

Liquid–vapour equilibria of the methyl esters of alkanolic acids: vapour pressures as a function of temperature and standard thermodynamic function changes

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Abstract

The vapour pressures as a function of temperature of the methyl esters of alkanolic acids from butanoic to eicosanoic acid, have been measured using two different techniques: the static diaphragm and spinning rotor manometry and the combined torsion mass-loss effusion. Combined with data available from literature, the new data have been processed using the thermodynamic regression equation proposed by Clarke and Glew. The results of this research are reliable vapour pressures and the thermodynamic properties of vaporisation.

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1. Introduction

In our laboratory, the vapour pressures have been measured of a number of methyl and ethyl esters of alkanolic acids. The experimental details and the results of the investigation were presented by van Bommel in his thesis [1]. In order to make van Bommel's data more accessible, we have opted for an approach in which the data are combined with data available from other sources to arrive at critically assessed sets of vapour pressure, valid over a large range of temperature.

In this communication, we present experimental data and the results of our assessment on the methyl esters of alkanolic acids, from butanoic to eicosanoic acid.

For the mathematical processing of the data, we use the three-parameter form of the thermodynamic regression equation introduced by Clarke and Glew [2].

$$R \ln \left(\frac{p}{p^0} \right) = \frac{-\Delta_{\text{vap}} G_{\text{m}}^{\circ}(\theta)}{\theta} + \Delta_{\text{vap}} H_{\text{m}}^{\circ}(\theta) \left\{ \frac{1}{\theta} - \frac{1}{T} \right\} + \Delta_{\text{vap}} C_{p,\text{m}}^{\circ} \left\{ \frac{\theta}{T} - 1 + \ln \left(\frac{T}{\theta} \right) \right\} \quad (1)$$

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Table 1
Vapour pressure data [1], and static diaphragm manometry

<i>T</i> (K)	<i>p</i> (Pa)	<i>T</i> (K)	<i>p</i> (Pa)	<i>T</i> (K)	<i>p</i> (Pa)	<i>T</i> (K)	<i>p</i> (Pa)
Methyl butanoate							
293.06	3216	300.78	4911	307.23	6766	313.34	9111
295.67	3711	300.97	4924	309.32	7500		
298.25	4282	305.63	6253	311.15	8199		
Methyl pentanoate							
293.34	1044	308.05	2446	318.03	4134	328.02	6726
297.75	1361	312.90	3174	322.47	5155		
Methyl hexanoate							
297.95	451.2	308.13	875.5	318.25	1545	328.05	2631
302.91	620.5	312.93	1139	323.02	2003	333.00	3356
Methyl heptanoate							
310.60	353.1	316.75	521.5	324.75	838.4	334.79	1474
311.50	374.3	320.89	669.4	329.71	1113	340.35	1982
Methyl octanoate							
312.98	149.5	322.60	282.4	332.95	533.5	348.42	127.1
317.86	207.3	327.91	394.0	337.93	714.0		
Methyl nonanoate							
308.71	39.72	328.28	157.0	345.97	465.8	350.03	588.9
312.45	52.75	333.21	214.0	357.68	714.6	353.40	894.7
316.38	70.46	336.60	263.9				
Methyl decanoate							
310.03	16.13	321.56	39.15	333.23	90.2	348.19	228.9
313.75	21.57	325.48	52.18	338.32	126.5	351.31	277.6
317.65	29.17	329.75	70.80	343.64	171.8		
Methyl undecanoate							
331.81	32.80	337.66	49.89	344.52	78.80	351.21	122.3
334.60	41.21	340.71	61.26	347.60	97.17		
Methyl dodecanoate							
332.38	13.97	338.35	21.89	346.01	38.66	350.24	51.95
335.33	17.54	340.25	25.30	348.06	44.47	357.29	84.76
Methyl tridecanoate							
338.54	9.439	344.30	14.91	351.43	24.72		
341.31	12.01	347.92	19.19	355.31	32.44		
Methyl tetradecanoate							
345.20	7.044	351.15	10.97	356.36	16.20		
348.06	8.683	353.20	12.69	359.13	19.75		
Methyl pentadecanoate							
343.20	2.658	349.42	4.384	354.04	6.005	359.29	9.137
345.38	3.215	351.83	5.254	355.35	6.843		
347.17	3.641	353.22	5.906	357.42	7.974		
Methyl hexadecanoate							
344.18	1.429	351.99	2.500	353.88	3.160	358.04	4.107
347.32	1.915	352.16	2.514	355.17	3.264	361.21	5.153
349.23	2.157						

where p is the saturation vapour pressure, T the thermodynamic temperature, θ a chosen reference temperature and p^0 a reference pressure; in this work we take $p^0 = 1$ Pa. The operator Δ_{vap} stands for the value of the quantity in the vapour state minus the value of the same quantity in the liquid state, G_{m}° is the molar Gibbs energy at $p = p^0$, H_{m}° the molar enthalpy and $C_{p,\text{m}}^{\circ}$ is the molar heat capacity. The value of the gas constant R is $8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$. The use of Eq. (1) implies that apart from the assessed vapour pressures, the result of the regression procedure consists of the thermodynamic vaporisation quantities at the reference temperature and at $p = 1$ Pa.

For a (pre-)screening of the data sets, to judge precision and mutual consistency, we make use of the ‘arc method’, which was proposed recently [3,4]. The arc method corresponds to a representation of data, in which the usual plot of $\ln p$ versus $1/T$ is replaced by a plot of $\ln f$ versus $1/T$. The function $\ln f$ is defined as

$$\ln f = \ln p - \alpha + \frac{\beta}{T} \quad (2)$$

In this expression, α and β are constants that are fixed such that $\ln f$ is (practically) zero for the two extreme (T, p) pairs of a given data set. The change from $\ln(p/p^0)$ to $\ln f$ corresponds to an amplification of the sensitivity of the ordinate axis by two orders of magnitude: details of the data that remain hidden in the traditional representation reveal themselves in the arc representation.

2. Experimental data

The experimental data by van Bommel [1] are given in Tables 1–3. The data in Table 1 were obtained by a static method, using an MKS baratron diaphragm manometer [5]. The data in Table 2 were obtained by simultaneous torsion and mass-loss effusion [6]. The data in Table 3 were obtained by means of the spinning rotor technique [7]. The experimental data by van Bommel are shown in Figs. 1–2, along with data from other sources. The latter are by Stage [8]; Rose and Supina [9]; Bonhorst et al. [10]; Jantzen and Witgert [11]; Rose et al. [12]; Scott et al. [13]; Husain et al. [14]; Spizzichino [15]; Norris and Terry [16]; Althouse and Triebold [17]; and Baccanari et al. [18].

Table 2

Vapour pressure data [1], torsion mass-loss effusion and temperatures (in K) for given pressure

	p (Pa)									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Methyl decanoate	260.41	265.89	269.20	271.60	273.49	275.06	276.40	277.57	278.61	279.54
Methyl undecanoate	271.35	276.95	280.33	282.78	284.71	286.31	287.67	288.87	289.93	290.88
Methyl dodecanoate	281.68	287.48	290.98	293.52	295.52	297.17	298.59	299.82	300.92	301.91
Methyl tridecanoate	291.53	297.46	301.03	303.62	305.66	307.35	308.79	310.05	311.17	312.18
Methyl tetradecanoate	300.94	307.08	310.79	313.48	315.60	317.35	318.84	320.15	321.31	322.36
Methyl pentadecanoate	310.17	316.45	320.24	322.98	325.14	326.93	328.45	329.79	330.97	332.04
Methyl hexadecanoate	319.11	325.52	329.39	332.20	334.41	336.23	337.79	339.15	340.36	341.45
Methyl heptadecanoate	327.60	334.15	338.11	340.98	343.23	345.10	346.69	348.08	349.32	350.43
Methyl octadecanoate	335.95	342.60	346.62	349.53	351.81	353.71	355.32	356.73	357.99	359.12
Methyl nonadecanoate	343.57	350.51	354.70	357.73	360.12	362.09	363.78	365.25	366.56	367.74
Methyl eicosanoate	351.50	358.49	362.71	365.76	368.16	370.15	371.85	373.33	374.65	375.84

Table 3
Vapour pressure data [1], and spinning rotor manometry

<i>T</i> (K)	<i>p</i> (mPa)	<i>T</i> (K)	<i>p</i> (mPa)	<i>T</i> (K)	<i>p</i> (mPa)	<i>T</i> (K)	<i>p</i> (mPa)
Methyl hexadecanoate							
303.46	14.66	303.54	14.10	305.75	19.48	310.89	35.84
303.48	14.99	304.82	17.22	305.75	19.49	310.92	36.10
303.48	16.30	304.82	17.36	308.67	27.58	312.88	44.67
Methyl heptadecanoate							
295.86	1.76	304.70	10.92	311.85	17.07	324.03	61.22
299.85	3.48	304.74	8.57	318.06	32.41	324.06	62.45
Methyl octadecanoate							
316.04	9.96	322.99	22.05	321.66	19.85	323.94	25.59

3. Discussion

3.1. Screening of experimental data

The arc representation of experimental vapour pressure data is a convenient, powerful tool for making a (pre-)screening of individual or combined data sets on a given substance.

The $\ln f$ function, underlying the arc representation and defined by Eq. (2), has the double advantage of being a physical representation and, at the same time, a representation which reveals details of the set(s) of data. As a physical representation, it distinguishes itself from the commonly used deviation plots. In contrast to the deviation plot, which is made after some mathematical treatment of the data, the $\ln f$ representation is equally useful before and after the mathematical treatment of the data.

The arc-like appearance of the $\ln f$ function, read the $\ln f$ representation of vapour pressure data, is the result of the influence of $\Delta_{\text{vap}} C_{p,m}^{\circ}$, the difference in molar heat capacity of vapour and liquid. From the Clausius–Clapeyron equation

$$\frac{d \ln p}{d(1/T)} = \frac{\Delta_{\text{vap}} H_m^{\circ}(T)}{R} \quad (3)$$

it follows that the slope of the $\ln f$ function, Eq. (2), is given by

$$\frac{d \ln f}{d(1/T)} = \frac{\Delta_{\text{vap}} H_m^{\circ}(T)}{R} + \beta \quad (4)$$

The difference properties in Eq. (1) can be ‘read’ easily from the arc, from Eq. (1):

$$\Delta_{\text{vap}} G_m^{\circ}(\text{at } T_{\text{max}}) = -R T_{\text{max}} \ln \left(\frac{p(T_{\text{max}})}{p^0} \right) \quad (5)$$

from Eq. (4):

$$\Delta_{\text{vap}} H_m^0(\text{at } T_{\text{max}}) = \beta R \quad (6)$$

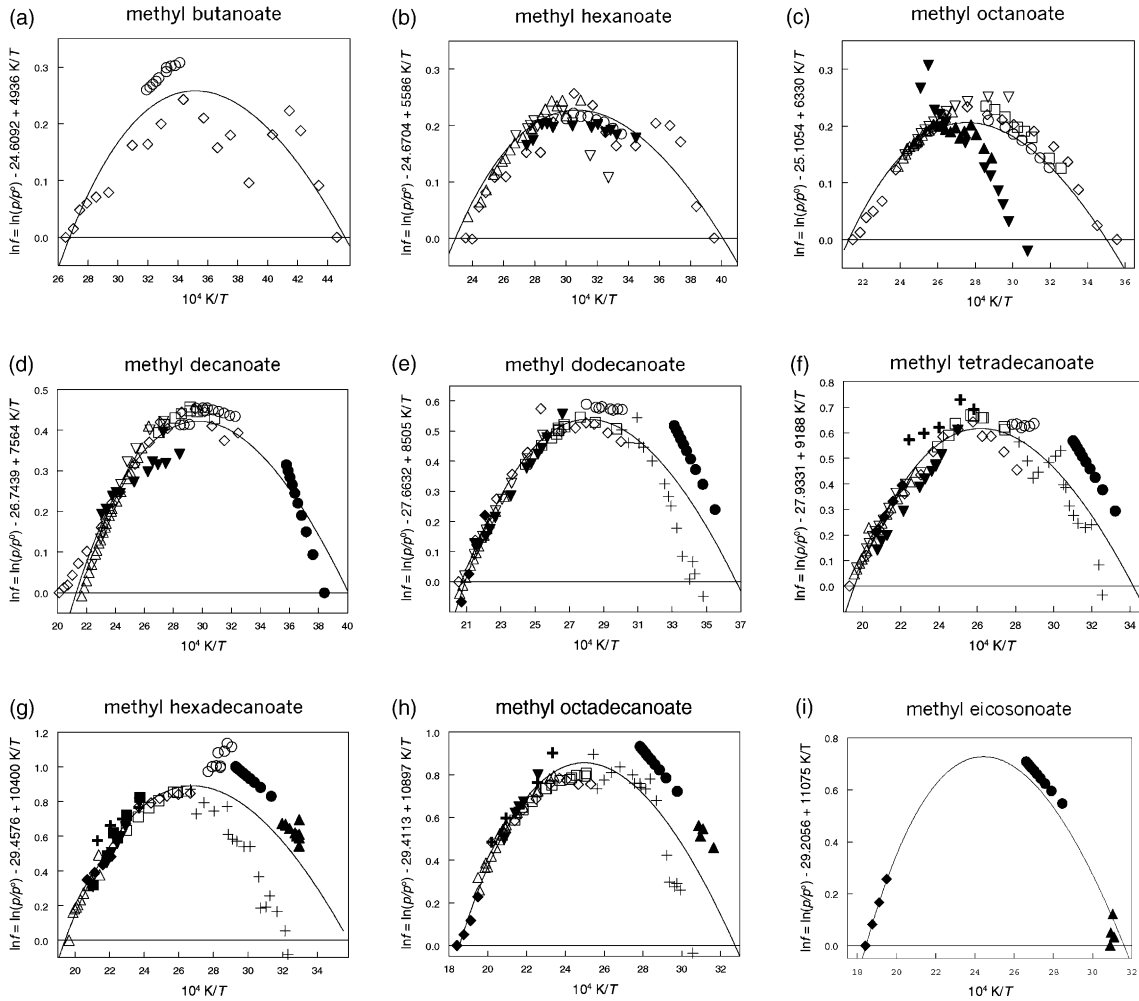


Fig. 1. (a–i) Vapour pressures for the methyl esters of the even carbonic acids, showing literature results and results obtained using the arc representation: (●) [1] (effusion); (○) [1] (static); (▲) [1] (spinning rotor); (△) [9]; (▼) [10]; (▽) [11]; (◇) [8]; (□) [13]; (◆) [14]; (⊕) [16]; (■) [17]; (+) [15].

and by Taylor's series expansion [4]:

$$\Delta_{\text{vap}} C_{p,m}^0 \cong -8R(T_{\text{max}}b)^{-2}h \quad (7)$$

where T_{max} is the temperature corresponding to the maximum of the arc, h the height of the arc, i.e. the $\ln f$ value at its maximum, and b is the width of the arc at its base. From the difference properties at T_{max} , the vapour pressures can be calculated at any temperature; by means of Eq. (1), and taking $\theta = T_{\text{max}}$. In addition, from the difference properties at T_{max} , the values of $\Delta_{\text{vap}} H_m^\circ$ and $\Delta_{\text{vap}} G_m^\circ$ at $T = 298.15$ K are easily calculated. These observations imply that Eqs. (5)–(7) allow a reliable 'manual' treatment of a set of experimental data, i.e. without the use of least squares (for examples, see refs. [4,19]).

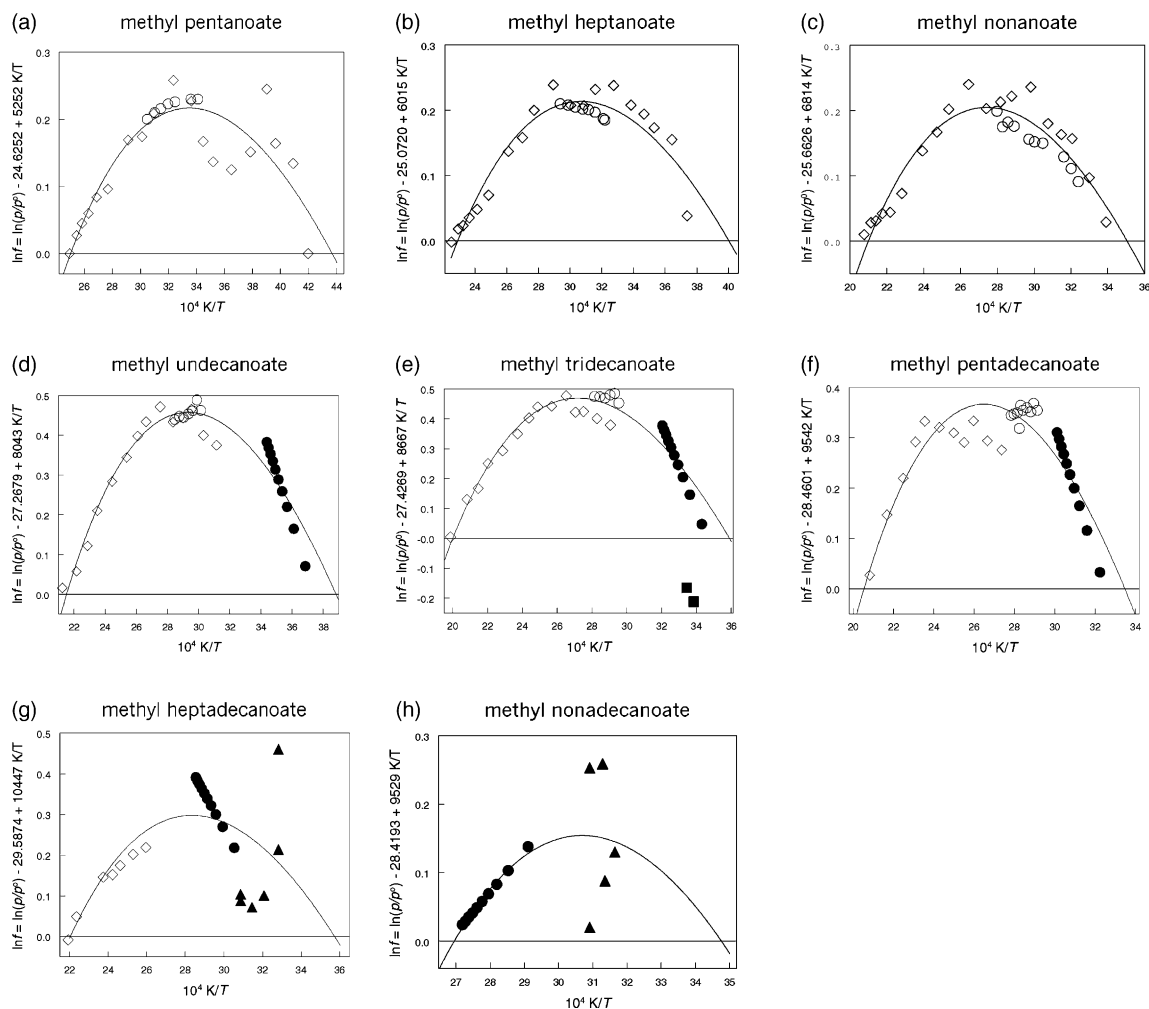


Fig. 2. (a–h) Vapour pressures for the methyl esters of the odd carbonic acids, showing literature results and results obtained using the arc representation: (●) [1] (effusion); (○) [1] (static); (▲) [1] (spinning rotor); (◇) [8]; (□) [13]; (■) [18].

As an example of the use of Eq. (7) for the calculation of $\Delta_{\text{vap}}C_{\text{m}}^{\circ}$, we take the combined sets of data for methyl octanoate, Fig. 1c. From Fig. 1c, it follows that the maximum of the arc is at about $(10^4 \text{ K}/T_{\text{max}}) = 28$, or $T_{\text{max}} \cong 357 \text{ K}$. The height of the arc is about $h \cong 0.23$, and the width at its base (taking the open diamonds by Stage) $b = 14 \times 10^{-4} \text{ K}^{-1}$. With these values Eq. (7) yields the value of $\Delta_{\text{vap}}C_{p,m}^{\circ} = -61 \text{ J K}^{-1} \text{ mol}^{-1}$.

An important issue, when comparing sets of data, is pertaining to the quality (as regards accuracy and precision) of an individual set of data. As an example we take the set of static data by van Bommel for methyl octanoate; its $\ln f$ representation is shown in Fig. 3. Realising that a difference of 0.01 in $\ln f$ corresponds to a difference of 1% in pressure, one can observe that the data have a high precision (absence of random errors). The data also have a high degree of accuracy in that they are in close

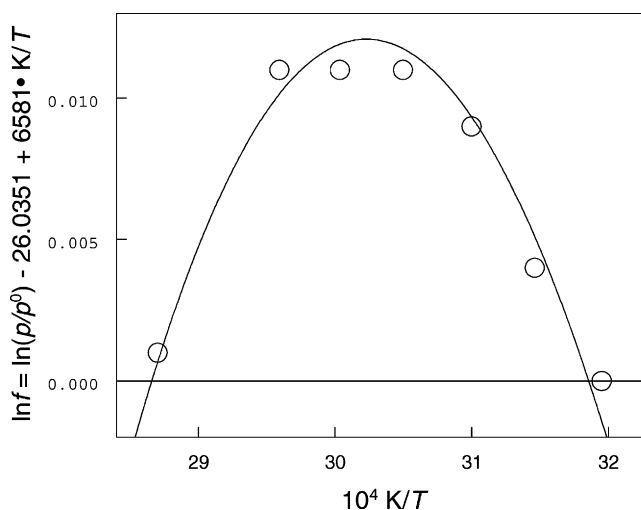


Fig. 3. Vapour pressures for methyl octanoate, showing literature results and results obtained using the arc representation: (○) [1] (static).

agreement with the data that set the overall trend. And, last but not least, Fig. 3 with Eq. (7) is giving rise to a $\Delta_{\text{vap}}C_{\text{m}}^{\circ}$ value of about $-60 \text{ J K}^{-1} \text{ mol}^{-1}$, i.e. in line with the value calculated from Fig. 1c (see earlier paragraph).

The situation sketched in the preceding paragraph is the exception rather than the rule. In most of the cases, an individual set over a limited range of temperature does not have the precision to reveal a ‘reasonable’ $\Delta_{\text{vap}}C_{\text{m}}^{\circ}$. As a matter of fact, the effusion instrument used by van Bommel does not yield any $\Delta_{\text{vap}}C_{\text{m}}^{\circ}$ at all. The instrument, designed by de Kruif et al. [5], is equipped with software which yields temperature values for evenly spaced pressures from 0.1 to 1.0 Pa, and such that $\ln p$ is linear in $(1/T)$.

The complete ensemble of experimental data, displayed by Figs. 1–2, allow us to make a number of additional observations.

1. For all of the substances, the combined data sets clearly display an arc-like behaviour. It implies that, for the mathematical processing of the data in terms of Eq. (1), three adjustable parameters ($\Delta_{\text{vap}}G_{\text{m}}^{\circ}$, $\Delta_{\text{vap}}H_{\text{m}}^{\circ}$ and $\Delta_{\text{vap}}C_{\text{p,m}}^{\circ}$) are justified and necessary (the addition of the temperature derivative of $\Delta_{\text{vap}}\Delta C_{\text{p,m}}^{\circ}$) as a fourth parameter is not justified: the data are not precise enough to reveal an asymmetric arc [20].
2. Individual data sets, as a rule, differ from the average trend, in a systematic sense. Systematic differences between data from different sources are most noticeable at the lowest pressures (because of the nature of the presentation and the fact that the measurement of low pressures makes high demands). As an example, van Bommel’s effusion (range 0.1–1.0 Pa) and spinning rotor data (0.001–0.1 Pa) are systematically higher in pressure than Spizzichino’s effusion data (0.013–13 Pa), see Fig. 2a–d.
3. For a given source/laboratory (eventually in combination with a given technique), the quality of the data sets (consistency with average trend, and precision) differs from substance to substance, in a rather random manner. For example, the data by Bonhorst are in line with the data from other sources, however, with the striking exception of methyl octanoate.

3.2. Thermodynamic vaporisation properties

Mathematical processing of the experimental data in terms of Eq. (1) is yielding the numerical values of the vaporisation quantities $\Delta_{\text{vap}}G_m^\circ(\theta)$, $\Delta_{\text{vap}}H_m^\circ(\theta)$, and $\Delta_{\text{vap}}C_{p,m}^\circ$. The computed value of $\Delta_{\text{vap}}C_{p,m}^\circ$ is independent of the choice of θ , whereas the computed values of $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ depend on the choice of θ . In other terms, there is only one mathematical result, in which the choice of θ is affecting the values computed for $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$.

As a first step, we took $\theta = 350$ K for all of the substances, including all data sets and giving them equal weight. The result of the computations is part of Table 4; the numerical values are given as integers, passing over the question of the number of significant digits. The computed $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ values are plotted in Fig. 2, as a function of the number of carbon atoms in the molecules of the parent acids. Similarly, the computed $\Delta_{\text{vap}}C_{p,m}^\circ$ values are displayed in Fig. 5.

Out of the three vaporisation quantities, $\Delta_{\text{vap}}G_m^\circ$ is the one which is most directly related to the measured vapour pressures. Therefore, it follows from Fig. 4 that the overall consistency, between the results for the different substances, is satisfactory. From the same figure, it follows that the dispersion of the $\Delta_{\text{vap}}H_m^\circ$ values is higher, the main cause being the inaccuracy of (some of) the computed $\Delta_{\text{vap}}C_{p,m}^\circ$ values (see Fig. 5).

In order to arrive at a collection of vaporisation properties for $T = 298.15$ K, we started from two (rather obvious) assumptions. In the first place, it is not implausible to assume that, for a given substance, the physical significance of the computed $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ values is maximal at the top of the arc, or rather at the temperature corresponding to the top. To bring the top values of $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ to their values at $T = 298.15$ K, the values of $\Delta_{\text{vap}}C_{p,m}^\circ$ are needed. Our second assumption is that more reliable results are obtained by using a calculated $\Delta_{\text{vap}}C_{p,m}^\circ$ (from a fit of all of the individual $\Delta_{\text{vap}}C_{p,m}^\circ$ values in column 4 of Table 4 as a function of number of carbon atoms) than by using the individually calculated $\Delta_{\text{vap}}C_{p,m}^\circ$ values in column 4 of Table 4.

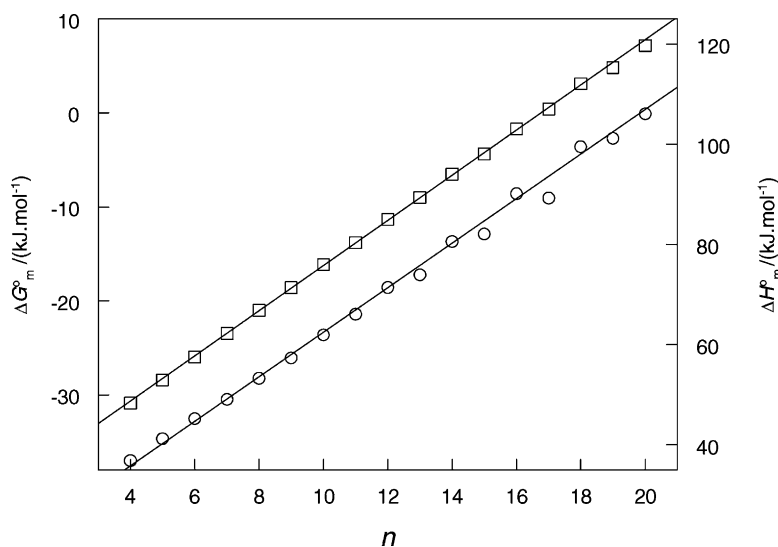


Fig. 4. Computed $\Delta_{\text{vap}}G_m^\circ$ (\square) and $\Delta_{\text{vap}}H_m^\circ$ (\circ), respectively as a function of the number of carbon atoms of the parent acids at $\theta = 350$ K.

Table 4
Survey of results of computations

n	ΔG_m° (J mol ⁻¹)	ΔH_m° (J mol ⁻¹)	$\Delta C_{p,m}^\circ$ (JK ⁻¹ mol ⁻¹)	S	θ (K)	ΔG_m° (J mol ⁻¹)	ΔH_m° (J mol ⁻¹)	$\Delta C_{p,m}^\circ$ (JK ⁻¹ mol ⁻¹)	ΔG_m° (kJ mol ⁻¹)	ΔH_m° (kJ mol ⁻¹)
$\theta = 350$ K						$T = 298.15$ K				
4	-30883	36890	-63.2	0.053	284	-17683 ± 33	41060 ± 172	-30	-20.60 ± 0.03	40.64 ± 0.22
5	-28428	41272	-46.7	0.038	299	-18090 ± 26	43653 ± 136	-39	-17.91 ± 0.03	43.69 ± 0.14
6	-25971	45188	-49.9	0.027	325	-20842 ± 13	46437 ± 57	-48	-15.23 ± 0.01	47.71 ± 0.10
7	-23489	49131	-45.9	0.023	326	-18470 ± 17	50232 ± 112	-56	-12.53 ± 0.02	51.80 ± 0.13
8	-21014	53341	-55.1	0.042	363	-23763 ± 17	52625 ± 125	-65	-9.71 ± 0.02	56.87 ± 0.14
9	-18602	57416	-51.7	0.068	364	-21629 ± 58	56692 ± 299	-74	-6.99 ± 0.07	61.59 ± 0.39
10	-16145	61952	-70.6	0.040	337	-13227 ± 53	62869 ± 87	-83	-4.26 ± 0.05	66.10 ± 0.17
11	-13799	66079	-88.0	0.037	340	-11504 ± 26	66959 ± 127	-92	-1.60 ± 0.05	70.82 ± 0.35
12	-11324	71421	-113.5	0.080	356	-12737 ± 81	70740 ± 166	-101	1.33 ± 0.10	76.59 ± 0.41
13	-8987	73955	-91.8	0.011	368	-13211 ± 34	72302 ± 150	-110	3.80 ± 0.07	79.99 ± 0.49
14	-6534	79828	-120.7	0.085	382	-14259 ± 76	75966 ± 178	-119	6.73 ± 0.15	85.94 ± 0.76
15	-4346	82100	-102.4	0.041	372	-9710 ± 345	79846 ± 209	-128	9.07 ± 0.40	89.29 ± 0.79
16	-1657	93363	-213.7	0.168	397	-13771 ± 101	83320 ± 405	-137	12.25 ± 0.22	96.84 ± 0.63
17	381	89299	-85.2	0.103	353	-380 ± 91	89043 ± 701	-146	14.17 ± 0.13	97.03 ± 1.23
18	3011	98021	-157.9	0.113	401	-10273 ± 79	89968 ± 280	-155	17.68 ± 0.23	105.87 ± 1.37
19	4827	101170	-159.0	0.060	326	11567 ± 71	104980 ± 2400	-164	19.75 ± 0.08	109.53 ± 2.72
20	7308	109200	-203.0	0.045	406	-8131 ± 66	97836 ± 204	-172	22.74 ± 0.27	116.43 ± 1.54

Column 1: number of carbon atoms in the molecules of the parent alkanolic acid. Columns 2–4: result of data processing in terms of Eq. (1), taking $\theta = 350$ K. Column 5: computed S.D. Columns 6–8: result of data processing in terms of Eq. (1), taking for θ the temperature corresponding to the maximum of the arc. Column 9: smoothed heat capacity difference. Columns 10 and 11: calculated standard Gibbs energy and enthalpy of vaporisation, respectively and valid for $T = 298.15$ K.

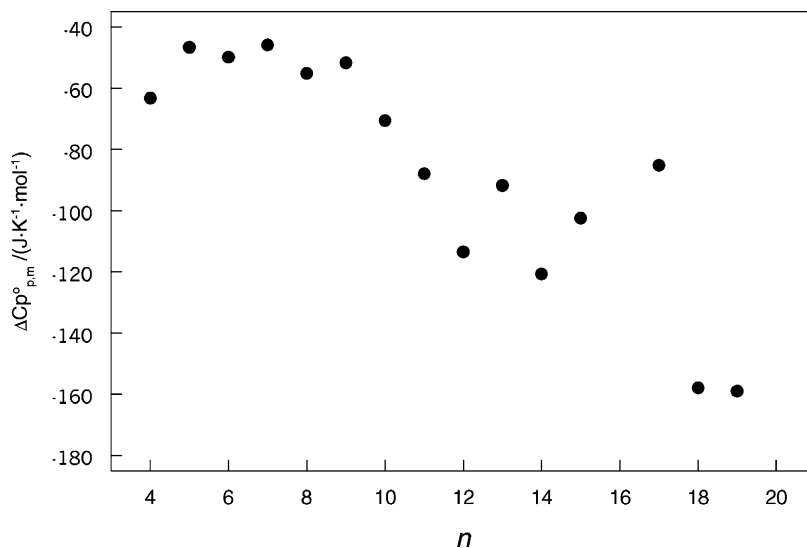


Fig. 5. Computed $\Delta_{\text{vap}}C_{p,m}^{\circ}$ as a function of the number of carbon atoms of the parent acids at $\theta = 350$ K.

The $\Delta_{\text{vap}}G_m^{\circ}$ and $\Delta_{\text{vap}}H_m^{\circ}$, calculated for the individual substances with their own θ , are included in Table 4 along with their mathematically computed standard deviations. The $\Delta_{\text{vap}}C_{p,m}^{\circ}$ values needed to transfer the $\Delta_{\text{vap}}G_m^{\circ}$ and $\Delta_{\text{vap}}H_m^{\circ}$ to 298.15, satisfy the equation

$$\Delta_{\text{vap}}C_{p,m}^{\circ}(n) = 5.64 - 8.929n \quad (8)$$

and are included in column 9 of Table 4.

The calculated $\Delta_{\text{vap}}H_m^{\circ}$ (at $T = 298.15$ K) and $\Delta_{\text{vap}}G_m^{\circ}$ (at $T = 298.15$ K) are given in Table 4, and graphically represented by Fig. 6. The data in Table 4 are provided with estimated uncertainties that reflect the standard deviations of the least-squares calculation along with the uncertainties introduced by the extrapolation from $T = \theta$ to 298.15 K.

Finally, we subjected the data for $T = 298.15$ K to a linear least-squares treatment, such that they were provided with weight factors. These factors were taken inversely proportional to the estimated uncertainties displayed in Table 4.

The final result is represented by the following two equations:

$$\Delta_{\text{vap}}G_m^{\circ}(\text{at } T = 298.15 \text{ K}, n) = -31.39 + 2.708n \quad (9)$$

$$\Delta_{\text{vap}}H_m^{\circ}(\text{at } T = 298.15 \text{ K}, n) = 19.39 + 4.741n \quad (10)$$

In our view, the last two equations are the most accurate representations of the two thermodynamic vaporisation quantities that can be derived from the complete amount of experimental vapour pressure data. The precisions of the numerical values, calculated by the Eqs. (9) and (10), are a function of n , reaching their lowest values for $n = 6$, i.e. for methyl hexanoate. We estimate that the uncertainties (δ) in $\Delta_{\text{vap}}G_m^{\circ}$ are given by

$$\delta(\Delta_{\text{vap}}G_m^{\circ}, n) = \{0.01 + 0.015(|n - 6|)\} \quad (11)$$

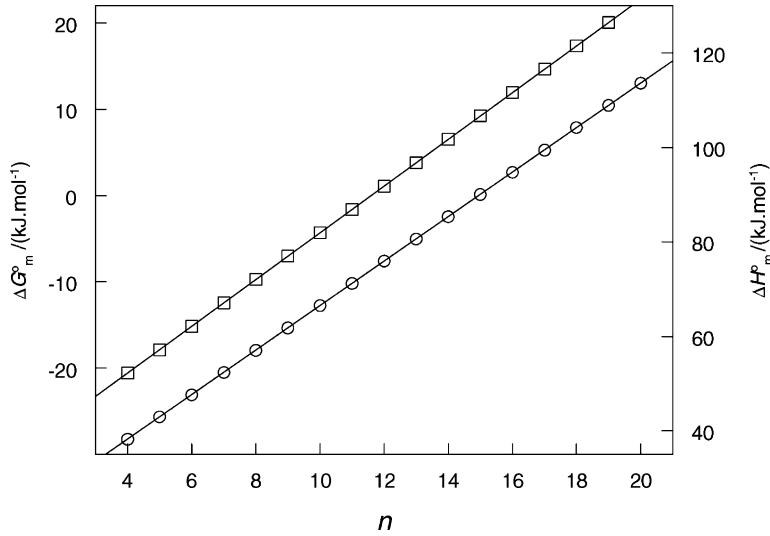


Fig. 6. Computed $\Delta_{\text{vap}}G_m^\circ$ (\square) and $\Delta_{\text{vap}}H_m^\circ$ (\circ), respectively as a function of the number of carbon atoms of the parent acids at $T = 298.15$ K.

and those in $\Delta_{\text{vap}}H_m^\circ$ by

$$\delta(\Delta_{\text{vap}}H_m^\circ, n) = \{0.10 + 0.053(|n - 6|)\} \quad (12)$$

4. Conclusions

- Vapour pressure data on the methyl esters of the normal alkanolic acids, $C_nH_{2n-1}O_2CH_3$, for $4 \leq n \leq 20$, from the sources available in literature, have been combined and mathematically processed in terms of Eq. (1).
- The computational result, for the chosen reference temperature of $\theta = 350$ K, is represented by the columns 2–5 of Table 4. Column 5 gives the calculated standard deviation between experimental and calculated vapour pressure in a relative sense.
- The physical significance of the computed vaporisation quantities $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$, for each of the substances, is maximal at the temperature corresponding to the maximum of the arc representation. The relevant information, i.e. T_{max} , $\Delta_{\text{vap}}G_m^\circ$ (at T_{max}), $\Delta_{\text{vap}}H_m^\circ$ (at T_{max}), is represented by the columns 6–8 of Table 4.
- The numerical information contained in columns 6–8 of Table 4, along with the smoothed $\Delta_{\text{vap}}\Delta C_{p,m}^\circ$ values, from Eq. (8) and given in column 9 of Table 4, has been used to calculate for $T = 298.15$ K, the $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ values in columns 10 and 11 in Table 4. The uncertainties in the $\Delta_{\text{vap}}G_m^\circ$ and $\Delta_{\text{vap}}H_m^\circ$ values, in columns 10 and 11 of Table 4, are estimated uncertainties.
- As a function of the number (n) of carbon atoms in the molecules of the parent acids, the overall result of the investigation, valid for $T = 298.15$ K, is represented by Eq. (9) for $\Delta_{\text{vap}}G_m^\circ$ and Eq. (10) for $\Delta_{\text{vap}}H_m^\circ$.

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