J. Chem. Eng. Data **2006,** *51,* 475−482

Evaluation of the Vaporization, Fusion, and Sublimation Enthalpies of the 1-Alkanols: The Vaporization Enthalpy of 1-, 6-, 7-, and 9-Heptadecanol, 1-Octadecanol, 1-Eicosanol, 1-Docosanol, 1-Hexacosanol, and Cholesterol at T = 298.15 K by Correlation Gas Chromatography

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The vaporization enthalpies and vapor pressures of 1-, 6-, 7-, and 9-heptadecanol, 1-octadecanol, 1-eicosanol, 1-docosanol, 1-hexacosanol and cholesterol at $T = 298.15$ K have been measured by correlation gas chromatography using as standards, the even carbon *n*-alkanols from 1-decanol to 1-octadecanol and 1-pentadecanol. Fusion enthalpies for the all of these compounds were either measured by DSC or obtained from the literature. Adjusted to $T = 298.15$ K, the fusion and vaporization enthalpies were combined to provide sublimation enthalpies. The sublimation enthalpies were compared to existing literature values. Agreement between the two sets of values when available was generally very good.

Introduction

Correlation gas chromatography is proving to be a useful technique for the reliable evaluation of vaporization enthalpies.[1−3] This technique does not measure vaporization enthalpies directly but rather correlates enthalpies of transfer from solution to the vapor as measured by gas chromatography to the vaporization enthalpy of the compounds at $T = 298.15$ K. It is the only direct means of obtaining vaporization enthalpies of materials at $T = 298.15$ K that are solids at this temperature.[4] As such it has proven useful for validating thermochemical cycles involving sublimation, fusion, and vaporization enthalpies.[5] The technique is also capable of providing pure component vaporization enthalpies of materials that exist as mixtures[6] and of measuring the vaporization enthalpies of complex mixtures of hydrocarbons.[7] The technique may also prove useful in the environmental field by providing vaporization enthalpies and vapor pressures at ambient temperatures of pollutants that are solids at these temperatures.[8] The distribution of some solid environmental pollutants appears to be modeled by their thermodynamic properties in the subcooled liquid state.[9]

The major limitation of the method is the need for reliable vaporization enthalpies that can be used in the correlations. The accuracy of the correlation is dependent largely on the nature of the standards chosen for the correlation. The most accurate results are obtained when the number and type of functional groups are maintained constant both in the series of standards used and in the compounds being evaluated. Accuracy appears much less sensitive to the nature of the carbon skeleton. Alkanes as a group give good correlations with other hydrocarbons, regardless of structure. The *n*-alkanes are excellent standards since most vaporization enthalpies up to *n*-C_{30} are known accurately, and this has recently been extended to *n*-C_{38}.[1] Applications of the correlation gas chromatographic method to determine vaporization enthalpies of solids at 298.15 K requires liquid standards that exhibit vapor pressures similar in magnitude to the solid compounds being investigated. This requires establishing reliable vaporization enthalpies of large liquid molecules with a variety of functional groups to be used as standards. This work extends the work reported on the *n*-alkanes to evaluate literature values of the 1-alkanols. Recommended values as well as the vaporization enthalpies of various alkanols not previously assessed are reported. The sublimation enthalpy of many of these homologous materials is also evaluated as a sum of the vaporization and fusion enthalpies.

Experimental Section

The 1-alkanols were obtained from Aldrich Chemical Co. The chemical purities were high, but this is not of concern since the chromatography generally separates the minor components. The GC correlation experiments reported in Tables 1 to 3 were performed on an HP 5890 series II gas chromatograph run isothermally at a head pressure of 204 kPa using He as the carrier gas as described previously.[1,10] Several different columns were used that included 30 m and 60 m DB-5 capillary columns. The column temperature was monitored independently using a Fluke 51 K/J thermometer. Constant temperature was maintained within ± 0.1 °C. Methylene chloride, chloroform, and acetone were used as solvents and as the non-retained standards. Their retention times increased with increasing temperature, a characteristic of a non-retained analyte. Adjusted retention times (t_a/min) were calculated by subtracting the corresponding retention time of the solvent from each value at each temperature. The corrected retention time measures the time a solute spends on the column, and this time is inversely proportional to the solute's vapor pressure above the solution formed from the solute and stationary phase. Enthalpies of transfer from solution to the gas phase ($\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H^\circ_{\mathrm{m}}$) were calculated from the product of the gas constant R and the slope of lines obtained by plotting of $\ln(t_o/t_a)$ versus $1/(T/\mathrm{K})$ (where $t_o = 1$ min).

Several separate mixtures were prepared because of the large differences in retention times. The composition of the mixtures

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10.1021/je0503857 CCC: $33.50

Table 1. Experimental Enthalpies of Vaporization of the Alcohols

	$\Delta_l^gH°_m(T_m)$	T_m	$C_p(l)$	$\Delta C_p \Delta T$	$\Delta_l^gH°_m(298\ K)/kJ\cdot mol^{-1}$	
compound	$kJ\cdot mol^{-1}$	K	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$	value	mean value
methanol						*37.83*[a]
ethanol						*42.46*[a]
1-propanol						*47.50*[a]
1-butanol						*51.42*[a]
1-hexanol						*60.61*[a]
1-heptanol						*66.81*[a]
1-octanol			311.3			*70.98*[a]
1-nonanol						*76.86*[a]
1-decanol			375.1			*81.50*[a]
1-undecanol	85.7[b,c]	308	407	1.2 ± 0.3	86.8	**85.8 ± 2.1**
	84.7[d]	298	407	0	84.7	all entries
1-dodecanol	92.0[e]	298	438.9	0	92.0	**90.8 ± 1.2**
	84.7[f]	343	438.9	5.62 ± 1.4	90.3	entries 1−3
	90.0[d]	298	438.9	0	90.0	
	95.4[g]	305	438.9	0.9 ± 0.3	96.3	
	69.6[h]	421	438.9	15.3 ± 4.6	85.0	
	66.7[i]	440	438.9	17.7 ± 5.3	84.4	
	73.5[b,h]	392	438.9	11.8 ± 3.5	85.2	
	81.8[c]	318	438.9	2.5 ± 0.7	84.2	
1-tridecanol	90.6[b,c]	328	470.8	4.0 ± 1.2	94.6	94.7 ± 0.4
	95.8[d]	298	470.8	0	95.8	all entries
1-tetradecanol	98.7[d]	298	502.7	0	98.7	**98.9 ± 2.5**
	77.3[h]	449	502.7	21.2 ± 6.3	98.5	entries 1−4
	88.9[b,c]	348	502.7	7.1 ± 2.1	96.0	
	102.2[e]	298	502.7	0	102.2	
	104.1[g]	320	502.7	3.0 ± 0.6	107.2	
	109.0[b,j,l]	332	502.7	4.8 ± 1.0	113.8	
1-pentadecanol	95.5[g,k]	358.1	534.6	9.0 ± 1.8	104.5	**103.5 ± 3.3**
	102.5[d]	298	534.6	0	102.5	entries 1−2
	72.4[b,j,l]	468	534.6	25.4 ± 5.1	97.8	
	75.0[b,j,l]	453	534.6	23.2 ± 4.6	98.2	
1-hexadecanol	108.9[g,k]	298	566.5	0	108.9	107.8 ± 4.2
	103.6[c]	358	566.5	9.5 ± 2.8	113.1	all entries
	82.9[b,k]	431	566.5	21.0 ± 6.3	103.9	
	69.9[i]	514	566.5	34.1 ± 6.5	104.0	
	109.4[g]	329	566.5	4.9 ± 0.9	114.3	
	75.4[h]	469	566.5	26.9 ± 5.0	102.3	
1-heptadecanol	78.3[b,l]	475	598.4	29.4 ± 5.3	107.7	107.6 ± 0.2
	75.9[b,l]	488	598.4	31.5 ± 5.7	107.4	all entries
1-octadecanol	76.7[i]	512	630.3	37.3 ± 6.4	114.0	115.9 ± 2.9
	85.6[k]	451	630.3	26.7 ± 4.6	112.2	all entries
	113.4[g,j]	345	630.3	8.2 ± 1.4	121.6	
1-eicosanol	83.5[b,l]	503	694.1	39.1 ± 6.1	122.6	124.9± 2.6
	83.4[b,l]	508	694.1	40.1 ± 6.3	123.5	all entries
	118.8[g]	348	694.1	9.7 ± 1.5	128.5	
1-docosanol	115.3[g]	351	757.9	11.0 ± 1.6	126.3	126.3
cholesterol	114.9[b,l]	426	757.3	26.5 ± 3.8	141.4	141.4

[a] Recommended value from ref 12. [b] Vaporization enthalpies were calculated from experimental vapor pressures or those generated from the Antoine constants reported in the text over a 30 K range followed by a Clausius−Clapeyron treatment of the resulting data. [c] From ref 13. [d] From ref 14. [e] From ref 15. [f] From ref 16. [g] From ref 17. [h] From ref 18. [i] From ref 19. [j] Not included in the calculation of the mean and standard deviations. [k] From ref 21. [l] From ref 20.

varied in concentration, but each component was present in comparable amounts. Some experiments were repeated. Several other series of experiments were performed using slightly different standards in the mixture at different times by different co-workers. The vaporization enthalpies obtained were reproducible within the uncertainties reported. The results reported below are based on the data reported in the Supporting Information.

Adjustments of the experimental vaporization enthalpies from the mean temperature of measurement to $T = 298.15$ K, whenever necessary, was accomplished using eq 1 as described previously:[11]

$$\Delta_l^gH°_m(98.15\ K)/kJ\cdot mol^{-1} = \Delta_l^gH°_m(T_m) + (10.58 + 0.26C_p(l))(T_m - 298.15)/1000 \quad (1)$$

The term C_p(l) represents the heat capacity of the liquid phase, which was estimated by a group additivity method.

Fusion enthalpies were measured on a Perkin-Elmer DSC-7. Each fusion enthalpy determination is the mean of three to five separate measurements. Errors are reported as two standard deviations of the mean. The long chain 1-alkanols are known to exhibit polymorphism. This may explain the differences in fusion enthalpies reported in the literature for some of these materials. No additional transitions were observed between room temperature and T_{fus}, although in some cases the fusion process may have involved several transitions that were not resolved by the DSC at the scan rate of the experiments (5 K/min). The samples were analyzed by gas chromatography. Purities are as follows: 1-octadecanol, 99+ %; 1-eicosanol, 98+ %; 1-docosanol, 98+ %; 1-hexacosanol, 98+ %.

Vaporization Enthalpies of the 1-Alkanols

Vaporization enthalpies at $T = 298.15$ K for the 1-alkanols up to 1-decanol have been critically reviewed previously by Majer and Svoboda.[12] The values recommended by Majer and

Table 2. Vaporization Enthalpies Obtained for a Standard Test Mixture[a]

compound	−slope	intercept	$\Delta_{sln}{}^{g}H°_m$(489 K) kJ·mol^{-1}	$\Delta_l{}^{g}H°_m$(298.15 K) (lit) kJ·mol^{-1}	$\Delta_l{}^{g}H°_m$(298.15 K) (calc) kJ·mol^{-1}
1-hexanol	3971.6	10.983	33.02	60.6	61.4 ± 1.7
1-heptanol	4386.8	11.366	36.47	66.8	66.1 ± 1.7
1-octanol	4816.9	11.827	40.05	71.0	70.9 ± 1.7
1-decanol	5703.0	12.874	47.41	81.5	80.8 ± 1.7
1-undecanol	6206.4	13.571	51.60	85.8	86.5 ± 1.7

[a] $\Delta_l{}^{g}H°_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.35 \pm 0.054)\Delta_{sln}{}^{g}H_m(402) + (16.86 \pm 0.84)\quad (r^2 = 0.9951)$ (2)

Table 3. Summary of the Vaporization Enthalpies

	$\Delta_l{}^{g}H°_m$(298.15 K)/kJ·mol^{-1}									
		mix								
compound	mean	1	2	3	4	5	6	7	8	9
1-decanol	**81.5**[a]	81.9			82.0	82.0				
1-dodecanol	**90.8**[a]	90.2			90.3	90.3		91.0	91.0	90.8
1-tetradecanol	**98.9**[a]	98.8	98.9	99.0	98.9	98.9				
1-pentadecanol	**103.5**[a]	103.8	103.5	103.3	103.2	103.2				
1-hexadecanol	107.7 ± 1.2[b]	107.7		107.9	107.7	107.8		107.1	107.2	107.5
1-heptadecanol	112.5 ± 0.5[c]		112.4	112.6						
6-heptadecanol								108.6		
7-heptadecanol									108.2	
9-heptadecanol										108.5
1-octadecanol	1116.8 ± 1.2[b]	116.8	116.8	116.7	117.0	116.9	116.7	117.0	116.9	116.8
1-eicosanol	125.9 ± 0.8[d]				125.9	126.0	126.2	126.0	126.0	125.8
1-docosanol	135.9 ± 0.8[e]				135.4	136.3	135.8			
cholesterol					147.9	147.3	148.9			
1-hexacosanol					153.9	153.4				

[a] Values in bold were used to evaluate values for the remaining alcohols (see Table 1). [b] Evaluated in mix 1 and used as a reference compound in mixes 3 to 5, 7, and 8; uncertainty derived from the uncertainty in the intercept (± 2σ, mix 1, Table 4). [c] Evaluated in mixes 2 and 3; uncertainty derived from the uncertainty in the intercept (± 2σ, mix 3, Table 4). [d] Evaluated in mix 4 and used as a reference compound in mixes 5 to 8; uncertainty derived from the uncertainty in the intercept (± 2σ, mix 4, Table 4). [e] Evaluated in mixes 4 and 5 and used as a reference compound in mix 6; uncertainty derived from the uncertainty in the intercept (± 2σ, mix 4, Table 4).

Svoboda (in italics in Table 1) were used, and additional values for other 1-alkanols found in the literature are provided in Table 1. Values were also recommended for 1-dodecanol and 1-tetradecanol by Majer and Svoboda. Since their recommendations were based only on a single experimental value, we have included other values in our assessment. The recommended values and other values used as reference materials in this work are reported in Table 1 in bold. Values for 1-dodecanol, 1-tetradecanol, and 1-pentadecanol were obtained by averaging several of the values available in the literature, provided a source to the primary literature was available. Additional experimental values can be found for most 1-alkanols up to 1-docosanol. The difficulty associated with the 1-alkanols larger than C_{15} is that, in addition to the uncertainty associated with experimental measurements on compounds exhibiting very low vapor pressures, additional uncertainty is introduced in adjusting the experimental vaporization enthalpy values to $T = 298.15$ K. This is illustrated in Figure 1. Note the excellent linearity observed between the vaporization enthalpy and the number of carbon atoms from methanol to decanol. 1-Alkanols larger than dodecanol suggest continued linearity as a function of the number of carbon atoms (N_C) but show significantly more scatter. Consequently, we have used the experimental values up to C_{15} as reference values to derive vaporization enthalpies at $T = 298.15$ K for the remaining even alkanols evaluated, 1-hexadecanol to 1-docosanol. The vaporization enthalpies of a few other alcohols including 1-heptadecanol were also evaluated in this process. The compounds selected as standards were selected because experimental data are available at or near $T = 298.15$ K and relatively good agreement is found between reported measurements.

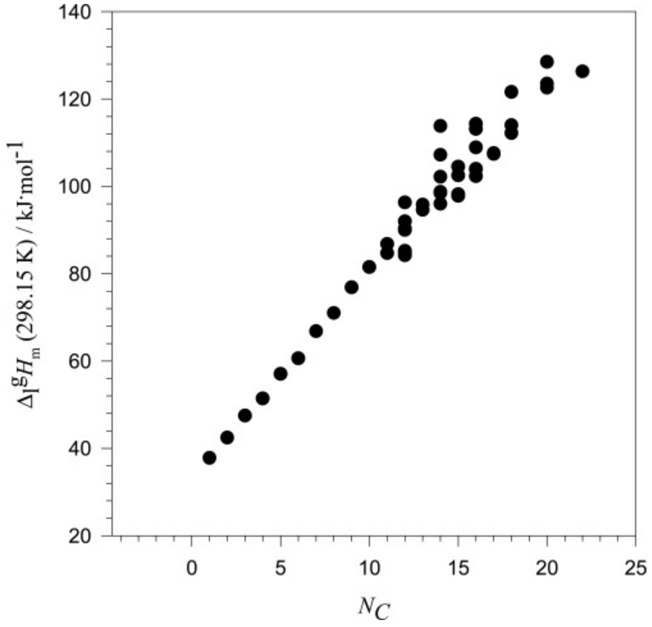

Figure 1. Plot of available experimental vaporization enthalpies vs the number of carbon atoms for the 1-alkanols from methanol to 1-docosanol.

As a demonstration of the linearity expected between experimental vaporization enthalpies measured at $T = 298.15$ K and the enthalpies of transfer measured by gas chromatography for a homologous series, the retention times of a series of five 1-alkanols from C_6 to C_{11} exclusive of C_9 were measured as a function of temperature. The measured retention times are reported in the Supporting Information. Figure 2 illustrates the linear relationship obtained between recommended and literature

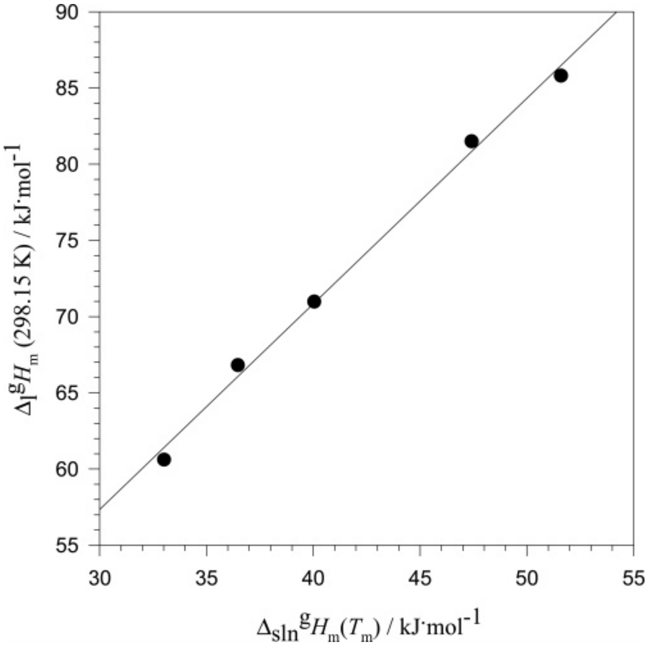

Figure 2. Comparison of literature vaporization enthalpies at $T = 298.15$ K with experimental enthalpies of transfer measured at a mean temperature of $T = 402$ K for the following 1-alkanols: C_6-C_8, C_{10}, C_{11}. The equation of the line is given by $\Delta_l^g H°_m$(298 K)/kJ·mol^{-1} = (1.35 ± 0.054)-$\Delta_{sln}^g H_m$(402) + (16.86 ± 0.84), ($r^2 = 0.9951$).

Table 4. Equations Resulting from Correlating Vaporization Enthalpies at $T = 298.15$ K with Enthalpies of Transfer

mix	−slope	intercept	T_m/K[a]	r^2
1	1.33 ± 0.047	27.38 ± 0.59	489	0.9975
2	1.462 ± 0.007	25.80 ± 0.06	520	0.9999
3	1.462 ± 0.024	25.13 ± 0.22	519	0.9994
4	1.617 ± 0.023	22.97 ± 0.40	559	0.9992
5	1.583 ± 0.015	24.54 ± 0.35	559	0.9996
6	1.479 ± 0.036	25.60 ± 0.33	558	0.9994
7	1.295 ± 0.025	24.64 ± 0.50	458	0.9992
8	1.335 ± 0.02	19.32 ± 0.38	450	0.9996
9	1.271 ± 0.008	27.67 ± 0.17	453	0.9999

[a] Mean oven temperature of the gas chromatograph.

vaporization enthalpies and enthalpies of transfer as measured by gas chromatography. The results are also summarized in Table 2. The correlation obtained between enthalpies of transfer and vaporization enthalpies is given by eq 2 in the footnote of Table 2.

Nine additional mixtures were evaluated. The gas chromatographic retention times are reported in the Supporting Information. Tables 3 and 4 summarize the results obtained for all mixtures. The following protocol was followed in evaluating the vaporization enthalpies listed in Table 3. The first mixture in the table, mix 1, contained the even carbon alcohols from 1-decanol to 1-octadecanol and the odd carbon alcohol, 1-pentadecanol. In this mixture, 1-hexadecanol and 1-octadecanol were treated as unknowns. Once the vaporization enthalpies of these two compounds were evaluated, they were used as reference compounds in subsequent mixtures. Similarly, the vaporization enthalpy of 1-eicosanol, evaluated in mix 4, was used as a reference compound in mixes 5 to 8. A similar protocol was followed once the vaporization enthalpy of 1-docosanol was evaluated. Table 4 lists the equations generated in correlating vaporization enthalpies with enthalpies of transfer. The correlation coefficient (r^2), listed in Table 4, is an indicator of the quality of the linear correlation.

Table 5. Summary of Vaporization Enthalpies

	$\Delta_l^g H°_m$(298 K)/kJ·mol^{-1}	
compound	experimental	calculated[d]
methanol	37.83[a]	37.8
ethanol	42.46[a]	42.5
1-propanol	47.50[a]	47.2
1-butanol	51.42[a]	51.8
1-pentanol	57.04[a]	56.5
1-hexanol	61.61[a]	61.2
1-heptanol	66.81[a]	65.9
1-octanol	70.98[a]	70.5
1-nonanol	76.86[a]	75.2
1-decanol	81.50[a]	79.9
1-undecanol	85.8 ± 2.1[b]	84.6
1-dodecanol	90.8 ± 1.2[c]	89.3
1-tridecanol	94.7 ± 0.4[c]	93.9
1-tetradecanol	98.9 ± 2.5[c]	98.6
1-pentadecanol	103.5 ± 3.3[c]	103.3
1-hexadecanol	107.7 ± 1.2[c]	108.0
1-heptadecanol	112.5 ± 0.5[c]	112.6
6-heptadecanol	108.6 ± 1.0[c]	
7-heptadecanol	108.2 ± 0.8[c]	
9-heptadecanol	108.5 ± 0.4[c]	
1-octadecanol	116.8 ± 1.2[c]	117.3
1-eicosanol	125.9 ± 0.8[c]	126.7
1-docosanol	135.9 ± 0.8[c]	136.0
cholesterol	148.0 ± 0.8[c]	
1-hexacosanol	153.7 ± 0.8[c]	154.7

[a] Recommended values.[12] [b] See Table 1. [c] This work. [d] Calculated using the equation of Rogalski.[22]

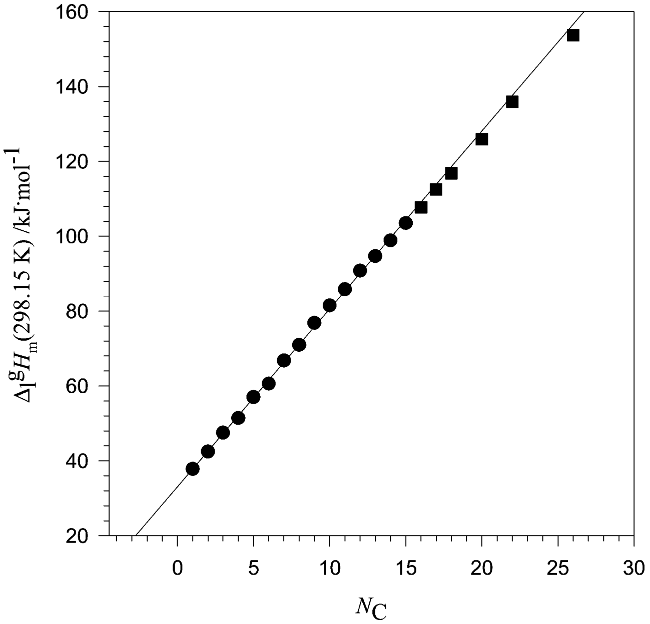

Figure 3. Vaporization enthalpies of the 1-alkanols as a function of the number of carbon atoms using literature values (●) and values determined in this work (■). The line was calculated using the relationship previously derived by Rogalski.[22]

A summary of the vaporization enthalpies obtained from the literature and those evaluated in this work is provided in Table 5 and illustrated in Figure 3. The solid circles correspond to literature values, and the solid squares represent values determined in this work. Also included are the values calculated from the equation reported by Rogalski[22] generated from the linearity observed between $\Delta_l^g H°_m$(298.15 K) and the number of carbon atoms (N_C) (eq 3):

$$\Delta_l^g H^\circ_m(298\ \text{K})/\text{kJ·mol}^{-1} = 33.16 + 4.6771 N_C \qquad (3)$$

Table 6. Coefficients of the Equation:[a] T/K·log $(p/p_o) = a_o/2 + \sum_{s=1}^{3} a_s E_s(x)$

	T_{min}/K	T_{max}/K	a_o	a_1	a_2	a_3
			Experimental Values			
1-decanol	400	529	1387.15	512.274	−13.792	1.418
1-dodecanol	425	550	1366.542	496.253	−11.973	1.221
1-hexadecanol	498	570	1411.797	286.998	−3.12	0.245
1-octadecanol	495	575	1098.181	330.631	−4.262	0.289
			Correlated Values			
1-pentadecanol	439	667	1837.30	897.45	−20.84	7.82
1-heptadecanol	461	695	1914.00	932.18	−17.29	7.91

[a] From ref 21. $E_s(x)$ is the Chebyshev polynomial: $a_1(x) + a_2(2x^2 - 1) + a_3(4x^2 - 3x)$, $x = [2T/\text{K} - (T_{max} + T_{min})]/(T_{max} - T_{min})$, and $p_o = 1$ kPa.

Table 7. Antoine Constants and the Temperature Range of Applicablity[a]

	A	B	C	temp range/K
1-decanol[b]	7.541	2270.427	192.322	283−388
1-dodecanol[b]	6.8	2011.634	162.769	303−413
1-tetradecanol[b]	6.916	2217.995	165.381	333−438
1-pentadecanol[b]	6.275	1911.956	136.738	343−453
1-hexadecanol[b]	5.964	1781.618	120.726	343−463
cholesterol[c]	11.056	6000	273.15	411−447

[a] Log $(p/p_o) = A - B/(C + T/°\text{C})$ where $p_o = 1$ kPa. [b] From ref 13. [c] From ref 20.

The standard deviation between calculated and experimental values is ± 0.8 kJ·mol^{-1}.

Vapor Pressures of the 1-Alkanols

In addition to obtaining vaporization enthalpies at $T = 298.15$ K, correlation gas chromatography can also be useful in obtaining vapor pressures as well. Vapor pressures are also obtained from a series of correlations and require experimental values to be used as standards. Reliable experimental values are available for a number of 1-alkanols. We have used experimental vapor pressures as calculated by the Chebshev polynomial reported by Ambrose et al.[21] for C_{10}, C_{12}, C_{16}, and C_{18} and by the Antoine constants for C_{10}, C_{12}, C_{14}, C_{15}, and C_{16} 1-alkanols as reported by N'Guimbi et al.[13] The parameters of the Chebshev polynomial are reported in Table 6. Table 7 lists the Antoine constants and the temperature range over which they are applicable. Vapor pressures and $\ln(t_o/t_a)$ were correlated using the following protocol. Values of $\ln(t_o/t_a)$ as a function of temperature, obtained from the experimental dependence of adjusted retention time with temperature over a 30 K temperature range at a mean temperature given in column 4 of Table 4, were calculated for all the alcohols in mix 1 using the equations in columns 2 and 3 of Table 8 over the temperature range $T = (298.15$ to $510)$ K in 30 K intervals. Vapor pressures at each of these temperatures were calculated for alcohols C_{10}, C_{12}, C_{16}, and C_{18} using Chebshev's polynomial. In addition, vapor pressures obtained from the Antoine equation was used for C_{10}, C_{12}, C_{14}, C_{15}, and C_{16}, only over the temperature range the constants are applicable (last column, Table 7) and averaged with those obtained using Chebshev's polynomial. At all other temperatures, experimental vapor pressures for C_{10}, C_{12}, C_{14}, C_{15}, and C_{16} were calculated from Chebshev's polynomial. Vapor pressures calculated using Chebshev's polynomial are believed to extrapolate favorably over a 75 K temperature range.[21] Values of $\ln(p/p_o)$ (where $p_o = 1$ kPa) were correlated with $\ln(t_o/t_a)$ (where $t_o = 1$ min) at each temperature, and the resulting equation from the correlation was used to calculate the vapor pressure for each compound present in the mixture. All correlations between $\ln(p/p_o)$ with $\ln(t_o/t_a)$ in this study were characterized by an $r^2 > 0.99$. Once vapor pressures for 1-alkanols C_{10}, C_{12}, C_{14}, C_{15}, and C_{16} were established over the temperature range cited above using this protocol, the vapor pressures were fit to the following third-order polynomial (eq 4) resulting in the coefficients listed under mix 1 in Table 9:

$$\ln(p/p_o) = A(T/\text{K})^{-3} + B(T/\text{K})^{-2} + C(T/\text{K}) + D \text{ where } p_o = 1 \text{ kPa} \quad (4)$$

These polynomials were then used to generate experimental vapor pressures for the compounds in Mix 1 in all the remaining mixes listed in Table 9. Values of $\ln(t_o/t_a)$ generated from the slopes and intercepts in Table 8 for mix 3 were combined with appropriate vapor pressures calculated using eq 4 for the compounds in mix 1 to evaluate the temperature dependence of vapor pressure for 1-heptadecanol. Similarly, the equations in Table 8 for mixes 5, 7, 8, and 9, combined with the appropriate vapor pressures calculated from eq 4 for the alcohols in mix 1 and 3, gave similar vapor pressure/temperature relationships for the remaining alcohols evaluated. Once the vapor pressure/temperature dependencies were evaluated, the temperature dependency of each alcohol was also fit to eq 4. This resulted in the remaining coefficients reported in Table 9.

The coefficients reported for eq 4 in Table 9 have for the most part been obtained from extrapolated or interpolated data. One means of testing the reliability of the data used to derive

Table 8. Slopes and Intercepts of Plots of Ln(t_o/t_a) versus 1/T(K^{-1}) for Various Mixes[a]

	mix											
	1		3		5		7		8		9	
compound	−slope	int	−slope	int	−slope	int	−slope	int	−slope	int	−slope	int
1-decanol	**4931.8**	**10.659**			4367.4	9.640						
1-dodecanol	**5676.2**	**11.442**			4999.0	10.206	6170.0	14.714	6460.1	15.306	5976.6	14.197
1-tetradecanol	**6461.4**	**12.338**	6074.1	11.54	5647.3	10.837	7657.5	16.374	7921.6	16.925	7558.2	16.111
1-pentadecanol	**6910**	**12.901**	6430.8	11.922	5979.9	11.176						
1-hexadecanol	**7262.7**	**13.282**	6811.4	12.354	6324.3	11.542						
1-heptadecanol			7194.9	12.758	7020.0	12.293						
6-heptadecanol							7794.5	16.593				
7-heptadecanol									8006.6	17.044		
9-heptadecanol											7644.3	16.235
1-octadecanol	**8084.1**	**14.276**	7537.9	13.164	7711.2	13.047						
1-eicosanol					8415.1	13.831	8577.4	17.587	8792.7	18.016	8449.6	17.264
1-docosanol					9792.1	15.365						
cholesterol					4367.4	9.6399						
1-hexacosanol					9327.6	13.932						

[a] The slopes and intercepts in bold along with the corresponding vapor pressures were used to generate vapors pressures for the remaining compounds in the table; $t_o = 1$ min.

Table 9. Coefficients of Equation 4 Evaluated to Calculate Vapor Pressure

mix 1	A	B	C	D	T_{b}/K(calc/exp)[a]
1-decanol	−1967359	−1364489	−1074.92	12.19	502/504.2[b]
1-dodecanol	191769066	−3001302	2583.48	8.98	537/(532, 538, 528)[b]
1-tetradecanol	379224562	−4584596	6042.84	6.04	572/(570, 536)[b]
1-pentadecanol	474000287	−5384735.7	7727.91	4.69	380/386[c]
1-hexadecanol	563379466	−6139805	9404.2	3.23	609/(617, 598)[b]
1-octadecanol	745807085	−7680233	12699.83	0.52	444/444[d]; 651/623[b]
Mix 3					
1-heptadecanol	665994534	−7005616	11275.51	1.67	632/610.5[e]
Mix 5					
1-eicosanol	925201968	−9201669	15942.72	−2.12	704/NA
1-docosanol	1105216248	−10725469	19186.20	−4.75	441/453[f]
1-hexacosanol	1457252181	−13705441	25528.55	−9.90	435/448[g]
cholesterol	1545929030	−14415329	27984.11	−13.33	
Mix 7					
6-heptadecanol	582128445	−6300989	9784.58	2.88	614/NA
Mix 8					
7-heptadecanol	577146478	−6257879	9704.25	2.93	613/NA
Mix 9					
9-heptadecanol	576848758	−6254496	9662.6	3.01	426/403[h]

[a] Extrapolated/normal boiling temperature (experimental) at $p = 101.325$ kPa unless noted otherwise. [b] From ref 19. [c] From ref 23 at 0.0266 kPa pressure. [d] From ref 24 at 0.266 kPa pressure. [e] From ref 20. [f] From the ref 24 at 0.029 kPa pressure. [g] From ref 25 at 0.00266 kPa pressure. [h] From ref 26 at 0.266 kPa pressure.

Table 10. Experimental Fusion Enthalpies and Their Adjustment to T = 298.15 K

compound	$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(T_{\mathrm{fus}})$[a] kJ·mol^{-1}	T_{fus} K	C_p(cr) J·mol^{-1}·K^{-1}	$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}$(298 K) kJ·mol^{-1}	ref
1-octanol	24.3 ± 0.6	282.3 ± 1.0	248.4	25.1 ± 0.7	this work
1-decanol	37.7	280.1	302.2	38.8	27
1-dodecanol	40.2	300.2	356	40.1	28
1-tridecanol	45.1 ± 0.4	304.6	382.9	44.6 ± 0.4	29
1-tetradecanol	49.4 ± 0.4[b]	311	409.8	48.4 ± 0.5	29
1-pentadecanol	54.7 ± 0.4	316.6	436.7	53.2 ± 0.6	29
1-hexadecanol	58.4 ± 0.4[c]	322.2	463.6	56.3 ± 0.7	29
1-heptadecanol	63.4 ± 0.6	325.3 ± 0.5	490.5	60.9 ± 1.0	this work
4-heptadecanol	35.7 ± 1.8	311.5 ± 0.5	472.6	34.5 ± 1.8	this work
6-heptadecanol	49 ± 0.5	315.8 ± 0.3	472.6	47.4 ± 0.7	this work
7-heptadecanol	28.8 ± 0.3	314.4 ± 0.8	472.6	27.3 ± 0.6	this work
9-heptadecanol	43.2 ± 0.6	330.2 ± 0.1	472.6	40.2 ± 1.1	this work
1-octadecanol	69.6 ± 0.8	325.6 ± 1.0	517.4	67.0 ± 1.1	this work
1-eicosanol	78.4 ± 0.2	337 ± 0.2	571.2	74.3 ± 1.2	this work
1-docosanol	82.8 ± 6.0	344.5 ± 1.1	625	77.6 ± 6.3	this work
1-hexacosanol	103.8 ± 3.9	353.1 ± 1.1	732.6	96.6 ± 3.6	this work
cholesterol	29.9	420.2	757.3	15.6 ± 4.3	26

[a] The sum of the fusion enthalpy and all phase transitions occurring above $T = 298.15$ K. [b] Other literature value:[30] 49.4 kJ·mol^{-1}. [c] Literature value:[31] 57.3 kJ·mol^{-1}.

Table 11. Comparison of Sublimation Enthalpies Calculated from Vaporization and Fusion Enthalpies to Those Measured Directly

compound	$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}$(298.15 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$(298.15 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$(298.15 K) + $\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}$(298.15K) kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$(298.15 K)[a] kJ·mol^{-1}
1-octanol	25.1 ± 0.7	70.98	96.1	103.4 ± 2.6
1-decanol	38.8	81.5	119.3	114.1 ± 6.3
1-dodecanol	40.1	90.8 ± 1.2	131.0	129.7 ± 1.3
1-tridecanol	44.6 ± 0.4	94.7 ± 0.4	139.3 ± 0.6	
1-tetradecanol	48.4 ± 0.5	98.9 ± 2.5	147.3 ± 2.6	144 ± 2.1
1-pentadecanol	53.2 ± 0.6	103.5 ± 3.3	156.7 ± 3.4	
1-hexadecanol	56.5 ± 0.7	107.7 ± 1.2	164.2 ± 1.4	168.5 ± 2.1
1-heptadecanol	60.9 ± 1.0	112.5 ± 2.9	173.4 ± 3.1	
6-heptadecanol	47.4 ± 0.7	108.6 ± 3.4	156.0 ± 3.5	
7-heptadecanol	27.3 ± 0.6	108.2 ± 2.6	135.5 ± 2.7	
9-heptadecanol	40.2 ± 1.1	108.5 ± 1.1	148.7 ± 1.6	
1-octadecanol	67.0 ± 1.1	116.8 ± 1.2	183.4 ± 1.6	189.5 ± 1.4
1-eicosanol	74.3 ± 1.2	125.9 ± 0.8	200.2 ± 1.4	220.9 ± 3.9
1-docosanol	77.6 ± 6.3	135.9 ± 0.8	213.7 ± 6.4	210.5 ± 10.1
1-hexacosanol	96.6 ± 3.6	153.7 ± 0.8	250.3 ± 3.7	
cholesterol	15.6 ± 4.3	148.0 ± 0.8	163.6 ± 4.4	

[a] From ref 17.

these coefficients is to use them in predicting normal boiling temperatures. The last column in Table 9 lists the predicted/experimental boiling temperatures when available. In some cases only the boiling temperature at reduced pressure is available.

Agreement with the available literature is reasonably good. In some instances more than one experimental boiling point is available. All values have been included to illustrate the scatter in the experimental data. The results reported for cholesterol represent a further test of these results. The vapor pressure of cholesterol has been reported in the temperature range $T = (411$ to $447)$ K.[20] The vapor pressure calculated from the Antoine constants in Table 7 at the mean temperature, $p = 1.09 \times 10^{-3}$ kPa at $T = 428$ K, can be compared to a value of $p = 9.86 \times 10^{-4}$ kPa calculated using eq 4 and the appropriate constants in Table 9. The vaporization enthalpy calculated at the mean temperature of measurement, $\Delta_l{}^gH^\circ_m(428\ \mathrm{K}) = 114.9\ \mathrm{kJ{\cdot}mol^{-1}}$ can be compared to a value of $\Delta_l{}^gH^\circ_m(428\ \mathrm{K}) = 117.0\ \mathrm{kJ{\cdot}mol^{-1}}$ calculated from vapor pressures generated by eq 4 over the same temperature range.

Fusion and Sublimation Enthalpies of the 1-Alkanols

Many of the larger 1-alkanols are solids at room temperature. Fusion enthalpies are available for some of these materials in the literature. For the remainder, fusion enthalpies were measured by DSC. These data can be found in Table 10. Experimental fusion enthalpies are also adjusted to $T = 298.15$ K using eq 5:

$$\Delta_{\mathrm{fus}}H^\circ_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = \Delta_{\mathrm{fus}}H^\circ_{\mathrm{m}}(T_{\mathrm{fus}}) + (0.15C_p(\mathrm{cr}) - 0.26C_p(\mathrm{l}) - 9.83)(T_{\mathrm{m}}/\mathrm{K} - 298.15)/1000 \quad (5)$$

This adjustment requires the heat capacities at $T = 298.15$ K for both the liquid and solid phases. The heat capacity of both phases was estimated using a group additivity approach that has been described previously.[11] Estimated heat capacities for the liquid and solid phases are provided in column 4 of Tables 1 and 10. Table 11 compares available sublimation enthalpies from the literature (column 5) and sublimation enthalpies calculated as the sum of experimental fusion and vaporization enthalpies. Experimental sublimation enthalpies were adjusted to $T = 298.15$ K using eq 6

$$\Delta_{\mathrm{cr}}{}^{g}H^\circ_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = \Delta_{\mathrm{cr}}{}^{g}H^\circ_{\mathrm{m}}(T_{\mathrm{m}}) + (0.75 + 0.15C_p(\mathrm{cr}))(T_{\mathrm{m}}/\mathrm{K} - 298.15)/1000 \quad (6)$$

as necessary. The two numbers are generally in good agreement with perhaps the exception of 1-docosanol, whose sublimation enthalpy measured directly, appears somewhat out of line with the other 1-alkanols.

Supporting Information Available:

Tables including retention times and a summary of each correlation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 23, 2005. Accepted November 21, 2005.

JE0503857