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The vaporization enthalpies and vapor pressures of fatty acid methyl esters C_{18}, C_{21} to C_{23}, and C_{25} to C_{29} by correlation – gas chromatography

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Abstract

Vapor pressures and vaporization enthalpies for methyl heptadecanoate and methyl heneicosanoate to methyl octacosanoate exclusive of methyl tricosanoate are evaluated as a function of temperature over the temperature range $T = 298.15$–450 K by correlation gas chromatography. The results are generated by an extrapolative process using literature values for methyl tetradecanoate to methyl eicosanoate as standards. Relationships for calculating vapor pressures of the title compounds from $T = 298.15$ to 450 K are provided. Experimental fusion enthalpies are also reported for the methyl esters from methyl hexadecanoate to methyl octacosanoate excluding methyl tridecanoate. Vaporization enthalpies and fusion enthalpies adjusted for temperature to $T = 298.15$ K are combined to provide sublimation enthalpies. The results are compared to available literature values. A rationale for the linear relationship observed between enthalpies of vaporization and enthalpies of transfer from solution to the vapor is also provided.

Keywords: Vaporization; Sublimation; Phase change; Enthalpy, Fatty acid methyl esters, Vapor pressures

1. Introduction

The methyl esters of fatty acids (FAMEs) are members of a group of esters that are promising substitutes for chlorinated hydrocarbons in industrial processes [1], diesel fuel substitutes [2] and lubricants. The larger esters are also useful in describing phase behavior of drilling fluids with gases for predicting the risk of violent gas kickbacks associated with petroleum recovery [3]. This has prompted interest in the thermochemical properties of these materials. Recently, van Genderen et al. [4] have evaluated the vapor pressures and vaporization enthalpies of methyl butanoate through methyl eicosanoate, using data from a variety of sources including their own measurements. Very few studies are available for the larger homologues. We would like to report the results of our studies on the vapor pressures and vaporization enthalpies of methyl heneicosanoate to methyl octacosanoate using the technique of correlation gas chromatography. Vaporization enthalpies are also combined with fusion enthalpies adjusted for temperature to provide sublimation enthalpies at $T = 298.15$ K.

Correlation gas chromatography has proven to be quite successful in providing vaporization enthalpies of both liquids and solids, particularly for homologous series [5]. The technique relies on the linear correlation observed between enthalpies of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$, as measured by gas chromatography and the vaporization enthalpy ($\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$) of a series of standards. The vaporization enthalpies of the standards have usually been chosen at $T = 298.15$ K but the correlation works for other temperatures as well. The linear correlation that is observed between $\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ is empirical. A simple mathematical basis for the linear correlation observed for hydrocarbons has recently been reported [6]. In this paper, the model is extended to include single and multi-substituted compounds. The model also provides a rational basis for understanding why the correlation fails when substituents are mixed or varied in a non-systematic manner.

2. Discussion

Enthalpies of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$, are measured by gas chromatography by measuring the retention times of a mixture consisting of both standards and

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target solutes as a function of temperature. The retention times, t, are adjusted for the dead volume of the column by measuring the retention time of an unretained solute, usually the solvent. The adjusted retention time, $t_a = t - t_{nrr}$, measures the amount of time the solute spends on the stationary phase and this time is inversely proportional to the compound's vapor pressure above the condensed phase. A plot of $\ln(1/t_a)$ versus $1/T$ (K^{-1}) results in a linear plot with a slope equal to $-\Delta_{sln}^{g}H_m(T_m)/R$.

The term, $\Delta_{sln}^{g}H_m(T_m)$ can be equated in a thermodynamic cycle to the sum of the vaporization enthalpy measured at $T = T_m$ and the enthalpy of solution or adsorption ($\Delta_{sln}^{g}H_m$) of each solute on the stationary phase of the column as shown below. The sensitivity of the flame ionization detector assures dilute concentrations of solute and since the solute "dissolves in" or is adsorbed on the stationary phase of the capillary column, the same thermodynamic cycle applies to both solids and liquids.

$$\Delta_{sln}^{g}H_m(T_m) = \Delta_{l}^{g}H_m(T_m) + \Delta_{sln}H_m(T_m) \quad (1)$$

In correlation gas chromatography, $\Delta_{sln}^{g}H_m(T_m)$ is correlated directly with the vaporization enthalpy of the standards at the temperature of interest, usually at $T = 298.15$ K. Provided the standards are appropriately chosen in relation to each other and to the target solutes, a linear correlation is obtained between $\Delta_{sln}^{g}H_m(T_m)$ and $\Delta_{l}^{g}H_m(T_m)$. The correlation equation derived from known vaporization enthalpies is then used to evaluate the vaporization enthalpies of the target solutes. The following narrative briefly describes the origin of this correlation.

In the thermodynamic cycle outlined by Eq. (1), all of the enthalpies are referenced to the same temperature. In c-gc, $\Delta_{sln}^{g}H_m(T_m)$ measured at $T = T_m$, is correlated to $\Delta_{l}^{g}H_m$ (298.15 K); the correlation results in the following slope:

$$\text{slope} = \frac{\Delta_{l}^{g}H_m\ (298.15\,\text{K})}{\Delta_{sln}^{g}H_m(T_m)} \quad (2)$$

Appropriate substitution of Eq. (1) into Eq. (2) results in the following:

$$\text{slope} = \frac{\Delta_{l}^{g}H_m\ (298.15\,\text{K})}{\Delta_{l}^{g}H_m(T_m) + \Delta_{sln}^{g}H_m(T_m)} \quad (3)$$

Vaporization enthalpies are known to exhibit excellent group properties [7]. Hydrocarbon derivatives containing a single functional group can be estimated quite accurately by a variety of simple relationships, including the following [8]:

$$\Delta_{l}^{g}H_m\ (298.15\,\text{K}) = 4.69(n_c - n_Q) + 1.3n_Q + b + 3.0 \quad (4)$$

In this equation, n_c and n_Q refer to the number of carbons and quaternary carbon atoms, respectively. The b term represents the contribution of the functional group. Table 1 lists values for a few functional groups. The b terms are constants whose value can be reformulated as equal to $4.69a_b$ where a_b refers to the functional group in question and $4.69a_b = b$. Eq. (4) can be rewritten as $m(n_c + a_b) + c$, where c is the sum of the constant, 3.0, and any negative contributions quaternary carbons may contribute or more generally as $mn_c' + c$ where n_c' equals to $n_c + a_b$.

Eq. (4) was derived for vaporization enthalpies at $T = 298.15$ K; this temperature selection however was arbitrary and it is reasonable to assume that similar equations of the same type, $m'n_{c''} + c'$, could also be derived for vaporization enthalpies at $T = T_m$ where m' and c' are appropriate values of constants and $n_{c''}$ refers to $(n_c + a_{b'})$ at this temperature. Although $a_{b'}$ would not be expected to equal a_b, any differences between the two can be accommodated by c' so that the vaporization enthalpy at $T = T_m$ can still be expressed by the expression: $m'n_{c'} + c'$. In fact, vaporization enthalpies at both $T = 298.15$ K and T_m can be modeled exactly by $mn_{c'} + c$ and $m'n_{c'} + c'$ by simply treating the intercepts, c and c', as variables.

Enthalpies of solution, $\Delta_{sln}H_m(T_m)$ at $T = 298.15$ K are small in comparison to vaporization enthalpies [8]; they can also can be modeled group additivity. Their value

Table 1
Contributions of various functional groups to vaporization enthalpies (kJ mol^{-1})[a]

Class of compounds	Functional group	b	Class of compounds	Functional group	b
Acid	–C(=O)OH	38.8	Iodide	–I	18.0
Alcohol	–OH	29.4	Ketone	>C=O	10.5
Aldehyde	–CHO	12.9	Nitrile	–CN	16.7
Amide [mono-substituted]			Nitro	–NO$_2$	22.8
	–C(=O)NH–	42.5	Heterocyclic aromatic	=NH–	
Amine (primary)	–NH$_2$	14.8	Nitrogen	=N–	[12.2]
Amine (secondary)	–NH–	8.9	Sulfide	>S	13.4
Amine (tertiary)	> N–	6.6	Disulfide	–SS–	[22.3]
Bromide	–Br	14.4	Sulfoxide	> SO	[42.4]
Chloride	–Cl	10.8	Sulfone	–SO$_2$–	[53.0]
Ester	–C(=O)O–	10.5	Thiolester	–C(=O)S–	[16.9]
Ether	> O	5.0	Thiol	–SH	13.9

[a] See Ref. [17].

is not known at $T = T_m$. However comparison of values of $\Delta_l^g H_m(T_m)$ computed at $T = T_m$ to measured values of $\Delta_{sln}^g H_m(T_m)$ suggest that the total contribution of $\Delta_{sln}^g H_m(T_m)$ is very small at this temperature, and often of the order of the uncertainty of the measurements. Using a similar relationship to model $\Delta_{sln}^g H_m(T_m)$, $m'''n_c' + c'''$ and treating c''' as a variable can reproduce $\Delta_{sln}^g H_m(T_m)$ exactly. Substituting these linear functions into Eq. (3) and combining similar terms results in Eq. (5), where $m_{sln} = m' + m'' + m'''$ and $c_{sln} = c' + c'' + c'''$. It is important to note that all the contributions to the constants c, c'', and c''' are small and can be of opposite sign. This assures that whatever their sum, the contribution of this second term to the total vaporization enthalpy will be small in comparison to the first term, particularly for large molecules.

$$\text{slope} = \frac{m_{sln}n_{c'} + c_{sln}}{mn_{c'} + c} \tag{5}$$

As long as c_{sln} and c are small in comparison to $m_{sln}n_{c'}$ and $mn_{c'}$, respectively, correlation of $\Delta_{sln}^g H_m(T_m)$ with $\Delta_l^g H_m$ (298.15 K), will be linear because Eq. (5) is a hyperbolic function approaching its asymptote, m_{sln}/m. This model explains the linear relationships observed between $\Delta_l^g H_m(T_m)$ and $\Delta_{sln}^g H_m(T_m)$ for hydrocarbons and substituted hydrocarbons when the number and type of functional group(s) remain constant. An examination of Table 1 also suggests that functional groups with similar b values should correlate with each other. This behavior has been observed when correlating $\Delta_{sln}^g H_m(T_m)$ with $\Delta_l^g H_m$ (298.15 K) of hydrocarbons with tertiary amines [9] and single and multi-substituted ethers [10]; similar correlations have been observed with esters and ketones [11].

3. Experimental

Most FAMEs were purchased from the Sigma Chemical Company and were used without any further purification. Each was analyzed by gas chromatography and found to be at least 99 mol% pure. Methyl hexadecanoate and methyl octadecanoate were recrystallized several times from acetone at 0 °C to a purity of 99+% as analyzed by gas chromatography before use. Correlation gas chromatography experiments were performed on an HP 5890A Series II Gas Chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of 100/1. Retention times were recorded to three significant figures following the decimal point on an HP 3989A Integrator. The instrument was run isothermally using both a 15 and 30 m SPB-5 capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent, CH_2Cl_2, increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion used to confirm that the solvent is not being retained on the column. The retention times of the solvent were used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the solvent from the retention time of each analyte as a function of temperature usually over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. Temperature was maintained constant by the gas chromatograph to ±0.1 K.

The retention times of the FAMEs are reported in Table 2A–F. The experiments were generally duplicated to insure reproducibility; only one of runs is reported. Since vapor pressures and vaporization enthalpies are determined relative to standards, the retention time data reported in Table 2 permit the reader to adjust the results should the values of the standards change as a result of future work. Table 3 contains a summary of the current results.

Fusion enthalpies were measure on a Perkin Elmer DSC-7 under a nitrogen purge in hermetically sealed aluminum cells at a scan rate of 5 K min^{-1}. Identification of the fusion temperature by DSC was complicated by various solid–solid transitions that accompanied the melting process thereby broadening the endotherms observed. DSC onset temperatures were not used for this reason. The DSC results were consistent with the fusion temperatures reported in the literature; literature melting temperatures were used in the calculations described below. All fusion enthalpy determinations were performed in triplicate.

4. Results: vaporization enthalpies

The vaporization enthalpies of FAMEs C_5 to C_{21} have previously been tabulated by van Genderen et al. [4]. In addition, the vaporization enthalpy of methyl docosanoate has been reported by Krop et al. [1]. These values are listed in Table 4 which also includes a summary of the results of this study. The details of plotting ln[1/t_a] versus 1/T are summarized in Table 3. Table 3A–F lists the slopes, intercepts, the literature vaporization enthalpies used as standards and the vaporization enthalpy calculated from the correlation equation reported at the bottom of each respective section of the table. We have repeated measurements for FAMEs C_{13} through to C_{21} to document whether a linear correlation is observed between $\Delta_{sln}^g H_m$ and $\Delta_l^g H_m$ (298.15) and because the literature value of one of the compounds, methyl heptadecanoate did not correlate well with the other FAMEs. These correlations are illustrated in Figs. 1 and 2. The literature value of methyl heptadecanoate, shown as a solid hexagon in Fig. 1, was treated as an unknown and is reported in Table 4 as an average of the values calculated by the correlation equations reported at the bottom of Table 3A–C. These values are identified as the empty circle and the empty square in Fig. 1 and as the empty circle in Fig. 2.

The literature values and the vaporization enthalpy results obtained in this study are summarized in Tables 3 and 4. While vaporization enthalpy values for methyl

Table 2
Retention times of the FAMEs

Compound		Retention times (min)						
(A) FAME mix 1								
	T/K	467.8	472.6	477.5	482.4	487.3	492.2	
CH_2Cl_2	methylene chloride	0.398	0.388	0.389	0.387	0.392	0.391	
$C_{13}H_{26}O_2$	methyl dodecanoate	1.637	1.46	1.329	1.209	1.121	1.035	
$C_{14}H_{28}O_2$	methyl tridecanoate	2.233	1.963	1.755	1.571	1.43	1.301	
$C_{15}H_{30}O_2$	methyl tetradecanoate	3.1	2.688	2.364	2.085	1.865	1.672	
$C_{16}H_{32}O_2$	methyl pentadecanoate	4.361	3.732	3.234	2.811	2.475	2.189	
$C_{17}H_{34}O_2$	methyl hexadecanoate	6.198	5.237	4.47	3.837	3.33	2.905	
$C_{18}H_{36}O_2$	methyl heptadecanoate	8.844	7.391	6.231	5.282	4.524	3.9	
(B) FAME mix 2								
	T/K	469.0	473.7	478.8	483.7	488.8	493.7	
CH_2Cl_2	methylene chloride	0.396	0.404	0.399	0.398	0.396	0.399	
$C_{15}H_{30}O_2$	methyl tetradecanoate	3.106	2.709	2.37	2.091	1.861	1.668	
$C_{16}H_{32}O_2$	methyl pentadecanoate	4.371	3.753	3.238	2.816	2.47	2.182	
$C_{17}H_{34}O_2$	methyl hexadecanoate	6.2	5.252	4.475	3.84	3.325	2.896	
$C_{18}H_{36}O_2$	methyl heptadecanoate	8.85	7.41	6.231	5.282	4.519	3.886	
$C_{19}H_{38}O_2$	methyl octadecanoate	12.709	10.498	8.72	7.311	6.183	5.255	
(C) FAME mix 3								
	T/K	508.9	513.9	518.8	523.8	528.8	533.8	
CH_2Cl_2	methylene chloride	0.396	0.396	0.407	0.402	0.41	0.415	
$C_{17}H_{34}O_2$	methyl hexadecanoate	4.468	3.874	3.393	2.99	2.645	2.352	
$C_{18}H_{36}O_2$	methyl heptadecanoate	6.227	5.332	4.615	4.016	3.51	3.081	
$C_{19}H_{38}O_2$	methyl octadecanoate	8.728	7.389	6.315	5.434	4.696	4.077	
$C_{20}H_{40}O_2$	methyl nonadecanoate	12.262	10.276	8.684	7.393	6.319	5.426	
$C_{21}H_{42}O_2$	methyl eicosanoate	17.255	14.318	11.971	10.093	8.545	7.26	
(D) FAME mix 4								
	T/K	508.9	513.9	518.8	523.8	528.8	533.8	538.7
					t_r/min			
CH_2Cl_2	methylene chloride	0.246	0.235	0.25	0.253	0.25	0.256	0.255
$C_{19}H_{38}O_2$	methyl octadecanoate	2.214	1.93	1.719	1.527	1.359	1.223	1.105
$C_{20}H_{40}O_2$	methyl nonadecanoate	2.915	2.517	2.214	1.945	1.713	1.524	1.363
$C_{21}H_{42}O_2$	methyl eicosanoate	3.859	3.302	2.872	2.495	2.176	1.914	1.696
$C_{22}H_{44}O_2$	methyl heneicosanoate	5.125	4.349	3.74	3.22	2.781	2.422	2.127
$C_{23}H_{46}O_2$	methyl docosanoate	6.823	5.745	4.895	4.174	3.573	3.079	2.679
$C_{25}H_{50}O_2$	methyl tetracosanoate	12.158	10.069	8.423	7.059	5.942	5.034	4.305
(E) FAME mix 5								
	T/K	533.9	539.0	543.9	549.0	553.9	558.8	
				t_r/min				
CH_2Cl_2	methylene chloride	0.252	0.255	0.255	0.255	0.258	0.26	
$C_{20}H_{40}O_2$	methyl nonadecanoate	1.518	1.358	1.223	1.105	1.006	0.923	
$C_{21}H_{42}O_2$	methyl eicosanoate	1.908	1.689	1.505	1.345	1.214	1.101	
$C_{22}H_{44}O_2$	methyl heneicosanoate	2.415	2.116	1.866	1.654	1.476	1.326	
$C_{23}H_{46}O_2$	methyl docosanoate	3.07	2.665	2.33	2.044	1.808	1.61	
$C_{25}H_{50}O_2$	methyl tetracosanoate	5.019	4.284	3.678	3.175	2.758	2.412	
$C_{26}H_{52}O_2$	methyl pentacosanoate	6.439	5.45	4.645	3.976	3.426	2.973	
$C_{27}H_{54}O_2$	methyl hexacosanoate	8.266	6.945	5.874	4.99	4.27	3.675	
(F) FAME mix 6								
	T/K	539.0	544.0	549.0	554.0	558.6	563.9	
				t_r/min				
CH_2Cl_2	methylene chloride	0.256	0.258	0.259	0.259	0.259	0.256	
$C_{22}H_{44}O_2$	methyl heneicosanoate	2.112	1.869	1.659	1.48	1.327	1.192	
$C_{23}H_{46}O_2$	methyl docosanoate	2.66	2.331	2.051	1.814	1.611	1.435	
$C_{25}H_{50}O_2$	methyl tetracosanoate	4.27	3.679	3.181	2.765	2.416	2.115	
$C_{26}H_{52}O_2$	methyl pentacosanoate	5.431	4.644	3.984	3.434	2.979	2.585	
$C_{27}H_{54}O_2$	methyl hexacosanoate	6.92	5.872	5.002	4.277	3.684	3.173	
$C_{28}H_{56}O_2$	methyl heptacosanoate	8.828	7.435	6.284	5.34	4.563	3.905	
$C_{29}H_{58}O_2$	methyl octacosanoate	11.271	9.421	7.91	6.676	5.663	4.812	

Table 3
Correlation of ln [1/*ta*] vs 1/*T* results with literature vaporization enthalpies

	−Slope[a]	Intercept[a]	$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) (literature)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) (calcd.)[b]
(A) FAME mix 1 ($T_{\mathrm{m}} = 480.0$ K)					
Methyl dodecanoate	6144.1 ± 63	12.928 ± 0.006	51.08	76.59	75.6 ± 2.6
Methyl tridecanoate	6598.9 ± 56	13.507 ± 0.005	54.86	79.99	80.9 ± 2.6
Methyl tetradecanoate	7028.4 ± 51	14.038 ± 0.004	58.43	85.94	85.8 ± 2.6
Methyl pentadecanoate	7448.7 ± 51	14.553 ± 0.005	61.93	89.29	90.7 ± 2.6
Methyl hexadecanoate	7878.5 ± 53	15.091 ± 0.005	65.50	96.84	95.6 ± 2.6
Methyl heptadecanoate	8282.9 ± 53	15.58 ± 0.005	68.86		100.3 ± 2.6
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.386±0.115)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (480 K) + (4.866 ± 1.30), $r^2 = 0.980$					
(B) FAME mix 2 ($T_{\mathrm{m}} = 481.3$ K)					
Methyl tetradecanoate	7071.0 ± 63	14.088 ± 0.006	58.79	85.94	85.5 ± 2.6
Methyl pentadecanoate	7472.7 ± 66	14.563 ± 0.006	62.13	89.29	90.7 ± 2.6
Methyl hexadecanoate	7861.0 ± 68	15.01 ± 0.006	65.35	96.84	95.7 ± 2.6
Methyl heptadecanoate	8258.1 ± 69	15.483 ± 0.006	68.65		100.8 ± 2.6
Methyl octadecanoate	8672.2 ± 79	15.991 ± 0.007	72.10	105.87	106.1 ± 2.6
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.548±0.135)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (481 K) + (4.61 ± 1.33), $r^2 = 0.985$					
(C) FAME mix 3 ($T_{\mathrm{m}} = 491.2$ K)					
Methyl hexadecanoate	7271.4 ± 57	13.783 ± 0.005	60.45	96.84	96.5
Methyl heptadecanoate	7658.4 ± 61	14.232 ± 0.005	63.67		101.2
Methyl octadecanoate	8049.9 ± 64	14.694 ± 0.005	66.92	105.87	106.0
Methyl nonadecanoate	8444.8 ± 64	15.156 ± 0.005	70.21	109.53	110.8
Methyl eicosanoate	8829.5 ± 69	15.617 ± 0.006	73.41	116.43	115.5
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.464±0.119)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (491 K) + (7.99 ± 1.14), $r^2 = 0.987$					
(D) FAME mix 4 ($T_{\mathrm{m}} = 523.8$ K)					
Methyl octadecanoate	7725.4 ± 15	14.507 ± 0.001	64.23	105.87	105.4 ± 1.8
Methyl nonadecanoate	8089.8 ± 18	14.918 ± 0.002	67.26	109.53	110.6 ± 1.8
Methyl eicosanoate	8462.3 ± 21	15.348 ± 0.002	70.35	116.43	115.8 ± 1.8
Methyl heneicosanoate	8820.6 ± 25	15.752 ± 0.002	73.33		120.9 ± 1.8
Methyl docosanoate	9192.3 ± 20	16.183 ± 0.002	76.42	126.1	126.2 ± 1.8
Methyl tetracosanoate	9931 ± 25	17.041 ± 0.002	82.56		136.6 ± 1.8
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.70±0.10)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (524 K) − (3.872 ± 0.91), $r^2 = 0.993$					
(E) FAME mix 5 ($T_{\mathrm{m}} = 546.3$ K)					
Methyl nonadecanoate	7753 ± 17	14.287 ± 0.001	64.46	109.53	110.2 ± 1.2
Methyl eicosanoate	8115.7 ± 11	14.698 ± 0.001	67.47	116.43	115.6 ± 1.2
Methyl heneicosanoate	8474.2 ± 20	15.103 ± 0.001	70.45	120.9	120.9 ± 1.2
Methyl docosanoate	8819 ± 16	15.484 ± 0.001	73.32	126.1	126.1 ± 1.2
Methyl tetracosanoate	9529.5 ± 23	16.289 ± 0.002	79.22	136.6	136.7 ± 1.2
Methyl pentacosanoate	9878.6 ± 21	16.682 ± 0.001	82.13		142.0 ± 1.2
Methyl hexacosanoate	10219 ± 21	17.062 ± 0.001	84.96		147.1 ± 1.2
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.80±0.054) $\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (546 K) − (5.842 ± 0.614), $r^2 = 0.997$					
(F) FAME mix 6 ($T_{\mathrm{m}} = 553.9$ K)					
Methyl heneicosanoate	8402.5 ± 57	14.971 ± 0.004	69.86	120.9	120.9 ± 0.1
Methyl docosanoate	8741.9 ± 61	15.343 ± 0.004	72.68	126.1	126.0 ± 0.1
Methyl tetracosanoate	9442.6 ± 60	16.13 ± 0.004	78.50	136.6	136.6 ± 0.1
Methyl pentacosanoate	9791.8 ± 58	16.523 ± 0.004	81.40	142.0	141.9 ± 0.1
Methyl hexacosanoate	10132 ± 59	16.902 ± 0.004	84.23	147.1	147.1 ± 0.1
Methyl heptacosanoate	10475 ± 65	17.287 ± 0.004	87.09		152.2 ± 0.1
Methyl octacosanoate	10824 ± 68	17.6840.005	90.00		157.5 ± 0.1
$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (1.818±0.004)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (554 K) − (6.106 ± 0.05), $r^2 = 0.999$					

[a] Each equation was characterized by a correlation coefficient (r^2) of better than 0.999.

[b] The uncertainty represents two standard deviations and was calculated from the uncertainty in the intercept of the correlation equation given at the bottom of each respective section.

Table 4
A summary of the results of this work and the literature values used in conjunction with this study

	$\Delta_l^g H_m$ (298.15 K) (kJ mol^{-1})							
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Literature	This work
Methyl butanoate							40.64	
Methyl pentanoate							43.69	
Methyl hexanoate							47.71	
Methyl heptanoate							51.8	
Methyl octanoate							56.87	
Methyl nonanoate							61.59	
Methyl decanoate							66.1	
Methyl indecanoate							70.82	
Methyl dodecanoate	75.6						76.59	75.6
Methyl tridecanoate	80.9						79.99	80.9
Methyl tetradecanoate	85.8	85.5					85.94	85.7
Methyl pentadecanoate	90.7	90.6					89.29	90.7
Methyl hexadecanoate	95.6	95.6	96.1				96.84	95.6
Methyl heptadecanoate	100.3	100.8	101.2				97.03	100.8 ± 1.0
Methyl octadecanoate		105.9	105.8	105.4			105.87	106.1 ± 2.5
Methyl nonadecanoate			110.7	110.6	110.2		109.53	110.8 ± 2.5
Methyl eicosanoate			115.5	115.8	115.6		116.43	115.6 ± 2.5
Methyl heneicosanoate				120.9	120.9	120.9		120.9 ± 2.5
Methyl docosanoate				126.2	126.1	126.0	126.1	126.1 ± 2.5
Methyl tetracosanoate				136.6	136.7	136.6		136.6 ± 2.5
Methyl pentacosanoate					142.0	141.9		142.0 ± 4.5
Methyl hexacosanoate					147.1	147.1		147.1 ± 4.5
Methyl heptacosanoate						152.2		152.2 ± 4.5
Methyl octacosanoate						157.5		157.5 ± 4.5

The uncertainties represent $\pm 2\sigma$ of the probable error as discussed in the text.

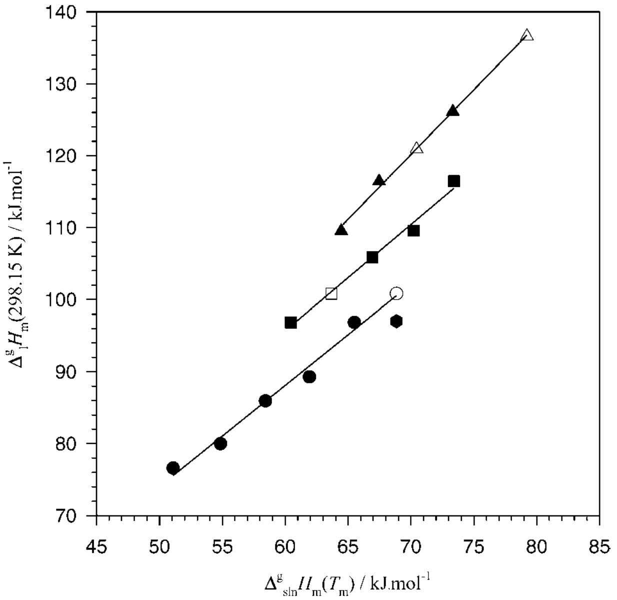

Fig. 1. Plots of $\Delta_l^g H_m$ (298.15 K) vs. the corresponding of $\Delta_{sln}^g H_m$ (T_m) for mixes 1, 3, and 5: solid symbols represent literature values; empty symbols represent values evaluated in this work; circles: n-$C_{12}O_2Me$ through to n-$C_{17}O_2Me$; hexagon: literature value for n-$C_{17}O_2Me$ (see text); solid squares: n-$C_{16}CO_2Me$ through to n-$C_{20}O_2Me$; triangles: n-$C_{19}O_2Me$ through to n-$C_{24}O_2Me$ excluding n-$C_{23}O_2Me$.

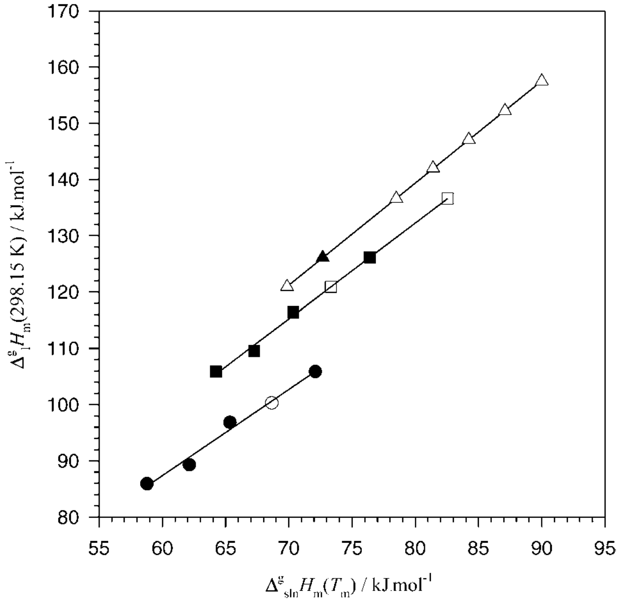

Fig. 2. Plots of $\Delta_l^g H_m$ (298.15 K) of the standards vs. the corresponding $\Delta_{sln}^g H_m(T_m)$ for mixes 2, 4 and 6; solid symbols represent literature values; empty symbols represent the values evaluated in this work; circles: n-$C_{14}CO_2Me$ through to n-$C_{18}CO_2Me$; squares: n-C_{18} CO_2Me through to n-$C_{22}CO_2Me$ excluding n-$C_{23}CO_2Me$; triangles: n-$C_{21}CO_2Me$ through to n-$C_{28}CO_2Me$ excluding n-$C_{23}CO_2Me$.

heptadecanoate, and heneicosanoate were obtained by interpolation, the corresponding values for methyl tricosanoate to methyl octacosanoate are extrapolated values and subject to a larger uncertainty. As a means of arriving at an estimate of the magnitude of this uncertainty, literature vaporization enthalpy values of methyl dodecanoate to methyl tetradecanoate were combined with $\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ values of the FAMEs given in Table 3A to evaluate the vaporization enthalpies of methyl pentadecanoate to methyl heptadecanoate by an extrapolative process. The vaporization enthalpies of methyl pentadecanoate to methyl heptadecanoate evaluated by this process were then used as knowns in mix 2 to evaluate the vaporization enthalpies of methyl octadecanoate. This procedure was repeated in mix 3 to evaluate the vaporization enthalpies of methyl nonadecanoate and methyl eicosanoate. A comparison of the calculated values with literature values resulted in errors that ranged from 0.5 to 4.5 kJ mol^{-1} with the largest error occurring in the last of the three correlations. The average error was ±2.5 kJ mol^{-1}. This is the origin of the errors reported in the last column of Table 4. The average error has been assigned to the results of mix 4 and an uncertainty of ±4.5 kJ mol^{-1} has been assigned to the results of mixes 5 and 6.

A plot of the vaporization enthalpies of the FAMEs from methyl butanoate to methyl octacosanoate as a function of the number of carbon atoms is given in Fig. 3. The line drawn in the figure was evaluated by a linear regression analysis using the vaporization enthalpies of methyl butanoate to methyl docosanoate exclusive of the values determined in this study. The values are identified by the solid circles in Fig. 3. If this equation is used to calculate the vaporization enthalpies of methyl tetracosanoate through methyl octacosanoate, the values calculated on average are +3.0 kJ mol^{-1} lower in magnitude than the values of this study. These values are however within the probable uncertainty associated with the values obtained by this study. The linear regression equation derived using only literature data and the equation derived using all the data are given in the caption of Fig. 3.

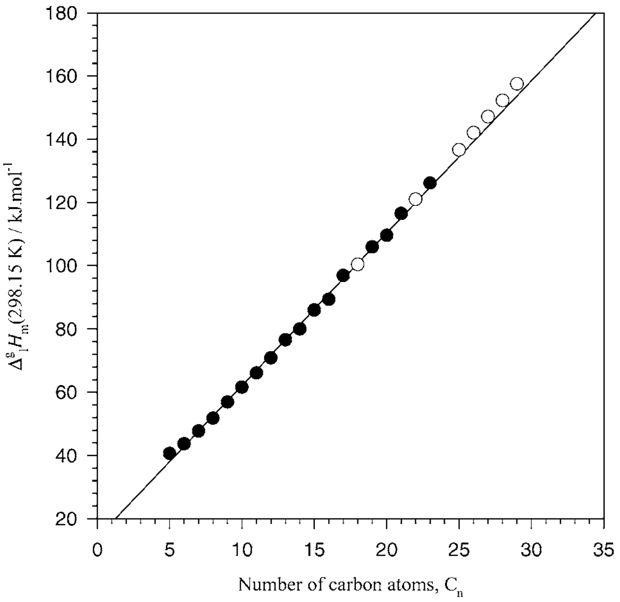

Fig. 3. Vaporization enthalpies of the FAMES from C_5 to C_{29} as a function of the total number of carbon atoms: solid circles: literature values; circles: results from this study. The line was calculated from of a linear regression analysis of the data using values for C_5 to C_{21} and C_{23}. The equation of the line obtained from using only literature data is: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)/kJ mol^{-1} $= (4.818 \pm 0.053)C_n + (13.83 \pm 1.165)$ ($r^2 = 0.9981$). The equation derived using all the data is given by $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) (kJ mol^{-1}) $= (4.954 \pm 0.0367)C_n + (12.36 \pm 1.30)$ ($r^2 = 0.9988$).

4.1. Vapor pressures

In addition to the vaporization enthalpies, the article by van Genderen et al. [4] also provides evaluated vapor pressure data processed in the form of the regression equation introduced by Clarke and Glew [12]:

$$R\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta_{\mathrm{l}}^{\mathrm{g}}G_{\mathrm{m}}(\theta)}{\theta} + \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\theta)\left[\frac{1}{\theta}-\frac{1}{T}\right] + \Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0}\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{\theta}{T}\right)\right] \qquad (6)$$

where p is the saturation vapor pressure, T the thermodynamic temperature, θ a chosen reference temperature and p_0 a reference pressure; p_0 was taken as 1 Pa. Molar values for the Gibbs' free energy, the vaporization enthalpy, and the heat capacity difference between the gas and liquid phases, $\Delta_{\mathrm{l}}^{\mathrm{g}}G_{\mathrm{m}}(\theta)$, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\theta)$, and $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0}(\theta)$, respectively, were computed at several temperatures including $T = 298.15$ and 350 K. Since much of the interest in vapor pressures of the FAMEs is at ambient temperatures and above, we chose for our correlations, a range of temperatures centered around $T = 350$ K. Vapor pressures calculated at $T = 298.15$ K using the parameters reported by van Genderen et al. [4] for $\theta = 350$ K were in good agreement with vapor pressures calculated using the parameters for $\theta = 298.15$ K. The parameters used in calculating vapor pressures are reported in Table 5. The vapor pressures calculated from these parameters are also expressed in the form of a third-order polynomial Eq. (7), that is used in this work to model the temperature dependence of vapor pressure. The parameters (A–D) of Eq. (7) for methyl dodecanoate to methyl eicosanoate exclusive of methyl heptadecanoate are also included in Table 5:

$$\ln\left(\frac{p}{p_0}\right) = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (7)$$

Vapor pressures were calculated using the protocol recently reported for the n-alkanes [6,13]. Values of $\ln(p/p_0)$ calculated using Eq. (6) were correlated with $\ln(1/t_{\mathrm{a}})$ values calculated from the equations in Table 3. As with the vaporization enthalpy, vapor pressures for methyl heptadecanoate were treated as unknown and calculated from the resulting correlation equation.

Table 5
Literature parameters for Eq. (6) and the A–D parameters used in Eq. (7)

	$\Delta G^{\circ}_{\mathrm{m}}$ [a] (J mol^{-1})	$\Delta H^{\circ}_{\mathrm{m}}$ [a] (J mol^{-1})	$\Delta C^{0}_{p,\mathrm{m}}$ [a] (J K^{-1} mol^{-1})	A [b] ($\times 10^{-8}$)	B [b] ($\times 10^{-6}$)	C [b]	D [b]
Methyl dodecanoate	−11324	71421	−113.5	2.18708	−2.72723	1633.21	4.862
Methyl tridecanoate	−8987	73955	−91.8	1.76893	−2.20581	−626.33	7.233
Methyl tetradecanoate	−6534	79828	−120.7	2.32582	−2.90023	1270.55	5.341
Methyl pentadecanoate	−4346	82100	−102.4	1.97319	−2.46051	−651.20	7.312
Methyl hexadecanoate	−1657	93363	−213.7	4.11787	−5.13488	8019.92	−1.553
Methyl octadecanoate	3011	98021	−157.9	3.04264	−3.79409	2433.18	4.364
Methyl nonadecanoate	4827	101170	−159	3.06384	−3.82052	2153.49	4.705
Methyl eicosanoate	7308	109200	−203	3.91169	−4.87777	5151.12	1.941

[a] Literature parameters for Eq. (6) at $\theta = 350$ K [4].
[b] Evaluated using the vapor pressures calculated from Eq. (6).

The data from mix 2 were used for this calculation since methyl heptadecanoate is more intermediate in volatility relative to the standards. Table 6 illustrates the protocol used to calculate vapor pressures at $T = 298.15$ K. Values of $\ln(1/t_a)$ were calculated for mix 2 using the appropriate equations in Table 3B; values of $\ln(p/p_0)$ were similarly calculated using Eq. (6) using the appropriate constants given in Table 5. The equation produced by the correlation, Eq. (8), was used to generate the $\ln(p/p_0)$ value for methyl heptadecanoate. This was the value used in each subsequent correlation. The results reported in the last column of Table 6A for mix 1 and the fourth column in Table 6B, illustrates the quality of the fit when this value for methyl heptadecanoate is used in correlations with other FAMEs.

The result obtained by extrapolation are provided in Table 6B and C. Mix 4 uses $\ln(p/p_0)$ values for FAMEs C_{19} to C_{21} generated from Eq. (6) to evaluate corresponding values for FAMEs C_{22} to C_{25}. Once evaluated, these values were used to expand the extrapolation to include FAMEs C_{26} to C_{29}. This process was then repeated using the equations in Tables 3 and 5 to calculate values of $\ln(1/t_a)$ and $\ln(p/p_0)$ over the temperature range $T = 298.15$–450 K at 30 K intervals, respectively. The resulting vapor pressures (not shown) were then fit to Eq. (7). The observed temperature dependence reproduced by the constants in Eq. (7) are reported in Table 7 and illustrated in Fig. 4.

The use of such an extrapolation is risky since errors present in early correlations can be amplified in subsequent ones. Unfortunately, very little experimental vapor pressure data appear to have been reported for the larger FAMEs, even at elevated temperatures. The only vapor pressure data we have been able to locate are for methyl docosanoate reported by Krop et al. [1]. They report a value for $\log p$ (mmHg) of −7.17 at $T = 298.15$ K; converted to $\ln(p/p_0)$, this corresponds to a value of −23.1 which is in good agreement with the value of −23.0 evaluated in mix 4 of Table 6B.

As an estimate of the magnitude of the error that might be expected in such an extrapolation, the following was used as a model. The vapor pressures of methyl dodecanoate to methyl tetradecanoate in mix 1 at $T = 298.15$ K were used as knowns to evaluate $\ln(p/p_0)$ of the remaining FAMEs up to methyl docosanoate in the manner described above. A total of four extrapolations were included in the evaluation, similar to the number used to evaluate $\ln(p/p_0)$ values for methyl heneicosanoate to methyl octacosanoate. The results of the extrapolation were then compared to experimental results. Methyl heptadecanoate and methyl heneicosanoate were excluded from the comparisons. The absolute error associated with calculated $\ln(p/p_0)$ values ranged from a low of 0.18 to a high of 0.53 with an average of 0.24; the absolute fractional error ranged from a low of 0.0013 to a high of 0.026 with an average of 0.015 natural log units. The scatter between experimental data calculated by Eq. (1) and the extrapolated data as measured by the standard deviation was ±0.3 $\ln(p/p_0)$ units. As might be expected, the uncertainty gradually increased with each successive extrapolation. As a result of the lack of any other suitable tests of these data, these uncertainties seem reasonable estimates of the uncertainties associated with the use of the parameters in Table 7 to calculate $\ln(p/p_0)$ values of the larger FAMEs. It should be emphasized here that the constants in Table 7

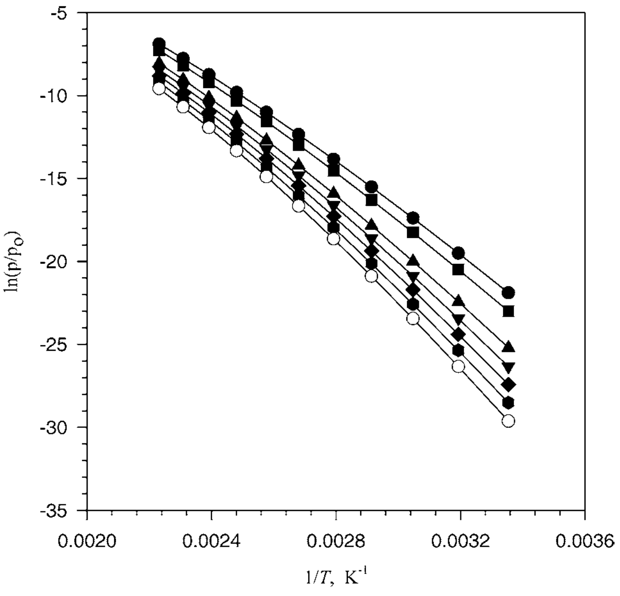

Fig. 4. The dependence of $\ln(p/p_0)$ on $1/T$ of FAMEs C_{22} (top), C_{23} and C_{25} to C_{29} (bottom).

Table 6
Calculation of $\ln(p/p_0)$ at $T = 298.15$ K for the FAMEs C_{18}, and C_{22} to C_{28} by correlation of $\ln(p/p_0)$ values calculated from Eq. (6) with corresponding $\ln(1/t_a)$ values

	$\ln(1/t_a)$[a], mix 2	$\ln(p/p_0)$[b]	$\ln(p/p_0)$[c], Eq. (8)	$\ln(1/t_a)$[a], mix 1	$\ln(p/p_0)$[b]	$\ln(p/p_0)$[d], Eq. (9)
(A) FAMEs C_{13} to C_{18}						
Methyl dodecanoate				−7.68	−12.09	−11.92
Methyl tridecanoate				−8.63	−13.01	−13.12
Methyl tetradecanoate	−9.638	−14.25	−14.23	−9.54	−14.25	−14.28
Methyl pentadecanoate	−10.50	−15.11	−15.38	−10.43	−15.11	−15.42
Methyl hexadecanoate	−11.36	−16.89	−16.51	−11.33	−16.89	−16.57
Methyl heptadecanoate	−12.21		−17.64	−12.2	−17.64[c]	−17.67
Methyl octadecanoate	−13.10	−18.68	−18.8			
$\ln(p/p_0)_{\text{calc}} = (1.316 \pm 0.133)\ln(1/t_a)_{\text{mix 2}} - (1.562 \pm 0.342)$; $r^2 = 0.9799$					(8)	
$\ln(p/p_0)_{\text{calc}} = (1.272 \pm 0.065)\ln(1/t_a)_{\text{mix 1}} - (2.152 \pm 0.246)$; $r^2 = 0.9990$					(9)	
	$\ln(1/t_a)$[a], mix 3	$\ln(p/p_0)$[b]	$\ln(p/p_0)$[e], Eq. (10)	$\ln(1/t_a)$[a], mix 4	$\ln(p/p_0)$[b]	$\ln(p/p_0)$[f], Eq. (11)
(B) FAMEs C_{13} to C_{18}						
Methyl hexadecanoate	−10.61	−16.89	−16.74			
Methyl heptadecanoate	−11.45	−17.64[c]	−17.73			
Methyl octadecanoate	−12.31	−18.68	−18.72	−11.4	−18.68	−18.58
Methyl nonadecanoate	−13.17	−19.49	−19.72	−12.22	−19.49	−19.68
Methyl eicosanoate	−14.0	−20.90	−20.68	−13.03	−20.90	−20.8
Methyl heneicosanoate				−13.83		−21.88
Methyl docosanoate				−14.65		−23.0
Methyl tetracosanoate				−16.27		−25.2
$\ln(p/p_0)_{\text{calc}} = (1.161 \pm 0.077)\ln(1/t_a)_{\text{mix 3}} - (4.425 \pm 0.206)$; $r^2 = 0.9870$					(10)	
$\ln(p/p_0)_{\text{calc}} = (1.361 \pm 0.205)\ln(1/t_a)_{\text{mix 4}} - (3.058 \pm 0.236)$; $r^2 = 0.9778$					(11)	
	$\ln(1/t_a)$[a], mix 5	$\ln(p/p_0)$	$\ln(p/p_0)$[e], Eq. (12)	$\ln(1/t_a)$[a], mix 6	$\ln(p/p_0)$	$\ln(p/p_0)$[h], Eq. (13)
(C) FAMEs C_{19} to C_{28}						
Methyl nonadecanoate	−11.72	−19.49[b]	−19.61			
Methyl eicosanoate	−12.52	−20.9[b]	−20.75			
Methyl heneicosanoate	−13.32	−21.88[f]	−21.89	−13.21	−21.88[f]	−21.89
Methyl docosanoate	−14.1	−23.0[f]	−22.99	−13.98	−23.0[f]	−22.98
Methyl tetracosanoate	−15.67	−25.2[f]	−25.23	−15.54	−25.2[f]	−25.22
Methyl pentacosanoate	−16.45		−26.34	−16.32	−26.34[g]	−26.33
Methyl hexacosanoate	−17.21		−27.42	−17.08	−27.42[g]	−27.42
Methyl heptacosanoate				−17.85		−28.51
Methyl octacosanoate				−18.62		−29.62
$\ln(p/p_0)_{\text{calc}} = (1.422 \pm 0.0355)\ln(1/t_a)_{\text{mix 5}} - (2.947 \pm 0.108)$; $r^2 = 0.9981$					(12)	
$\ln(p/p_0)_{\text{calc}} = (1.429 \pm 0.0041)\ln(1/t_a)_{\text{mix 6}} - (3.010 \pm 0.014)$; $r^2 = 0.9999$					(13)	

[a] Calculated at $T = 298.15$ K using the equations in Table 3 for each appropriate mixture.
[b] Calculated at $T = 298.15$ K using Eq. (6).
[c] Calculated using Eq. (8).
[d] Calculated at $T = 298.15$ K using Eq. (9).
[e] Calculated at $T = 298.15$ K using Eq. (10).
[f] Calculated at $T = 298.15$ K using Eq. (11).
[g] Calculated at $T = 298.15$ K using Eq. (12).
[h] Calculated at $T = 298.15$ K using Eq. (13).

were derived using results from Eq. (6) for $\theta = 350$ K. To the extent that the quality of fit to the experimental data provided by Eq. (6) improves going from $T = 298.15$ to 350 K, this improvement in fit should also be reflected by the predictions given by Eq. (7).

As noted above, the vapor pressures reported for methyl heptadecanoate were not used in these correlation because of the poor fit observed in Fig. 1 for this compound. Nevertheless, it is possible to compare literature vapor pressures calculated by Eq. (6) to those obtained by interpolation, using Eq. (7). Table 8 compares vapor pressures calculated from $T = 298.15$ to 448.15 K using the two equa-

Table 7
Vapor pressure parameters (*A*–*D*) evaluated for FAMEs C_{18}, C_{22} to C_{23} and C_{25} to C_{28}

	A ($\times 10^{-8}$)	B ($\times 10^{-6}$)	C	D
Methyl heptadecanoate	3.20885	−3.99382	3615.89	3.0564
Methyl heneicosanoate	4.20126	−5.23876	5943.62	1.2615
Methyl docosanoate	4.62998	−5.77717	7293.43	0.0632
Methyl tetracosanoate	5.48008	−6.84544	9971.29	−2.3130
Methyl pentacosanoate	5.98677	−7.47838	11631.82	−3.8127
Methyl hexacosanoate	6.43086	−8.03301	13047.85	−5.0815
Methyl heptacosanoate	6.85197	−8.56341	14379.54	−6.2620
Methyl octacosanoate	7.29147	−9.11763	15787.58	−7.5139

Table 8
A comparison of $\ln(p/p_0)$ values for methyl heptadecanoate obtained by interpolation with literature values

T (K)	$\ln(p/p_0)$[a]	$\ln(p/p_0)$[b]
298.15	−17.64	−17.13
328.15	−13.93	−13.72
358.15	−11.00	−10.96
388.15	−8.65	−8.69
418.15	−6.75	−6.80
448.15	−5.20	−5.22

[a] This work.
[b] Literature values [4].

tions. The comparison is good and improves as $T = 350$ K is approached.

4.2. Fusion enthalpies

The fusion enthalpies of methyl octadecanoate to methyl octacosanoate were measured by DSC; the results are listed in Table 9. Fusion enthalpies for methyl hexadecanoate to methyl eicosanoate and for methyl dodecanoate have previously been measured. However, since most of this work was published in 1936, we decided to repeat the measurements. As shown in this table, our DSC results are very good agreement with heats of crystallization measured by King and Gardner [14]. The uncertainties cited in this work represent two standard deviations of the mean.

Most FAMEs examined exhibited complex solid–solid phase behavior just prior to melting as illustrated by methyl heneicosanoate in Fig. 5. In many instances this behavior could be isolated by examining the cooling curve which apparently resolves a number of these transitions as shown in the figure. In some instances, these transitions perturbed calculation of the onset temperature for fusion. Conventional melting temperatures were used in adjusting the fusion enthalpies from $T = T_{\mathrm{fus}}$ to $T = 298.15$ K.

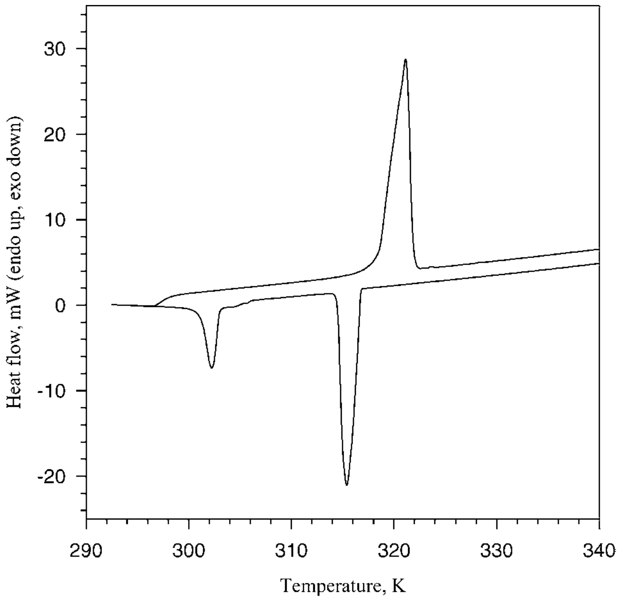

Fig. 5. The DSC heating/cooling curve for methyl heneicosanoate illustrating the separation of transitions upon cooling.

4.3. Sublimation enthalpies

Temperature adjustments were performed using Eqs. (14) and (15) where $C_{p_{\mathrm{c}}}$ and $C_{p_{\mathrm{l}}}$ refer to the heat capacity of the crystalline and liquid phases, respectively [15]. Heat capacities were estimated by group additivity using the group values cited in the footnotes of Table 8 and are listed in the last two columns of Table 9. Eq. (14) was used to adjust sublimation enthalpies and Eq. (15) was used to adjust fusion enthalpies to $T = 298.15$ K.

$$\begin{aligned}&\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}\,(298.15\,\mathrm{K})\ (\mathrm{kJ\,mol^{-1}})\\&\quad = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(T) + (0.75 + 0.15C_{p_{\mathrm{c}}}) \times \frac{T - 298.15}{1000}\end{aligned} \tag{14}$$

Table 9
Experimental fusion enthalpies (kJ mol^{-1}) of methyl hexadecanoate to methyl octadecanoate exclusive of methyl tridecanoate

	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$, this work	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$, literature[b]	T_{fus} (K)	$C_{p_{\mathrm{l}}}$[a]	$C_{p_{\mathrm{c}}}$[a]
Methyl hexadecanoate	56.0 ± 2.1	55.4	305.15	579.6	490.1
Methyl heptadecanoate	48.1 ± 2.8		304.2	611.5	517
Methyl octadecanoate	61.7 ± 1.7	64.4	310.9	643.4	543.9
Methyl nonadecanoate	63.8 ± 1.8	62.2	313.2	675.3	570.8
Methyl eicosanoate	74.3 ± 2.7	73.7	319.2	707.2	597.7
Methyl heneicosanoate	75.1 ± 1.1		321.15	739.1	624.6
Methyl docosanoate	83.5 ± 0.4	82.3	327.2	771	651.5
Methyl tetracosanoate	90.0 ± 0.4		331.2	834.8	705.3
Methyl pentacosanoate	92.0 ± 1.8		332.2	866.7	732.2
Methyl hexacosanoate	101.3 ± 0.6		336.2	898.6	759.1
Methyl heptacosanoate	100.7 ± 0.6		336.2	930.5	786
Methyl octacosanoate	109.7 ± 3.3		340.2	962.4	812.9

[a] Calculated using the following group values for the liquid and solid, respectively: CH_3: 34.9, 36.6; CH_2: 31.9, 26.9; $–CO_2–$: 63.2, 40.3 J mol^{-1}.
[b] Ref. [14].

Table 10
Fusion, vaporization and sublimation enthalpies at $T = 298.15\,\mathrm{K}$

	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$, mean value[a]	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ (298.15 K)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)[b]
Methyl hexadecanoate	55.7 ± 0.7	55.1 ± 0.7	96.8 ± 1.3	151.9 ± 1.4	151.2 ± 2
Methyl heptadecanoate	48.1 ± 2.8	48.7 ± 2.8	100.8 ± 1.0	148.9 ± 3.0	
Methyl octadecanoate	63.1 ± 2.7	61.9 ± 2.7	105.9 ± 2.7	167.7 ± 3.8	158.7 ± 2.5
Methyl nonadecanoate	63.0 ± 1.5	61.5 ± 1.6	109.5 ± 5.4	171.0 ± 5.6	
Methyl eicosanoate	74.0 ± 0.6	71.5 ± 0.7	116.4 ± 3.0	188.0 ± 3.2	192 ± 10
Methyl heneicosanoate	75.1 ± 1.1	72.6 ± 1.3	120.9 ± 2.5	193.5 ± 2.8	
Methyl docosanoate	82.9 ± 0.6	79.6 ± 1.2	126.1 ± 2.5	205.7 ± 2.8	
Methyl tetracosanoate	90.0 ± 0.4	86.0 ± 1.3	136.6 ± 2.5	222.6 ± 2.8	
Methyl pentacosanoate	92.00 ± 1.8	87.7 ± 2.2	142 ± 4.5	229.7 ± 5.0	
Methyl hexacosanoate	101.3 ± 0.6	96.4 ± 1.6	147.1 ± 4.5	243.5 ± 4.8	
Methyl heptacosanoate	100.7 ± 0.6	95.6 ± 1.7	152.2 ± 4.5	247.8 ± 4.8	
Methyl octacosanoate	109.7 ± 3.3	103.8 ± 3.8	157.5 ± 4.5	261.3 ± 5.9	

[a] Average of this work and the literature where applicable; uncertainty represents two standard deviations of the mean.
[b] Ref. [16,18].

$$\Delta_{\mathrm{cr}}{}'H_{\mathrm{m}}\,(298.15)\,(\mathrm{kJ\,mol^{-1}}) = \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}}) + (0.15C_{p_{\mathrm{c}}} - 0.26C_{p_{\mathrm{l}}} - 9.83) \times \frac{T_{\mathrm{fus}} - 298.15}{1000} \qquad (15)$$

Fusion, vaporization and sublimation enthalpies each adjusted to $T = 298.15\,\mathrm{K}$ are listed in Table 10. Column 2 lists the mean value of the fusion enthalpies measured in this work; if a literature value was previously available, the value reported represents the average of the results of this work with the literature value. Uncertainties represent two standard deviations of the mean. Sublimation enthalpies were calculated by combining the fusion and vaporization enthalpy. When available, the resultant sum is compared to the sublimation enthalpy in the literature (last column of Table 10); comparison of the two values gives good agreement.

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