_c = 535.15 K for triethylamine. Best values of A, B, and C (determined by employing the method described by Rose et al. (*7*) and tested by Naik et al. (*8*)), least-squares values of D, E, and F, and deviations defined as

percent deviation

$$e = 100[(P^\circ_{\text{obsd}} - P^\circ_{\text{calcd}}/P^\circ_{\text{obsd}}] \quad (3)$$

overall percent deviation

$$\bar{e} = \frac{\sum |e|}{N} \quad (4)$$

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Table III. Vapor Pressure of Triethylamine

temp, °C	vapor press., mmHg	ref	% deviation in using Antoine eq	Angus et al. eq
10.0	31.3	*4*	−4.44	−3.62
12.4	38.0	*2*	+2.75	+3.47
25.0	67.75	*3*	−0.14	+0.45
28.6	80.0	this work	+0.07	+0.54
31.2	90.0	this work	+0.25	+0.60
33.5	100.0	this work	+0.68	+1.00
35.0	106.0	this work	+0.01	+0.35
35.7	110.0	this work	+0.70	+1.02
38.2	120.0	this work	−1.26	−1.02
40.1	130.0	this work	−1.23	−0.93
42.1	140.0	this work	−2.13	−1.91
43.3	150.0	this work	−0.13	+0.02
44.8	160.0	this work	+0.22	+0.37
46.2	170.0	this work	+0.64	+0.74
47.7	180.0	this work	+0.37	+0.54
49.1	190.0	this work	+0.24	+0.32
49.8	195.0	this work	+0.08	+0.18
50.0	195.0	*6*	−0.70	−0.57
50.7	200.0	this work	−0.91	−0.77
55.0	237.5	*6*	−0.26	−0.28
56.6	247.0	*2*	−2.41	−2.45
60.0	289.5	*6*	+0.84	+0.85
60.5	282.0	*2*	−3.69	−3.75
64.4	328.0	*2*	−2.69	−2.76
65.0	350.0	*6*	+1.67	+1.65
65.4	350.0	this work	+0.26	+0.26
68.5	400.0	*6*	+0.26	+2.58
72.35	450.0	*6*	+1.13	+1.04
75.5	500.0	*6*	+0.99	+0.90
78.2	550.0	*6*	+1.53	+1.44
81.0	600.0	*6*	+1.05	+0.93
83.5	650.0	*6*	+0.99	+0.92
86.0	700.0	*6*	+0.44	+0.29
88.5	755.0	*6*	+0.16	+0.02
88.85	760.0	*6*	−0.27	+0.38
90.55	800.0	*6*	−0.40	−0.49
92.65	850.0	*6*	−0.77	−0.87
94.60	900.0	*6*	−0.97	−1.03
overall % deviation			1.1	1.1

[a] $A = 7.7001$, $B = 171.9269$, $C = 26.7943$, $D = 0.7455$, $E = -8.2501$, $F = 0.0997$.

Table IV. Comparison of Vapor Pressure Data of Triethylamine with Bittrich and Kauer (*6*)

vapor press., mmHg	temp, °C this work	ref *6*
195	49.8	50.0
350	65.4	65.0

are the other entries in Tables II and III. Table II shows that the deviations for trimethyl phosphite ranged between −6.4% and +7.5% in the case of the Antoine equation and −5.7% and +5.6% in the case of the Angus et al. equation. The corresponding values for triethylamine as reported in Table III are −4.4% and +2.8% and −3.8% and +2.6%. The results presented in Tables II, III, and IV indicate that (i) the experimental observations of this work are in fair agreement with literature data and (ii) vapor pressure measurements on both trimethyl phosphite and triethylamine can be approximately represented by the Antoine equation (eq 1) and the Angus et al. (*9*) equation (eq 2).

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Glossary

A, B, C	constants in eq 1
D, E, F	constants in eq 2
e	percent deviation defined by eq 3
$\bar{e}$	overall percent deviation defined by eq 4
N	number of data points
P°	vapor pressure, mmHg
P_c	critical pressure, mmHg
P°_{calcd}	calculated value of vapor pressure, mmHg
P°_{obsd}	observed value of vapor pressure, mmHg
T	temperature, K
T_c	critical temperature, K
t	temperature, °C
$\sum$	summation

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