Heats of Vaporization of the *n*-Fatty Acid Esters

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ABSTRACT: Heats of vaporization at both 25°C and normal boiling points are given for the *n*-fatty acid methyl and ethyl esters and the *n*-alkyl acetates. The validity of the reported heats of vaporization is supported by: (i) their agreement with those estimated by alternate methods, and (ii) the equations correlating heats of vaporization with homolog carbons have the proper slopes (approximately 4.96). Equations also are given for correlating heats of vaporization with boiling points, and boiling points and molar volumes with homolog chainlength.
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KEY WORDS: Boiling points, densities, heats of vaporization, *n*-alkanes, *n*-alkanols, *n*-alkyl acetates, *n*-fatty acid ethyl esters, *n*-fatty acid methyl esters, solubility parameters.

Although both the *n*-fatty acid esters and heats of vaporization (H_v) are important (1,2), many of the published H_v and H_vM values (M, molecular weight) disagree widely with each other (1–14). The present paper reports work on H_v (at 25°C and at boiling points), boiling points, densities, and molar volumes of the *n*-fatty acid methyl and ethyl esters and *n*-alkyl acetates, but H_v of the methyl esters (at 25°C) and efforts to evaluate their accuracy received most attention.

Criteria for assessing accuracy included (i) linearity (Eq. 1) of molar H_v (H_vM or ΔH_v) with homolog chainlength (measured by total carbons, *C*, or molecular weight, M), (ii) observing whether the slopes, *m*, in Equation 1 resemble the proposed proper slope of 4.96 (15), and (iii) ascertaining how well the literature H_vM data agree with those estimated by some of the recommended methods (13,16–18).

$$H_vM\ (25°C) = b + mC \qquad [1]$$

DATA SOURCES AND METHODS

The principal sources of H_v were References 3, 4, 6, and 12–14. Normal boiling points, molar volumes at 25°C, and solubility parameters were needed to estimate H_v; boiling points (T_bK) were obtained from References 4, 6, 7, 12, and 19; densities (d_4^{25}) from References 6, 7, and 12; and solubility parameters (S) from References 12, 13, and 16.

Calories were multiplied by 4.184 to get Joules, and solubility parameters (Hildebrands) were multiplied by 2.046 to get solubility parameters in S.I. (international standard) units.

In developing equations to correlate ester properties with the number of carbons, *C*, total carbons (instead of carbons in the acyl group) were used.

The solubility parameters (lacking for most aliphatic esters), needed to calculate H_vM (25°C) by Equations 2 and 3, were estimated by Equation 4 (20):

$$H_vM,\ \text{cal/mol} = S^2V + RT;\ RT = 592.5 \qquad [2]$$

$$H_vM,\ \text{J/mol} = 4.184(S^2V) + 2479 \qquad [3]$$

$$S\ (\text{Hildebrands}) = T_bK/4V^{1/2} \qquad [4]$$

To get the S^2 needed in Equations 2 and 3, the expression $T/4V^{1/2}$ was squared to get $T^2/16V$; it follows that S^2V becomes $T^2/16$ and that the simple Equations 5 and 6 can be used to estimate H_vM at 25°C:

$$H_vM,\ \text{cal/mol} = T^2/16 + 592.5 \qquad [5]$$

$$H_vM,\ \text{J/mol} = 0.2615\ T^2 + 2479 \qquad [6]$$

Primarily to get information on the proper slope of H_vM vs. *C* equations, the H_v of the *n*-alkanes were studied briefly. Equations that correlate *n*-alkane H_vM values with homolog carbons, *C*, are:

$$H_vM,\ \text{kJ/mol}\ (25°C) = 1.5450 + 4.9778\ C \qquad [7]$$

[C_4–C_{17}; r = 0.999979; Zwolinski and Wilhoit (Ref. 4)]

$$H_vM,\ \text{kJ/mol}\ (25°C) = 1.7315 + 4.9687\ C \qquad [8]$$

[C_4–C_{17}; r = 0.999987; Majer and Svoboda (Ref. 3)]

The slopes of Equations 7 and 8 are similar to that (4.959) reported by Somayajula (15).

The *n*-alkanol Equation 9, based on Majer and Svoboda's data (3), has a slope similar to those of the *n*-alkanes (Eqs. 7 and 8):

$$H_vM,\ \text{kJ/mol}\ (25°C) = 32.595 + 4.9264\ C \qquad [9]$$

(C_1–C_{14}; r = 0.999765)

The intercept of Equation 9 is much higher than the intercepts of Equations 7 and 8, illustrating the effects of polarity on H_vM. (It will be shown later that the methyl ester intercept is approximately 12, which is compatible with the intermediate polarity of esters.)

The *n*-alkane H_v, kJ/mol, at normal boiling points are linear with $C^{1/2}$. Their squares are linear with carbons, C (Eqs. 10 and 11):

$$H_vM, \text{kJ/mol(b.p.)} = -6.5861 + 14.485\, C^{1/2} \quad [10]$$

[C_5–C_{19}; r = 0.999973; Rossini *et al.* (Ref. 14)]

$$[H_vM(\text{b.p.})]^2 = -262.11 + 181.16\, C \quad [11]$$

[C_5–C_{19}; r = 0.999921; Rossini *et al.* (Ref. 14)]

Equations for correlating boiling points (T_b,K), heats of vaporization (H_v, g, 25°C), and densities (d_4^{25}) with homolog chainlength were developed (21) by plotting carbons (C) against $1/(P-P_\infty)$, where P is property and P_∞ is the limiting property (property of an amorphous, infinite-length homolog) to get:

$$C = -k + m/(P-P_\infty) \quad [12]$$

which was rearranged to:

$$P = P_\infty + m/(C + k) \quad [13]$$

The following P_∞ values were used: $T_{b\infty}$K = 1190 (Huddle, B.P., Jr., private communication) at 760 torr; 926 at 1 torr; 354 Joules (15,21); and d_4^{25} = 0.851 (21,22).

METHYL ESTERS: CORRELATING H_VM (25°C) WITH CHAINLENGTH

The Majer H_v (3) at 25°C [identical with those published by Sellers *et al.* (23)] are well defined (except for the lower and the pentadecanoic esters) by Equations 14 and 15:

$$H_vM, \text{kJ/mol, 25°C} = 11.051 + 5.0632\, C \quad [14]$$

(C_8–C_{15}; r = 0.999763)

$$H_vM, \text{kJ/mol, 25°C} = 11.809 + 4.9911\, C \quad [15]$$

(C_8–C_{19}; r = 0.999837)

Equation 15 resulted when Riddick *et al.* (12) value (106.32 kJ/mol for methyl oleate) was added to Equation 14. The H_v calculated by Equation 15 agree with the Majer and Svoboda (3) and Sellers *et al.* (23) values (Table 1). Moreover, the slope is similar to the 4.96 slope proposed by Somayajulu (15) for the H_vM (25°C) vs. C equations.

The molar quotients (M/H_v), like the molar products, H_vM, also are linear with chainlength (Eq. 16):

$$M/H_v = M^2/H_vM = 86.627 + 39.422\, C \quad [16]$$

(C_8–C_{19}: r = 0.999842)

The methyl ester H_v, estimated by different methods, agree with the Majer and Svoboda values (3) (Table 1). The first estimation method consisted in adding the contributions of the methyl (4.71), methylene (4.94), and ester (18.0) groups (13,24). The calculated values from Equation 17, based on these group contributions, agree with previous data (3) over chainlengths, C_6–C_{19}:

$$H_vM, \text{kJ/mol(25°C)} = 12.60 + 4.94\, C \quad [17]$$

H_v calculated by Equations 3 and 6 also agree with these values (Table 1).

The usefulness of solubility parameters and Equation 3 to estimate heats of vaporization is illustrated by the data in Table 2.

The ratios (H_vM/T_b,K) of the methyl esters are linear with chainlength:

$$\text{ratio} = 17.233 + 1.3061\, C \quad [18]$$

(C_7–C_{16}; r = 0.999720)

TABLE 1
***n*-Fatty Acid Methyl Esters: Molar Heats of Vaporization, Solpars[a], Molar Volumes[b], and Normal Boiling Points[c]**

				H_vM, kJ/mol (25°C)			
Carbons (C)	Solpars[a]	V_{25}[b,c]	T_b,K[d]	Ref. 3	Eq. 15	Eq. 17	Eqs. 3 and 6
6	8.728	131.61	400.5	43.10		42.24	44.42
7	8.702	148.18	423.7	48.04		47.18	49.42
8	8.677	164.76	445.5	51.62	51.74	52.12	54.38
9	8.655	181.33	466.2	56.41	56.73	57.06	59.31
10	8.631	197.91	485.7	61.99	61.72	62.00	64.17
11	8.607	214.48	504.2	66.75	66.71	66.94	68.96
12	8.580	231.05	521.7	71.37	71.70	71.88	73.65
13	8.554	247.63	538.4	77.17	76.69	76.82	78.28
14	8.524	264.20	554.2	82.68	81.68	81.76	82.80
15	8.495	280.78	569.4	86.98	86.68	86.70	87.26
16	8.464	297.35	583.8	93.49	91.67	91.64	91.60
19	8.363	347.07	623.2	106.3	106.6	106.5	104.0

[a] Solubility parameters (Hildebrands): $S = T_b,K/4V^{1/2}$.
[b] Calculated: $V_{25} = 32.165 + 16.574\, C$.
[c] These values agree with those published recently (Ref. 27) for the C_3–C_{15} methyl *n*-alkanoates.
[d] From Stephenson and Malanowski (19) and T_b,K = 1190 − 26123/(C + 27.09).

TABLE 2
Heats of Vaporization (H_vM, kJ/mol, 25°C) and Solubility Parameters (S)[a]

Carbons (*C*)		Solpars[a]	V_{25}	H_vM (Calcd.)[b]	Ref. 3
4	Et acetate	8.91	98.49	35.19	35.60
5	Bu formate	8.7	115.16	38.95	41.1
5	Et propionate	8.77	115.54	39.66	39.21
5	Pr acetate	8.80	115.66	39.95	39.72
6	Bu acetate	8.69	132.55	44.36	43.86
8	$(Bu)_2O$	7.76	170.44	45.42	44.97
6	*n*-Hexane	7.27	131.61	31.58	31.56
10	*n*-Decane	7.72	195.88	51.32	51.38
12	*n*-Dodecane	7.91	228.58	62.32	61.51

[a] The Bu formate solubility parameter (Hildebrand) is from Riddick *et al.* (Ref. 12), the others from Hoy (Ref. 16).
[b] Calculated by Equation 3: $H_vM = 2479 + 4.184\ (S^2V)$.

Equation 18 can be used to calculate H_v from normal boiling points.

ADDITIONAL ESTERS: HEATS OF VAPORIZATION AT 25°C

The H_vM (25°C) of the *n*-fatty acid ethyl esters and the *n*-alkyl acetates (Tables 3 and 4) are generally similar to the H_vM values of the isomeric methyl esters. H_vM (25°C) of the ethyl esters and acetates were estimated, by using Equations 3 and 6, from solubility parameters, molar volumes, and normal boiling points; the estimated values agree reasonably well with the literature values (Tables 3 and 4).

The H_vM of the acetates were also estimated by multiplying Joules (from Eq. 19) by molecular weights:

$$H_v,\ \text{Joules} = 354 + 87.892/(C - 2.333) \qquad [19]$$

Equation 19 was obtained by rearranging Equation 20 (354 is the limiting value) (15,21):

$$C = 2.333 + 87.892/(H_v - 354) \qquad [20]$$

$$(C_4\text{–}C_6,\ C_\infty;\ r = 0.99156)$$

Majer and Svoboda (3) have published H_v (kJ/mol, 25°C) for the following additional esters: *n*-Pr formate 37.53; *n*-Pr propionate, 43.45; *n*-Bu formate, 41.11; glycol diacetate, 61.44; glycol dipropionate, 67.59; glycol dibutyrate, 73.21; triacetin, 85.74; tripropionin, 91.36; and tributyrin, 107.07.

HEATS OF VAPORIZATION AT BOILING POINTS

The H_vM of the methyl and ethyl esters at their boiling points (both at 760 and 1 torr), like those of the *n*-alkanes (Eqs. 10 and 11), are linear with $C^{1/2}$ and $M^{1/2}$; the squares of the H_vM values are linear with chainlength (Eqs. 21–26) (Table 5):

$$H_vM,\ \text{kJ/mol (b.p.)} = 17.893 + 7.1367\ C^{1/2} \qquad [21]$$

$$(\text{Me esters})\ (C_2\text{–}C_6;\ r = 0.99974)$$

$$H_vM,\ \text{kJ/mol (b.p.)} = 9.2293 + 2.4339\ M^{1/2} \qquad [22]$$

$$(\text{Me esters})\ (C_2\text{–}C_6;\ r = 0.99871)$$

$$[H_vM(\text{b.p.})]^2 = 560.44 + 116.41\ C \qquad [23]$$

$$(\text{Me esters})\ (C_2\text{–}C_6;\ r = 0.99804)$$

$$H_vM,\ \text{kJ/mol(b.p.)} = 16.493 + 7.7459\ C^{1/2} \qquad [24]$$

$$(\text{Et esters})\ (C_3\text{–}C_7;\ r = 0.999885)$$

$$[H_vM(\text{b.p.})]^2 = 546.95 + 118.08\ C \qquad [25]$$

$$(\text{Et esters})\ (C_3\text{–}C_7;\ r = 0.999221)$$

$$[H_vM(\text{b.p.})]^2 = 277.55 + 8.4182\ M \qquad [26]$$

$$(\text{Et esters})\ (C_3\text{–}C_7;\ 0.999224)$$

TABLE 3
***n*-Fatty Acid Ethyl Esters: Molar Heats of Vaporization, Solpars[a], Molar Volumes[b] and Normal Boiling Points[c]**

Carbons					H_vM, kJ/mol (25°C)	
(*C*)	Solpars[a]	V_{25}[b]	T_b,K[c]	Ref. 3	Eqs. 3 and 6	Me esters, (3)[d]
3	9.101	80.93	327.5	31.96	30.44	32.29
4	8.827	98.43	350.3	35.60	34.49	35.85
5	8.657	115.54	372.2	39.21	38.67	39.28
6	8.559	132.92	394.7	42.68	43.28	43.10
7	8.558	149.95	419.2	47.01	48.38	48.04
8	8.546	166.52	441.1	51.72	53.32	51.62
10	8.523	199.65	481.7		63.23	61.99
12	8.485	232.78	517.8		72.58	71.37
14	8.440	265.91	550.5		81.86	82.68
15	8.415	282.47	565.7		86.24	86.98

[a] Solubility parameters (Hildebrands): $S = T_b,K/4V^{1/2}$.
[b] Molar volumes: C_3–C_6 from Riddick *et al.* (Ref. 12); C_7–C_{15} from $V_{25} = 33.998 + 16.565\ C$.
[c] From Stephenson and Malanowski (Ref. 19) and $T_b,K = 1190 - 26264/(C + 27.07)$.
[d] For comparison.

TABLE 4
n-Alkyl Acetates: Molar Heats of Vaporization (25°C), Solpars[a], Molar Volumes (25°C)[b], and Normal Boiling Points[c]

				H_vM, kJ/mol (25°C)			
Carbons (C)	Solpars[a]	V_{25}[b]	T_b,K[c]	Ref. 3	Calcd.[d]	Eqs. 3 and 6	Me esters (3)[e]
3	9.233	79.84	330.4	32.29		30.96	32.29
4	8.824	98.49	350.3	35.60	35.84	34.57	35.85
5	8.710	115.66	374.7	39.72	39.52	39.19	39.28
6	8.668	132.55	399.2	43.86	43.90	44.15	43.10
7	8.620	150.09	422.4		48.54	49.14	48.04
8	8.606	166.12	443.7		53.29	53.96	51.62
10	8.566	199.27	483.7		62.96	63.66	61.99
12	8.519	232.41	519.5		72.73	73.05	71.37
14	8.467	265.55	551.9		82.57	82.13	82.68
15	8.438	282.12	655.9		87.50	86.52	86.98

[a] Solubility parameters (Hildebrands): $S = T_b,K/4V^{1/2}$ (Ref. 20).

[b] C_3–C_8 values from Riddick *et al.* (Ref. 12); the others from: $V_{25} = 33.581 + 16.569\ C$.

[c] From Riddick *et al.* (Ref. 12) and $T_b,K = 1190 - 26424/(C + 29.41)$.

[d] Joules calculated by Joules = 354 + 87.892/(C – 2.333) multiplied by molecular weights [354 is the limiting value (Refs. 15,21)].

[e] Given for comparison.

The group contribution values for calculating entropies of vaporization (Me = 40.140; CH_2 = 0.97069; ester = 5.8752; and acetate = 11.663) of Hoshino (26) were used to develop Equations 27 and 28:

$$\text{esters: } \Delta S_v = 83.243 + 0.97069\ C \qquad [27]$$

$$\text{acetates: } \Delta S_v = 89.031 + 0.97069\ C \qquad [28]$$

The ΔS_v values calculated by Equations 27 and 28 were multiplied by the appropriate normal boiling points (K) to get Hoshino's (25) estimated H_vM data; agreement with other H_vM values is good (Table 5).

Scott's H_vM data and boiling points at 1 torr of the n-fatty acid methyl esters (26) were used to develop Equations 29–32; the calculated values agree with Scott's data (Table 6):

$$H_vM\text{, kJ/mol (b.p.)} = -9.0127 + 21.694\ C^{1/2} \qquad [29]$$

$$\text{(Me esters) } (C_9\text{–}C_{19};\ r = 0.999895)$$

$$[H_vM(\text{b.p.})]^2 = -625.20 + 417.38\ C \qquad [30]$$

$$\text{(Me esters) } (C_9\text{–}C_{19};\ r = 0.999880)$$

$$H_vM\text{, kJ/mol (b.p.)} = -20.220 + 0.24525\ T_b,K \qquad [31]$$

$$\text{(Me esters) } (C_9\text{–}C_{19};\ r = 0.999867)$$

$$T_b,K(1\text{ torr}) = 926 - 25340/(C+32.17) \qquad [32]$$

$$\text{(Me esters) } (C_9\text{–}C_{19};\ r = 0.999893)$$

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TABLE 5
Molar Heats of Vaporization (H_vM, kJ/mol) at Normal Boiling Points[a]

	Methyl esters			Ethyl esters			Acetates	
Carbons (C)	Ref. 3	Eq. 21	Eq. 27[b]	Ref. 3	Eq. 24	Eq. 27[b]	Ref. 3	Eq. 28[c]
2	27.92	27.99	25.97					
3	30.32	30.25	28.47	29.91	29.91	28.22	30.32	30.38
4	32.24	32.17	30.74	31.94	31.98	30.52	31.94	32.55
5	33.79	33.85	33.12	33.88	33.81	32.79	33.92	35.18
6	35.36	35.37	35.67	35.47	35.47	35.15	36.28	37.88
7	38.55		38.15	36.96	36.99	37.74		

[a] The $(H_vM)^2$ vs. C equations gave calculated values similar to those calculated from the H_vM vs. $C^{1/2}$ equations.

[b] The ΔS_v values calculated by Equation 27 were multiplied by T_b,K.

[c] The ΔS_v values calculated by Equation 28 were multiplied by T_b,K.

TABLE 6
***n*-Fatty Acid Methyl Esters: Heats of Vaporization at Boiling Points (1 torr)**[a]

	T_b, K, 1 torr		Heats of vaporization, kJ/mol			
Carbons (*C*)	Ref. 26	Eq. 32	Ref. 26	Eq. 29	Eq. 30	Eq. 31
9	311.1	310.5	55.94	56.07	55.96	56.08
11	339.0	339.0	63.05	62.94	62.98	62.92
13	365.0	365.0	69.33	69.21	69.29	69.30
15	387.7	388.8	75.06	75.01	75.07	74.86
17	410.5	410.6	80.17	80.43	80.44	80.46
19	431.4	430.8	85.65	85.55	85.47	85.58

[a]Data from Scott *et al.* (Ref. 26).

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