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Subatmospheric Vapor Pressure Curves for Propionic Acid, Butyric Acid, Isobutyric Acid, Valeric Acid, Isovaleric Acid, Hexanoic Acid, and Heptanoic Acid

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Vapor pressure data were measured for the following carboxylic acids: propionic, butyric, isobutyric, valeric, isovaleric, hexanoic, and heptanoic acids. The pressure ranged between ~5 kPa and atmospheric pressure (at sea level), and the corresponding temperatures were between 85 and 180 °C, depending on the acid being measured. The data were regressed using both the Antoine and Wagner equations, and the parameters obtained for each equation are presented. The experimental data were also compared to literature data, and the results are discussed.

Introduction

Carboxylic acids are important chemicals from a commercial viewpoint and are widely utilized in a great variety of industrial applications. The acids are employed as a raw material in the manufacture of nylon, biodegradable plastics, and soaps; they are used as buffers and acidulents (food preservatives) in the food industry and as builders (included in washing powders to enhance the detergency of the powder) and are particularly beneficial in the pharmaceutical sector, where the acids are utilized as chemical intermediates. In addition, carboxylic acids form stable oxidation products and, consequently, they frequently appear as byproducts of various industrial processes and in the aqueous waste streams resulting from those processes. These streams often consist of large volumes of various carboxylic acid mixtures. Hence, data relating to carboxylic acids are necessary to determine how these byproducts may be removed and separated, so as to limit their impact on the environment. Furthermore, these separated acids may then be purified (if necessary) and utilized to increase profitability. A literature survey was completed, and this revealed a considerable scarcity of data relating to carboxylic acid vapor−liquid equilibrium (VLE) and vapor pressures. Previous vapor pressure measurements were conducted for certain acids studied in this work by Sewnarain et al.,[1] Ambrose and Ghiassee,[2] Muñoz and Krähenbühl,[3] Dreisbach and Shrader,[4] Pool and Ralston,[5] Jasper and Miller,[6] and Rose et al.[7] In addition, comparisons with the vapor pressure data provided in the form of equation parameters by the Dortmund Data Bank (DDB)[8] and Korea Thermophysical Properties Data Bank (KDB)[9] were carried out.

Experimental Section

Materials. The carboxylic acids were purchased through Capital Labs Supplies cc from Fluca Enterprises. The acids were used without further purification after gas chromatographic analysis revealed no significant impurities. The purities were confirmed via refractive index measurement; comparisons with literature values are presented in Table 1.

Table 1. Component Purities and Refractive Indices

reagent	refractive index (293.15 K) exptl	lit.[a]	GC analysis, mass %	min purity,[b] mass %
propionic acid	1.3810	1.3809	99.8	99.5
butyric acid	1.3978	1.3980	99.8	99.5
isobutyric acid	1.3933	1.3930	99.7	99.5
valeric acid	1.4087	1.4085	99.1	99.0
isovaleric acid	1.4029	1.4033	99.4	98.0
hexanoic acid	1.4156	1.4163	99.5	99.5
heptanoic acid	1.4175	1.4170	99.3	99.0

[a] Weast et al.[15] [b] As stated by the supplier.

Apparatus. Figure 1 shows a schematic block diagram of the experimental setup. The experimental apparatus includes the following pieces of equipment: a VLE still, three Pyrex 5 L ballast flasks (two of which are joined to provide a 10 L ballast flask), a Julabo FT 200 coldfinger, a Hewlett-Packard 34401 A model multimeter, a Sensotec Super TJE pressure transducer, a vacuum pump, two solenoid valves, a differential mercury manometer, a LABOTECH water bath complete with pump and a glycol−water mixture, three DC power supplies (one providing power for the motors used to turn the magnetic stirrers, and one each for the two solenoid valves), two AC voltage regulators allowing adjustment of the internal and external heaters, and a computer. The setup is the same as that utilized by Joseph.[10]

Vapor−Liquid Equilibrium (VLE) Still. The VLE still that was used to measure the data presented in this paper is a highly refined, recirculating, dynamic vapor−liquid equilibrium still (Figure 2) developed by Raal[11] and has been described previously in extensive detail by Joseph[10] and Joseph et al.[12] The same experimental setup was used previously by Sewnarain et al.[1] to obtain vapor pressure curves and to measure VLE data for certain carboxylic acids combined with butyric acid at 14 kPa. The equipment is considered to be particularly suitable for vapor pressure measurements on hydrogen-bonding systems because superheat in the mixture resulting from the Cottrell pump is effectively discharged in the packing before impinging on the temperature sensor.

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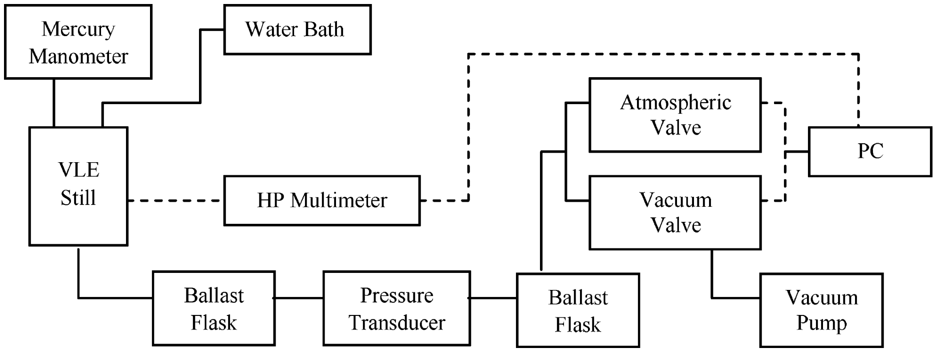

Figure 1. Schematic diagram of the VLE experimental system showing electronic connections (- - -).

Table 2. Vapor Pressure Data for the Carboxylic Acids

propionic acid		butyric acid		isobutyric acid		valeric acid		isovaleric acid		hexanoic acid		heptanoic acid	
P/kPa	*T*/°C	*P*/kPa	*T*/°C	*P*/kPa	*T*/°C	*P*/kPa	*T*/°C	*P*/kPa	*T*/°C	*P*/kPa	*T*/°C	*P*/kPa	*T*/°C
14.56	88.37	14.56	110.40	14.55	102.06	14.56	130.00	14.56	122.90	9.52	140.25	4.70	140.33
19.58	95.22	19.58	117.72	19.58	108.99	19.59	137.56	19.59	129.75	14.56	149.73	8.63	153.33
29.65	105.80	29.65	128.17	29.65	118.62	24.63	143.92	29.65	139.72	19.59	156.77	12.56	161.92
39.73	113.59	39.72	135.85	39.72	126.28	29.65	149.04	39.72	147.55	24.63	162.47	16.57	168.18
49.79	119.78	49.79	141.85	49.79	132.29	39.72	156.93	49.78	154.03	29.64	166.88	20.63	173.25
59.86	124.94	59.86	147.07	59.85	137.60	49.78	163.33	59.86	159.47	34.68	171.11	24.65	177.85
69.92	129.50	69.92	151.66	69.92	142.36	59.85	168.74	69.92	164.29	39.72	174.73	27.67	180.65
79.99	133.65	79.99	155.81	79.99	146.62	69.92	173.30	79.99	168.45	44.75	178.28		
90.07	137.18	90.07	159.46	90.07	150.21	74.96	175.33	90.07	172.01				
95.10	138.82	95.10	161.36	95.10	151.71	79.99	177.20	95.10	173.45				
101.21	140.59	100.04	162.90	100.59	153.01	85.03	178.77	100.08	174.77				

The VLE still was computer-controlled, allowing the still to be run in either isobaric or isothermal mode, as discussed by Joseph et al.[12] A Hewlett-Packard multimeter was used to display the resistance of the PT-100 temperature sensor that was then converted to a temperature using the relationship $T = mR + c$, with m and c obtained from the temperature calibration. The system was calibrated for pressure using a differential mercury manometer (refer to Figure 1), whereas for temperature a careful, in situ, chemical calibration was conducted using a pure component. The accuracy of the measured temperature is estimated from the calibration to be within ±0.02 °C, whereas the accuracy of the temperature control varied between 0.01 and 0.05 °C depending on the volatility of the species. A SENSOTEC Super TJE pressure transducer was utilized to measure the system pressure, and the measured pressure accuracy (again, via the in situ calibration discussed above) is estimated at ±0.03 kPa. When the still was being run isobarically, the pressure was controlled to within 0.01 kPa.

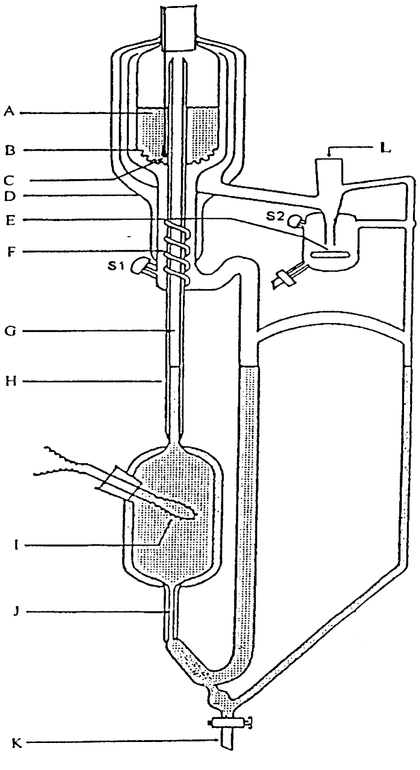

Figure 2. Schematic diagram of the VLE still: A, stainless steel wire mesh packing; B, drainage holes; C, PT-100 sensor; D, vacuum jacket; E, magnetic stirrer; F, stainless steel mixing spiral; G, insulated Cottrell pump; H, vacuum jacket; I, internal heater; J, capillary leg; K, drainage valve; L, condenser attachment; S1, liquid sampling septum; S2, vapor sampling septum.

Results and Discussion

Vapor pressure data were measured for the following acids: propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, hexanoic acid, and heptanoic acid. The data are presented in Table 2 and plotted in Figure 3. The pressures ranged between ~5 kPa and atmospheric pressure at sea level (which varied between 100.04 kPa and 101.21 kPa depending on the prevailing weather conditions). The equipment imposed a constraint on the upper bound of the temperature (and, hence, pressure) range because the septa used on the still (for liquid and vapor sampling when VLE data were obtained) began to degrade at temperatures >180 °C. Furthermore, the still itself was not designed for high-temperature work. Thus, the temperatures ranged from ~85 °C to just over 180 °C. Due to this constraint on the maximum system temperature, fewer data points were measured for hexanoic and heptanoic acid because the temperatures rapidly exceeded 180 °C (even at low pressures). The data were fitted to find parameters for both the Antoine equation

$$\ln(P/\text{kPa}) = A - \frac{B}{(T/C) + C} \tag{1}$$

Table 3. Parameters and Critical Properties[2,9] for the Wagner[13] Equation

	propionic acid	butyric acid	isobutyric acid	valeric acid	isovaleric acid	hexanoic acid	heptanoic acid
T_c/K	604.0	624.0	605.0	643.0	629.0	662.0	679.0
P_c/kPa	4530	4030	3700	3580	3400	3200	2900
A	7.518161	−36.10190	0.962296	17.48437	33.06715	−54.58281	−19.89683
B	−37.61987	72.08083	−23.63434	−63.03654	−106.8467	118.08454	33.07344
C	58.78732	−145.5125	42.54900	97.25152	206.65935	−231.6407	−88.38105
D	−164.2785	470.1079	−200.7284	−244.7591	−813.6062	698.1327	298.2216
$\Sigma(\Delta P_i^2)$	0.282225	0.142438	3.196343	0.414071	1.549875	0.076878	0.031384

Table 4. Parameters for the Antoine Equation

	propionic acid	butyric acid	isobutyric acid	valeric acid	isovaleric acid	hexanoic acid	heptanoic acid
A	18.105654	14.511627	15.176238	36.410366	18.084913	13.46595	20.05208
B	5640.3443	3164.4707	3527.8614	30029.229	5702.4431	2642.198	7018.304
C	277.46143	156.56122	180.5140	760.44819	247.98837	95.20133	238.8097
$\Sigma(\Delta P_i^2)$[a]	0.35682507	0.43389429	3.43419821	0.4604351	2.99353347	0.131165	0.036790

[a] Where $\Sigma(\Delta P_i^2)$ is the sum of the squared differences between the experimental and calculated pressures (kPa).

Table 5. ΔP_{av} Values Resulting from a Comparison between the Experimental Data Measured in This Work and the Available Literature Data[2−9]

acid	DDB	KDB	Dresibach and Schrader	Muñoz and Krähenbühl	Ambrose and Ghiassee	Jasper and Miller	Rose et al.	Pool and Ralston
propionic	0.48	0.55	0.46		0.40			
butyric	0.42	4.22	0.39	0.37	0.64	2.06		
isobutyric	1.21	1.66			1.13			
valeric	0.77	0.98			1.24			
isovaleric	3.30	1.36			1.11			
hexanoic	0.92	0.70			0.61		0.76	0.78
heptanoic	0.58	1.13			0.67			0.58

Table 6. ΔP_{av} Values for the Data of Ambrose and Ghiassee[2] Compared to the Experimental Data Measured in This Work and the Available Literature Data[3−9]

acid	this work	Muñoz and Krähenbühl	Dresibach and Shrader	Pool and Ralston	Jasper and Miller	Rose et al.	DDB	KDB
propionic	0.40		0.70				0.16	0.35
butyric	0.64	0.66	0.71		2.39		0.72	3.90
isobutyric	1.13						0.32	2.65
valeric	1.24						1.26	0.69
isovaleric	1.11						4.19	2.12
hexanoic	0.61			0.43		0.64	0.71	0.17
heptanoic	0.67			0.37			0.45	0.48

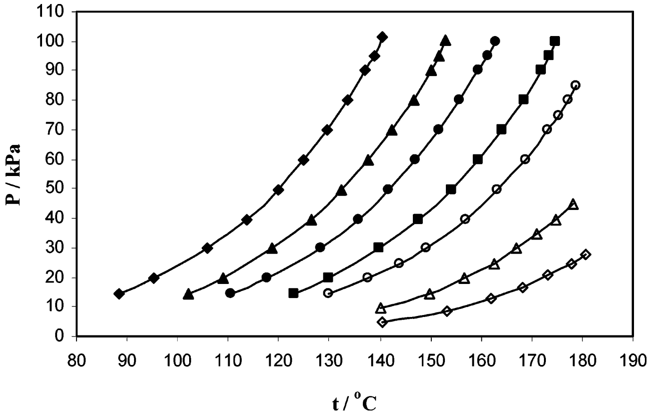

Figure 3. Vapor pressure curves for the carboxylic acids: ◆, propionic; ●, butyric, ▲, isobutyric; ○, valeric; ■, isovaleric; △, hexanoic; ◇, heptanoic.

and the Wagner[13] equation

$$\ln\left(\frac{P}{P_c}\right) = (1 - x)^{-1}[Ax + Bx^{1.5} + Cx^3 + Dx^6] \quad (2)$$

where

$$x = 1 - \frac{T}{T_c} \quad (3)$$

In all cases, the Wagner[13] equation (eq 2) was found to give a superior correlation of the vapor pressure data when compared to the simpler Antoine equation (eq 1). This is clearly evidenced by the significantly lower $\sum(\Delta P_i^2)$ values for the Wagner[13] equation (eq 2) presented in Tables 3 and 4. However, both equations fitted the data extremely well.

Table 5 shows the comparison between the experimental data measured in this work and the available literature data. The average pressure difference per point was calculated for each acid using the equation

$$\Delta P_{av} = \frac{\sum_{i=1}^{n} |P_{exptl,i} - P_{lit.,i}|}{n} \quad (4)$$

where n stands for the number of experimental points measured and ΔP_{av} is expressed in units of kPa.

Figure 3 shows the measured carboxylic acid vapor pressure data. It is clear that as the acids increase in size, the boiling point temperature at a particular pressure also increases. The effect of branching on the boiling points of the acids is also demonstrated in Figure 3. Isobutyric acid and isovaleric acid both boil at a lower temperature than butyric and valeric acid, respectively (provided the pressure is the same), despite the fact that the respective acids correspond in terms of size. Thus, it may be deduced that

Table 7. ΔP_{av} Values for the Data of Muñoz and Krähenbühl[3] and Dreisbach and Shrader[4] Compared to the Experimental Data Measured in This Work and the Available Literature Data[2−4,6,8,9]

	Muñoz and Krähenbühl	Dreisbach and Shrader	
data set	butyric acid	propionic acid	butyric acid
Ambrose and Ghiassee	0.66	0.70	0.71
DDB	0.07	0.54	0.03
Jasper and Miller	1.73		1.67
KDB	4.55	0.37	4.61
Dresibach and Shrader	0.07		
this work	0.37	0.49	0.40
Muñoz and Krähenbühl			0.07

branching has the effect of reducing the boiling point of a compound.

The experimental data measured in this work were compared to several sources of literature data.[2−9] Although the agreement between the various sets of literature data is fair, the data do deviate to a certain degree. This deviation is clearly evident in Tables 5−7. Because the literature data differ when compared to one another (Tables 6 and 7), it is only natural that the data presented here would also show some deviation when compared to previously published data (Table 5). However, in most instances these differences are fairly small and are all of the same order of magnitude as the variations existing between the literature data sets.

The recently published vapor pressure data for butyric acid, measured by Muñoz and Krähenbühl[3] (Table 7), show good agreement with the data measured in this work ($\Delta P_{av} = 0.37$ kPa), whereas the Ambrose and Ghiassee[2] measurements differ slightly more in this instance ($\Delta P_{av} = 0.66$ kPa). However, the data set found in the DDB[8] and that measured by Dreisbach and Shrader[4] are in excellent agreement with the Muñoz and Krähenbühl[3] data (both have a $\Delta P_{av} = 0.07$ kPa). The KDB[9] data set differs to a significant degree with the other published data for butyric acid (ΔP_{av} varying from 3.90 kPa in Table 6 to 4.61 kPa in Table 7), as does the data measured by Jasper and Miller[6] [ΔP_{av} fluctuating between 1.67 kPa (Table 7) and 2.39 kPa (Table 6)]. For all of the other acids, the measured data differ to some degree from one another with no two data sets possessing a conspicuously good agreement.

The largest deviations from literature data[2,8,9] occurred for isobutyric acid and isovaleric acid (Table 5). However, the data measured by Ambrose and Ghiassee[2] show similar differences when compared to the data located on the DDB[8] and KDB[9] (Table 6).

The fact that experimental vapor pressure data differ to such an extent for the carboxylic acids is attributed to the difficulties involved in measuring the acids (discussed below). In addition, the average deviations shown in Table 5 appear to be rather large when compared to the claimed uncertainty on the pressure of ±0.03 kPa. However, these values are representative of the differences that exist between the various literature data sets and do not reflect the accuracy of the equipment used in this work; rather, they are an indication of the complications associated with measuring carboxylic acid properties experimentally.

These difficulties include the fact that the acids form hydrogen bonds, which cause the acid molecules to dimerize. The effects of dimerization were also noted by Ambrose and Ghiassee.[2] Furthermore, Ambrose and Ghiassee[2] found that the acids may decompose depending on the experimental conditions. This decomposition is only likely to significantly affect the results at elevated temperatures. The dimerization, on the other hand, is known to occur even at low pressures and temperatures (Prausnitz et al.[14]) and will therefore have an effect on the vapor pressure measurements throughout the pressure range considered in this paper.

Conclusion

Subatmospheric vapor pressure data were measured for seven commonly occurring carboxylic acids, namely, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, hexanoic acid, and heptanoic acid. These data were regressed to obtain parameters for the Antoine and Wagner[13] equations. A comparison between available literature data and the experimental data presented in this paper revealed a satisfactory agreement, although the literature data sets[2−9] differed from one another to varying degrees.

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