



Prediction of heat capacities and heats of vaporization of organic liquids by group contribution methods

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ABSTRACT

In the present work a group contribution method is proposed for the estimation of the heat capacity of organic liquids as a function of temperature for fatty compounds found in edible oil and biofuels industries. The data bank used for regression of the group contribution parameters (1395 values for 86 types of substances) included fatty compounds, such as fatty acids, esters, alcohols and triacylglycerols, and hydrocarbons. The performance of this method is compared with other published group contribution methods [Z. Kolská, J. Kukal, M. Záborský, V. Růžicka, Ind. Eng. Chem. Res. 47 (2008) 2075–2085] and the Rowlinson–Bondi equation. Also, the predictive performance of general correlations of heats of vaporization based on the corresponding-states method, such as Carruth and Kobayashi [G.F. Carruth, R. Kobayashi, Ind. Eng. Chem. Fundam. 11 (1972) 509–516], Sivaraman et al. [A. Sivaraman, J.W. Magee, R. Kobayashi, Ind. Eng. Chem. Fundam. 23 (1984) 97–100], and Morgan and Kobayashi [D.L. Morgan, R. Kobayashi, Fluid Phase Equilib. 94 (1994) 51–87], as well as of a group contribution model [C.H. Tu, C.P. Liu, Fluid Phase Equilib. 121 (1996) 45–65], have been studied for fatty compounds. An alternative method in the prediction of heats of vaporization of fatty compounds based on the vapor pressure model of Ceriani and Meirelles [R. Ceriani, A.J.A. Meirelles, Fluid Phase Equilib. 215 (2004) 227–236] and its combination with the Clausius–Clapeyron equation has been studied.

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1. Introduction

Liquid heat capacity is a measure of the amount of energy required by a unit mass (or mole) of a substance to raise its temperature by a unit degree. Heat of vaporization, on the other hand, always involves a change of state (liquid–gas). Both properties are of great importance in the design of processes, such as distillation, evaporation, stripping and heating, found in the petrochemical, pharmaceutical and food (edible oil) industrial sectors, to name a few.

In the particular case of edible oil industry, there is a growing demand for reliable predictive methods for physical properties of fatty compounds, vegetable oils and fats, and compounds related to biofuels. Considering the complexity of these edible oil products, the diversity of the chemicals found in them, their compositions, and the range of normal processing conditions, methods for estimation of relevant physical properties are of great practical interest.

The widely known concept of group contribution has been used previously for the prediction of physical properties of fatty compounds and oils: viscosity [1] and vapor pressure [2]. In these works, all fatty compounds were represented through a small set of functional groups: CH₃, CH₂, COOH, CH=, COO, OH and CH₂–CH–CH₂.

Heat capacity data for fatty compounds, such as fatty acids, triacylglycerols (TAG), fatty alcohols and fatty esters, and hydrocarbons have been reported in the literature as a function of temperature [3–27]. Recently, Kolská et al. [28] developed a model for estimating the temperature dependence of heat capacities of pure organic liquids based on the three-level group contribution method of Marrero and Gani [29]. Two sets of parameters were established for prediction of this property.

In this work, our goal has been to develop a flexible and simple group contribution method for estimating the heat capacities of fatty compounds and hydrocarbons using only the small set of functional groups as proposed by Ceriani and Meirelles [2]. The results have been compared with the hierarchic and the non-hierarchic methods described by Kolská et al. [28] and the Rowlinson–Bondi equation [14,30].

Following the work of Cachadiña and Mulero [31], the predictive capabilities of three empirical correlations based on the corresponding-states method, i.e., the expressions of Carruth and

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Table 1
Experimental heat capacity data bank of fatty compounds and hydrocarbons.

Class of compounds	Saturated FA	Unsaturated FA	Fatty esters	Fatty alcohols	Saturated TAG	Unsaturated TAG	Hydrocarbons	Total
Number of data points	123	27	125	557	94	74	395	1395
References	[3,5–7,15,25–27]	[3,15,25]	[22,24,25,27]	[16,18,19,21]	[3,4,8,12,14]	[9,14,20]	[10,11,13,17,23]	[3,27]
Carbon chain length	5–26	18	8–21	5–22	21–57	47–57	6–50	6–57
Temperature range (°C)	25–250	25–150	25–93	25–126	40–180	35–180	25–200	25–250

FA = fatty acids and TAG = triacylglycerols.

Kobayashi [32], Sivaraman et al. [33] and Morgan and Kobayashi [34], and a group contribution method [35], have been compared through a collection of experimental data from the literature [3,25–27,36–42]. Also, an extension of the vapor pressure model of Ceriani and Meirelles [2] was established for fatty compounds by using the Clausius–Clapeyron equation [30], which gives a relation between these two properties.

2. Heat capacity model

The first step has been to collect representative experimental data for the classes of fatty compounds, including acids, alcohols, esters and triacylglycerols (TAG), and hydrocarbons. A total of 1395 experimental values of liquid heat capacity have been found for 86 types of substances. The distribution of the classes of compounds considered in this work is shown in Table 1. It can be noted that the data bank covers a wide range of temperatures and also of carbon chain lengths. The minimum temperature considered was 25 °C for all compounds, except those whose melting temperatures are higher than this value.

The following set of functional groups are able to represent all the molecular structures of the compounds in the database: CH₃, CH₂, COOH, CH=CH, COO, OH and CH₂–CH–CH₂. The last group describes the glycerol portion of acylglycerols. The group contribution equation chosen to correlate the liquid heat capacity, cp_i^l , in J/gmol K as a function of temperature, T , in K of component i is

$$cp_i^l = \sum_k N_k \cdot (A_k + B_k \cdot T) \quad (1)$$

where N_k is the number of groups k in the molecule, A_k , and B_k are parameters obtained from the regression of the experimental data, k represents the groups of component i .

Table 2 lists the regressed values of the parameters cited above. They were fitted using the Statistical Analysis System (SAS, Cary, NC) package with the well-known Marquardt method [43] with the following objective function:

$$f = \sum_{j=1}^n \left[\frac{|cp_{\text{exp}}^l - cp_{\text{calc}}^l|}{cp_{\text{exp}}^l} \right]_j \quad (2)$$

where n is the number of experimental data considered, and cp_{exp}^l and cp_{calc}^l are values of the experimental and calculated heat capacities, respectively. First, the values of the parameters A_k , and B_k were regressed only with data for the functional groups of hydrocarbons

Table 2
Adjusted parameters for Eq. (1).

Group	A_k	B_k
CH ₃	14.5504	0.05406
CH ₂	19.539	0.038211
COOH	−49.7595	0.42115
CH=CH	−130.42	0.54731
OH	−205.8	0.89618
COO	26.261	0.12317
CH ₂ –CH–CH ₂	181.89	−0.37671

and fatty acids. Next, the other classes and their representative groups were added.

Examples of calculation are presented in Appendix A.

The regression used all data sets shown in Table 1. Training and verification sets were not necessary in this case, considering that Eq. (1) is a group contribution (GC) model. Unlike QSAR (Quantitative Structure–Activity Relationship) models, the regression procedure of GC models should include as many experimental values as possible to cover the widest application and give safe extrapolations.

The predictive capability of the model has been tested against the hierarchic and the non-hierarchic methods described recently by Kolská et al. [28] and two versions of the Rowlinson–Bondi equation [14,30]. In the case of the GC-method of Kolská et al. [28], the complete model (using higher-order groups) as well as the model with only the first-order group contributions have been compared. The second-order group CH₂–CH_m=CH_n ($m, n = 0, \dots, 2$), has been used for unsaturated compounds and the second-order group COO–CH_n–CH_m–OOC ($n, m = 1, \dots, 2$) has been used for triacylglycerols.

The two versions of the Rowlinson–Bondi equation, reported by Poling et al. [30] and Morad et al. [14], are given below. As one can see, both are similar to the original equation given by Bondi [30], but with the two first constants refitted to give a better description of the liquid argon behavior.

$$\frac{cp_i^l - cp_i^o}{R} = 1.586 + \frac{0.49}{1 - T/T_c} + \omega \cdot \left[4.2775 + \frac{6.3 \cdot (1 - T/T_c)^{1/3}}{T/T_c} + \frac{0.4355}{1 - T/T_c} \right] \quad (3)$$

$$\frac{cp_i^l - cp_i^o}{R} = 1.45 + \frac{0.45}{1 - T/T_c} + \omega \cdot \left[4.2775 + \frac{6.3 \cdot (1 - T/T_c)^{1/3}}{T/T_c} + \frac{0.4355}{1 - T/T_c} \right] \quad (4)$$

Eq. (4) was also used by Morad et al. [14] to estimate the liquid heat capacities of fatty compounds, such as fatty acids and triacylglycerols.

The Rowlinson–Bondi equation requires the following physical properties as inputs: ideal gas heat capacity (cp^o), critical volume (V_c), critical pressure (P_c), which have been estimated by the Joback and Reid models [30]; critical temperature (T_c) (estimated using Fedors group contribution method [14]), and acentric factor (ω), which has been estimated by the following relation [14]:

$$\omega = 12.5 \cdot \left(0.291 - \frac{P_c \cdot V_c}{R \cdot T_c} \right) \quad (5)$$

where R is the gas constant.

Note that the choice for Fedors method for predicting critical temperatures was based on the fact that the method of Joback and Reid [30] requires experimental values of normal boiling temperatures as input. If instead of the experimental values, one uses the estimated values, poor predictions are obtained. In fact, for the heavy hydrocarbons and the long-chain triacylglycerols of the

Table 3

Experimental data bank for heat of vaporization of fatty compounds.

Class of compounds	Saturated fatty acids	Unsaturated fatty acids	Fatty esters	Fatty alcohols	Triacylglycerols	Total
Number of data points	119	1	98	37	9	264
References	[3,25–27,36,37,39]	[25]	[3,25,27,38,40,41]	[25,27]	[3,27]	[3,25–27,36–42]
Carbon chain length	5–20	18	7–23	5–22	12–57	5–57
Temperature range (°C)	20–299	360	20–156	20–158	20–358	20–358
Reduced temperature range	0.380–0.771	0.753	0.363–0.703	0.363–0.713	0.368–0.538	0.363–0.771
Vapor pressure range (mm Hg) ^a	3.5E–5–805.7	871.6	1.3E–7–720.8	6.9E–8–696.6	3.4E–5–8.4E–3	6.9E–8–871.6

^a The vapor pressure values were estimated using the model of Ceriani and Meirelles [2].

database shown in Table 1, the critical temperature values, calculated with predicted values of normal boiling points using also the method of Joback and Reid [30], were in total disagreement with those obtained with the models of Marrero and Gani [29], and Fedors [14].

3. Heat of vaporization

The database of experimental data for heats of vaporization has 264 values distributed over the classes of fatty compounds considered in this work as given in Table 3. Besides the reduced number of available experimental points, the database covers a satisfactory range of carbon chain lengths and temperatures. Unfortunately only one value was found for unsaturated fatty acids (oleic acid, in this case).

The predictive capability of one group contribution method proposed by Tu and Liu [35] and of three expressions based on the corresponding-states method, i.e., Carruth and Kobayashi [32], Sivaraman et al. [33], and Morgan and Kobayashi [34] has been tested against the collection of experimental values shown in Table 3. Tu and Liu method [35] requires only T_c as input, while the other three methods need also the acentric factor. Considering that the values of T_c and ω (calculated by Eq. (5)) would influence the results given by these four expressions for ΔH_i^{vap} , the required critical properties were predicted by two set of methods: (1) Marrero and Gani [29] for T_c , P_c and V_c and (2) Joback and Reid [30] for P_c and V_c and Fedors [14] for T_c .

The vapor pressure model suggested by Ceriani and Meirelles [2] can be expressed as follows:

$$P_i^{\text{vp}} = \exp \left[A'_i + \frac{B'_i}{T^{1.5}} - C'_i \cdot \ln T - D'_i \cdot T \right] \quad (6)$$

where P_i^{vp} is the vapor pressure in Pa and T is the temperature in K. Terms A'_i , B'_i , C'_i and D'_i are related to the group contribution parameters by the following expressions:

$$A'_i = \sum_k N_k \cdot (A_{1k} + M_i \cdot A_{2k}) + \alpha \cdot (f_0 + N_c \cdot f_1) + (s_0 + N_{cs} \cdot s_1) \quad (7)$$

$$B'_i = \sum_k N_k \cdot (B_{1k} + M_i \cdot B_{2k}) + \beta \cdot (f_0 + N_c \cdot f_1) \quad (8)$$

$$C'_i = \sum_k N_k \cdot (C_{1k} + M_i \cdot C_{2k}) + \gamma \cdot (f_0 + N_c \cdot f_1) \quad (9)$$

$$D'_i = \sum_k N_k \cdot (D_{1k} + M_i \cdot D_{2k}) + \delta \cdot (f_0 + N_c \cdot f_1) \quad (10)$$

where N_k is the number of groups k in the molecule, M_i is the component molecular weight, A_{1k} , B_{1k} , C_{1k} , D_{1k} , A_{2k} , B_{2k} , C_{2k} and D_{2k} , f_0 and f_1 , α , β , γ and δ , s_0 and s_1 are parameters obtained from the regression of the experimental data, k represents the groups of component i , N_c is the total number of carbon atoms in the molecules, and N_{cs} is related to the number of carbons of the substitute fraction in fatty esters [2].

The enthalpy of vaporization ΔH_i^{vap} of a compound i can be estimated by the Clausius–Clapeyron equation as a function of its vapor pressure (P_i^{vp}) and the temperature (T) [30]:

$$\frac{dP_i^{\text{vp}}}{dT} = \frac{\Delta H_i^{\text{vap}}}{T \cdot (V^v - V^\ell)} \quad (11)$$

Assuming that, at low pressures, V^ℓ is small compared to V^v and that the vapor phase shows an ideal behavior, Eq. (11) reduces to the simplified form given as

$$\frac{dP_i^{\text{vp}}}{dT} = \frac{P_i^{\text{vp}} \cdot \Delta H_i^{\text{vap}}}{R \cdot T^2} \quad (12)$$

The term dP_i^{vp}/dT in Eq. (12) is obtained from Eq. (6) by differentiating the right hand side of the equation with respect to T :

$$\frac{dP_i^{\text{vp}}}{dT} = -P_i^{\text{vp}} \cdot \left(\frac{1.5 \cdot B'_i}{T^{2.5}} + \frac{C'_i}{T} + D'_i \right) \quad (13)$$

The final expression for ΔH_i^{vap} as a function of T is then obtained as

$$\Delta H_i^{\text{vap}} = -R \cdot \left(\frac{1.5 \cdot B'_i}{\sqrt{T}} + C'_i \cdot T + D'_i \cdot T^2 \right) \quad (14)$$

where R is the gas constant (8.3144 J/gmol K for ΔH_i^{vap} in J/gmol). Values of all parameters required to estimate B'_i , C'_i and D'_i can be found in Ceriani and Meirelles [2]. Note that no further regression is necessary in this case, as the values of the model parameters needed for the prediction of ΔH_i^{vap} are exactly the same as reported by Ceriani and Meirelles [2].

At high temperatures and, consequently, high vapor pressures, the simplifications assumed in Eq. (12) are no longer valid, and ΔH_i^{vap} falls rapidly to zero. In these cases, a correction term should be included as proposed by Haggenmacher [44], and Eq. (14) becomes

$$\Delta H_i^{\text{vap}} = -R \cdot \left(\frac{1.5 \cdot B'_i}{\sqrt{T}} + C'_i \cdot T + D'_i \cdot T^2 \right) \cdot \left(1 - \frac{T_c^3 \cdot P_i^{\text{vp}}}{T^3 \cdot P_c} \right)^{0.5} \quad (15)$$

4. Results and discussion

Table 4 shows the average relative deviations ($\text{ARD} = \sum_{i=1}^n 1/n \cdot [100 \cdot |cp_{\text{exp}}^\ell - cp_{\text{calc}}^\ell| / cp_{\text{exp}}^\ell]$) between experimental and estimated values of heat capacities for the classes of compounds studied in this work. It can be seen that a good representation of the heat capacity of fatty compounds and hydrocarbons has been achieved. In comparison with the models suggested by Kolská et al. [28], the new expression gives lower deviations for all classes of compounds with the exception of hydrocarbons. Note also that the inclusion of the second-order group contributions for unsaturated compounds and triacylglycerols for the methods of Kolská et al. [28] improved their performance. In the case of Rowlinson–Bondi equations [14,30], the new expression gives better predictions in all cases. Fig. 1

Table 4
Average relative deviations (ARD) for heat capacities of fatty compounds and hydrocarbons.

Class of compounds	This work	Rowlinson–Bondi equations		Kolská et al. [28]		Non-Hierarchical complete model	Hierarchic complete model
		Poling et al. [30]	Morad et al. [14]	Non-Hierarchical 1st order parameters	Hierarchic 1st order parameters		
Fatty acids	2.79 (17.5–0.0009)	5.78 (20.88–0.06)	5.54 (20.0–0.15)	3.19 (15.9–0.008)	2.93 (15.9–0.04)	2.98 (15.9–0.006)	2.94 (15.9–0.002)
Fatty esters	0.46 (3.2–0.004)	8.86 (11.3–5.96)	8.49 (11.0–5.41)	3.27 (6.7–1.3)	0.58 (4.8–0.0009)	3.27 (6.7–1.3)	0.58 (4.8–0.0009)
Fatty alcohols	3.15 (10.0–0.003)	11.58 (26.5–4.37)	12.04 (27.0–4.63)	6.44 (15.0–0.9)	7.52 (17.0–0.05)	6.44 (15.0–0.9)	7.52 (17.0–0.05)
Triacylglycerols	2.82 (28.3–0.005)	5.90 (43.2–0.03)	5.88 (42.9–0.05)	6.19 (22.0–1.2)	4.07 (29.5–0.004)	5.20 (23.9–0.005)	3.58 (34.5–0.005)
Hydrocarbons	2.32 (11.7–0.02)	7.94 (12.1–0.04)	7.66 (11.9–0.01)	1.79 (13.3–0.002)	2.18 (16.2–0.004)	1.79 (13.3–0.002)	2.18 (16.2–0.004)
Total	2.60 (28.3–0.0009)	9.00 (43.2–0.03)	9.04 (42.9–0.01)	4.46 (22.0–0.002)	4.48 (29.5–0.0009)	4.32 (23.9–0.002)	4.42 (34.5–0.0009)

$$^a \text{ARD} = \sum_{i=1}^n \left[100 \cdot \frac{|C_{p,\text{exp}}^i - C_{p,\text{calc}}^i|}{C_{p,\text{exp}}^i} \right] \cdot \frac{1}{n}$$

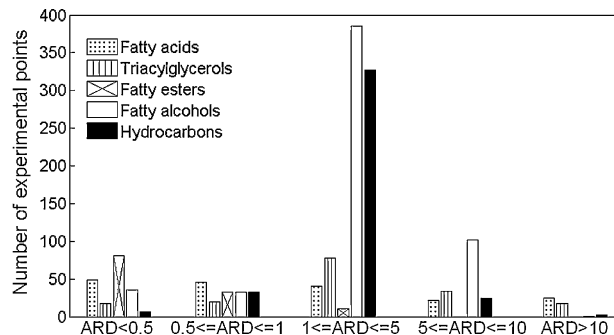


Fig. 1. Distribution of the average relative deviations of heat capacities for fatty acids, triacylglycerols, fatty esters, fatty alcohols and hydrocarbons.

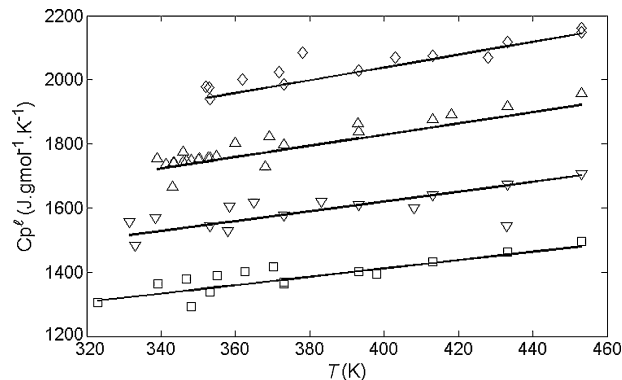


Fig. 2. Experimental and predicted values of heat capacities of saturated triacylglycerols. Code for experimental data: trilaurin (\square); trimiristin (∇); tripalmitin (Δ) and tristearin (\diamond).

illustrates the distribution of the ARD for each class of compounds. As one can see, most of the relative deviations are between $\pm 1\%$ and $\pm 5\%$ for all classes of compounds, with the exception of fatty acids and fatty esters. In these cases, there is a predominance of deviations lower than $\pm 0.5\%$. Fig. 2 shows the agreement achieved for experimental and predicted heat capacities of some saturated triacylglycerols. One interesting feature of the model developed in this work is that it allows the estimation of heat capacity values for fatty compounds for which experimental data is not available. Fig. 3 illustrates the predicted values for diacylglycerols (SO, SS, PP and PO) and monoacylglycerols (P, S and O) that can be produced by the hydrolysis reaction of two triacylglycerols (SOS and POP) commonly found in palm oil. In this nomenclature, P stands for palmitic acid, S for stearic acid and O for oleic acid.

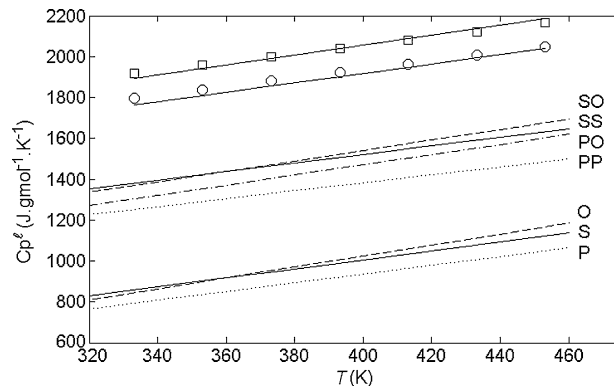


Fig. 3. Predicted lines for the triacylglycerols SOS and POP, the diacylglycerols SO, SS, PO and PP, and the monoacylglycerols O, S and P. Code for experimental data: POP (\circ) and SOS (\square).

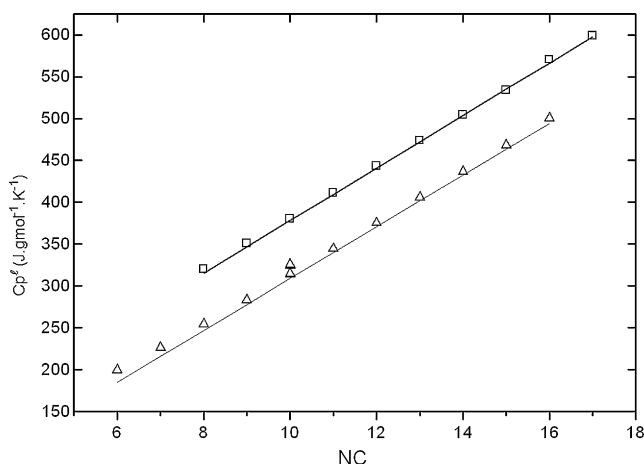


Fig. 4. Experimental and predicted values of heat capacities of methyl esters of *n*-alkanoic acids (C8–C17) at 310 K and hydrocarbons (C6–C16) at 298.15 K. Code for experimental data: methyl esters (□); hydrocarbons (Δ).

Experimental [14] and predicted values for SOS and POP are also shown in Fig. 3.

Fig. 4 shows the comparison between experimental and predicted values of heat capacities of methyl esters of *n*-alkanoic acids (C8–C17) and hydrocarbons (C6–C16) at selected temperature. In addition, Table 5 brings the calculated values of heat capacities for some substances distributed in all classes of compounds considered in this work at 350 ± 0.5 K.

Table 6 gives the average relative deviations between experimental and the predicted values of heats of vaporization of fatty acids, esters, alcohols and triacylglycerols obtained through Eq. (14) and the models suggested by Tu and Liu [35], Carruth and

Kobayashi [32], Sivaraman et al. [33], Morgan and Kobayashi [34]. It can be noted that Eq. (14) gives lower deviations for all classes of compounds with the exception of the unsaturated fatty acid class (19.98%). Note, however, that only one experimental data point was available in the literature (oleic acid), and that the method of Ceriani and Meirelles [2] gave a relative deviation of 16.14% for the vapor pressure of oleic acid at 360 °C (same temperature of the reported heat of vaporization). Therefore, inaccuracy in the prediction of this value can be a consequence of the poor prediction of the vapor pressure by the model in this case. For the whole database (264 experimental points), the proposed model overestimated 122 points or 46.2% (53 of fatty acids, 12 of alcohols, 54 of esters and 3 of triacylglycerols) and underestimated 142 points or 53.8% (67 of fatty acids, 25 of alcohols, 44 of esters and 6 of triacylglycerols). It should be noted that the performances of the four models tested [32–35], besides Eq. (14), were influenced by the methods selected for the prediction of T_c and ω . Use of the Marrero and Gani [29] methods generally improved the predictive capacity of Tu and Liu [35] model. In the case of the expressions derived from corresponding-states, the ARD values oscillated: sometimes they were higher by using Marrero and Gani [29], sometimes lower. In general, all models gave a wide range of relative deviations (RD). However, most of the ARD (221 values) are between 0% and 5% for all classes of compounds, and only thirteen values are higher than 10%. In contrast, none of the models tested [32–35] can reproduce the collection of experimental values shown in Table 3 with ARD lower than 10%. In fact, Carruth and Kobayashi [32] model gives the poorest predictions with $ARD \leq 5\%$ only for 19 values (using Fedors [14], and Joback and Reid [30]) while Morgan and Kobayashi [34] model gives better predictions with $ARD \leq 5\%$ for 94 values (using Marrero and Gani [29]).

Despite the accuracy of Eq. (14) discussed above, its applicability is limited to the range of processing conditions in which V^ℓ is small

Table 5

Calculated values of heat capacities for some compounds from all classes considered at 350 ± 0.5 K.

	Compound (reference)	T (K)	M (g/gmol)	cp_{exp}^ℓ (J/gmol K)	cp_{calc}^ℓ (J/gmol K)	RD ^a
Alcohols	Eicosanol [16]	349.75	298.55	794.69	766.26	3.58
	Dodecanol [19]	349.79	186.34	507.22	503.09	0.81
	Nonadecanol [16]	349.96	284.52	758.48	733.70	3.27
	Pentadecanol [19]	350.07	228.42	615.00	602.22	2.08
	Heptadecanol [19]	350.17	256.47	682.70	668.21	2.12
	Docosanol [16]	350.48	326.60	868.92	833.35	4.09
	Tridecanol [19]	350.19	200.36	543.91	536.56	1.35
Esters	M-octanoate [22]	350	158.24	336.19	333.79	0.71
	M-nonanoate [22]	350	172.27	368.16	366.70	0.40
	M-decanoate [22]	350	186.29	400.20	399.62	0.15
	M-undecanoate [22]	350	200.32	431.52	432.53	0.23
	M-dodecanoate [22]	350	214.35	467.86	465.44	0.52
	M-tetradecanoate [22]	350	242.40	528.04	531.27	0.61
	M-hexadecanoate [22]	350	270.45	597.66	597.09	0.09
	M-heptadecanoate [22]	350	284.48	622.81	630.01	1.16
	M-octadecanoate [22]	350	298.51	664.03	662.92	0.17
	M-nonadecanoate [22]	350	312.53	693.78	695.83	0.30
	M-eicosanoate [22]	350	326.56	732.20	728.74	0.47
Acids	E-undecanoate [24]	350.22	214.35	465.10	465.58	0.10
	Heptadecanoic acid [6]	350	270.45	624.12	624.81	0.11
	Stearic acid [7]	350	284.48	656.08	657.72	0.25
	Nonadecanoic acid [6]	350	298.51	691.19	690.63	0.08
Hydrocarbons	Arachidic acid [7]	350	312.53	727.00	723.55	0.48
	Nonadecane [11]	350.02	268.53	637.99	626.48	1.80
Triacylglycerols	Eicosane [11]	350.31	282.55	671.97	659.62	1.84
	Alfa-trielaidin [20]	350.15	885.45	1963.03	1924.83	1.95
	Beta-tripalmitin [12]	350.16	807.33	1751.30	1741.19	0.58
	Alfa-tripalmitin [12]	350.38	807.33	1754.50	1741.58	0.74

^a $RD = 100 \cdot \frac{|cp_{\text{exp}}^\ell - cp_{\text{calc}}^\ell|}{cp_{\text{exp}}^\ell}$.

Table 6

Average relative deviations (ARD) for heats of vaporization of fatty compounds.

ARD ^a										
Class of compounds	Fedors [14], and Joback and Reid [30] for critical properties				Marrero and Gani [29] for critical properties				Eq. (14)	Eq. (15) ^f
	T&L ^b	C&K ^c	SM&K ^d	M&K ^e	T&L ^b	C&K ^c	SM&K ^d	M&K ^e		
Saturated fatty acids	20.48	13.31	13.32	8.83	18.09	8.46	9.96	10.46	3.83	4.30
Unsaturated fatty acid	8.24	4.73	6.15	11.86	4.67	3.55	6.06	9.56	19.96	7.81
Fatty acids	20.38	13.23	13.26	8.86	17.97	8.41	9.93	10.46	3.96	4.33
Fatty esters	8.72	10.21	8.09	25.60	7.96	7.43	10.15	6.06	2.98	2.99
Fatty alcohols	2.66	24.83	17.44	21.69	2.13	28.45	20.06	23.47	1.66	1.82
Triacylglycerols	40.22	21.22	5.38	48.56	39.56	34.18	31.87	27.54	3.00	3.00
Total	14.24	14.01	11.66	18.22	12.77	11.74	12.18	11.23	3.24	3.43
RD (max. value–min. value)										
Class of compounds	Fedors [14], and Joback and Reid [30] for critical properties				Marrero and Gani [29] for critical properties				Eq. (14)	Eq. (15) ^f
	T&L ^b	C&K ^c	SM&K ^d	M&K ^e	T&L ^b	C&K ^c	SM&K ^d	M&K ^e		
Saturated fatty acids	48.8–1.8	65.5–0.8	47.4–0.48	81.1–0.18	51.5–1.1	39.3–0.16	34.1–0.27	0.06–49.2	59.1–0.24	58.8–0.2
Unsaturated fatty acid	8.22	4.7	6.1	11.9	4.7	3.5	6.1	9.6	20.0	7.8
Fatty acids	48.8–1.8	65.5–0.8	47.4–0.48	81.1–0.18	51.5–1.1	39.3–0.16	34.1–0.27	0.06–49.2	59.1–0.24	58.8–0.2
Fatty esters	16.1–0.34	24.9–1.3	21.7–0.19	45.0–9.1	15.9–0.04	27.3–0.06	30.1–0.05	0.28–14.1	22.7–0.05	22.7–0.05
Fatty alcohols	9.5–0.12	34.7–5.1	27.2–5.3	30.6–2.4	8.7–0.07	34.8–21.9	35.6–6.8	16.2–30.1	9.2–0.06	9.2–0.06
Triacylglycerols	63.1–15.1	34.8–0.41	12.0–0.86	66.2–17.9	62.3–14.7	66.4–10.8	54.4–12.4	1.3–66.4	11.2–0.50	11.2–0.50
Total	63.1–0.12	65.5–0.41	47.4–0.19	81.1–0.18	62.3–0.04	66.4–0.06	54.4–0.05	0.06–66.4	59.1–0.05	58.8–0.05

$$^a \text{ARD} = \sum_{i=1}^n \frac{1}{n} \cdot \left[100 \cdot \frac{|\Delta H_i^{\text{vap}} - \Delta H_i^{\text{vap}}|}{\Delta H_i^{\text{vap}}} \right]_i$$

^b Tu and Liu [35].^c Carruth and Kobayashi [32].^d Sivaraman et al. [33].^e Morgan and Kobayashi [34].^f Marrero and Gani [29] for critical properties.

compared to V^v and the vapor phase shows an ideal behavior. The correction term included in Eq. (15), as suggested by Haggemacher [44], is supposed to handle these deviations. The last column of Table 5 gives the average relative deviations using Eq. (15). Note that the inclusion of the correction term improved the prediction of the heat of vaporization of oleic acid notably. For the other compounds, the prediction altered slightly.

5. Conclusion

We have presented a simple group contribution method for estimating the liquid heat capacities of fatty compounds commonly found in processes of the edible oil industry and also hydrocarbons, as a function of temperature. The new model has been compared with two types of models (one recently released [28]), and it has been found to be more accurate for the fatty compounds. Also, the capabilities of four correlations [32–35] for predicting heats of vaporization of fatty compounds has been reviewed and compared with a new equation (Eq. (14)). It has been shown that none of four correlations published earlier, could give ARD lower than 10% for all the selected fluids. The proposed equation was found to be more accurate, although its range of applicability is limited to low pressures and/or temperatures in the range investigated. At higher pressures, a correction to the new equation has been proposed. However, further evaluations are necessary before its use can be recommended. Here, lack of available experimental data is a factor and perhaps the lack of a suitable model will motivate more data collection so that appropriate models can be developed.

List of symbols

 $A_{1k}, \dots, D_{1k}, A_{2k}, \dots, D_{2k}, f_0, f_1, s_0, s_1$ constants of Eqs. (7)–(10)

 A'_i, B'_i, C'_i, D'_i constants of Eqs. (7)–(10)

 cp^0 ideal gas heat capacity

cp^ℓ liquid heat capacity
 FA fatty acid
 ΔH_i^{vap} heat of vaporization
 M_i molecular weight of component i
 N_c total number of carbon atoms in the molecules
 N_{cs} number of carbons of the alcoholic part in fatty esters
 N_k number of groups k in the molecule
 P_c critical temperature in Kelvin
 p_i^{vp} vapor pressure of component i in Pa
 T temperature in K
 V^ℓ volume of the liquid phase
 V^v volume of the vapor phase
 V_c critical volume

Greek symbols

 $\alpha, \beta, \gamma, \delta$ constants of Eqs. (7)–(10)

 ω acentric factor

Subscripts

c related to the critical state
 calc calculated
 exp experimental
 i component
 k group of component i
 r related to the reduced property

Superscript

 vp vapor pressure

Abbreviations

ARD average relative deviation
 exp exponential
 O stands for oleic acid and monoolein

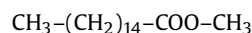
P	stands for palmitic acid and monopalmitin
PO	stands for 1-palmitin-2-olein
PP	stands for dipalmitin
POP	stands for 1,3-dipalmitin-2-olein
R	gas constant
S	stands for stearic acid
SOS	stands for 1,3-distearin-2-olein
SO	stands for 1-stearin-2-olein
SS	stands for diestearin
TAG	triacylglycerol

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Appendix A. Calculation of liquid heat capacities of methyl hexadecanoate at 340.0 K and of 1,2-dimyristin-3-olein at 389.15 K.

Methyl hexadecanoate (270.45 g/gmol) has the following structure



Thus according to the group contribution method described above, the group count is

CH ₃	2
CH ₂	14
COO	1

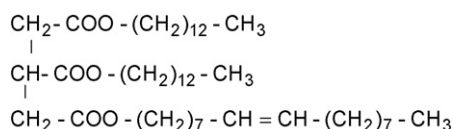
From Eq. (1), using the adjusted parameters from Table 2:

$$cp_i^L (\text{J/gmol K}) = [2 \cdot (14.5504) + 14 \cdot (19.539) + 1 \cdot (26.261)] + [2 \cdot (0.05406) + 14 \cdot (0.038211) + 1 \cdot (0.12317)] \cdot T$$

$$cp_i^L (T=340.0 \text{ K}) = 328.9078 + 0.766244 \cdot 340.0 = 589.431 \text{ J/gmol K}$$

The experimental value is 590.14 J/gmol K [22], corresponding to a deviation of 0.12%

1,2-dimyristin-3-olein (777.26 g/gmol) has the following structure



Thus according to the group contribution method described above, the group count is

CH ₃	3
CH ₂	38
COO	3
CH=CH	1
CH ₂ -CH-CH ₂	1

From Eq. (1), using the adjusted parameters from Table 2:

$$cp_i^L (\text{J/gmol K}) = [3 \cdot (14.5504) + 38 \cdot (19.539) + 3 \cdot (26.261) + 1 \cdot (-130.42) + 1 \cdot (181.89)] + [3 \cdot (0.05406) + 38 \cdot (0.038211) + 3 \cdot (0.12317) + 1 \cdot (0.54731) + 1 \cdot (-0.37671)] \cdot T$$

$$cp_i^L (T = 389.15 \text{ K}) = 916.3862 + 2.154308 \cdot 389.15 = 1754.735 \text{ J/gmol K}$$

The experimental value is 1683.35 J/gmol K [9], corresponding to a deviation of 4.24%.

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