



# The vaporization enthalpies and vapor pressures of a series of fatty acids methyl esters for C<sub>18</sub>, C<sub>21</sub> to C<sub>23</sub>, C<sub>25</sub> to C<sub>29</sub> 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  $T = 298.15\text{--}450\text{ K}$  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  $450\text{ K}$  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  $T = 298.15\text{ K}$  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.

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## 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  $T = 298.15\text{ K}$ .

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,  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}$ , as measured by gas chromatography and the vaporization enthalpy ( $\Delta_1^{\text{g}} H_{\text{m}}$ ) of a series of standards. The vaporization enthalpies of the standards have usually been chosen at  $T = 298.15\text{ K}$  but the correlation works for other temperatures as well. The linear correlation that is observed between  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}$  and  $\Delta_1^{\text{g}} H_{\text{m}}$  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,  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}$ , 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,  $t_a = t - t_{\text{nr}}$ , 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  $1/T$  ( $\text{K}^{-1}$ ) results in a linear plot with a slope equal to  $-\Delta_{\text{sln}}^{\text{g}} H_m(T_m)/R$ .

The term,  $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$  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 ( $\Delta_{\text{sln}}^{\text{g}} H_m$ ) 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.

$$\Delta_{\text{sln}}^{\text{g}} H_m(T_m) = \Delta_1^{\text{g}} H_m(T_m) + \Delta_{\text{sln}} H_m(T_m) \quad (1)$$

In correlation gas chromatography,  $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$  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  $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$  and  $\Delta_1^{\text{g}} H_m(T_m)$ . 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,  $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$  measured at  $T = T_m$ , is correlated to  $\Delta_1^{\text{g}} H_m(298.15 \text{ K})$ ; the correlation results in the following slope:

$$\text{slope} = \frac{\Delta_1^{\text{g}} H_m(298.15 \text{ K})}{\Delta_{\text{sln}}^{\text{g}} H_m(T_m)} \quad (2)$$

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

$$\text{slope} = \frac{\Delta_1^{\text{g}} H_m(298.15 \text{ K})}{\Delta_1^{\text{g}} H_m(T_m) + \Delta_{\text{sln}}^{\text{g}} H_m(T_m)} \quad (3)$$

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]:

$$\Delta_1^{\text{g}} H_m(298.15 \text{ K}) = 4.69(n_c - n_Q) + 1.3n_Q + b + 3.0 \quad (4)$$

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,  $\Delta_{\text{sln}} H_m(T_m)$  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 ( $\text{kJ mol}^{-1}$ )<sup>a</sup>

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 <sub>2</sub>	22.8
	-C(=O)NH-	42.5	Heterocyclic aromatic	=NH-	
Amine (primary)	-NH <sub>2</sub>	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 <sub>2</sub> -	[53.0]
Ester	-C(=O)O-	10.5	Thiolester	-C(=O)S-	[16.9]
Ether	> O	5.0	Thiol	-SH	13.9

<sup>a</sup> See Ref. [17].

is not known at  $T = T_m$ . However comparison of values of  $\Delta_1^g H_m(T_m)$  computed at  $T = T_m$  to measured values of  $\Delta_{\text{sln}}^g H_m(T_m)$  suggest that the total contribution of  $\Delta_{\text{sln}}^g H_m(T_m)$  is very small at this temperature, and often of the order of the uncertainty of the measurements. Using a similar relationship to model  $\Delta_{\text{sln}}^g H_m(T_m)$ ,  $m'''n_c + c'''$  and treating  $c'''$  as a variable can reproduce  $\Delta_{\text{sln}}^g H_m(T_m)$  exactly. Substituting these linear functions into Eq. (3) and combining similar terms results in Eq. (5), where  $m_{\text{sln}} = m' + m'' + m'''$  and  $c_{\text{sln}} = c' + c'' + c'''$ . 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.

$$\text{slope} = \frac{m_{\text{sln}}n_c + c_{\text{sln}}}{mn_c + c} \quad (5)$$

As long as  $c_{\text{sln}}$  and  $c$  are small in comparison to  $m_{\text{sln}}n_c$  and  $mn_c$ , respectively, correlation of  $\Delta_{\text{sln}}^g H_m(T_m)$  with  $\Delta_1^g H_m$  (298.15 K), will be linear because Eq. (5) is a hyperbolic function approaching its asymptote,  $m_{\text{sln}}/m$ . This model explains the linear relationships observed between  $\Delta_1^g H_m(T_m)$  and  $\Delta_{\text{sln}}^g H_m(T_m)$  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  $a_b$  values should correlate with each other. This behavior has been observed when correlating  $\Delta_{\text{sln}}^g H_m(T_m)$  with  $\Delta_1^g H_m$  (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,  $\text{CH}_2\text{Cl}_2$ , 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  $\pm 0.1$  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 measured on a Perkin Elmer DSC-7 under a nitrogen purge in hermetically sealed aluminum cells at a scan rate of 5 K  $\text{min}^{-1}$ . 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  $\text{C}_5$  to  $\text{C}_{21}$  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 the last column of 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  $\text{C}_{13}$  through to  $\text{C}_{21}$  to document whether a linear correlation is observed between  $\Delta_{\text{sln}}^g H_m$  and  $\Delta_1^g H_m$  (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

Table 2

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

Table 3

	–Slope <sup>a</sup>	Intercept <sup>a</sup>	$\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$	$\Delta_1^{\text{g}} H_m$ (298.15 K) (literature)	$\Delta_1^{\text{g}} H_m$ (298.15 K) (calcd.) <sup>b</sup>
(A) FAME mix 1 ( $T_m = 480.0$ 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
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.386±0.115) $\Delta_{\text{sln}}^{\text{g}} H_m$ (480 K) + (4.866 ± 1.30), $r^2 = 0.980$					
(B) FAME mix 2 ( $T_m = 481.3$ 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
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.548±0.135) $\Delta_{\text{sln}}^{\text{g}} H_m$ (481 K) + (4.61 ± 1.33), $r^2 = 0.985$					
(C) FAME mix 3 ( $T_m = 491.2$ 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
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.464±0.119) $\Delta_{\text{sln}}^{\text{g}} H_m$ (491 K) + (7.99 ± 1.14), $r^2 = 0.987$					
(D) FAME mix 4 ( $T_m = 523.8$ 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
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.70±0.10) $\Delta_{\text{sln}}^{\text{g}} H_m$ (524 K) – (3.872 ± 0.91), $r^2 = 0.993$					
(E) FAME mix 5 ( $T_m = 546.3$ 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
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.80±0.054) $\Delta_{\text{sln}}^{\text{g}} H_m$ (546 K) – (5.842 ± 0.614), $r^2 = 0.997$					
(F) FAME mix 6 ( $T_m = 553.9$ 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	17.684±0.005	90.00		157.5 ± 0.1
$\Delta_1^{\text{g}} H_m$ (298.15 K) = (1.818±0.004) $\Delta_{\text{sln}}^{\text{g}} H_m$ (554 K) – (6.106 ± 0.05), $r^2 = 0.999$					

<sup>a</sup> Each equation was characterized by a correlation coefficient ( $r^2$ ) of better than 0.999.

<sup>b</sup> 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

	$\Delta_f^g H_m(298.15\text{ K}) / (\text{kJ mol}^{-1})$						Literature	This work
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6		
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 undecanoate							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

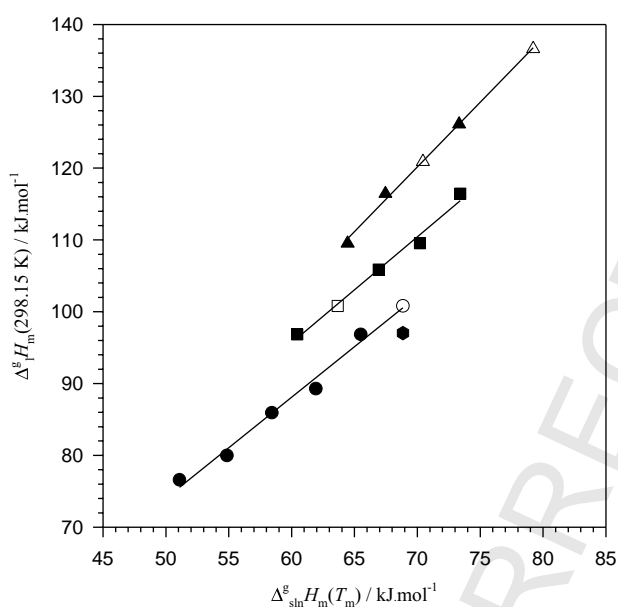
The uncertainties represent  $\pm 2\sigma$  of the probable error as discussed in the text.

Fig. 1. Plots of  $\Delta_f^g H_m(298.15\text{ K})$  vs. the corresponding of  $\Delta_{\text{sln}}^g H_m(T_m)$  for mixes 1, 3, and 5: solid symbols represent literature values; empty symbols represent values evaluated in this work; circles:  $n\text{-C}_{12}\text{O}_2\text{Me}$  through to  $n\text{-C}_{17}\text{O}_2\text{Me}$ ; hexagon: literature value for  $n\text{-C}_{17}\text{O}_2\text{Me}$  (see text); solid squares:  $n\text{-C}_{16}\text{CO}_2\text{Me}$  through to  $n\text{-C}_{20}\text{O}_2\text{Me}$ ; triangles:  $n\text{-C}_{19}\text{O}_2\text{Me}$  through to  $n\text{-C}_{24}\text{O}_2\text{Me}$  excluding  $n\text{-C}_{23}\text{O}_2\text{Me}$ .

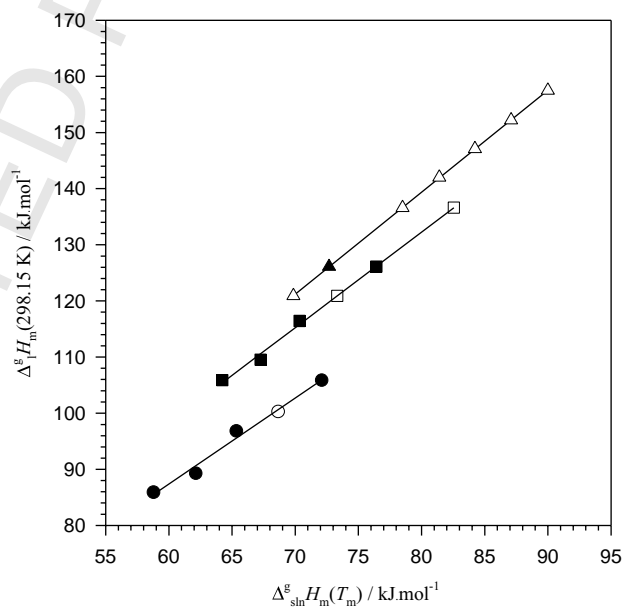


Fig. 2. Plots of  $\Delta_f^g H_m(298.15\text{ K})$  of the standards vs. the corresponding  $\Delta_{\text{sln}}^g H_m(T_m)$  for mixes 2, 4 and 6; solid symbols represent literature values; empty symbols represent the values evaluated in this work; circles:  $n\text{-C}_{14}\text{CO}_2\text{Me}$  through to  $n\text{-C}_{18}\text{CO}_2\text{Me}$ ; squares:  $n\text{-C}_{18}\text{CO}_2\text{Me}$  through to  $n\text{-C}_{22}\text{CO}_2\text{Me}$  excluding  $n\text{-C}_{23}\text{CO}_2\text{Me}$ ; triangles:  $n\text{-C}_{21}\text{CO}_2\text{Me}$  through to  $n\text{-C}_{28}\text{CO}_2\text{Me}$  excluding  $n\text{-C}_{23}\text{CO}_2\text{Me}$ .

4. While vaporization enthalpy values for methyl 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  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}(T_{\text{m}})$  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<sup>-1</sup> with the largest error occurring in the last of the three correlations. The average error was  $\pm 2.5$  kJ mol<sup>-1</sup>. 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  $\pm 4.5$  kJ mol<sup>-1</sup> 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 us-

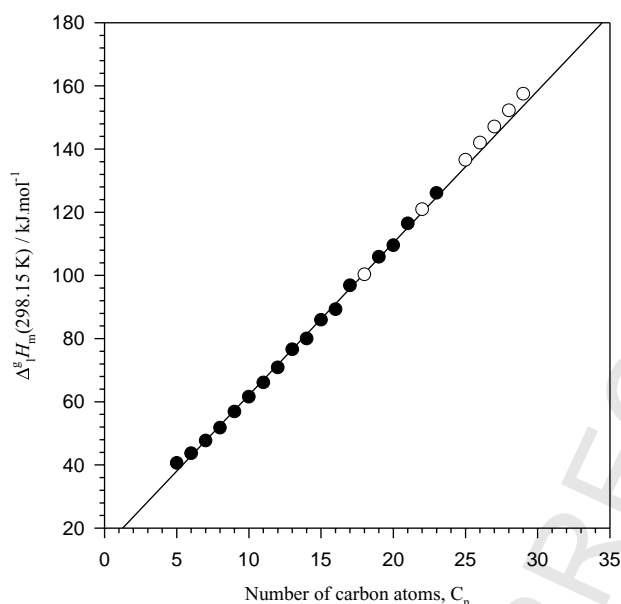


Fig. 3. Vaporization enthalpies of the FAMES from C<sub>5</sub> to C<sub>29</sub> as a function of the total number of carbon atoms: circles: literature values; triangles: results from this study. The line was calculated from of a linear regression analysis of the data using values for C<sub>5</sub> to C<sub>21</sub> and C<sub>23</sub>. The equation of the line obtained from using only literature data is:  $\Delta_1^{\text{g}} H_{\text{m}}(298.15 \text{ K})/\text{kJ mol}^{-1} = (4.818 \pm 0.053)C_n + (13.83 \pm 1.165)$  ( $r^2 = 0.9981$ ). The equation derived using all the data is given by  $\Delta_1^{\text{g}} H_{\text{m}}(298.15 \text{ K}) (\text{kJ mol}^{-1}) = (4.954 \pm 0.0367)C_n + (12.36 \pm 1.30)$  ( $r^2 = 0.9988$ ).

ing 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<sup>-1</sup> 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.

#### 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]:

$$R \ln \left( \frac{p}{p_0} \right) = -\frac{\Delta_1^{\text{g}} G_{\text{m}}(\theta)}{\theta} - \Delta_1^{\text{g}} H_{\text{m}}(\theta) \left[ \frac{1}{\theta} - \frac{1}{T} \right] - \Delta_1^{\text{g}} C_{p,\text{m}}^0(\theta) \left[ \left( \frac{\theta}{T} - 1 + \ln \frac{\theta}{T} \right) \right] \quad (6)$$

where  $p$  is the saturation vapor pressure,  $T$  the thermodynamic temperature,  $\theta$  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,  $\Delta_1^{\text{g}} G_{\text{m}}(\theta)$ ,  $-\Delta_1^{\text{g}} H_{\text{m}}(\theta)$ , and  $-\Delta_1^{\text{g}} C_{p,\text{m}}^0(\theta)$ , 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:

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

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  $\ln(1/t_a)$  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)

	$\Delta G_m^{\circ a}$ (J mol <sup>-1</sup> )	$\Delta H_m^{\circ a}$ (J mol <sup>-1</sup> )	$\Delta C_{p,m}^{\circ a}$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$A^b$ ( $\times 10^{-8}$ )	$B^b$ ( $\times 10^{-6}$ )	$C^b$	$D^b$
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

<sup>a</sup> Literature parameters for Eq. (6) at  $\theta = 350$  K [4].

<sup>b</sup> Evaluated using the vapor pressures calculated from Eq. (6).

312 The data from mix 2 were used for this calculation since  
313 methyl heptadecanoate is more intermediate in volatility re-  
314 lative to the standards. Table 6 illustrates the protocol used to  
315 calculate vapor pressures at  $T = 298.15$  K. Values of  $\ln(1/t_a)$   
316 were calculated for mix 2 using the appropriate equations in  
317 Table 3B; values of  $\ln(p/p_0)$  were similarly calculated using  
318 Eq. (6) using the appropriate constants given in Table 5. The  
319 equation produced by the correlation, Eq. (8), was used to  
320 generate the  $\ln(p/p_0)$  value for methyl heptadecanoate. This  
321 was the value used in each subsequent correlation. The re-  
322 sults reported in the last column of Table 6A for mix 1 and  
323 the fourth column in Table 6B, illustrates the quality of the  
324 fit when this value for methyl heptadecanoate is used in cor-  
325 relations with other FAMES.

326 The result obtained by extrapolation are provided in  
327 Table 6B and C. Mix 4 uses  $\ln(p/p_0)$  values for FAMES C<sub>19</sub>  
328 to C<sub>21</sub> generated from Eq. (6) to evaluate corresponding  
329 values for FAMES C<sub>22</sub> to C<sub>25</sub>. Once evaluated, these values  
330 were used to expand the extrapolation to include FAMES  
331 C<sub>26</sub> to C<sub>29</sub>. This process was then repeated using the equa-  
332 tions in Tables 3 and 5 to calculate values of  $\ln(1/t_a)$  and  
333  $\ln(p/p_0)$  over the temperature range  $T = 298.15$ –450 K at  
334 30 K intervals, respectively. The resulting vapor pressures  
335 (not shown) were then fit to Eq. (7). The observed tempera-  
336 ture dependence reproduced by the constants in Eq. (7) are  
337 reported in Table 7 and illustrated in Fig. 4.

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

348 As an estimate of the magnitude of the error that might be  
349 expected in such an extrapolation, the following was used  
350 as a model. The vapor pressures of methyl dodecanoate to  
351 methyl tetradecanoate in mix 1 at  $T = 298.15$  K were used  
352 as knowns to evaluate  $\ln(p/p_0)$  of the remaining FAMES up  
353 to methyl docosanoate in the manner described above. A to-

tal of four extrapolations were included in the evaluation, 354  
similar to the number used to evaluate  $\ln(p/p_0)$  values for 355  
methyl heneicosanoate to methyl octacosanoate. The results 356  
of the extrapolation were then compared to experimental 357  
results. Methyl heptadecanoate and methyl heneicosanoate 358  
were excluded from the comparisons. The absolute error asso- 359  
ciated with calculated  $\ln(p/p_0)$  values ranged from a low 360  
of 0.18 to a high of 0.53 with an average of 0.24; the abso- 361  
lute fractional error ranged from a low of 0.0013 to a high of 362  
0.026 with an average of 0.015 natural log units. The scat- 363  
ter between experimental data calculated by Eq. (1) and the 364  
extrapolated data as measured by the standard deviation was 365  
 $\pm 0.3 \ln(p/p_0)$  units. As might be expected, the uncertainty 366  
gradually increased with each successive extrapolation. As 367  
a result of the lack of any other suitable tests of these data, 368  
these uncertainties seem reasonable estimates of the uncertan- 369  
tainties associated with the use of the parameters in Table 7 370  
to calculate  $\ln(p/p_0)$  values of the larger FAMES. It should 371  
be emphasized here that the constants in Table 7 were der- 372  
ived using results from Eq. (6) for  $\theta = 350$  K. To the extent 373

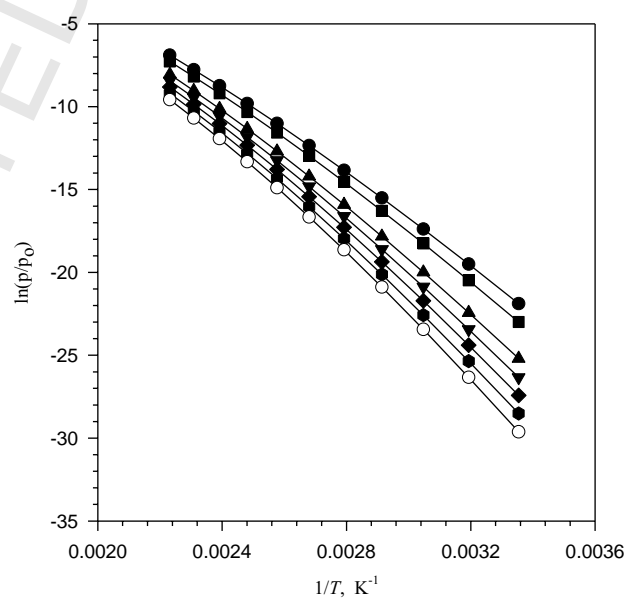


Fig. 4. The dependence of  $\ln(p/p_0)$  on  $1/T$  of FAMES C<sub>22</sub> (top), C<sub>23</sub> and C<sub>25</sub> to C<sub>28</sub> (bottom).

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 <sup>c</sup>	-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 <sup>c</sup>	-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
Methyl pentacosanoate						
Methyl hexacosanoate						
$\ln(p/p_0)_{\text{calc}} = (1.161 \pm 0.077) \ln(1/t_a)_{\text{mix 3}} - (4.425 \pm 0.206)$ ; $r^2 = 0.9870$					(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	$\ln(p/p_0)$	$\ln(p/p_0)^g$ , 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 <sup>b</sup>	-19.61			
Methyl eicosanoate	-12.52	-20.9 <sup>b</sup>	-20.75			
Methyl heneicosanoate	-13.32	-21.88 <sup>f</sup>	-21.89	-13.21	-21.88 <sup>f</sup>	-21.89
Methyl docosanoate	-14.1	-23.0 <sup>f</sup>	-22.99	-13.98	-23.0 <sup>f</sup>	-22.98
Methyl tetracosanoate	-15.67	-25.2 <sup>f</sup>	-25.23	-15.54	-25.2 <sup>f</sup>	-25.22
Methyl pentacosanoate	-16.45		-26.34	-16.32	-26.34 <sup>g</sup>	-26.33
Methyl hexacosanoate	-17.21		-27.42	-17.08	-27.42 <sup>g</sup>	-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)	

<sup>a</sup> Calculated at  $T = 298.15$  K using the equations in Table 3 for each appropriate mixture.

<sup>b</sup> Calculated at  $T = 298.15$  K using Eq. (6).

<sup>c</sup> Calculated using Eq. (8).

<sup>d</sup> Calculated at  $T = 298.15$  K using Eq. (9).

<sup>e</sup> Calculated at  $T = 298.15$  K using Eq. (10).

<sup>f</sup> Calculated at  $T = 298.15$  K using Eq. (11).

<sup>g</sup> Calculated at  $T = 298.15$  K using Eq. (12).

<sup>h</sup> Calculated at  $T = 298.15$  K using Eq. (13).

374 that the quality of fit to the experimental data provided by  
375 Eq. (6) improves going from  $T = 298.15$  to  $350$  K, this im-  
376 provement in fit should also be reflected by the predictions  
377 given by Eq. (7).

378 As noted above, the vapor pressures reported for methyl  
379 heptadecanoate were not used in these correlation because of  
380 the poor fit observed in Fig. 1 for this compound. Neverthe-  
381 less, it is possible to compare literature vapor pressures cal-  
382 culated by Eq. (6) to those obtained by interpolation, using  
383 Eq. (7). Table 8 compares vapor pressures calculated from

$T = 298.15$  to  $448.15$  K using the two equations. The compar- 384  
385 ison is good and improves as  $T = 350$  K is approached.

#### 4.2. Fusion enthalpies 386

The fusion enthalpies of methyl octadecanoate to methyl 387  
388 octacosanoate were measured by DSC; the results are listed  
389 in Table 9. Fusion enthalpies for methyl hexadecanoate to  
390 methyl eicosanoate and for methyl dodecanoate have previ-  
391 ously been measured. However, since most of this work was

Table 7  
Vapor pressure parameters (A–D) evaluated for FAMES C<sub>18</sub>, C<sub>22</sub> to C<sub>23</sub> and C<sub>25</sub> to C<sub>28</sub>

	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

<sup>a</sup> This work.

<sup>b</sup> Literature values [4].

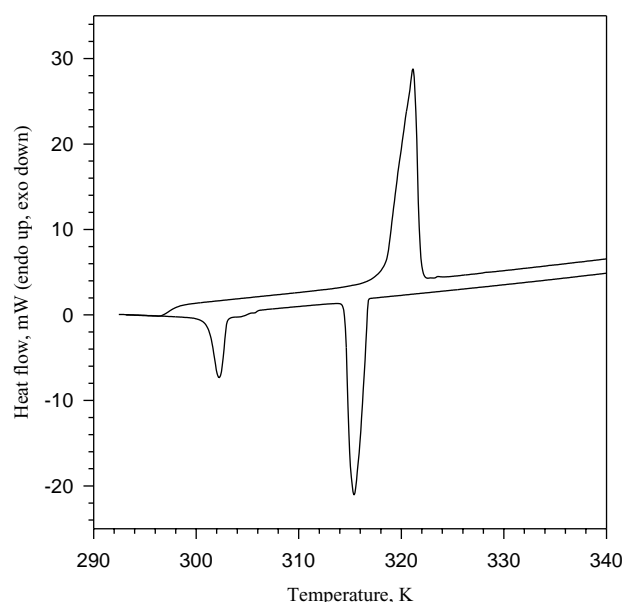


Fig. 5. The DSC heating/cooling curve for methyl heneicosanoate illustrating the separation of transitions upon cooling.

#### 4.3. Sublimation enthalpies

Temperature adjustments were performed using Eqs. (14) and (15) where  $C_{pc}$  and  $C_{pl}$  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.

$$\begin{aligned} \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15 \text{ K}) (\text{kJ mol}^{-1}) \\ = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(T_{\text{fus}}) + (0.75 + 0.15C_{pc}) \times \frac{T - 298.15}{1000} \end{aligned} \quad (14)$$

published in 1936, we decided to repeat the measurements. As shown in this table, our DSC results are in 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  $T = T_{\text{fus}}$  to  $T = 298.15$  K.

Table 9  
Experimental fusion enthalpies of methyl hexadecanoate to methyl octadecanoate exclusive of methyl tridecanoate

	$\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}(T_{\text{fus}})$ , this work	$\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}(T_{\text{fus}})$ , literature <sup>b</sup>	$T_{\text{fus}}$ (K)	$C_{pl}^a$	$C_{pc}^a$
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

<sup>a</sup> Calculated using the following group values for the liquid and solid, respectively: CH<sub>3</sub>: 34.9, 36.6; CH<sub>2</sub>: 31.9, 26.9; −CO<sub>2</sub>−: 63.2, 40.3 J mol<sup>−1</sup>.

<sup>b</sup> Ref. [14].

Table 10

Fusion, vaporization and sublimation enthalpies at  $T = 298.15$  K

	$\Delta_{\text{cr}}^1 H_{\text{m}}(T_{\text{fus}})$ , mean value <sup>a</sup>	$\Delta_{\text{cr}}^1 H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15 \text{ K})^{\text{b}}$
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	

<sup>a</sup> Average of this work and the literature where applicable; uncertainty represents two standard deviations of the mean.<sup>b</sup> Ref. [18].

$$\begin{aligned} 419 \quad & \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15) \text{ (kJ mol}^{-1}\text{)} \\ 420 \quad & = \Delta_{\text{cr}}^1 H_{\text{m}}(T_{\text{fus}}) + (0.15C_{p_c} - 0.26C_{p_l} - 9.83) \\ 421 \quad & \times \frac{T_{\text{fus}} - 298.15}{1000} \end{aligned} \quad (15)$$

422 Fusion, vaporization and sublimation enthalpies each ad-  
 423 justed to  $T = 298.15$  K are listed in Table 10. Column 2  
 424 lists the mean value of the fusion enthalpies measured in  
 425 this work; if a literature value was previously available, the  
 426 value reported represents the average of the results of this  
 427 work with the literature value. Uncertainties represent two  
 428 standard deviations of the mean. Sublimation enthalpies  
 429 were calculated by combining the fusion and vaporization  
 430 enthalpy. When available, the resultant sum is compared  
 431 to the sublimation enthalpy in the literature (last column  
 432 of Table 10); comparison of the two values gives good  
 433 agreement.

#### 434 Uncited reference

435 [16].

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