Determination of Environmentally Relevant Physical–Chemical Properties of Some Fatty Acid Esters

Hildo B. Krop*, Martin J.M. v. Velzen, John R. Parsons, and Harrie A.J. Govers

Department of Environmental and Toxicological Chemistry, Amsterdam Research Institute for Substances in Ecosystems,
University of Amsterdam, 1018 WV Amsterdam, The Netherlands

ABSTRACT: Fat models frequently use input parameters that are defined at environmental conditions. In a recently developed gas–liquid chromatography method (GC–VAP), vapor pressures, heats of vaporization, and heat capacity differences (gas–liquid) of fatty acid esters are determined over a large temperature range that includes environmental temperatures. This method also allows an accurate determination of the normal boiling point temperature of a substance. Literature values of vapor pressure, boiling point temperature, and heat of vaporization at 298.15 K for the chosen esters are all in excellent agreement with those determined with the developed method. Correlations between carbon number and heat of vaporization are high.

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KEY WORDS: Fatty acid esters, heat capacity, heat of vaporization, QSAR, solubility parameter, vapor pressure.

Fatty acid esters of natural origin are promising products for use as fuels, lubricants, or cleaning agents. The introduction and use of fatty acid esters as possible substitutes for (chlorinated) hydrocarbons as industrial cleaning agents are being investigated in the recently started project "**V**egetable **O**ils and their **F**atty **A**cid esters as substitutes for organic solvents in industrial **PRO**cesses (VOFA**Pro**; sponsored by the EU)." As part of this project, an environmental and human risk assessment of the products is being carried out. Some environmentally important parameters, such as the vapor pressures of the fatty acid esters, are difficult to determine accurately at environmental conditions because of their low volatility. The values in the literature are usually extrapolated from measurements at higher temperatures, often leading to substantial errors.

Indirect vapor pressure measurement by gas–liquid chromatography (GC) has several advantages over other methods. It is a fast and easy method where low concentrations are used and relatively impure substances are tolerated. The method described in this paper is based on the use of relative retention times, determined on a nonpolar stationary phase under isothermal conditions. The retention of a solute, however, depends on both its vapor pressure in the pure liquid phase and its activity in the column stationary phase. In addition to the measured retention parameters, the value of the activity coefficient is required (1). In an earlier version of the GC method, this problem was solved by using one or two reference compounds with known vapor pressure in the measured temperature range (2–4). In the thermodynamic relationship used to calculate the pressures at environmental conditions, the heats of vaporization of the unknown substance and the reference compound appeared, which were assumed to be independent of the temperature. This assumption leads to substantial errors in the extrapolation to environmental conditions.

In a novel version of the GC method (GC–VAP), reported by Spieksma *et al.* (1), Kováts retention indices and liquid *n*-alkanes as reference compounds are used. The Kováts retention indices of these compounds are by definition independent of the temperature. The retention of the unknown substance is expressed relative to those of the *n*-alkanes that elute just before and after the compound. An expression is derived that relates the vapor pressure, P, of the unknown compound at a certain temperature to those of the corresponding nearest *n*-alkanes and some correction factors. The difference in activities to the column of the unknown substance and the nearest eluting *n*-alkane is incorporated by the McReynolds number of a model compound.

In this study, the vapor pressures of a number of fatty acid esters are measured. The esters are divided into three groups: (i) a series of methyl esters of different saturated fatty acids with even carbon number (C_{12}–C_{22}); (ii) a series of esters of lauric acid and different alcohol groups; and (iii) a series of methyl esters of C_{18}-acids with different degrees of saturation. Special attention is paid to comparison of the results, extrapolated outside of the measured temperature interval, with values obtained by different methods. From the temperature dependence of vapor pressure, heat of vaporization, and gas–liquid heat capacity, differences are derived.

METHODS

Physical–Chemical Model

Detailed descriptions of the method used can be found elsewhere (1,5,6). In short, the Kováts retention indices of the un-

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*To whom correspondence should be addressed at Department of Environmental and Toxicological Chemistry, Amsterdam Research Institute for Substances in Ecosystems, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

known substance (I_i) and the *n*-alkanes are determined after correction by the retention time of an unretarded compound (in our case methane) on a gas chromatograph at different temperatures. The index is defined as follows:

$$I_i = \frac{100\left[\log\left(t_{r,i} - t_0\right) - \log\left(t_{r,z} - t_0\right)\right]}{\left[\log\left(t_{r,z+1} - t_0\right) - \log\left(t_{r,z} - t_0\right)\right]} + 100z \qquad [1]$$

where ($t_{r,i} - t_0$) is the net retention time (min) of the test compound, ($t_{r,z} - t_0$) is that of the *n*-alkane, and t_0 is the retention time of the unretarded component at different temperatures T(K). The numbers of carbon atoms of *n*-alkanes eluting just before and after i are z and $z + 1$, respectively.

This index is then transformed into the compound's vapor pressure, P, and the activity in the column stationary phase, γ_i. The vapor pressure of the unknown substance is related to those of the nearest *n*-alkanes and a correction factor. The correction factor takes into account that the Kováts retention index of the unknown substance does not coincide exactly with those of the nearest *n*-alkanes and the different activities of the unknown substance and the nearest *n*-alkane in the column. The value of the correction factor in the pressure equation, which is the logarithm of the ratio of the activity coefficients of the unknown substance and of the nearest *n*-alkane, is assumed to be constant in the derivation, whereas the ratio of the activity coefficients of the *n*-alkane (with z carbon atoms) and the following one (with $z + 1$ carbon atoms) is assumed to be 1.0. The constant ratio γ_i/γ_z is found from tabulated values based on the McReynolds number. For the fatty acid esters, the value of 2-pentanone was chosen (1). The same procedure is used to derive equations for the heats of vaporization and the heat capacity differences. The following basic equations can be derived (6):

$$\log P_i = \log P_z + \frac{\left(100z - I_i\right)\left(\log P_z - \log P_{z+1}\right)}{100} + \log\left(\gamma_i/\gamma_z\right) \qquad [2]$$

$$\Delta H_i(T) = \Delta H_z + \frac{\left(100z - I_i\right)\left(\Delta H_z - \Delta H_{z+1}\right)}{100} - \frac{2.30259RT^2\left(\log P_z - \log P_{z+1}\right)\left(dI_i/dT\right)}{100} \qquad [3]$$

$$\Delta C_{P,i}(T) = \Delta C_{P,z} + \frac{\left(100z - I_i\right)\left(\Delta C_{P,z} + \Delta C_{P,z+1}\right)}{100} - \left[\frac{RT\left(\log P_z - \log P_{z+1}\right)\left(dI_i/dT\right)}{50} + \frac{\left(\Delta H_z - \Delta H_{z+1}\right)\left(dI_i/dT\right)}{100} + \frac{RT^2\left(\log P_z - \log P_{z+1}\right)\left(d^2I_i/dT^2\right)}{100}\right] \qquad [4]$$

Equations 3 and 4 can be derived from Equation 2 by using the thermodynamic definitions $\Delta H_v = RT^2(d \ln P/dT)$ and $\Delta C_p = d\Delta H_v/dT$.

Because the Kováts retention indices of the *n*-alkanes are, by definition, independent of the temperature, a (small) correction is necessary if the substance is not an *n*-alkane. The nature of this correction is not known exactly, but good results are found by using a simple quadratic relationship of the Kováts index and the temperature according to the following equation (5):

$$I_i(T) = I_0 + I_1 \cdot T^2 \qquad [5]$$

After determination of the Kováts indices of the unknown compound and the square of the temperature, I_0 and I_1 can be determined by linear regression.

The next step is the calculation of log P_z of the *n*-alkanes by fitting T and z to experimental values of the vapor pressure, heat of vaporization, and heat capacity differences according to the following equation:

$$\log P_z = A_z + \frac{B_z}{T} + \frac{C_z}{T^2} \qquad [6]$$

with $A_z = 4.877735\ (\pm\ 0.014939) + 0.303157\ (\pm\ 0.00222)z - 0.007281\ (\pm\ 0.00007)z^2$; $B_z = 485.68961\ (\pm\ 5.613) - 261.5436\ (\pm\ 0.47628)z + 5.8678\ (\pm\ 0.005539)z^2$; $C_z = -86487.5\ (\pm\ 55.09) + 344.999\ (\pm\ 14.2985)z - 874.879\ (\pm\ 0.8257)z^2$.

The corresponding equations for the heat of vaporization and heat capacity difference for the *n*-alkanes can be found by using again the thermodynamic definitions for these properties given before.

A_z, B_z, and C_z in Equation 6 have been derived from independent measurements of vapor pressures, heats of vaporization, and heat capacity differences of the *n*-alkanes. Thus, A_z, B_z, and C_z are empirical parameters for *n*-alkanes, A_z and B_z being similar to constants in the Clausius–Clapeyron equation. Heat capacity differences of the *n*-alkanes at 298.15 K have been used for the C_z factors, which span a range of z = 3–14. The B_z factors have been derived from calorimetric determination of the heats of vaporization of the *n*-alkanes at 298.15 K, spanning a range of z = 6–17, and the A_z factors from 297 experimental P values in the range of z = 3–35, determined at 150–763 K (log P_z–values between −4.56 and +3.31). No experimental values were omitted, even if the difference between the experimental value and the model was more than three times the standard deviation.

The errors in log P_i, $\Delta H(T)$, and $\Delta C_{P,i}(T)$ were calculated from the standard error of each factor (A_z, B, C_z, I_i). In the calculated error function, the temperature and the retention index can still be found, resulting in an increase of the error with increasing temperature and retention index.

All calculations, including the statistical ones, were performed in the spreadsheet program Excel 5.0 for Windows (Microsoft, Redmond, WA).

Experimental

All esters, with the exception of 2-ethylhexyl laurate, were purchased from Sigma (Zwijndrecht, The Netherlands).

2-Ethylhexyl laurate was a gift from Unichema (Gouda, The Netherlands). The esters were stored at 5°C.

The even, C_{12}–C_{18}, *n*-alkanes were purchased from Polyscience (Niles, IL), analytical standard (purity >99%), and the even, C_{20}–C_{24}, *n*-alkanes were from Sigma (purity >99%). No peak interference was found by GC. All substances were dissolved in trimethylpentane (TMP) [Rathburn (glass-distilled grade), Walkerburn, Scotland].

A Hewlett-Packard model 5890 series II (Amstelveen, The Netherlands), equipped with a flame-ionization detector, was used. A 30 m × 0.32 mm DB1 column from J&W Scientific (Interscience, Breda, The Netherlands) (film thickness 25 µm) was applied. Helium was used as the carrier gas.

The injector was used in the split mode with a split ratio of 1:24.2. The column flow amounted to 1.64 mL/min, and the septum purge flow to 1.12 mL/min.

The oven temperature of the isothermal runs depended on the volatility of the fatty acid esters. For methyl caprate, the temperature varied between 373 and 433 K in steps of 10 K, for methyl laurate between 393 and 463 K, for methyl myristate from 393 to 473 K, and the other esters from 433 to 535 K, all in steps of 10 K. The oven temperature was accurate to within 1% of the temperature in Kelvin.

Retention indices of the saturated methyl fatty acid esters were measured in quadruplicate for most temperatures and in sextuplicate for the end and middle temperature of the chosen range to improve the stability of the regression line. For the other esters, all indices were measured in quadruplicate.

At each temperature, all indices were checked for outliers, defined as the index value above or below the average and three times the standard deviation. None were found. The Fisher *F*-value of the average retention index at each measured temperature for each fatty acid ester was calculated. Its value is found by dividing the square of the standard deviation of the pertinent temperature over the same value of a reference temperature, corrected for the number of degrees of freedom.

RESULTS AND DISCUSSION

In this study, the GC–VAP method was found to provide accurate vapor pressure data at different temperatures, which can be extrapolated to temperatures outside the measured range. Accurate measurements of the Kováts retention indices within the measured temperature range diminish the extrapolation error. The curvature of the vapor pressure–temperature relationship (*P–T* model) determines the heat of vaporization, ΔH_v. This property is sometimes measured by a different, e.g., calorimetric, method at temperatures other than where the vapor pressures were determined. Some values are available, and they will provide an extra validation of the *P–T* model.

The heat of vaporization is an important parameter in the prediction of partitioning properties. For example, its value can be used to calculate a total solubility parameter, δ, frequently used in relationships to predict solubility behavior (7). The heat capacity difference (gas – liquid) under constant pressure (ΔC_{Pi}) is derived from the curvature of the heat of vaporization vs. temperature relationship.

Because the heat of vaporization is an important thermodynamic property, a number of estimation methods (QSAR) are known (8). A simple one is frequently found for the unsaturated methyl esters, where the number of C atoms of the fatty acids is used as descriptor. This correlation will be reexamined.

Kováts Retention Indices at Different Temperatures

It was noted that the *F* values increased when the calculated retention index was derived from a retention time of the unknown substance that was less than twice the unretarded component. These indices were omitted from the calculation. No other irregularities could be found in the measured values. The results of the regression according to Equation 5 are summarized in Table 1. It shows that the temperature effect of the Kováts retention index (I_1) is extremely small, indicating that the fatty acid esters behave similarly to the corresponding nearest *n*-alkane on the GC column. This leads sometimes to small correlation coefficients (r^2) of the regression equation, whereas the calculated prediction interval of the retention index of the unknown substance at 298.15 K (the environmentally relevant temperature) never exceeds 1.5 units, which is a sufficiently small error compared to the experimental error of the retention index.

No significant temperature dependence could be found for methyl myristate and ethyl laurate in the measured temperature range. As Table 1 shows, these fatty acid esters mark the change of sign in the I_i values in this series. The origin of this change in sign is not known yet.

Thermodynamic Properties

Vapor pressure. Values of the vapor pressure, heat of vaporization, and difference in heat capacity at 298.15 K were obtained *via* Equations 2–4 (Table 2). The standard errors turned out to be small. A comparison is made between these results and literature diagrams at 273.15 to 623.15 K (0–350°C) for methyl myristate (9–11) in Figures 1–3. The literature curves of Ohé (9) and Scott (10) are derived from the Antoine equation [$\log P = A - B/(T + C)$], while the curve of Spizzichino (11) is obtained by application of a Rankine-type equation ($\log P = A + B/T + C \cdot \log T$). The last equation can be defined rigorously from thermodynamics by assuming ideal behavior of the vapor and a temperature independence of the heat capacities (12).

All curves are extrapolated outside their measured temperature range. Other fatty acid esters for which Antoine or Rankine constants could be found in the literature (9–11) showed similar figures. The difference in log *P* values in the measured temperature ranges amounts to a maximum of 0.1 log unit. The *P–T* curve closest to that from the GC–VAP method in the low-temperature range is that of Spizzichino (11). However, these data points are determined at

TABLE 1
Gas–Liquid Chromatography (GC) Kováts Retention Indices (I_i) as a Function of Temperature According to Equation 5[a]

Substance	I_0	I_1	r^2	s.e.r.	Temperature range (°C)	$N(T)$	$N_{regr.}$
Me caprate	1310.80	−2.63e − 05	0.56	0.376	100–160	6	30
Me laurate	1510.04	−1.58e − 05	0.39	0.410	120–190	8	38
Me myristate	1707.97	0.00	0.00	0.222	120–200	9	44
Me palmitate	1906.62	1.10e − 05	0.13	0.850	190–250	7	34
Me stearate	2104.17	2.69e − 05	0.54	0.750	190–250	7	34
Me arachidate	2303.93	2.94e − 05	0.90	0.210	190–250	7	34
Me behenate	2504.38	3.18e − 05	0.93	0.190	190–250	7	34
Ethyl laurate	1576.53	0.00	0.00	0.490	150–210	7	28
Propyl laurate	1669.44	1.63e − 05	0.41	0.370	150–210	7	28
Butyl laurate	1760.94	3.70e − 05	0.91	0.260	150–220	8	32
2-Ethyl hexyl laurate	2069.08	9.04e − 05	0.97	0.360	170–240	8	32
Me oleate	2045.06	1.60e − 04	1.00	0.095	150–210	7	28
Me linolate	2024.75	2.12e − 04	1.00	0.138	150–210	7	28
Me linolenate	2022.87	2.38e − 04	1.00	0.100	150–210	7	28
Me erucate	2458.84	1.21e − 04	0.97	0.520	190–250	7	28

[a]Abbreviations: *I*, regression coefficients; r^2, correlation coefficient; s.e.r., standard error of regression; *N(T)*, number of temperature data points; $N_{regr.}$, number of measurements used for the regression; Me, methyl.

320–360 K, which is much closer to environmentally relevant temperatures than the other curves. Consequently, these curves may deviate more when extrapolated to lower temperatures.

No Antoine constants could be found for the pertinent methyl esters, but some boiling points under reduced pressure are available. Table 3 shows values compared to the boiling temperature calculated by the GC–VAP method. A good agreement is found considering the possible error in the literature values, although it seems that the GC–VAP method determines the boiling points under reduced pressure a few degrees higher (2–10 K).

The GC–VAP method allows an estimation of the normal (at 760 mm Hg) boiling point temperature as well. Table 3 includes the results for the chosen esters compared to literature data. Some data are close to the experimental value, although our values are again slightly higher than the literature values. Our values show a calculated error of 2 K (around 0.06 log units in pressure). The literature values (13) of the boiling points of methyl palmitate and methyl stearate at 747 mm Hg seem to be out of the range. The origin of these values could not be traced. These results indicate that the GC–VAP method seems to obtain reliable normal boiling point temperatures, which shows that the extrapolation of the log *P–T*-curve to higher temperature and pressure is correctly made.

Heat of vaporization. Experimental values of the heat of vaporization at 298.15 K are known for some methyl esters (14,15). These values allow a validation of the GC–VAP method at lower temperatures because the heat of vaporization can be determined from the curvature of the log *P–T* curve. Figure 1 shows that, in the lower temperature range, the curvatures of the different *P–T* diagrams deviate considerably, which is also shown in Figure 2, where large deviations in the heat of vaporization at 298.15 K are found.

The values of Spizzichino (11), derived from the Rankine equation, are close to the GC–VAP method. The relationship

TABLE 2
(Subcooled) Liquid Vapor Pressures (log P_i), Heats of Vaporization (ΔH_v) and Gas–Liquid Heat Capacity Differences ($\Delta C_{p,i}$) at 298.15 K (25°C) According to the GC–VAP Method[a]

Substance	log P_i (mm Hg)	ΔH_v (cal/mol)	$\Delta C_{p,i}$ (cal/mol/K)	Substance	log P_i (mm Hg)	ΔH_v (cal/mol)	$\Delta C_{p,i}$ (cal/mol/K)
Me caprate	−1.50 (0.05)	15982 (40)	−23.9 (0.2)	Ethyl laurate	−2.83 (0.05)	19132 (45)	−30.7 (0.6)
Me laurate	−2.50 (0.05)	18346 (43)	−28.9 (0.3)	Propyl laurate	−3.29 (0.05)	20232 (47)	−33.4 (0.6)
Me myristate	−3.47 (0.06)	20691 (47)	−34.6 (0.6)	Butyl laurate	−3.74 (0.05)	21319 (48)	−36.3 (0.2)
Me palmitate	−4.43 (0.06)	23047 (52)	−41.0 (0.4)	2-Ethylhexyl laurate	−5.22 (0.06)	24968 (55)	−46.8 (0.6)
Me stearate	−5.36 (0.07)	25389 (56)	−48.1 (0.5)				
Me arachidate	−6.26 (0.07)	27762 (61)	−55.9 (0.3)	Me oleate	−5.14 (0.06)	24678 (55)	−46.0 (0.6)
Me behenate	−7.17 (0.08)	30137 (66)	−64.6 (0.4)	Me linolate	−5.06 (0.06)	24433 (55)	−45.4 (0.6)
				Me linolenate	−5.07 (0.06)	24409 (55)	−45.3 (0.6)
				Me erucate	−7.00 (0.08)	29595 (65)	−62.7 (0.7)

[a]Errors are given in parentheses. Other abbreviation in Table 1.

TABLE 3
Comparison of Normal Boiling Point Temperatures T_{bp}, in °C, and Those Under Reduced Pressure for Those Fatty Acid Esters Where No P–T Relationship Could Be Found[a]

Compound	Pressure (mm Hg)	T_{bp} (GC–VAP)[a]	T_{bp} (lit.)[b,c]
Me caprate	760	229	224
Me laurate	766	265	262
Me myristate	751	296	295
Me palmitate	747	322	415–418
	15	198	196[e]
	5	174	148[e]
Me stearate	747	347	442–443
	15	220	215
Me arachidate	10	228	215.6
	1.95	192	188
	760	369	
Me behanate	15	259	224–225[d]
	3.75	226	215.5
	2.5	217	221
	760	393	
Ethyl laurate	15	158	154
	8	145	141
	5	135	121.7
	760	275	277
Propyl laurate	8	156	155
	4	142	140
	760	291	
Butyl laurate	18	187	180
	30	199	194
	4.5	156	153.5
	3	148	145
	760	304	
2-Ethylhexyl laurate	760	345	
Me oleate	760	346	
Me linolate	760	346	
Me linolenate	760	347	
Me erucate	760	393	

[a] T_{bp} (GC–VAP), boiling point temperature as determined by the gas–liquid chromatography vapor method.
[b] T_{bp} (lit.), boiling point temperature as determined from the literature.
[c] Reference 17.
[d] Reference 13.
[e] Reference 19. Other abbreviation in Table 1.

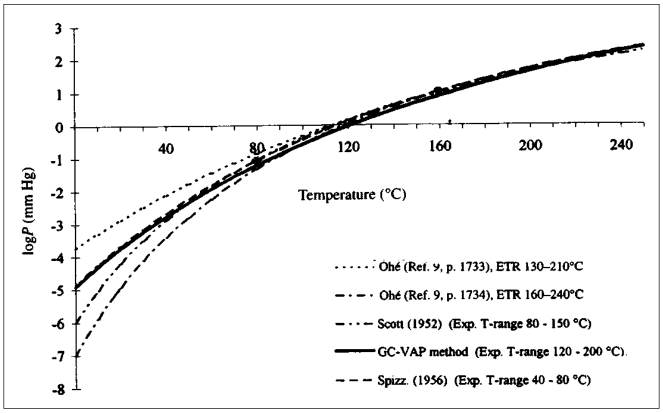

FIG. 1. Literature and experimental gas–liquid chromatography vapor method (GC–VAP method) log P–T diagrams of methyl myristate. The experimental temperature range (ETR) is indicated in the legend.

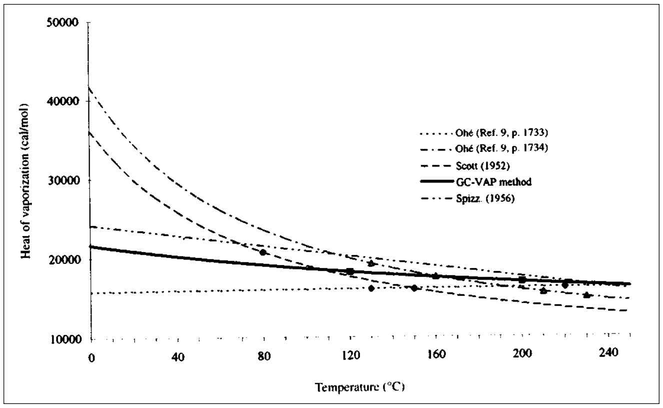

FIG. 2. Curves for heats of vaporization of methyl myristate derived from the log P–T diagrams. The ETR is indicated by paired symbols for each curve. See Figure 1 for abbreviations.

used, however, gives values of the heat of vaporization that are linearly dependent on the temperature. A maximum error of 9% in the values is cited in the reference. Table 4 compares the results of the different experiments. The heat of vaporization at 298.15 K derived from the pressure–temperature relationship of Spizzichino (11) is the only one that is near the calorimetric values. The GC–VAP method determines a P–T relationship that not only derives the heat of formation at environmentally relevant temperatures closest to the calorimetric ones but is also the most accurate one. It indicates that the curvature of the P–T diagram of the GC–VAP method is correct at 298.15 K.

Heat capacity differences. No experimental gas–liquid heat capacity differences at 298.15 K are known for the fatty acid esters chosen. Furthermore, many P–T diagrams seem to estimate unrealistic values (Fig. 3) at environmental temperatures. The values estimated by the GC–VAP method seem to approach those expected on thermodynamic grounds. They also approach, as the others do, the necessary high temperature limit. Because the P–T relationship used by Spizzichino (11) is a Rankine type, heat capacities are independent of tempera-

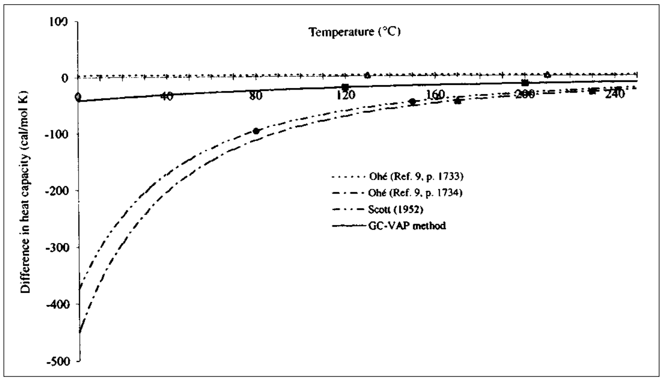

FIG. 3. Temperature dependences of the heat capacity difference (gas – liquid) of methyl myristate derived from the log P–T relationships. The ETR is indicated by paired symbols for each curve. See Figure 1 for abbreviations.

TABLE 4
Heats of Vaporization (cal/mol) Determined at 298.15 K

		Literature values		
Substance	GC–VAP	GC-Calorimetric[a]	Calorimetric[b]	*P–T* diagram[c]
Me caprate	15982 (40)	15846 (120)	15956 (141)	19262 (1734)
Me laurate	18346 (43)	18300 (170)	18448 (129)	21326 (1919)
Me myristate	20691 (47)	20619 (230)	20801 (220)	23288 (2096)
Me palmitate	23047 (52)			25620 (2306)

[a]Reference 15. [b]Reference 14. [c]Reference 11. For other abbreviations, see Tables 1 and 2. Errors are given in parentheses.

ture. In a large temperature range, as indicated in the graph, this is unrealistic. Its line is therefore omitted from the graph.

Solubility parameter. Because our method accurately predicts heats of vaporization at environmental temperatures, the total solubility parameter, δ, can be estimated according to $\delta^2 = (\Delta H_v - RT)V_M$ if the molar volume, V_M, of the pure substance is known. Liquid densities of all chosen fatty acid esters could be found in the literature or were obtained from the suppliers. Table 5 shows the results of the calculations. The values are of the same order of magnitude as those of similar fatty acid esters (16). That the parameter hardly varies in the chosen set of methyl esters of different fatty acids is remarkable. This change is more pronounced in the others. However, these changes are small.

Quantitative Structure–Activity Relationships (QSAR)

The correlation of the heat of vaporization and the number of C atoms of the fatty acid esters is greatly improved, compared to the calorimetric measurement (14), with the GC–VAP method, as is shown in Figure 4. The calculated prediction interval of the established QSAR was tested by predicting the heat of vaporization of methyl octanoate and methyl hexanoate. Their literature values (14) are close to the extrapolated values of the QSAR. A methylene incremental value of 1179 ± 3 cal/mol is found. This agrees with literature values (14,15). A similar correlation is established between the number of C atoms of the different alcohol groups and the heat of vaporization (Fig. 5). A somewhat lower accuracy is found in the correlation with an incremental value of 861 ± 33 cal/mol per methylene group. This is caused by the lower number of data points used in the equation. The most likely cause of the different incremental values of the methylene group is that the lower value is for a methylene close to the ester bond in contrast to the acid incremental value. Consequently, the influence of the oxygen atoms is higher in the lower incremental value.

We conclude that the GC–VAP method accurately estimates the liquid vapor pressure of the chosen fatty acid esters, not only in the measured temperature range but also when extrapolated to lower and high temperatures. This method may be used to accurately predict the normal boiling point temperature, which is frequently used in estimation methods for other thermodynamic properties. It also predicts accurately the curvature of the log *P–T* relationship and can therefore be used as an estimation method for the heat of va-

TABLE 5
Values of the Parameters for the Calculation of the Solubility Parameters at 298 K (25°C)

Substance	ΔH_v[a] (298 K) (cal/mol)	Liquid density[b] (25°C) (g/cm^3)	Molecular mass	Molar volume	δ (cal/cm^3)$^{1/2}$
Me caprate	15982	0.8688	186.30	214.4	8.472
Me laurate	18346	0.8655	214.35	247.7	8.466
Me myristate	20691	0.8633	242.41	280.8	8.460
Me palmitate	23047	0.8603[c]	270.46	314.4	8.451
Me stearate	25389	0.8607[c]	298.52	346.9	8.455
Me arachidate	27762				
Me behenate	30138				
Ethyl laurate	19132	0.8591	228.38	265.8	8.352
Propyl laurate	20232	0.8560	242.40	283.2	8.328
Butyl laurate	21319	0.8555	256.43	299.7	8.316
2-Ethylhexyl laurate	24968	0.860[d]	312.54	363.4	8.19
Me oleate	24678	0.8704	296.50	340.6	8.409
Me linolate	24433	0.8824	294.48	333.7	8.452
Me linolenate	24409	0.8961	292.46	326.4	8.542
Me erucate	29595	0.850[d]	352.60	414.8	8.36

[a]GC–VAP method. [b]Reference 18. [c]Extrapolated values from Reference 18. [d]Value from suppliers. For other abbreviations see Tables 1 and 2.

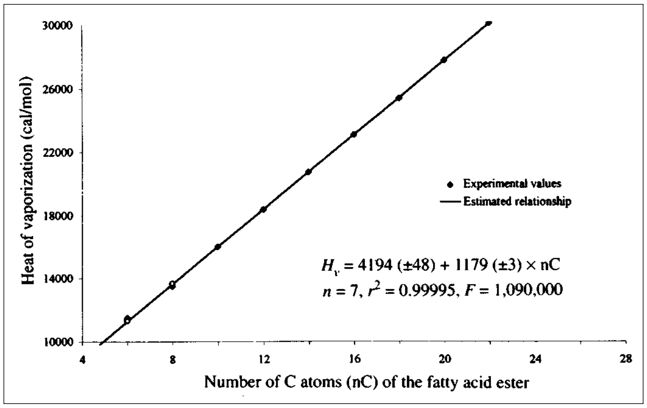

FIG. 4. Quantitative structure-activity relationships (QSAR) for the heat of vaporization and the number of carbon atoms (*n*C) in the saturated methyl fatty acid esters. Open marks are literature values not used in the derivation of the QSAR. In the equation of the line, values within parentheses represent the 95% confidence interval.

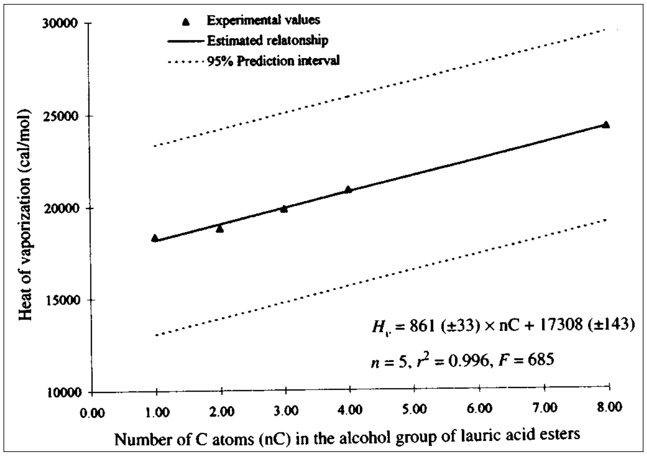

FIG. 5. QSAR for the heat of vaporization and the number of carbon atoms (*n*C) in the alcohol group of lauric acid esters. The 95% prediction interval is indicated in the figure. See Figure 4 for abbreviation.

porization at any relevant temperature. The model also includes an estimation of heat capacity differences of the substance, dependent on the temperature. The GC–VAP method seems to be a promising method to determine a number of environmentally relevant thermodynamic parameters, at both low and high temperatures.

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