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Vapor Pressure Determination of the Aliphatic C_5 to C_8 1-Alcohols

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A precise static method is used to measure vapor pressures of 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol from 298.15 up to the boiling points of these alcohols. The vapor pressure data are correlated with the Antoine and Wagner equations. From the measured vapor pressures, the enthalpies of vaporization are calculated. The results are compared with literature values.

Introduction

The vapor pressure of a pure substance is an important thermodynamic property that is essential in chemical process design and fate analysis of environmental contaminants. Experimental data over a wide temperature range, however, are scarce, especially for the alcohols with a higher boiling point. Besides, the available results on vapor pressures and enthalpies of vaporization[1−4] are not always as consistent as they should be when these data are used for comparison with predictive calculations. In our previous works,[5,6] the vaporization enthalpies and vapor pressures of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, propylene carbonate, and *N*,*N*-dimethylformamide were measured by a static method. As a continuation, the vapor pressures and the standard molar enthalpies of 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol are studied in this work.

Experimental Section

Materials. The purity of the alcohols after distillation under dry nitrogen and drying with molecular sieves was checked with gas chromatography (HP-6890) equipped with a flame ionization detector (FID). The purities were determined with GC as follows: for 1-pentanol (Fluka, min 99 %) 99.97 %, 1-hexanol (Lancaster, min 99 %) 99.81 %, 1-heptanol (Merck, min 99 %) 99.90 %, and 1-octanol (Aldrich, min 99 %, anhydrous) 99.95 %. The water content detected by Karl Fischer titration (mci, model CA-02) was less than 0.011 %, 0.014 %, 0.013 %, and 0.007 % for 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, respectively. All alcohols were degassed prior to making the measurements.

Vapor Pressure Measurements. The vapor pressure measurements were performed with a precise vapor pressure apparatus that yields total vapor pressure of solutions. The apparatus was designed especially for vapor pressure measurements of pure fluids and of electrolyte solutions over a wide temperature range from $T = (278.15 \text{ to } 473.15)$ K with an overall uncertainty in temperature of 0.01 K and a reproducibility of 0.1 % in pressure. Due to uncertainties of the zero point pressure of the manometer, volatile impurities, incomplete degassing of the samples, and leakage, an overall uncertainty of at least 5 Pa can be estimated. The temperature is based on the international temperature scale ITS-90. The apparatus and the measuring method as well as the degassing procedure are described in detail elsewhere.[5]

Table 1. Experimental Vapor Pressures of 1-Pentanol, 1-Hexanol, 1-Heptanol, and 1-Octanol at Different Temperatures

	p/kPa			
T/K	1-pentanol	1-hexanol	1-heptanol	1-octanol
298.15	0.337[a]	0.115[a]	0.029[a]	0.011[a]
303.15	0.488[a]	0.171[a]	0.045[a]	0.017[a]
308.15	0.694[a]	0.250[a]	0.069[a]	0.027[a]
313.15	0.969[a]	0.362[a]	0.104[a]	0.041[a]
318.15	1.359	0.517[a]	0.156[a]	0.063[a]
323.15	1.866	0.729[a]	0.230[a]	0.093[a]
328.15	2.528	1.015	0.335[a]	0.138[a]
333.15	3.381	1.395	0.481[a]	0.200[a]
338.15	4.467	1.895	0.681[a]	0.287[a]
343.15	5.873	2.544	0.951[a]	0.406[a]
348.15	7.633	3.377	1.312	0.569[a]
353.15	9.828	4.433	1.787	0.786[a]
358.15	12.520	5.759	2.403	1.072
363.15	15.808	7.408	3.194	1.446
368.15	19.861	9.436	4.196	1.929
373.15	24.685	11.911	5.451	2.544
378.15	30.467	14.905	7.005	3.319
383.15	37.357	18.500	8.910	4.285
388.15	45.451	22.786	11.223	5.479
393.15	54.875	27.863	14.002	6.938
398.15	65.845	33.842	17.315	8.706
403.15	78.450	40.846	21.230	10.830
408.15		49.015	25.822	13.362
413.15		58.504	31.170	16.357
418.15		69.487	37.361	19.876
423.15		82.163	44.485	23.986
428.15			52.641	28.758
433.15			61.936	34.271
438.15			72.487	40.612
443.15			84.398	47.876
448.15				56.167
453.15				65.454
458.15				75.948
463.15				87.733

[a] Data not used for fitting.

Table 2. Constants of the Antoine Equation $\ln(p/\text{kPa}) = A - B/(T/\text{K} + C)$

compound	temp range/K	*A*	*B*	*C*	SD[a]/kPa
1-pentanol	318−403	14.9571	3231.225	−98.138	0.043
1-hexanol	328−423	15.1869	3545.833	−94.190	0.032
1-heptanol	348−443	13.2516	2604.808	−147.696	0.014
1-octanol	358−463	13.6860	2985.671	−139.026	0.014

[a] $\mathrm{SD} = [\sum(p - p_{\mathrm{calc}})^2/(n-3)]^{0.5}$, where *n* is the number of experimental points.

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Table 3. Constants of the Wagner Equation ($\ln(p_r) = (1/T_r)(a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5)$)

compound	temp range/K	$p_c{}^a$/MPa	$T_c{}^a$/K	a	b	c	d	SD^b/kPa
1-pentanol	318−403	3.897	588.1	−11.806	12.0699	−20.477	13.884	0.014
1-hexanol	328−423	3.417	610.3	−10.738	8.9016	−15.725	4.070	0.137
1-heptanol	348−443	3.058	632.6	−10.255	6.7106	−10.331	−15.240	0.022
1-octanol	358−463	2.777	652.5	−8.413	1.6281	−5.078	−17.052	0.015

[a] Ref 8. [b] SD = $[\Sigma(p - p_{calc})^2/(n - 4)]^{0.5}$, where n is the number of experimental points.

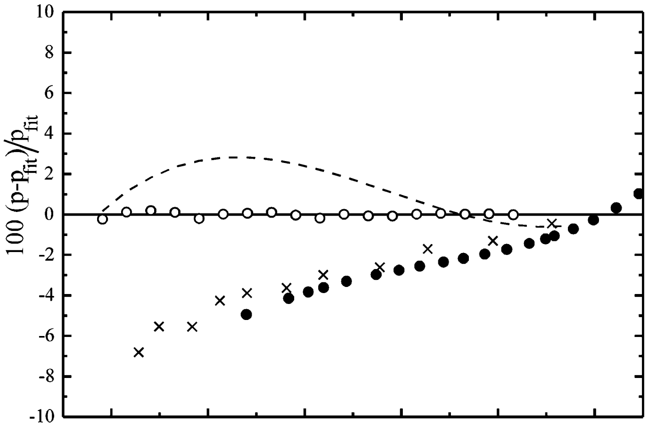

Figure 1. Comparison of literature vapor pressures for 1-pentanol with those obtained using the Wagner equation and the parameters listed in Table 3: ○, our experimental data; ×, data from Kemme and Kreps;[9] ●, Ambrose and Sprake;[10] - - -, calculated with the Antoine correlation of Wilhoit and Zwolinski.[11]

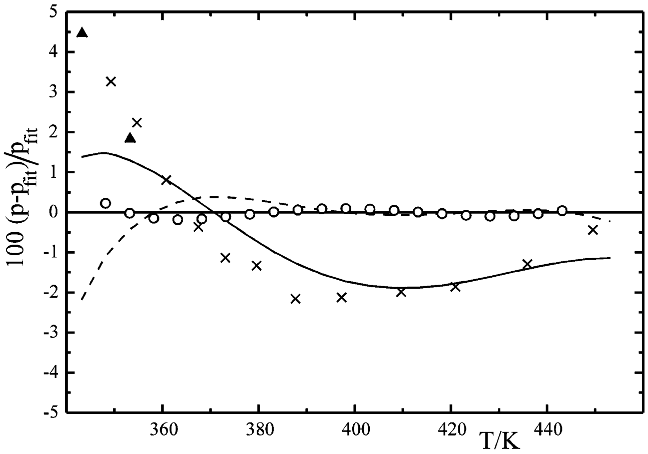

Figure 3. Comparison of literature vapor pressures for 1-heptanol with those obtained using the Wagner equation and the parameters listed in Table 3: ○, our experimental data; ×, data from Kemme and Kreps;[9] - - -, calculated from the Antoine correlation of Wilhoit and Zwolinski;[11] —, calculated from the Antoine correlation of Stephenson and Malanowski;[12] ▲, N'Guimbi et al.[16]

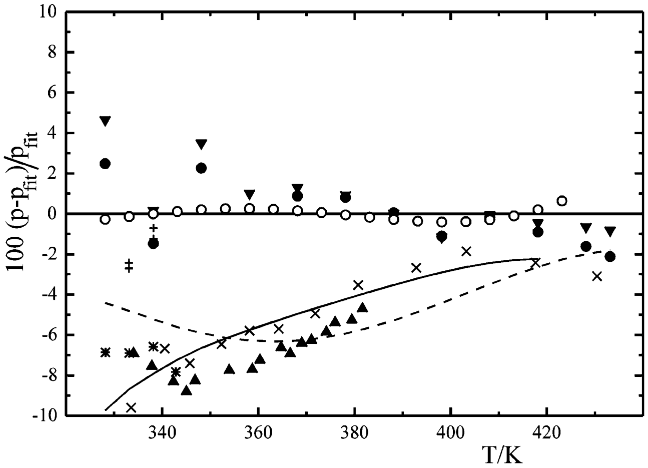

Figure 2. Comparison of literature vapor pressures for 1-hexanol with those obtained using the Wagner equation and the parameters listed in Table 3: ○, our experimental data; ×, data from Kemme and Kreps;[9] - - -, calculated from the Antoine correlation of Wilhoit and Zwolinski;[11] —, calculated from the Antoine correlation of Stephenson and Malanowski;[12] ●, Hovorka et al.;[13] ▲, Rose and Supina;[14] *, Wieczorek and Stecki;[15] +, N'Guimbi et al.;[16] ▼, Reddy et al.[28]

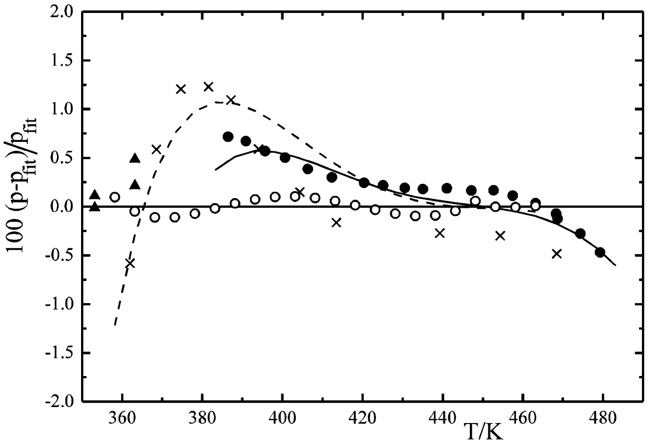

Figure 4. Comparison of literature vapor pressures for 1-octanol with those obtained using the Wagner equation and the parameters listed in Table 3: ○, our experimental data; ×, data from Kemme and Kreps;[9] ●, Ambrose and Sprake;[10] - - -, calculated from the Antoine correlation of Wilhoit and Zwolinski;[11] —, calculated from the Antoine correlation of Stephenson and Malanowski;[12] ▲, N'Guimbi et al.[16]

Results and Discussion

The temperature-dependent vapor pressure of pure 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol were measured from $T = (298.15 \text{ to } 403.15)$ K for 1-pentanol, $T = (298.15 \text{ to } 423.15)$ for 1-hexanol, $T = (298.15 \text{ to } 443.15)$ for 1-heptanol, and $T = (298.15 \text{ to } 453.15)$ K for 1-octanol in 5 K intervals. The results are reported in Table 1.

The data of Table 1 are fitted with the help of the Antoine equation:

$$\ln(p/\text{kPa}) = A - B/(T/\text{K} + C) \qquad (1)$$

where p is pressure; T is temperature; and A, B, and C are the Antoine constants. These constants are given in Table 2. To obtain reliable fitting parameters, all vapor pressures below 1 kPa were excluded from the calculations.

For the Wagner equation,[7] the fitting parameters were derived by a nonlinear least-squares fit of the vapor pressures listed in Table 1 using the formulation given by Poling et al.:[7]

$$\ln(p_r) = (1/T_r)(a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5) \qquad (2)$$

where p_r is the reduced vapor pressure, $p_r = p/p_c$; T_r is the reduced temperature, $T_r = T/T_c$; and τ is $1 - T_r$. The critical

Table 4. Comparison of the Enthalpy of Vaporization Values for 1-Pentanol, 1-Hexanol, 1-Heptanol, and 1-Octanol with Literature Values

compound	T/K	$\Delta_{vap}H$/kJ·mol^{-1}	$\Delta_{vap}H_{lit}$/kJ·mol^{-1}	$\delta\Delta_{vap}H$[b]
1-pentanol	298	55.4	57.4[a]	−3.5
			55.4[d]	0.0
			56.9[e]	−2.6
	313	54.8	55.7[f]	1.6
	322	53.9	56.2[g]	−4.1
	328	53.2	54.2[f]	−1.8
	343	52.4	52.8[f]	−0.8
	358	50.7	51[f]	−0.6
	374	49.5	49.2[h]	0.6
	392	47.6	47.1[h]	1.1
1-hexanol	298	59.9	61.1[i]	−2.0
			61.5[c]	−2.6
			59.1[d]	1.4
			60.8[j]	−1.5
			61.4[e]	−2.4
	313	58.7	57.7[k]	1.7
	323	58.3	57.9[l]	0.7
	328	58.1	58.3[m]	−0.4
	343	56.5	57.4[m]	−1.6
	349	56.0	56[n]	0.0
	358	54.8	55[m]	−0.4
	368	53.9	53.8[m]	0.2
1-heptanol	298	67.1	65.5[c]	2.4
			67[j]	0.1
	310	66.8	65.2[o]	2.5
	328	65.9	*[r]	
	348	63.5	65.2[l]	−2.6
	351	62.7	62.6[k,g]	0.2
	378	58.4	*	
	398	54.8	*	
	418	51.7	*	
	438	49.4	*	
1-octanol	298	69.3	70.1[i]	−1.1
			71.6[c]	−3.2
			71.0[j]	−2.4
	303	69.3	69.6[i]	−0.4
	318	68.7	68.7[o]	−0.0
	343	66.9	67.3[k]	−0.6
	358	65.1	67.5[l]	−3.6
	380	61.2	61.6[p]	−0.6
	401	57.9	58.3[k,q]	−0.7
	412	56.4	56.6[k]	−0.4
	428	54.4	*	
	445	52.9	52.5[k]	0.8
	458	50.7	*	

[a] Ref 4. [b] $\delta\Delta_{vap}H = (\Delta_{vap}H - \Delta_{vap}H_{lit}) \times 100/\Delta_{vap}H_{lit}$. [c] Ref 21. [d] Ref 22. [e] Ref 23. [f] Ref 24. [g] Ref 9. [h] Ref 25. [i] Ref 18. [j] Ref 26. [k] Ref 12. [l] Ref 11. [m] Ref 27. [n] Ref 14. [o] Ref 16. [p] Ref 20. [q] Ref 10. [r] An asterisk indicates not a sufficient number of literature data in the measured range.

temperatures and critical pressures for the alcohols studied are taken from Gude and Teja[8] and are presented in Table 3 together with the Wagner parameters.

For all alcohols studied, we compared the experimental data of this work with literature data in the appropriate temperature range:

(1) In the case of 1-pentanol, our results are lower than the vapor pressure data of Wilhoit and Zwolinski[11] but higher than the data of Kemme and Kreps[9] and of Ambrose and Sprake,[10] especially at lower temperatures. Figure 1 shows the comparison of literature vapor pressure values for 1-pentanol with our experimental values and with their fit using the Wagner equation and the parameters listed in Table 3.

(2) In the case of 1-hexanol, our results are in medium agreement with the literature data,[11−18] as can be seen in Figure 2. Best agreement is found with the data reported by Hovorka et al.[13] and by Reddy et al.[28] It seems that Stephenson and Malanowski[12] used the data of Kemme and Kreps[9] when reporting their Antoine constants. We note that 8 % relative deviation is equal to about 9 Pa in vapor pressure for 1-hexanol at 298.15 K.

(3) Concerning 1-heptanol, precise temperature-dependent literature data over all the temperature range studied are rare. Figure 3 shows the comparison of relative deviation of literature vapor pressures values for 1-heptanol with those obtained using the Wagner equation and the parameters listed in Table 3. For temperatures higher than 360 K, there is good agreement between our data and values calculated from the Antoine constants of Wilhoit and Zwolinski.[11] At temperatures lower than 360 K, there are larger deviations from literature values.[9,11,12,16] It appears again that Stephenson and Malanowski[12] used the data of Kemme and Kreps[9] when reporting the Antoine constants for 1-heptanol.

(4) For 1-octanol, several vapor-pressure measurements are reported in the literature. As shown in Figure 4, there is good agreement between our measurements and literature values[9−12] in the given temperature range.

The Clapeyron equation is a general equation originally relating vapor pressure, temperature, volume change, and enthalpy of vaporization of a pure liquid in equilibrium with the gas phase. If the volume of the liquid is much smaller than that of the gas and therefore is neglected and the gas-phase behavior is treated as ideal, then this equation becomes[19]

$$\frac{\mathrm{d}\ln(p)}{\mathrm{d}(1/T)} = \frac{-\Delta_{vap}H}{R} \tag{3}$$

where p is the vapor pressure, $\Delta_{vap}H$ is the enthalpy of vaporization, T is the absolute temperature, and R is the gas constant. A linear relationship between ln(p) and 1/T as we found in our measurements shows that the enthalpy of vaporization is only weakly temperature-dependent in the temperature range studied. The corresponding values for the alcohols studied are given in Table 4 together with a comparison with literature values. Some of the values compared are from calorimetric measurements,[18,21−27] and there is good agreement between our calculated data and literatures values at some temperatures. Enthalpy of vaporization or sufficient data in the literature for the calculation of the enthalpy of vaporization is not available at some temperatures.

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