3326 © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 3326—3328 (1988) [Vol. 61, No. 9

Vapor Pressures of Diethyl, Diisopropyl, and Dibutyl Phthalates at Reduced Pressures

Hirotake KATAYAMA
Department of Mechanical Engineering, College of Engineering, Hosei University,
Kajino-cho, Koganei, Tokyo 184
(Received January 26, 1988)

Synopsis. Vapor pressures of the three phthalates noted above were measured over the ranges 0.3—30, 0.3—10, and 0.3—9 kPa, respectively. The correlations of vapor pressures using the Cragoe equation with 4 constants give the percent root mean square deviations of 0.21, 0.33, and 0.28, respectively.

Few experimental data of vapor pressure for dialkyl phthalates have been published. Their accuracies are not good. Accordingly the vapor pressures of diethyl, diisopropyl, and dibutyl phthalates were measured over the ranges 0.3—30, 0.3—10, and 0.3—9 kPa, respectively. The results were checked by the Chebyshev polynomial[1] and the Cragoe,[2] Frost-Kalkwarf,[3] and Antoine[4] equations. The enthalpies of vaporization for the phthalates were also obtained from the slopes of the vapor pressure against the temperature (dP/dt).

Experimental

Special grade materials from Tokyo Kasei Co., Ltd., were used without further purification. The purity of each was determined by gas chromatographic analyses with a 3 mm I.D. and 2 m length column of 5% Silicone SE-52 on Celite. In all cases it exceeded 99%.

Table 1 shows the densities and refractive indices compared with published values.[5-8]

The experimental apparatus and procedure have already been described elsewhere.[9-11] The part of the equilibrium still unit with the Cottrell pump, which was of the vapor circulation type, was made of Pyrex glass. The measurement and the control of pressure were carried out with the Multi-Range Model 157/100 pressure standard from Texas Instruments Inc., which had a spiral quartz Bourdon guage and a servo controlled valve in a vacuum line. The accuracy of the gauge was ±0.002 kPa for 10—34 kPa range and ±0.001 kPa for 0.24—10 kPa. The variation of the pressure control on the operation was read from the attached deviation meter. It was found to be within ±0.00003 kPa for the 1—34 kPa, and within ±0.0004 kPa for the 0.3—1 kPa.

Four mercury thermometers with immersion lines marked at the 18 cm points from their bulb ends, i.e., the set of 40—100, 100—150, 150—200, and 200—250 °C graduations, were used for temperature measurements. They were calibrated at 5 °C intervals with accuracies of ±0.04 K by Watanabe Keiki Seisakusho Co., Ltd., Tokyo. The intermediate temperatures in the intervals were interpolated. After the circulation of vapor for one hour, no fluctuations of the thermometers were observed greater than 0.02 K.

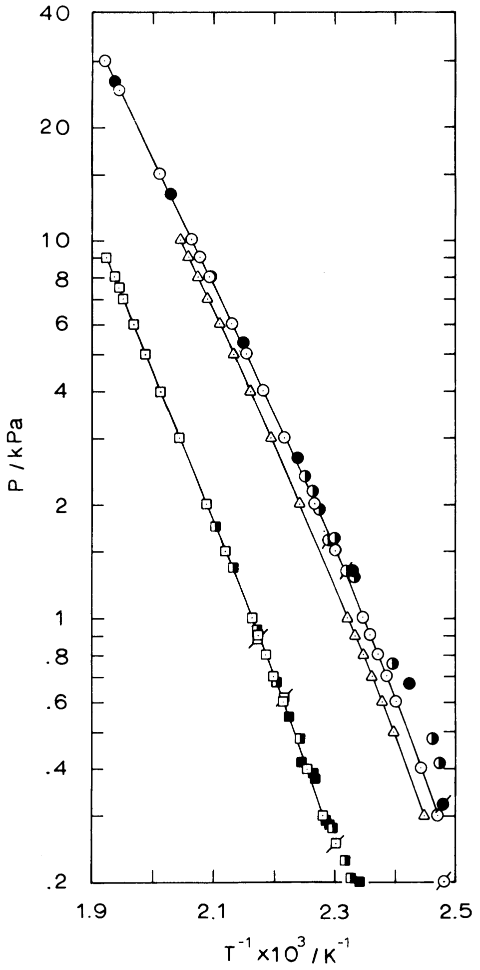

Fig. 1. Vapor pressures of three phthalates vs. T^{-1}. ○, △, □: diethyl, diisopropyl and dibutyl phthalates, respectively, in this work. Diethyl phthalate (◑: Ishii and Nakayama,[12] ●: Stull,[13] Ø: Matsuda and Kikkawa,[5] ◑: Wegscheider and Amann,[14] ●: Hickman[15]). Dibutyl phthalate (◧: Hammer and Lydersen,[16] ■: Gardner and Brewer,[17] □: Bonhorst et al.[18]).

Table 1. Densities ρ and Refractive Indices n_D of Three Phthalates

	T/K	ρ/g cm^{-3} Exptl	ρ/g cm^{-3} Lit	T/K	n_D Exptl	n_D Lit
Diethyl phthalate	293.15	1.11881	1.1185[5]	287.45	1.50459	1.50490[6]
Diisopropyl phthalate	293.15	1.06286		293.15	1.49042	1.4900[7]
Dibutyl phthalate	293.15	1.04633	1.0474[5]	298.15	1.49122	1.4907[8]

Table 2. Vapor Pressure of Three Phthalates

Diethyl phthalate			Diisopropyl phthalate			Dibutyl phthalate		
P/kPa	T/K	ΔH_v kJ mol^{-1}	P/kPa	T/K	ΔH_v kJ mol^{-1}	P/kPa	T/K	ΔH_v kJ mol^{-1}
30.000	520.81		10.000	489.00		9.000	520.09	
25.000	514.37		9.000	485.79		8.000	516.56	
15.000	497.17	63.3	8.000	482.27	66.4	7.500	514.74	
10.000	484.51	63.8	7.000	478.57	66.6	7.000	512.58	74.9
9.000	481.27	64.0	6.000	474.24	66.9	6.000	508.05	74.9
8.000	477.77	64.2	5.000	469.21	67.3	5.000	502.90	75.0
6.000	469.48	65.0	4.000	463.05	67.9	4.000	496.96	75.4
5.000	464.33	65.6	3.000	455.75	69.0	3.000	489.23	75.9
4.000	458.47	66.5	2.000	445.96	70.8	2.000	478.88	77.2
3.000	450.99	67.8	1.000	430.78	74.8	1.500	471.77	78.3
2.000	441.25	70.0	0.900	428.68	75.5	1.000	462.59	80.4
1.500	434.75	71.8	0.800	426.30	76.3	0.900	460.35	81.0
1.000	426.30	74.6	0.700	423.57	77.3	0.800	457.76	81.7
0.900	424.15	75.4	0.600	420.60	78.4	0.700	454.90	82.5
0.800	412.92	76.3	0.500	417.22	79.8	0.600	451.75	83.6
0.700	419.33	77.4	0.300	408.54	84.0	0.400	443.75	
0.600	416.52	78.7				0.300	438.55	
0.400	409.27							
0.300	404.53							

Results and Discussion

The experimental results are presented in Table 2. The results are also plotted in Fig. 1 including a comparison with values from the literature.[5,12–18]

The Chebyshev polynomial,[1] and the Cragoe,[2] Frost-Kalkwarf,[3] and Antoine[4] equations were used to fit the results.

The Chebyshev polynomial is :

$$t\ln(P) = a_0/2 + \textstyle\sum a_i E_i(X). \tag{1}$$

where P kPa, $t(=T-273.15)$°C, T K, $E_1(x)=x$, $E_2(x)=2x^2-1$, $E_i(x)=2xE_{i-1}(x)-E_{i-2}(x)$, and x is a function of temperature defined as

$$x = \frac{2T-(T_{\max}+T_{\min})}{T_{\max}+T_{\min}} \tag{2}$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures of the related substances, respectively. The polynomial with 4 parameters is identical to the Cragoe equation.

The Cragoe equation is:

$$\ln(P) = A_c + B_c/t + C_c t + D_c t^2 \tag{3}$$

or

$$t\ln(P) = A_c t + B_c + C_c t^2 + D_c t^3. \tag{4}$$

The Frost-Kalkwarf equation is:

$$\ln(P) = A_f + B_f/t + C_f \ln t + D_f P/t^2 \tag{5}$$

or

$$t\ln(P) = A_f t + B_f + C_f t\ln t + D_f P/t. \tag{6}$$

The Antoine equation is:

$$\ln(P) = A_a - B_a/(t+C_a) \tag{7}$$

or

$$t\ln(P) = A_a t + D_a - C_a \ln(P) \tag{8}$$

where $D_a=A_aC_a-B_a$.

All the constants of the expressions mentioned above were determined by least-square fits of $t\ln(P)$.

The percent root mean square deviations of pressure (prms) using Cragoe, Frost-Kalkwarf, and Antoine equations were estimated as 0.21, 0.21, and 1.25 for diethyl phthalate, respectively; 0.33, 0.33, and 1.88 for diisopropyl phthalate, respectively; and 0.28, 0.30, and 2.14 for dibutyl phthalate, respectively.

The prms using the Chebyshev polynomial for diethyl phthalate were taken as 0.33 with 3 parameters, 0.21 with 4 parameters, 0,20 with 5 parameters, 0.15 with 6 and 7 parameters, 0.14 with 8 and 9 parameters, and 0.11 with 10 parameters. The prms of diisopropyl phthalate were 0.34 with 3 parameters, 0.30 with 4 and 5 parameters, 0.24 with 6 parameters, 0.13 with 7 parameters, and 0.12 with 8—10 parameters. The prms of dibutyl phthalate were 0.37 with 3 parameters, 0.28 with 4 parameters, 0.26 with 5 and 6 parameters, 0.25 with 7 parameters, 0.18 with 8 parameters, and 0.15 with 9 and 10 parameters.

Conversely the temperatures were calculated from the pressures by using the Cragoe, Frost-Kalkwarf, and Antoine equations. The mean temperature differences of the Cragoe, Frost-Kalkwarf, and Antoine equations with the experimental values were taken as 0.04, 0.04, and 0.28 K for diethyl phthalate, respectively; 0.07, 0.06, and 0.32 K for diisopropyl phthalate, respectively; and 0.06, 0.06, and 0.46 K for dibutyl phthalate, respectively.

The constants of the Cragoe and Frost-Kalkwarf equations are listed in Table 3. The constants of the Antoine equation are not listed, because they give large errors. Those of the Chebyshev polynomial are omitted, because the polynomial with 4 parameters gives satisfactory fits.

The enthalpies of vaporization, ΔH_v, were calculated from the Clapeyron equation via the slopes of the

Table 3. Constants of Cragoe and Frost-Kalkwarf Equations

	Diethyl phthalate	Diisopropyl phthalate	Dibutyl phthalate
Constants of Cragoe equation			
A_c	4.55623	4.00826	7.50802
B_c	−903.1363	−892.0324	−1396.648
C_c	0.665139×10^{-2}	0.840047×10^{-2}	-0.769651×10^{-2}
D_c	0.137763×10^{-4}	0.131916×10^{-4}	0.368429×10^{-4}
prms[a)]	0.21	0.33	0.28
ΔT_m[b)]	0.04K	0.07K	0.06K
Constants of Frost-Kalkwarf equation			
A_f	−14.06478	−14.61002	−13.51560
B_f	−596.764	−606.515	−920.178
C_f	3.56600	3.64239	3.49727
D_f	452.28	687.37	1178.09
prms[a)]	0.21	0.33	0.30
ΔT_m[b)]	0.04K	0.06K	0.06K

a) Percent root mean square deviation defined by $100[\sum_i(P_{\mathrm{exptl}}-P_{\mathrm{calcd}})/P_{\mathrm{exptl}})_i^2/n]^{1/2}$. n: number of data. b) Mean temperature difference defined by $\sum_i|T_{\mathrm{exptl}}-T_{\mathrm{calcd}}|_i/n$, K.

pressure against the temperature (dP/dt) using three expressions, the Chebyshev polynomial with 4 parameters (equivalent to the Cragoe equation), that with 5 parameters and the Frost-Kalkwarf equation. The ΔH_v values, of which the differences at their respective temperatures was less than 0.2 kJ mol^{-1}, are only listed in Table 2.

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