

The vaporization enthalpies and vapor pressures of a series of unsaturated fatty acid methyl esters by correlation gas chromatography

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Abstract

Vaporization enthalpies for methyl myristoleate (methyl Z 9-tetradecenonate), methyl 10-pentadecenoate, methyl palmitoleate (methyl Z 9-hexadecenoate), methyl Z 10-heptadecenoate, methyl oleate (methyl Z 9-octadecenoate), methyl linoleate (methyl Z,Z 9,12-octadecadienoate), methyl linolenate (methyl Z,Z,Z 9,12,15-octadecatrienoate), methyl Z 11-eicosenoate, methyl Z,Z 11,14-eicosadienoate, methyl Z,Z,Z 11,14,17-eicosatrienoate, methyl arachidonate (methyl Z,Z,Z,Z 5,8,11,14-eicosatetraeneoate), methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaeneoate, methyl erucate (methyl Z 13-docosanoate), methyl Z,Z 13,16-docosadienoate, methyl Z,Z,Z,Z,Z 4,7,10,13,16,19-docosahexaenoate and methyl nervonate (methyl Z 15-tetracosanoate) are evaluated at $T=298.15$ and vapor pressures are evaluated over the temperature range $T=298.15$ –450 K by correlation gas chromatography. The results are generated by an interpolative process using literature values for the saturated fatty acid methyl esters (FAMES) from methyl decanoate to methyl tetracosanoate, exclusive of methyl nonadecanoate, heneicosanoate and tricosanoate, as standards. Relationships for calculating vapor pressures for all of the compounds studied from $T=298.15$ to 450 K are 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], for diesel fuel [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, using previous work by van Genderen et al. [4], the vapor pressures and vaporization enthalpies of a series of eight of the larger methyl esters of saturated fatty acids at $T=298.15$ K were reported using correlation gas chromatography [5]. In this article, we would like to report the results of our studies on the vapor pressures and vaporization enthalpies of a series of unsaturated FAMES using the same technique.

Correlation gas chromatography has proven to be quite successful in providing vaporization enthalpies of both liquids and solids, particularly for homologous series [6]. 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 ($\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$) of a series of standards. The results are dependent on the quality of the vaporization enthalpies and vapor pressures used as standards. The vaporization enthalpies of the standards have usually been chosen at $T=298.15$ K but the correlation should work for other temperatures as well. The linear correlation that is observed between $\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$ and $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ is empirical. A simple mathematical basis for the linear correlation observed for hydrocarbons and their derivatives has recently been reported [5,6].

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 target solutes as a function of temperature. The retention times, t , are adjusted

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for the dead volume of the column by measuring the retention time of an unretained reference, t_{nr} , 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 $\ln(t_o/t_a)$ versus $1/T$ (K^{-1}) where $t_o = 1$ min, results in a linear plot with a slope equal to the negative of the enthalpy of transfer from the stationary phase of the column to the gas phase, $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)/R$. The enthalpy of transfer is then correlated with the vaporization enthalpy of the standards, usually at $T = 298.15$ K, and the resulting equation, along with the appropriate values of $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ are then used to calculate the vaporization enthalpy of the unknowns.

3. Experimental

FAMEs were purchased as standard mixtures in methylene chloride from Restek and were used without any further purification. Three mixtures were purchased, FAME #13 (cat. #35034, reported as Mix 1; Table 1), Food Industry FAME

Mix (cat. #35077, reported in Mix 2; Table 2) and Marine Oil FAME Mix (cat. #35066, reported in Mixes 3 and 4; Tables 3 and 4). Most compounds were identified by the supplier's chromatograms and relative composition and a few of the standards were checked with authentic samples from Aldrich Chemical Co. A few FAMEs co-eluted and could not be identified conclusively. Results for these FAMEs are not included. 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 approximately 50/1. The chromatograms were recorded on an HP GC Chemstation. Retention times were recorded to three significant figures following the decimal point. The instrument was run isothermally on a 30 m Restek StabilwaxTM capillary column. The elution order was very similar to the chromatograms supplied by Restek, although the supplier's chromatograms were performed on a FamewaxTM column. Helium was used as the carrier gas. At the temperatures of some 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

Table 1
Retention times of FAME Mix 1

	<i>t</i> (min)						
	<i>T</i> = 489.7 K	<i>T</i> = 494.8 K	<i>T</i> = 499.8 K	<i>T</i> = 504.8 K	<i>T</i> = 509.9 K	<i>T</i> = 514.9 K	<i>T</i> = 520.0 K
Methylene chloride	1.19	1.204	1.209	1.213	1.217	1.224	1.244
Methyl hexadecanoate	3.929	3.576	3.265	3.009	2.793	2.604	2.487
Methyl Z 9-hexadecenoate	4.236	3.843	3.494	3.209	2.967	2.757	2.624
Methyl octadecanoate	6.223	5.508	4.891	4.389	3.969	3.609	3.364
Methyl Z 9-octadecenoate	6.681	5.888	5.217	4.67	4.218	3.824	3.552
Methyl Z,Z 9,12-octadecadienoate	7.571	6.641	5.849	5.207	4.674	4.214	3.895
Methyl Z,Z,Z 9,12,15-octadecatrienoate	9.00	7.842	6.852	6.054	5.39	4.822	4.427
Methyl eicosanoate	10.348	8.933	7.731	6.77	5.971	5.3	4.823
Methyl Z 11-eicosenoate	11.098	9.56	8.266	7.225	6.369	5.641	5.118
Methyl Z,Z 11,14-eicosadienoate	12.691	10.895	9.372	8.153	7.145	6.296	5.693
Methyl docosanoate	17.715	14.963	12.675	10.858	9.367	8.132	7.231
Methyl Z 13-docosenoate	19.136	16.08	13.622	11.648	10.078	8.731	7.723
Methyl Z,Z 13,16-docosadienoate	21.869	18.41	15.513	13.218	11.348	9.793	8.66
Methyl tetracosanoate	30.727	25.478	21.187	17.809	15.073	12.83	11.193
Methyl Z 15-tetracosenoate	32.922	27.321	22.707	19.081	16.144	13.732	11.956

Table 2
Retention times of FAME Mix 2

	<i>t</i> (min)					
	<i>T</i> = 444.5 K	<i>T</i> = 449.4 K	<i>T</i> = 459.3 K	<i>T</i> = 464.2 K	<i>T</i> = 469.1 K	<i>T</i> = 474.1 K
Methylene chloride	0.649	0.646	0.641	0.636	0.642	0.662
Methyl dodecanoate	2.093	1.881	1.553	1.424	1.333	1.288
Methyl tridecanoate	2.781	2.453	1.953	1.761	1.621	1.541
Methyl tetradecanoate	3.786	3.278	2.521	2.234	2.022	1.891
Methyl Z 9-tetradecenoate	4.328	3.729	2.835	2.498	2.247	2.089
Methyl pentadecanoate	5.243	4.469	3.324	2.899	2.58	2.373
Methyl Z 10-pentadecenoate	6.024	5.109	3.764	3.265	2.891	2.644
Methyl hexadecanoate	7.368	6.184	4.462	3.831	3.356	3.039
Methyl Z 9-hexadecenoate	8.132	6.819	4.897	4.195	3.664	3.306
Methyl heptadecanoate	10.432	8.637	6.062	5.133	4.429	3.951
Methyl Z 10-heptadecenoate	11.507	9.521	6.659	5.628	4.846	4.312
Methyl octadecanoate	14.86	12.164	8.318	6.954	5.92	5.205

Table 3
Retention times of FAME Mix 3

	<i>t</i> (min)						
	<i>T</i> = 488.5 K	<i>T</i> = 493.5 K	<i>T</i> = 498.5 K	<i>T</i> = 503.5 K	<i>T</i> = 508.4 K	<i>T</i> = 513.5 K	<i>T</i> = 518.5 K
Methane	0.859	0.851	0.854	0.859	0.861	0.86	0.871
Methyl tetradecanoate	1.818	1.696	1.598	1.517	1.445	1.38	1.335
Methyl Z 9-tetradecenoate	1.969	1.827	1.712	1.616	1.533	1.458	1.404
Methyl hexadecanoate	2.645	2.403	2.203	2.037	1.892	1.768	1.672
Methyl Z 9-hexadecenoate	2.844	2.572	2.349	2.164	2.004	1.867	1.759
Methyl octadecanoate	4.133	3.653	3.257	2.932	2.654	2.421	2.233
Methyl Z 9-octadecenoate	4.422	3.904	3.474	3.12	2.815	2.562	2.356
Methyl Z,Z 9,12-octadecadieneoate	4.997	4.38	3.874	3.459	3.108	2.812	2.571
Methyl Z,Z,Z 9,12,15-octadecatrieneoate	5.935	5.161	4.529	4.012	3.576	3.211	2.912
Methyl eicosanoate	6.799	5.855	5.089	4.467	3.947	3.515	3.161
Methyl Z 11-eicosenoate	7.286	6.28	5.45	4.777	4.207	3.74	3.356
Methyl Z,Z 11,15-eicosadieneoate	8.333	7.133	6.16	5.371	4.714	4.168	3.719
Methyl Z,Z,Z,Z 5,8,11,14-eicosatetraeneoate	9.691	8.27	7.115	6.176	5.396	4.748	4.215
Methyl Z,Z,Z 11,14,17-eicosatrieneoate	10.006	8.513	7.3	6.321	5.505	4.748	4.215
Methyl docosanoate	11.66	9.896	8.462	7.109	6.138	5.348	4.698
Methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaeneoate	11.66	9.896	8.462	7.299	6.329	5.534	4.877
Methyl Z 13-docosenoate	12.379	10.448	8.873	7.611	6.564	5.71	5.009
Methyl tetracosanoate	19.957	16.51	13.777	11.591	9.819	8.387	7.218
Methyl Z 15-tetracosenoate	21.402	17.716	14.769	12.428	10.52	8.982	7.719
Methyl Z,Z,Z,Z,Z,Z 4,7,10,13,16,19-docosahexaeneoate	21.988	18.271	15.304	12.922	10.965	9.385	8.087

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. Methane, which is also non-retained, was used in other mixtures. 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 Tables 1–4. Since vapor pressures and vaporization enthalpies are determined relative to standards, the retention time data reported in these tables permit the reader to adjust the results should the values of the standards change as a result of future work. Tables 5–8 contain a summary of each run.

4. Results: vaporization enthalpies

The vaporization enthalpies of FAMES C₁₂ to C₂₀ used in this study have previously been evaluated by van Genderen et al. [4].

Table 4
Retention times of FAME Mix 4

	<i>t</i> (min)						
	<i>T</i> = 488.5 K	<i>T</i> = 493.5 K	<i>T</i> = 498.4 K	<i>T</i> = 503.5 K	<i>T</i> = 508.5 K	<i>T</i> = 513.5 K	<i>T</i> = 518.5 K
Methane	0.852	0.8541	0.841	0.861	0.864	0.867	0.867
Methyl tetradecanoate	1.81	1.691	1.577	1.512	1.442	1.383	1.328
Methyl Z 9-tetradecenoate	1.962	1.821	1.691	1.612	1.53	1.461	1.397
Methyl hexadecanoate	2.633	2.389	2.174	2.026	1.886	1.769	1.663
Methyl Z 9-hexadecenoate	2.833	2.56	2.322	2.155	1.999	1.867	1.75
Methyl octadecanoate	4.116	3.629	3.22	2.914	2.643	2.418	2.221
Methyl Z,Z 9,12-octadecadieneoate	4.981	4.357	3.837	3.441	3.096	2.808	2.559
Methyl Z,Z,Z 9,12,15-octadecatrieneoate	5.912	5.133	4.49	3.991	3.562	3.205	2.899
Methyl eicosanoate	6.773	5.822	5.044	4.44	3.93	3.506	3.145
Methyl Z 11-eicosenoate	7.255	6.231	5.394	4.741	4.187	3.73	3.337
Methyl Z,Z 11,15-eicosadieneoate	8.302	7.093	6.112	5.34	4.692	4.157	3.702
Methyl Z,Z,Z,Z 5,8,11,14-eicosatetraeneoate	9.657	8.222	7.059	6.139	5.369	4.734	4.196
Methyl Z,Z,Z 11,14,17-eicosatrieneoate	9.968	8.464	7.243	6.282	5.479	4.813	4.196
Methyl docosanoate	11.615	9.829	8.387	7.06	6.108	5.328	4.673
Methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaeneoate	11.615	9.829	8.387	7.247	6.297	5.515	4.853
Methyl Z 13-docosenoate	12.335	10.371	8.797	7.556	6.53	5.69	4.981
Methyl tetracosanoate	19.867	16.395	13.667	11.515	9.764	8.354	7.184
Methyl Z 15-tetracosenoate	21.314	17.598	14.661	12.346	10.464	8.946	7.685
Methyl Z,Z,Z,Z,Z,Z 4,7,10,13,16,19-docosahexaeneoate	21.881	18.152	15.175	12.824	10.902	9.342	8.048

Table 5
Summary of FAME Mix 1

	Slope	Intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$ (505 K) (kJ mol ⁻¹)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) (kJ mol ⁻¹) lit. [4,5]	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) (kJ mol ⁻¹) calcd. ^a
Methyl hexadecanoate	-6710	12.70	55.784	96.84	96.4 ± 3.3
Methyl Z 9-hexadecenoate	-6726	12.63	55.919		96.7 ± 3.3
Methyl octadecanoate	-7334	13.37	60.975	105.87	106.4 ± 3.6
Methyl Z 9-octadecenoate	-7336	13.29	60.995		106.4 ± 3.6
Methyl Z,Z 9,12-octadecadienoate	-7442	13.35	61.873		108.1 ± 3.7
Methyl Z,Z,Z 9,12,15-octadecatrienoate	-7612	13.50	63.282		110.8 ± 3.8
Methyl eicosanoate	-7964	14.06	66.209	116.43	116.4 ± 3.9
Methyl Z 11-eicosenoate	-7950	13.95	66.092		116.2 ± 3.9
Methyl Z,Z 11,14-eicosadienoate	-8053	14.01	66.952		117.8 ± 4.0
Methyl docosanoate	-8596	14.76	71.466	126.1	126.4 ± 4.0
Methyl Z 13-docosenoate	-8589	14.66	71.408		126.3 ± 4.2
Methyl Z,Z 13,16-docosadienoate	-8687	14.72	72.220		127.9 ± 4.3
Methyl tetracosanoate	-9211	15.43	76.579	136.6	136.2 ± 4.5
Methyl Z 15-tetracosenoate	-9191	15.32	76.411		135.9 ± 4.5

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K}) = (1.915 \pm 0.027) \Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(505\text{ K}) - (10.42 \pm 0.47), \quad r^2 = 0.9993 \quad (1)$$

^a The uncertainties reported represent two standard deviations of the uncertainty calculated from the uncertainties in the slope and intercept of Eq. (1).

Table 6
Summary of FAME Mix 2

	Slope	Intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) lit. [4,5]	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) calcd. ^a
Methyl dodecanoate	-6063.3	13.285	50.408	76.59	75.8 ± 3.1
Methyl tridecanoate	-6418	13.693	53.357	79.99	80.7 ± 3.3
Methyl tetradecanoate	-6776.6	14.114	56.338	85.94	85.7 ± 3.5
Methyl Z 9-tetradecenoate	-6850.2	14.12	56.950		86.7 ± 3.5
Methyl pentadecanoate	-7136.6	14.543	59.331	89.29	90.7 ± 3.6
Methyl Z 10-pentadecenoate	-7206.5	14.543	59.912		91.7 ± 3.7
Methyl hexadecanoate	-7500.9	14.982	62.360	96.84	95.8 ± 3.8
Methyl Z 9-hexadecenoate	-7509.3	14.893	62.429		95.9 ± 3.8
Methyl heptadecanoate	-7861.6	15.418	65.358	100.8	100.8 ± 4.0
Methyl Z 10-hexadecenoate	-7863.1	15.317	65.371		100.8 ± 4.0
Methyl octadecanoate	-8219.2	15.849	68.331	105.87	105.8 ± 4.2

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K}) = (1.675 \pm 0.059) \Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(460\text{ K}) - (8.68 \pm 0.94), \quad r^2 = 0.9938 \quad (2)$$

^a The uncertainties reported represent two standard deviations of the uncertainty calculated from the uncertainties in the slope and intercept of Eq. (2).

Table 7
Summary of FAME Mix 3

	Slope	Intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) lit. [4,5]	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ (298.15 K) calcd. ^a
Methyl tetradecanoate	-6140	12.613	51.046	85.94	86.3 ± 2.8
Methyl Z 9-tetradecenoate	-6201.3	12.593	51.555		87.2 ± 2.8
Methyl hexadecanoate	-6783.6	13.309	56.396	96.84	96.3 ± 3.0
Methyl Z 9-hexadecenoate	-6796.5	13.231	56.503		96.5 ± 3.0
Methyl octadecanoate	-7413	13.993	62.460	105.87	106.1 ± 3.3
Methyl Z 9-octadecenoate	-7401	13.884	61.529		105.9 ± 3.3
Methyl Z,Z 9,12-octadecadienoate	-7512.3	13.963	62.454		107.6 ± 3.3
Methyl Z,Z,Z 9,12,15-octadecatrienoate	-7692.4	14.128	63.952		110.4 ± 3.4
Methyl eicosanoate	-8046.2	14.696	66.893	116.43	115.9 ± 3.5
Methyl Z 11-eicosenoate	-8032.3	14.587	66.777		115.7 ± 3.5
Methyl Z,Z 11,14-eicosadienoate	-8143.2	14.665	67.699		117.4 ± 3.5
Methyl Z,Z,Z,Z 5,8,11,14-eicosatetraenoate	-8199.8	14.614	68.170		118.3 ± 3.6
Methyl Z,Z,Z 11,14,17-eicosatrienoate	-8515.2	15.219	70.792		123.2 ± 3.7
Methyl docosanoate	-8810	15.659	73.243	126.1	127.8 ± 3.8
Methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaenoate	-8376.7	14.774	69.641		121.1 ± 3.6
Methyl Z 13-docosenoate	-8650.5	15.27	71.917		125.3 ± 3.8
Methyl tetracosanoate	-9300.7	16.097	77.322	136.6	135.5 ± 4.0
Methyl Z 15-tetracosenoate	-9274.8	15.971	77.107		135.1 ± 4.0
Methyl Z,Z,Z,Z,Z,Z 4,7,10,13,16,19-docosaheptaenoate	-9071.8	15.527	75.419		131.9 ± 3.9

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K}) = (1.875 \pm 0.050) \Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(503\text{ K}) + (9.4 \pm 1.12), \quad r^2 = 0.9971 \quad (3)$$

^a The uncertainties reported represent two standard deviations of the uncertainty calculated from the uncertainties in the slope and intercept of Eq. (3).

Table 8
Summary of FAME Mix 4

	Slope	Intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}} (T_{\text{m}})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}} (298.15 \text{ K})$ lit.	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}} (298.15 \text{ K})$ calcd. ^a
Methyl tetradecanoate	−6154.2	12.649	51.164	85.94	86.4 ± 3.3
Methyl Z 9-tetradecenoate	−6213.7	12.625	51.658		87.4 ± 3.4
Methyl hexadecanoate	−6771.9	13.294	56.299	96.84	96.1 ± 3.6
Methyl Z 9-hexadecenoate	−6796.3	13.238	56.502		96.5 ± 3.6
Methyl octadecanoate	−7402.7	13.981	61.543	105.87	105.9 ± 3.9
Methyl Z,Z 9,12-octadecadieneoate	−7507.2	13.959	62.412		107.6 ± 4.0
Methyl Z,Z,Z 9,12,15-octadecatrieneoate	−7681.2	14.112	63.858		110.3 ± 4.1
Methyl eicosanoate	−8040.1	14.69	66.842	116.43	115.9 ± 4.2
Methyl Z 11-eicosenoate	−8016.1	14.562	66.643		115.5 ± 4.2
Methyl Z,Z 11,14-eicosadieneoate	−8134.1	14.653	67.624		117.4 ± 4.3
Methyl Z,Z,Z,Z 5,8,11,14-eicosatetraeneoate	−8190.6	14.601	68.093		118.3 ± 4.3
Methyl Z,Z,Z 11,14,17-eicosatrieneoate	−8430	15.053	70.084		122.0 ± 4.4
Methyl docosanoate	−8825.5	15.694	73.372	126.1	128.2 ± 4.6
Methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaeneoate	−8362.2	14.752	69.520		120.9 ± 4.4
Methyl Z 13-docoseneoate	−8640.2	15.256	71.831		125.3 ± 4.5
Methyl tetracosanoate	−9280	16.062	77.150	136.6	135.3 ± 4.8
Methyl Z 15-tetracosenoate	−9256.2	15.94	76.952		134.9 ± 4.8
Methyl Z,Z,Z,Z,Z,Z 4,7,10,13,16,19-docosahexaeneoate	−9053.1	15.496	75.264		131.7 ± 4.7

$\Delta_{\text{l}}^{\text{g}}H_{\text{m}} (298.15 \text{ K}) = (1.880 \pm 0.06) \Delta_{\text{sln}}^{\text{g}}H_{\text{m}} (503 \text{ K}) + (9.76 \pm 1.34), \quad r^2 = 0.9960$ (4)

^a The uncertainties reported represent two standard deviations of the uncertainty calculated from the uncertainties in the slope and intercept of Eq. (4).

In addition, the vaporization enthalpy of methyl docosanoate has been reported by Krop et al. [1]. We recently used these values to extend these measurements to methyl octacosanoate, exclusive of methyl tricosanoate [5]. The literature value of one FAME, methyl heptadecanoate, was adjusted as a result of our previous

work and we have used the adjusted value in this work. Values for methyl dodecanoate through to methyl tetracosanoate, exclusive of methyl nonadecanoate, heneicosanoate and tricosanoate, were used to evaluate the vaporization enthalpies and vapor pressures of a series of unsaturated FAMES. The vaporization

Table 9
Summary of FAME vaporization enthalpies at $T = 298.15 \text{ K}$

Compounds ^a	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}} (298.15 \text{ K}) (\text{kJ mol}^{-1})$					Lit. [4,5]
	Mix 1	Mix 2	Mix 3	Mix 4	Mean ^a	
Methyl dodecanoate		75.8			75.8	76.6
Methyl tridecanoate		80.7			80.7	80.0
Methyl tetradecanoate		85.7	86.3	86.4	86.1 ± 0.8	85.9
Methyl Z 9-tetradecenoate		86.7	87.2	87.4	87.1 ± 0.7	
Methyl pentadecanoate		90.7			90.7	90.2
Methyl Z 10-pentadecenoate		91.7			91.7	
Methyl hexadecanoate	96.4	95.8	96.3	96.1	96.2 ± 0.5	96.8
Methyl Z 9-hexadecenoate	96.7	95.9	96.5	96.5	96.4 ± 0.7	
Methyl heptadecanoate		100.8			100.8	100.8
Methyl Z 10-heptadecenoate		100.8			100.8	
Methyl octadecanoate	106.4	105.8	106.1	105.9	106.1 ± 0.5	105.9
Methyl Z 9-octadecenoate	106.4		105.9		106.2 ± 0.7	
Methyl Z,Z 9,12-octadecadieneoate	108.1		107.6	107.6	107.8 ± 0.6	
Methyl Z,Z,Z 9,12,15-octadecatrieneoate	110.8		110.4	110.3	110.5 ± 0.5	
Methyl eicosanoate	116.4		115.8	115.9	116.0 ± 0.6	116.4
Methyl Z 11-eicosenoate	116.2		115.7	115.5	115.8 ± 0.7	
Methyl Z,Z 11,14-eicosadieneoate	117.8		117.4	117.4	117.5 ± 0.5	
Methyl Z,Z,Z,Z 5,8,11,14-eicosatetraeneoate			118.3	118.3	118.3	
Methyl Z,Z,Z 11,14,17-eicosatrieneoate			123.2	122.0	122.6 ± 1.6	
Methyl docosanoate	126.4		127.8	128.2	127.5 ± 1.9	126.1
Methyl Z,Z,Z,Z,Z 5,8,11,14,17-eicosapentaeneoate			121.1	120.9	121.0 ± 0.3	
Methyl Z 13-docoseneoate	126.3		125.3	125.3	125.6 ± 1.2	
Methyl Z,Z 13,16-docosadieneoate	127.9				127.9	
Methyl tetracosanoate	136.2		135.5	135.3	135.7 ± 1.0	136.6
Methyl Z 15-tetracosenoate	135.9		135.1	134.9	135.3 ± 1.1	
Methyl Z,Z,Z,Z,Z,Z 4,7,10,13,16,19-docosahexaeneoate			131.9	131.7	131.8 ± 0.2	

^a The uncertainties reported represent two standard deviations.

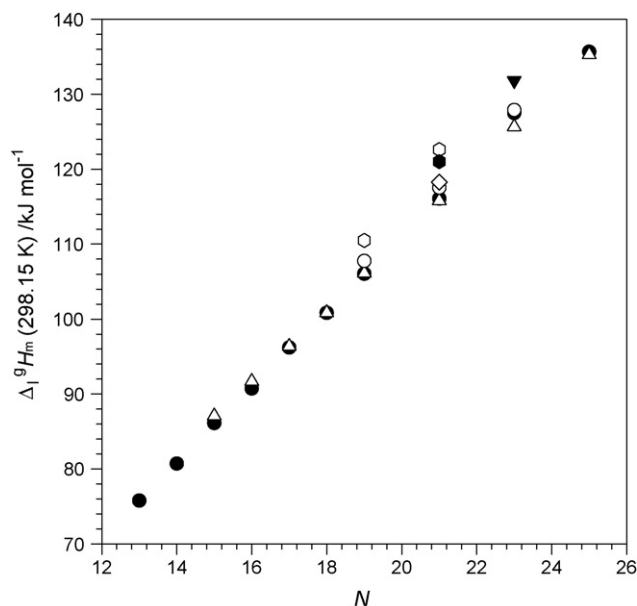


Fig. 1. Vaporization enthalpies of the FAMES from C₁₃ to C₂₅ as a function of the total number of carbon atoms, *N*; solid circles, literature values of the saturated FAMES; triangles, results of this study on the mono-unsaturated FAMES; empty circles, dienes; hexagons, trienes; diamond, tetraenes; solid hexagon, pentaene; solid triangle, hexadiene.

enthalpies of all of the unsaturated FAMES were evaluated by interpolation and their vaporization enthalpies at $T = 298.15$ are summarized in Table 9. The uncertainties listed in Tables 5–8 were calculated from the uncertainties associated with Eqs. (1)–(4) and represent two standard deviations. These uncertainties are a reasonable estimate of the uncertainty associated in the absolute value of the vaporization enthalpy which in turn depends on the accuracy of the standards used. The uncertainties reported in Table 9 represent two standard deviations of the uncertainty associated in reproducing vaporization enthalpies and is likely a good measure of the relative accuracy of the measurements. Fig. 1 illustrates the linear relationship observed for the saturated FAMES (solid circles) as a function of the number of carbon atoms and the relationship obtained between the saturated and unsaturated analogs. Most unsaturated FAMES

appear to have vaporization enthalpies slightly larger than their saturated counterparts.

5. Vapor pressures

In addition to an analysis of vaporization enthalpies, the article by van Genderen et al. [4] also evaluated vapor pressure data and processed the data in the form of the regression equation introduced by Clarke and Glew [7].

$$R \ln \left(\frac{p}{p_o} \right) = \frac{-\Delta_1^g G_m(\theta)}{\theta} + \Delta_1^g H_m(\theta) \left[\frac{1}{\theta} - \frac{1}{T} \right] + \Delta_1^g C_{p,m}^\circ \left[\left(\frac{\theta}{T} - 1 \right) + \ln \left(\frac{T}{\theta} \right) \right] \quad (5)$$

In this equation, p is the saturation vapor pressure, T the thermodynamic temperature, θ a chosen reference temperature and p_o is a reference pressure; p_o was taken as 1 Pa. Molar values for the Gibbs' energy, the vaporization enthalpy and the heat capacity difference between the gas and liquid phases, $\Delta_1^g G_m(\theta)$, $-\Delta_1^g H_m(\theta)$ and $-\Delta_1^g C_{p,m}^\circ$, 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 10. The vapor pressures calculated from these parameters have been also expressed in the form of a third order polynomial Eq. (6), used by us previously to model the temperature dependence of vapor pressure [6]. The parameters (A–D) for methyl dodecanoate to methyl tetracosanoate, exclusive of methyl nonadecanoate, heneicosanoate and tricosanoate, are also included in Table 10.

$$\ln \left(\frac{p}{p_o} \right) = AT^{-3} + BT^{-2} + CT^{-1} + D \quad (6)$$

Vapor pressures were calculated for the standards using the protocol recently reported [5,6]. Values of $\ln(p/p_o)$ for the saturated

Table 10
Literature A–D parameters for Eqs. (5) and (6) used as standards

Standards	ΔG_m° ^a (J mol ⁻¹)	ΔH_m° ^a (J mol ⁻¹)	$\Delta C_{p,m}^\circ$ ^a (J K ⁻¹ mol ⁻¹)	$10^{-8}A^b$	$10^{-6}B^b$	C^b	D^b
Methyl dodecanoate	-11324	71421	-113.5	2.18708	-2.72723	1633.21	4.862
Methyl tridecanoate				1.76893	-2.20581	-626.3	7.233
Methyl tetradecanoate	-6534	79828	-120.7	2.32582	-2.90023	1270.55	5.341
Methyl pentadecanoate				1.97319	-2.460510	-651.2	7.312
Methyl hexadecanoate	-1657	93363	-213.7	4.11787	-5.13488	8019.92	-1.553
Methyl heptadecanoate				3.20885	-3.993820	3615.9	3.056
Methyl octadecanoate	3011	98021	-157.9	3.04264	-3.79409	2433.18	4.364
Methyl eicosanoate	7308	109200	-203	3.91169	-4.87777	5151.12	1.941
Methyl docosanoate				4.629987	-5.777174	7293.4	0.063
Methyl tetracosanoate				5.480083	-6.845442	9971.3	-2.313

^a Literature parameters for Eq. (5) at $\theta = 350$ K [4].

^b Evaluated using the vapor pressures calculated from Eq. (6) [6].

Table 11
The A–D parameters of Eq. (6) of each FAME evaluated in this study

Compound evaluated ^a	A	B	C	D
Methyl 9-tetradecenoate	267312930	−3309709	2550.5	3.055
Methyl 10-pentadecenoate	315724757	−3943316	3451.8	3.227
Methyl 9-hexadecenoate	323007181	−4002347	4046.2	2.473
Methyl 10-heptadecenoate	329937369	−4076398	3847	2.708
Methyl 9-octadecenoate	382679646	−4765679	5734.1	0.97
Methyl 9,12-octadecadienoate	357332987	−4565417	5053	1.606
Methyl 9,12,15-octadecatrienoate	373598925	−4758558	5426.5	1.269
Methyl 11-eicosenoate	393530777	−5029377	5888.1	1.006
Methyl 11,14-eicosadienoate	436511436	−5408822	6789.1	0.201
Methyl 11,14,17-eicosatrienoate	455603381	−5667481	7234.8	−0.04
Methyl 5,8,11,14-eicosatetraenoate	452129069	−5558050	7142.3	−0.23
Methyl 5,8,11,14,17-eicosapentaenoate	460779146	−5695443	7384.8	−0.465
Methyl 13-docosenoate	472562883	−5872503	7620.5	−0.39
Methyl 13,16-docosadienoate	476350411	−5936572	7628.0	−0.33
Methyl 4,7,10,13,16,19-docosahexaenoate	527651044	−6482281	8966.2	−1.79
Methyl 15-tetracosenoate	519525244	−6460574	8702.7	−1.23

^a All the unsaturated compounds in this table have the Z configuration.

FAMES were calculated using Eq. (6) and correlated with respective $\ln(t_o/t_a)$ values calculated from the slopes and intercepts reported in Tables 5–8. Values of $\ln(p/p_o)$ for each unsaturated FAME were calculated using the correlation equation between $\ln(p/p_o)$ and $\ln(t_o/t_a)$ obtained from the standards. Values of $\ln(p/p_o)$ were evaluated at temperatures from $T = 298.15$ to 450 K at 30 K intervals. The correlations were generally characterized by correlation coefficients better than 0.99. Once $\ln(p/p_o)$ values for each unsaturated FAME in Mixes 1–4 were evaluated over the entire temperature range, these values were averaged together and the plot of $\ln(p/p_o)_i$ versus $1/T$ (K^{-1}) was fit to Eq. (6). The results of the fit are illustrated in Fig. 2. The fits were generally characterized with correlation coefficients greater than 0.999. The coefficients of the polynomial (Eq. (6)) evaluated

are provided in Table 11 for each unsaturated FAME. Most of the unsaturated FAMES investigated, exhibited longer retention times than their saturated counterparts, resulting in slightly lower vapor pressures.

The vaporization enthalpies and vapor pressures of the unsaturated FAMES examined in this study, to our knowledge, are not known. However, the boiling temperatures at reduced pressure are available for several of the saturated and unsaturated FAMES. While pressure and temperature measurements under distillation conditions may not always be made under optimal conditions, they do provide a qualitative measure of the reliability of the measurements. Experimental boiling temperatures at reduced pressures were obtained by searching SciFinder Scholar for each compound by name and opening the appropriate window

Table 12
Experimental and estimated boiling temperatures at reduced pressures^a

	$\ln(p/p_o)$ (lit.)	T (K) (lit.)	T (K) (calc.)	$\ln(p/p_o)$ (lit.)	T (K) (lit.)	T (K) (calc.)
Standards ^b						
Methyl dodecanoate	−4.35	406	407			
Methyl tridecanoate	−6.63	92	104			
Methyl tetradecanoate	−5.02	428	420	−3.23	457	459
Methyl hexadecanoate	−5.25	162	162	−5.02	428	439
Methyl heptadecanoate	−4.44	458	465			
Methyl octadecanoate	−7.33	436	418	−5.25	453	458
Methyl eicosanoate	−4.33	488	495			
Methyl docosanoate	−3.93	498	521			
Methyl tetracosanoate	−9.16	450	432			
Compounds evaluated						
Methyl 9-octadecenoate	−5.94	441	443	−3.64	491	490
Methyl 9,12-octadecadienoate	−4.69	463	474			
Methyl 9,12,15-octadecatrienoate	−8.75	405	404			
Methyl 5,8,11,14-eicosatetraenoate	−6.99	468	447			
Methyl 13-docosenoate	−4.33	502	513	−6.86	463	458

^a All experimental pressures and boiling temperatures were obtained by searching SciFinder Scholar.

^b All the unsaturated compounds in this table have the Z configuration.

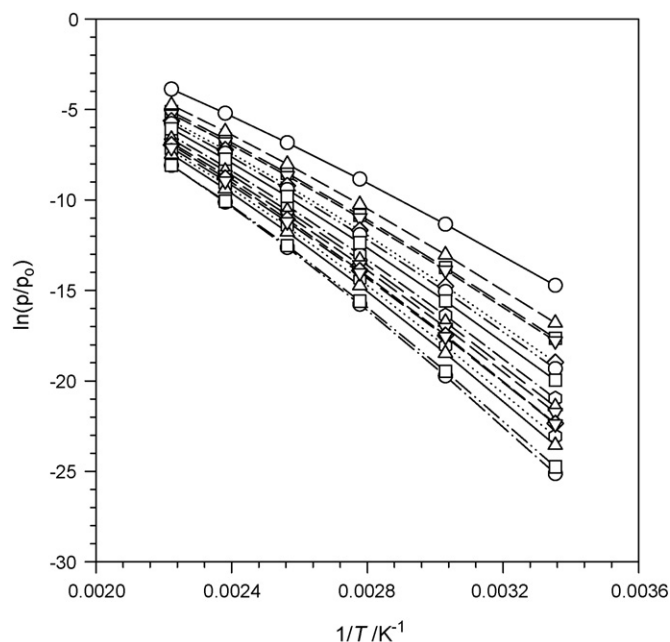


Fig. 2. The dependence of $\ln(p/p_0)$ on $1/T$ (K^{-1}) of the unsaturated FAMES of this study. From top to bottom, methyl *Z* esters of 9-tetradecenoate, 9-hexadecenoate, 10-pentadecenoate, 10-heptadecenoate, 9-octadecenoate, 9,12-octadecadienoate, 9,12,15-octadecatrienoate, 11-eicosenoate, 11,14-eicosadienoate, 5,8,11,14-eicosatetraenoate, 11,14,17-eicosatrienoate, 5,8,11,14,17-eicosapentaenoate, 13-docosenoate, 13,16-docosadienoate, 4,7,10,13,16,19-docosapentaenoate and 15-tetracosenoate.

listing experimental properties. For some compounds, several boiling temperatures at different reduced pressures are available. In this case values chosen were in the pressure range, 0.01–4 kPa. Available experimental boiling temperatures and pressures are provided in Table 12 along with the appropriate temperature necessary to reproduce the experimental vapor pressure. Predicted boiling temperatures are provided both for compounds used as standards and for those evaluated in this study. The absolute average deviation between experimental temperatures and those calculated using Eq. (6) was approximately 8 K and was similar for both the saturated and unsaturated FAMES.

References

- [1] H.B. Krop, M.J.M. Velzen, J.R. Parsons, H.A.J. Govers, *J. Am. Oil Chem. Soc.* 74 (1997) 309–315.
- [2] Y. Ali, M.A. Hanna, *Bioresour. Technol.* 50 (1994) 153–163.
- [3] N. Bureau, J. Jose, I. Mokbel, J.C. de Hemptinne, *J. Chem. Thermodyn.* 33 (2001) 1485–1498.
- [4] A.C.G. van Genderen, J.C. van Miltenburg, J.G. Bolk, M.J. van Bommel, P.J. Ekeren, G.J.K. van den Berg, H.A.J. Oonk, *Fluid Phase Equilib.* 202 (2002) 109–120.
- [5] J.S. Chickos, H. Zhao, G. Nichols, *Thermochim. Acta* 424 (2004) 111–121.
- [6] J.S. Chickos, W. Hanshaw, *J. Chem. Eng. Data* 49 (2004) 77–85.
- [7] E.C.W. Clarke, D.N. Glew, *Trans. Faraday Soc.* 62 (1966) 539–547.