Vapor Pressure–Boiling Point Measurements of Five Organic Substances by Twin Ebulliometry

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Vapor pressure–boiling point measurements are reported for propylene trimer, 1-nonanol, n-nonylphenol, benzyl benzoate, and α-bromonaphthalene from 100 to 900 mmHg. The twin ebulliometry method was selected for the measurements. Temperatures were measured to ± 0.01 °C and pressures to ± 0.3 mmHg. Deionized, degassed water was used as the reference substance. The data were fitted to the Antoine equation. For 1-nonanol the agreement with the Thermodynamics Research Center selected values is very good. The Antoine constants and the Clapeyron equation were used to calculate the enthalpy of vaporization at the normal boiling point.

As part of the program for the measurement of physical and thermodynamic properties of pure organic substances, vapor pressure data from 100 to 900 mmHg for propylene trimer, 1-nonanol, n-nonylphenol, benzyl benzoate, and α-bromonaphthalene were measured using the comparative ebulliometry technique (9). Literature data are available for 1-nonanol (4, 5, 7, 8) and α-bromonaphthalene (4, 8), but the data for α-bromonaphthalene are very old and unreliable.

Materials

(*a*) *Reference Substance Water.* Water was deionized and distilled over potassium permanganate and sodium hydroxide to give a conductivity less than $1.0 \ \mu\Omega^{-1}$. The effect of any impurity on the measured boiling point was within ± 0.01 °C.

(*b*) *Compounds Investigated.* 1-Nonanol, and α-bromonaphthalene were AR grade samples and were used without further purification. Propylene trimer, n-nonylphenol, and benzyl benzoate were lab grade reagents and were purified by fractional distillation in a 20 plate sieve column of 2.54 cm i.d. at a 5:1 reflux ratio. The sample purity was determined by the density measurements at 20 °C and by noting the difference between the boiling and condensing temperatures in the differential ebulliometer. A rough calculation of sample purity was made by using the following formula (2) based upon the elevation of boiling point in the presence of an impurity.

$$x_B = \Delta H_v(T_b - T_0)/RT_0^2 \qquad (1)$$

where x_B = mole fraction of the impurity; ΔH_v = enthalpy of vaporization calculated at $(T_b + T_0)/2$, cal mol^{-1}; T_0 = boiling point of the pure compound, K; $T_b - T_0$ = boiling point elevation, K; R = gas constant, 1.9871 cal K^{-1} mol^{-1}. The $(T_b - T_0)$ value

was taken as the difference between the boiling and the condensing temperatures. T_0 was calculated from the experimental vapor pressure data using the Antoine equation. ΔH_v value at $(T_b + T_0)/2$ was calculated using the Antoine constants and the Clapeyron equation assuming vapor phase ideality. In this manner, approximate purity of each sample was estimated and is reported in Table I along with the source, normal boiling point, and density at 20 °C. Table I also includes comparison of the physical properties with the available literature values.

Apparatus and Experimental Procedure

The apparatus was similar to the one used by Osborne and Douslin (6) and the Swietoslawski type differential ebulliometer formed the heart of the apparatus. Details of the apparatus and the experimental method used in the present investigation have been described elsewhere (3). The temperatures were measured to an accuracy of ± 0.01 °C with copper–constantan thermocouples and a Leeds and Northrup (L and N) type K-3 potentiometer capable of reading the voltage with a precision of 0.0001% or better. The thermocouples were calibrated against a L and N 25-Ω platinum resistance thermometer certified by the U.S. National Bureau of Standards and the temperatures were reproducible to at least 0.01 °C. Each thermocouple was placed in the ebulliometer thermowell containing silicone fluid for better thermal contact. The pressures were roughly measured in a long U-tube glass manometer 1500 mm high, 10 mm i.d., and 15 mm o.d. containing triple distilled mercury. Hence the maximum operating pressure in this apparatus was restricted to about 1400 mmHg. The correct operating pressure in the system was calculated at the boiling temperature of the reference substance water whose vapor pressure data were taken from the Thermodynamics Research Center Tables (7). The error of ± 0.01 °C in temperature measurement corresponds to a maximum error of ± 0.3 mmHg in the measured pressure. Each ebulliometer was provided with sample entry tube with a high vacuum stopcock and ground glass joint for charging the sample without contaminating it with air and moisture.

Results

The experimental temperature and pressure measurements for five substances are reported in Table II. Each set of data was regressed to the Antoine equation

$$\log P \text{ (mmHg)} = A - \frac{B}{C + t(\text{°C})} \qquad (2)$$

Table I. Source, Purity, and Physical Properties of Compounds Studied

Compound	Source	Approx purity [e]	Nbp, °C		d_4^{20}, g cm^{-3}	
			Present	Lit.	Present	Lit.
Propylene trimer	LR [a]	99.6	136.96	—	—	—
1-Nonanol	AR [b]	99.8	213.17	213.3 (5)	0.8281	0.828 (1)
n-Nonylphenol	LR [a]	99.8	317.61	—	—	—
Benzyl benzoate	LR [c]	99.6	323.24	323.5 (1)	1.1208	1.12 (1)
α-Bromonaphthalene	AR [d]	99.9	280.66	281.1 (4, 8)	1.4830	1.482 (1)

[a] Aniline Dyestuffs, Bombay, India. [b] Aldrich, Wisc. [c] S. H. Kelkar, Bombay, India. [d] Hungary. [e] See text.

Table II. Experimental Vapor Pressure–Boiling Point Data

Propylene trimer		1-Nonanol		n-Nonylphenol		Benzyl benzoate		α-Bromonaphthalene	
t, °C	P, mmHg	t, °C	P, mmHg	t, °C	P, mmHg	t, °C	P, mmHg	t, °C	P, mmHg
57.82	158.79	152.15	95.11	214.78	49.18	224.70	76.66	196.27	140.12
64.65	191.99	170.20	190.14	251.33	150.00	229.52	88.42	213.14	211.56
72.02	233.12	181.03	278.62	261.87	200.11	251.64	162.59	228.08	294.29
77.04	262.67	187.49	345.85	274.76	279.40	263.98	220.54	234.45	335.58
81.01	287.95	194.80	437.56	283.74	350.00	273.42	274.58	244.51	408.81
85.42	317.36	203.95	580.19	289.28	400.26	276.54	295.09	245.13	413.66
96.75	398.90	207.76	649.89	298.78	499.96	278.31	306.76	250.71	458.98
105.34	467.73	213.44	764.68	303.76	561.59	279.93	318.21	256.24	506.85
116.76	566.91	213.97	776.52	307.72	612.26	285.79	360.51	262.78	568.24
126.31	656.87	217.73	864.74	310.82	655.87	295.05	439.68	275.35	698.69
133.04	721.44	221.35	956.44	314.17	707.09	305.60	543.72	279.49	746.39
135.94	750.24			317.10	751.34	316.13	666.88	281.40	768.62
139.07	781.06			321.81	829.98	320.01	716.10	284.04	800.59
147.44	866.96					325.25	788.48	285.93	824.04
						329.09	845.59		

Table III. Antoine Constants and Derived Quantities

Compound	Antoine constants			t_{760}, °C	ΔH_v at t_{760}, kcal mol^{-1}	Std dev	
	A	B	C			$\sigma(t)$	$\sigma(P)$
Propylene trimer	4.28106	338.76	104.97	136.96	4.4	0.08	0.78
1-Nonanol	7.60022	1793.77	166.91	213.17	13.4	0.02	0.57
n-Nonylphenol	7.74950	2550.67	206.28	317.61	14.8	0.05	0.58
Benzyl benzoate	6.42726	1594.49	126.36	323.24	12.8	0.08	0.66
α-Bromonaphthalene	5.38175	929.64	91.06	280.66	9.4	0.02	0.18

by the least-squares regression analysis using an IBM 7044 computer. The Antoine constants and the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(v_g - v_l)} \simeq \frac{\Delta H_v P}{RT^2} \tag{3}$$

were used to compute the enthalpy of vaporization at the normal boiling point. Table III reports the derived values for these compounds along with the standard deviation, σ in temperature and pressure defined as $[\sum_N \Delta D^2 / N]^{1/2}$. Here ΔD is the difference in the experimental and calculated value and N is the total number of measurements for each compound.

The present vapor pressure–boiling point data for 1-nonanol are in excellent agreement with recent literature values (5, 7). No experimental ΔH_v data at the normal boiling point are available in the literature for comparison with the present calculated values.

Literature Cited

(1) Dean, J. A., "Lange's Handbook of Chemistry", 11th ed, McGraw-Hill, New York, N.Y., 1973.
(2) Denbigh, K., "The Principles of Chemical Equilibrium", Cambridge, 1964.
(3) Hon, H. C., M. Tech. Thesis, Indian Institute of Technology, Kanpur, India, 1972.
(4) Jordan, T. E., "Vapor Pressure of Organic Compounds", Interscience, New York, N.Y., 1954.
(5) Kemme, H. R., Kreps, H. S., J. Chem. Eng. Data, 14, 98 (1969).
(6) Osborne, A. G., Douslin, D. R., J. Chem. Eng. Data, 11, 502 (1966).
(7) "Selected Values of Properties of Chemical Compounds", Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Tex. (loose leaf data sheets, extant 1975).
(8) Stull, D. R., Ind. Eng. Chem., 39, 517 (1947).
(9) Swietoslawski, W., "Ebulliometric Measurements", Reinhold, New York, N.Y., 1945.