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Vapor Pressures of Morpholine, Diethyl Methylmalonate, and Five Glycol Ethers at Temperatures up to 473.15 K

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Vapor pressures were measured for seven polar organic compounds including morpholine, diethyl methylmalonate, diethylene glycol diethyl ether, diethylene glycol hexyl ether, diethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, and diethylene glycol monoethyl ether acetate at temperatures ranging from 308.15 K to 473.15 K. The measured vapor pressures of morpholine, 2-methoxyphenol, and *tert*-butyl alcohol agree reasonably well with literature values. The Antoine equation correlates the vapor pressure data to AADs of 0.28 % to 0.50 % for the investigated substances.

Introduction

Vapor pressure data are fundamentally important in phase equilibrium calculations and some other engineering applications. The present study measures the vapor pressures for seven polar organic compounds, including morpholine, diethyl methylmalonate, diethylene glycol diethyl ether, diethylene glycol hexyl ether, diethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, and diethylene glycol monoethyl ether acetate. Among these substances, morpholine is a corrosion inhibitor and an important intermediate for textile lubricants, softening agents, dyes, and catalysts. Diethyl methylmalonate is used as an intermediate for pharmaceuticals. The glycol ethers are widely used in the semiconductor industry to strip photoresist materials and can be used for glass cleaning and to remove flux, solder paste, oils, grease, etc. For the substances listed above, some vapor pressure data are available in the literatures, which are Wu et al.[1] (morpholine, 346.188 K to 401.563 K), Palczewska-Tulinska et al.[2] (morpholine, 317.676 K to 401.991 K), Verevkin[3] (morpholine, 273.6 K to 303.5 K), Delzenne[4] (diethylene glycol diethtyl ether, 330.25 K to 460.95 K), Chylinski et al.[5] (diethylene glycol monohexyl ether, 402.96 K to 432.15 K), and Wilson et al.[6] (diethylene glycol monoethyl ether acetate, 484.6 K to 672.6 K). It appears that the data are still limited in the temperature range of 308.15 K to 473.15 K. In the present study, the vapor pressures of the above-mentioned compounds were thus measured over this temperature range. The experimental results are compared with literature, if available. The Antoine equation was applied to correlate the new data for each investigated substance.

Experimental Section

Chemicals. The chemicals used in the present study include morpholine (purity = 99+ mass %, Acros, USA; CAS Registry No. 110-91-8), diethyl methylmalonate (99+ mass %, Acros, USA; CAS Registry No. 609-08-5), diethylene glycol diethyl ether (99+ mass %, Acros, USA; CAS Registry No. 112-36-7), diethylene glycol hexyl ether (98+ mass %, Fluka, Swiss; CAS Registry No. 112-59-4), diethylene glycol dibutyl ether (98+ mass %, Acros, USA; CAS Registry No. 112-73-2), ethylene glycol monobutyl ether acetate (98+ mass %, Acros, USA; CAS Registry No. 112-07-2), and diethylene glycol monoethyl ether acetate (99+ mass %, Aldrich, USA; CAS Registry No. 112-15-2). All the compounds were degassed by heating and vacuum before used. The impurity was less than 1 % by chromatographic analysis for each chemical after degassing process.

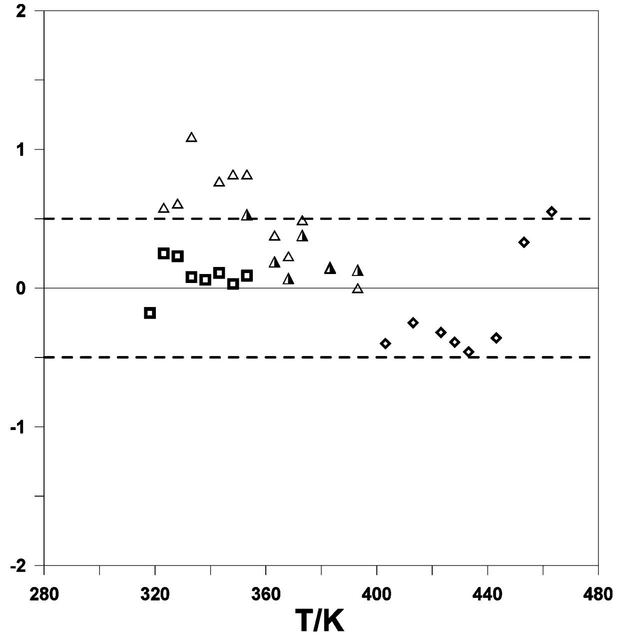

Figure 1. Comparison of vapor pressures measured from this study and those from literature values: ▲, morpholine;[1] △, morpholine;[2] ◇, 2-methoxyphenol;[8] □, *tert*-butyl alcohol.[9]

Apparatus and Procedure. A static vapor−liquid equilibrium apparatus was used in this study to measure the vapor pressures. The schematic diagram has been given by Hwang et al.[7] The degassed sample was transferred into a blind equilibrium cell, which was immersed in a thermostatic bath (model HT-250, stability = ± 0.03 K, Neslab, USA). The liquid phase was circulated by a liquid pump through vapor phase to promote the equilibration. After

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Table 1. Experimental Vapor Pressures and Calculated Deviations

T	P_{expt}	$\Delta P/P$	T	P_{expt}	$\Delta P/P$	T	P_{expt}	$\Delta P/P$
K	kPa	%[a]	K	kPa	%[a]	K	kPa	%[a]
morpholine			diethyl methylmalonate			diethylene glycol diethyl ether		
308.15	2.33	0.92	373.15	3.15	−0.56	363.15	2.61	1.38
313.15	3.13	−1.34	383.15	5.02	0.97	373.15	4.29	−1.18
323.15	5.17	−0.15	393.15	7.94	−0.55	383.15	6.69	−0.91
328.15	6.59	−0.18	403.15	11.84	0.46	393.15	10.08	0.25
333.15	8.28	0.35	413.15	17.40	−0.06	403.15	15.08	−0.12
343.15	12.93	−0.01	423.15	24.82	−0.27	413.15	22.08	−0.27
348.15	15.93	0.08	433.15	34.43	−0.10	423.15	31.51	0.19
353.15	19.49	0.15	443.15	46.74	0.07	428.15	37.58	−0.05
363.15	28.71	−0.13	453.15	62.44	−0.12	433.15	44.45	0.08
368.15	34.50	−0.22	458.15	71.52	0.01	438.15	52.47	0.03
373.15	41.04	0.12	463.15	81.75	−0.07	443.15	61.68	−0.01
383.15	57.60	−0.02	468.15	92.85	0.08	448.15	72.21	−0.01
393.15	79.04	0.05				453.15	84.21	0.01
diethylene glycol hexyl ether			diethylene glycol dibutyl ether			ethylene glycol monobutyl ether acetate		
413.15	1.97	0.04	403.15	2.50	−1.95	363.15	2.92	0.95
423.15	3.09	−1.20	413.15	3.61	0.40	373.15	4.57	−1.27
433.15	4.58	0.65	423.15	5.26	−0.38	383.15	6.72	0.48
443.15	6.79	0.14	433.15	7.39	0.80	393.15	9.96	−0.13
453.15	9.86	−0.52	443.15	10.43	−0.46	403.15	14.42	−0.18
458.15	11.71	−0.16	453.15	14.23	0.02	413.15	20.44	0.34
463.15	13.89	−0.11	458.15	16.61	−0.26	423.15	28.85	−0.15
468.15	16.36	0.19	463.15	19.19	0.09	428.15	33.94	0.04
473.15	19.26	0.12	468.15	22.18	0.05	433.15	39.87	0.08
			473.15	25.58	−0.09	438.15	46.80	−0.16
						443.15	54.64	−0.16
						448.15	63.48	0.02
						458.15	85.24	0.03
						463.15	98.36	0.02
			diethylene glycol monoethyl ether acetate					
			363.15	2.02	−2.10			
			373.15	2.95	−0.91			
			383.15	4.29	−0.80			
			393.15	6.04	0.62			
			403.15	8.53	0.19			
			413.15	11.91	−0.62			
			423.15	16.24	−0.42			
			433.15	21.85	−0.18			
			443.15	29.01	0.16			
			453.15	38.36	−0.22			
			463.15	49.87	0.01			
			468.15	56.75	−0.06			
			473.15	64.24	0.16			

[a] $\Delta P/P/\% = (P_{\mathrm{Antoine}} - P_{\mathrm{expt}}/P_{\mathrm{expt}}) \times 100\%$, where P_{Antoine} was calculated from the Antoine equation and P_{expt} is the experimental value.

the equilibrium state was attained, the temperature was measured by a precision thermometer (model 1560, Hart Scientific, USA) with a platinum RTD probe, and the pressure in the equilibrium cell was measured by a pressure transducer (model PDCR-330, 0 to 100.0 kPa, Druck, U.K.) together with a digital indicator (model DPI-262, Druck, U.K.). The uncertainty of the reported temperatures is about ± 0.02 K, and that of pressure is about ± 0.1 kPa.

Results and Discussion

Vapor pressures of morpholine, 2-methoxyphenol, and *tert*-butyl alcohol were determined experimentally in a temperature range from 308.15 K to 463.15 K for comparison purposes. Figure 1 shows the comparison of our measurements (P_{expt}) with the literature values[1,2,8,9] ($P_{\mathrm{literature}}$), where the deviation is defined as

$$\Delta P/P/\% = \left(\frac{P_{\mathrm{literature}} - P_{\mathrm{expt}}}{P_{\mathrm{expt}}}\right) \times 100\ \% \tag{1}$$

The experimental results agree with the literature values of Wu et al.[1] (morpholine), Boublik et al.[8] (2-methoxyphenol), and Brown et al.[9] (*tert*-butyl alcohol) to about within ± 0.5 %. Our vapor pressure data of morpholine are lower than the smooth values of Palczewska-Tulinska et al.[2] by about 0.5 % to 1.0 % at temperatures from 323.15 K to 353.15 K. The average absolute deviation (AAD) is 0.54 % over 323.15 K to 393.15 K for morpholine, in comparison with the smooth values of Palczewska-Tulinska et al.,[2] while the AAD is 0.24 % over 353.15 K to 393.15 K, in comparison with those of Wu et al.[1]

Table 1 lists the experimental results of morpholine, diethyl methylmalonate, diethylene glycol diethyl ether, diethylene glycol hexyl ether, diethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, and diethylene glycol monoethyl ether acetate. The vapor pressure data measured in the present study were correlated with the Antoine equation:

$$\ln(P/\mathrm{kPa}) = A - \frac{B}{T/\mathrm{K} + C} \tag{2}$$

where A, B, and C are the Antoine constants. The values of the Antoine constants were determined by minimizing

Table 2. Antoine Constants and Calculated Average Absolute Deviations

substance	A^a	B^a	C^a	AAD $\Delta P/P$ / %^{b}	temp range/K
tert-butanol	15.1536	2802.771	−89.425	0.12	313−353
2-methoxyphenol	13.6745	3378.850	−104.630	0.19	373−463
morpholine	14.5733	3384.26	−61.453	0.29	308−393
diethyl methylmalonate	12.8742	2742.831	−139.368	0.28	373−468
diethylene glycol diethyl ether	17.5759	5675.286	−21.321	0.35	363−453
diethylene glycol hexyl ether	15.1386	4633.638	−92.704	0.35	413−473
diethylene glycol dibutyl ether	14.8018	4797.646	−58.166	0.45	403−473
ethylene glycol monobutyl ether acetate	19.4095	7746.132	59.508	0.29	363−463
diethylene glycol monoethyl ether acetate	17.1753	6779.610	47.914	0.50	363−473

[a] $\ln(P/\text{kPa}) = A - (B/(T/\text{K} + C))$. [b] AAD $\Delta P/P/\% = (100\%/n)\sum_{k=1}^{n}(|P_{\text{Antoine}} - P_{\text{expt}}|/P_{\text{expt}})_k$, where n is the number of data points.

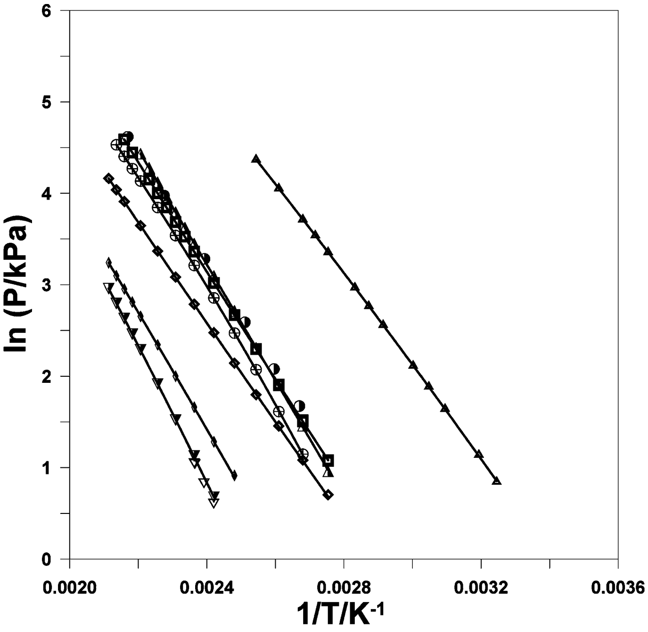

Figure 2. Temperature dependence of vapor pressures for the investigated substances: △, morpholine; ⊕, diethyl methylmalonate; ▲, diethylene glycol diethyl ether; ◑, diethylene glycol diethyl ether;[4] ▼, diethylene glycol hexyl ether; ▽, diethylene glycol hexyl ether;[5] half-solid diamond, diethylene glycol dibutyl ether; □, ethylene glycol monobutyl ether acetate; ◇, diethylene glycol monoethyl ether acetate.

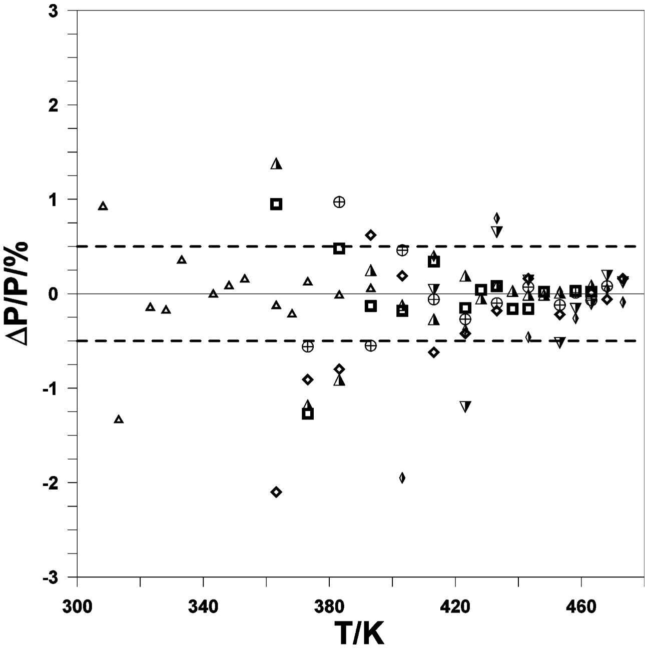

Figure 3. Deviation distributions of the calculated values of the Antoine equation from the experimental vapor pressures for the investigated substances: △, morpholine; ⊕, diethyl methylmalonate; ▲, diethylene glycol diethyl ether; ▼, diethylene glycol hexyl ether; half-solid diamond, diethylene glycol dibutyl ether; □, ethylene glycol monobutyl ether acetate; ◇, diethylene glycol monoethyl ether acetate.

the following objective function π:

$$\pi = \sum_{k=1}^{n}(P_{\text{Antoine}} - P_{\text{expt}})_k^{\;2} \qquad (3)$$

where n is the number of data points, P_{Antoine} is the calculated values from the Antoine equation (eq 2), and P_{expt} is the experimental results. The determined Antoine constants and the calculated deviations are reported in Table 2. Figure 2 illustrates the variation of vapor pressures with temperature for the investigated substances, where the smooth lines are the calculated results from the Antoine equation. Literature values of diethylene glycol diethyl ether[4] and diethylene glycol hexyl ether[5] are also presented in the graph for comparison. Good agreement is shown in the figure. Figure 3 shows the deviation distributions of the data correlations, where the deviation is defined as

$$\Delta P/P/\% = \left(\frac{P_{\text{Antoine}} - P_{\text{expt}}}{P_{\text{expt}}}\right) \times 100\ \% \qquad (4)$$

The individual deviations are within ± 0.5 % for a majority of data points, and the values of AAD of the correlations are within a range of 0.28 % to 0.50 %. It appears that the Antoine equation represents well the vapor pressures varying with temperature over the entire experimental range.

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