Liquid Specific Heat Capacity Estimation for Fatty Acids, Triacylglycerols, and Vegetable Oils Based on Their Fatty Acid Composition

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ABSTRACT: The liquid specific heat capacity of fatty acids can be accurately estimated using the Rowlinson-Bondi method. This method requires the specific heat capacity of ideal gases, the critical temperature, and the acentric factor for each acid. The liquid specific heat capacity of triacylglycerols and vegetable oils can be estimated using mixture properties corresponding to the fatty acid composition and a correction factor, which accounts for the triacylglycerol form. The experimental data of triacylglycerols were used to produce the generalized correction factor. The estimated values were compared to experimental values and the error was found to be within ± 5%.

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KEY WORDS: Estimation method, fatty acid, liquid specific heat capacity, Rowlinson-Bondi equation, triacylglycerol, vegetable oil.

A critical review of the existing estimation methods and their reliability in the estimation of physical properties of triacylglycerols and palm oil has been given by Noor Azian *et al.* (1). It can be deduced from this review that the method proposed by Phillips and Mattamal (2) for estimating liquid specific heat capacity is rather specific and no generalization can be drawn from this method.

On the other hand, the method proposed by Halvorsen *et al.* (3) for the estimation of liquid density of triacylglycerols and oil mixtures is rather attractive and may be extended to other properties. The fact that the properties of different types of oil can be estimated using the method makes it doubly attractive.

This paper proposes an estimation method for specific heat capacity of fatty acids, triacylglycerols, and vegetable oils utilizing experimental data obtained in this work based on the approach proposed by Halvorsen *et al.* (3) for liquid density

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EXPERIMENTAL PROCEDURES

The specific heat capacity of simple triacylglycerols (trilaurin, trimyristin, tripalmitin, and tristearin); mixed triacylglycerols [1,2-dimyristoyl-3-oleoyl (MMO), 1,2-dimyristoyl-3-palmitoyl (MMP), 1,2-dipalmitoyl-3-oleoyl (PPO), and 1,2-dioleoyl-3-palmitoyl (OOP)]; 1,3-dipalmitoyl-2-oleoyl (POP); 1-palmitoyl-2-oleoyl-3-stearoyl (POS); 1,3-distearoyl-2-oleoyl (SOS); 1-palmitoyl-2,3-dioleoyl (POO); 1,2-dioleoyl-3-stearoyl (OOS); triolein (OOO); refined, bleached, deodorized palm oil (RBDPO), and cocoa butter were determined using a Seiko (Seiko Instrument Inc., Tokyo, Japan) heat-flux differential scanning calorimeter (DSC). The temperature range conducted was between the melting temperature (T_m) and 250°C to ensure that only the liquid specific heat capacity was measured.

The experiments were conducted under improved conditions of the DSC developed for triacylglycerols and vegetable oils and described in detail by N.A. Morad *et al.* (4). Under the improved conditions, the sample weight was kept constant at 21 mg, the scan rate was kept constant at 17 deg/min, and 50 mL/min of nitrogen purge gas, only at a high temperature range (>150–250°C) was used. The round robin test procedure was used to measure the specific heat capacity of the mentioned samples (5,6).

The specific heat capacity results obtained under these conditions for triacylglycerols (trilaurin, trimyristin, tripalmitin, tristearin, MMO, MMP, PPO, and OOP) are documented by N.A. Morad *et al.* (7) and N.A. Morad (8), and for RBDPO by N.A. Morad (8). The specific heat of triacylglycerols (POP, POS, SOS, OOO, and OOS) and cocoa butter are documented by F. Panau (9). The experimental specific heat capacities determined are within ±1% precision.

Estimation of specific heat capacity. The Rowlinson-Bondi equation was used to estimate specific heat capacity (C_p) for pure component fatty acids. The equation, as quoted in Reid *et al.,* (10), is as follows:

$$(C_p - C_p^\circ)/R = 1.45 + 0.45\,(1 - T_r)^{-1} + 0.25\,\omega[17.11 + 25.2\,(1 - T_r)^{1/3}\,T_r^{-1} + 1.742\,(1 - T_r)^{-1}] \quad [1]$$

where C_p is the liquid specific heat capacity, C_p° is the ideal gas

specific heat capacity, R is the universal gas constant, T_r is the reduced temperature, and ω (Appendix II) is the acentric factor. C_p° is calculated using the method of Rihany and Doraisamy (11).

Triacylglycerols and vegetable oils can be viewed as substances consisting of mixtures of different fatty acids. For instance, a mixed triacylglycerol, POS, consists of mixtures of three different fatty acids: palmitic acid, oleic acid, and stearic acid in the proportion of 1:1:1 or a mole fraction of 0.333 for each fatty acid. Similarly, vegetable oils such as RBDPO and cocoa butter are also made up of various portions of fatty acids (8,9).

Therefore, the terms in Equation 1 have to take into account the mixture properties when applied to triacylglycerols and vegetable oils. Kay's rule (10) is applied where the mixture properties are based on the simple molar average of the properties.The following equations for the terms take into account the mixture properties. The ideal gas heat capacity (C_p°) of the mixture is given as:

$$C_p^\circ(\text{mix}) = \Sigma\, x_i C_{pi}^\circ \qquad [2]$$

where x is the mole fraction, the subscript i refers to each fatty acid, and mix refers to mixture of fatty acid, e.g., MMO contains a mixture of two different fatty acids i $^2/_3$ myristic acid and 1/3 oleic acid.

The acentric factor (ω) of the mixture is given as:

$$\omega(\text{mix}) = \Sigma x_i\, \omega_i \qquad [3]$$

The critical temperature (Tc) (Appendix I) of mixture,

$$Tc, \text{mix} = \Sigma x_i\, Tc_i \qquad [4]$$

The reduced temperature (T_r) is

$$T_r = T/Tc, \text{mix} \qquad [5]$$

The average molecular weight (Mw) is given as:

$$\text{Mw} = \Sigma\, x_i\, \text{Mw}_i \qquad [6]$$

The estimation of Tc uses Fedor's method (10) using the equation below:

$$Tc = 535 \log (\Sigma\, \Delta T) \qquad [7]$$

where ΔT is the critical temperature group contributions. This method is also recommended and used by J.D. Halvorsen *et al.* (3).

The acentric factor can be obtained using

$$Pc\ Vc/R\ Tc = 0.291 - 0.080\ \omega \qquad [8]$$

from Reid *et al.* (10), where Pc and Vc, obtained using Joback's method, are the critical pressure and temperature, respectively.

Input properties for the fatty acids. The fatty acids that are of interest in this study ranged from lauric acid (C_{12}) to stearic acid (C_{18}), where C_{18} occurs in four different forms: $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$. ($C_{18:0}$ denotes saturated fatty acid with 18 carbons and no double bond, $C_{18:1}$ is fatty acid with 18 carbons and a single double bond, and so on. Most of the fatty acids in the palm oil and cocoa butter mixture ranged in palmitic acid (C_{16}) and (C_{18}) (8,9). The estimated input properties for some fatty acids of interest are tabulated in Table 1. A sample calculation is given in the *Appendix*.

Correction factor (F_c). F_c is defined as the factor (a constant value) added to the calculated liquid specific heat capacity values [$C_{p(\text{est.})}$] so that the values are the same as the experimental values. F_c has to be derived to accommodate the triacylglycerol form. This F_c is derived from experimental values of all 13 triacylglycerols mentioned earlier.

The specific heat values obtained using the Rowlinson-Bondi equation, $C_{p(\text{est.})}$ and the experimental values, [$C_{p(\text{exp.})}$] are compared to the individual triacylglycerols. The averaged difference between the estimated and experimental values in the experimental range is the F_c. It is assumed that F_c is independent of temperature for each triacylglycerol type and independent of the degree of unsaturation. To simplify the analysis it is assumed that F_c is dependent only on molecular weight.

The F_c values for all triacylglycerols mentioned are plotted against $|850 - \text{Mw}|$, one plot is for Mw <850, the other is for Mw >850. The Mw value, 850, is chosen to give a fair number of points for each plot and also since the Mw of the triacylglycerols under analysis lies between 638 and 888. Apart from that, the Mw of RBDPO and cocoa butter are 847 and 864, respectively. The selection of other molecular weight values between 815 and 875 influence the accuracy of the method insignificantly.

The molecular weight of a triacylglycerol or vegetable oil can be estimated using the following equation:

$$\text{Mw} = 3\Sigma\, x_i\, \text{Mw}_i + 38 \qquad [9]$$

Therefore, F_c can be simply represented in two different forms: for oil of Mw <850, and for Mw >850. This is applicable to pure triacylglycerols as well as to vegetable oil mixtures.

For Mw < 850,

$$F_c = -0.3328 + 0.0001\ |850 - \text{Mw}| \qquad [10]$$

For Mw > 850,

$$F_c = -0.2836 - 0.0005\ |850 - \text{Mw}| \qquad [11]$$

TABLE 1
Primary Properties of Fatty Acids

Fatty acids	Carbon number	T_c (K)[a]	ω
Lauric	12:0	756.21	0.8422
Myristic	14:0	779.07	0.9760
Palmitic	16:0	799.88	1.1087
Palmitoleic	16:1	800.34	1.0524
Stearic	18:0	819.00	1.2369
Oleic	18:1	819.14	1.1850
Linoleic	18:2	819.82	1.1294
Linolenic	18:3	820.23	1.0724

[a] T_c, critical temperature; ω, acentric factor.

RESULTS AND DISCUSSION

Application of the method to vegetable oil mixtures. The above method was applied to two types of vegetable oils, namely RBDPO and cocoa butter. The major triacylglycerol components of RBDPO and cocoa butter are as cited by Morad (8) and F. Panau (9), respectively. The mixtures were then divided according to their respective fatty acid compositions. The RBDPO fatty acid composition in mole fractions was therefore given as: 0.4621 palmitic acid, 0.4205 oleic acid, 0.0013 myristic acid, 0.0911 linoleic acid, and 0.0252 stearic acid. The fatty acid composition in mole fractions of cocoa butter was 0.2780 palmitic acid, 0.3713 stearic acid, 0.3233 oleic acid, 0.0227 linoleic acid, and 0.0037 arachidic acid.

TABLE 2
Comparison of Specific Heat Capacities for Vegetable Oils and Pure Triacylglycerols[a]

T (°C)	$C_{p(\text{exp.})}$ (J/g K)	$C_{p(\text{est.})}$ (J/g K)	Error (%)	$C_{p(\text{exp.})}$ (J/g K)	$C_{p(\text{est.})}$ (J/g K)	Error (%)
	Cocoa butter[b]			Palm oil[c]		
60	2.1187	2.1328	–0.67	2.0615	2.0538	–0.38
80	2.1807	2.1790	0.08	2.1123	2.1002	–0.57
100	2.2427	2.2267	0.71	2.1631	2.1480	–0.70
120	2.3047	2.2754	1.27	2.2139	2.1968	–0.77
140	2.3667	2.3246	1.78	2.2647	2.2462	–0.82
160	2.4287	2.3743	2.24	2.3155	2.2960	–0.84
180	2.4907	2.4241	2.67	2.3663	2.3459	–0.86
	OOO[b]			MMP[c]		
60	2.0827	2.0952	–0.60			
80	2.1227	2.1417	–0.89	2.1265	2.1302	–0.17
100	2.1627	2.1894	–1.24	2.1681	2.1782	–0.47
120	2.2027	2.2382	–1.61	2.2097	2.2272	–0.79
140	2.2427	2.2875	–2.00	2.2512	2.2769	–1.14
160	2.2827	2.3371	–2.38	2.2928	2.3269	–1.49
180	2.3227	2.3869	–2.76	2.3343	2.3772	–1.84
	POP[b]			POS[b]		
60	2.1560	2.0745	3.78	2.1495	2.1352	0.67
80	2.2060	2.1209	3.86	2.1974	2.1814	0.73
100	2.2560	2.1687	3.87	2.2454	2.2292	0.72
120	2.3060	2.2174	3.84	2.2934	2.2779	0.68
140	2.3560	2.2668	3.78	2.3413	2.3272	0.60
160	2.4060	2.3166	3.71	2.3893	2.3769	0.52
180	2.4560	2.3666	3.64	2.4372	2.4268	0.43
	SOS[b]			OOP[c]		
60	2.1540	2.1574	–0.16	2.0798	2.1041	–1.17
80	2.2004	2.2036	–0.15	2.1326	2.1505	–0.84
100	2.2468	2.2512	–0.20	2.1854	2.1983	–0.59
120	2.2932	2.2999	–0.29	2.2382	2.2470	–0.39
140	2.3396	2.3491	–0.41	2.291	2.2964	–0.23
160	2.3860	2.3988	–0.54	2.3438	2.3461	–0.10
180	2.4324	2.4486	–0.67	2.3966	2.3959	0.03
	Trilaurin[c]			Trimyristin[c]		
80	2.0944	2.1414	–2.24	2.1356	2.1226	0.61
100	2.1433	2.1894	–2.15	2.1804	2.1708	0.44
120	2.1922	2.2384	–2.11	2.2252	2.2199	0.24
140	2.2410	2.2881	–2.10	2.2700	2.2696	0.02
160	2.2899	2.3381	–2.11	2.3147	2.3198	–0.22
180	2.3387	2.3884	–2.12	2.3595	2.3702	–0.45
	Tripalmitin[c]			Tristearin[c]		
80	2.1772	2.1142	2.89	2.1772	2.1790	–0.08
100	2.2267	2.1624	2.89	2.2267	2.2272	–0.02
120	2.2762	2.2115	2.84	2.2762	2.2763	0.00
140	2.3257	2.2612	2.77	2.3257	2.3260	–0.02
160	2.3751	2.3114	2.68	2.3751	2.3762	–0.04
180	2.4246	2.3618	2.59	2.4246	2.4266	–0.08

[a]$C_{p(\text{exp.})}$, liquid specific heat capacity from experimental values; $C_{p(\text{est.})}$, liquid specific heat capacity through estimation (calculation) method; OOO, triolein; MMP, 1,2-dimyristoyl-3-palmitoyl; POP, 1,3-dipalmitoyl-2-oleoyl; POS, 1-palmitoyl-2-oleoyl-3-stearoyl; SOS, 1,3-distearoyl-2-oleoyl; OOP, 1,2-dioleoyl-3-palmitoyl.
[b]$C_{p(\text{exp.})}$ data from Reference 9.
[c]$C_{p(\text{exp.})}$ data from Reference 8.

The estimated specific heat capacity is calculated using the following equation:

$$C_{p(\text{est.})} = C_{p(\text{F.A.})} + F_c \quad [12]$$

where $C_{p(\text{F.A.})}$ is the specific liquid heat capacity of the fatty acid mixtures in the vegetable oil calculated using Equation 1. Sample calculations of C_p (F.A.) and $C_{p(\text{est.})}$ are demonstrated in the Appendix (III).

The Mw in the calculation of F_c are those of the respective oil mixtures, i.e., 847 for palm oil and 864 for cocoa butter.

Table 2 gives the comparison of the estimated values and the experimental values when applied to the two vegetable oil mixtures, RBDPO and cocoa butter, and some of the triacylglycerols studied.

It was found that the the error (%) between the estimated specific heat capacity and the experimental values were within ±5% of the average absolute percentage error. In some cases the deviation increased with temperature. The assumption made in the derivation of F_c may have contributed to the inaccuracy of the method, i.e., independence of temperature and degree of unsaturation. In actual fact, F_c is dependent on three factors: Mw, temperature, and degree of unsaturation. However, Mw is the factor that affects F_c the most. Therefore, it is assumed that F_c is linearly related to Mw. Moreover, a linear relationship is preferred for simplified analysis and application.

The above method gives a good estimate for specific heat capacity of triacylglycerols and the method is applicable to all types of vegetable oils provided the fatty acid composition is known.

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APPENDIX

I. Sample Calculation for T_c Using Fedor's Method (10)

Formula:

$$T_c = 535 \log (\Sigma \Delta T)$$

For fatty acid, e.g., lauric acid: $CH_3(CH_2)_{10}COOH$
[please refer to Reid *et al.* (10) for group contributions]

Group Contributions	ΔT	Occurrence
CH_3	1.79	1
CH_2	1.34	10
COOH	10.72	1

$\Sigma \Delta T = (1 \times 1.79) + (10 \times 1.34) + (1 \times 10.72)$
$= 25.91$
$Tc = 535 \log 25.91$
$Tc = 756.21$ K

II. Sample Calculation of Acentric Factor ω (10)

For fatty acid, lauric acid: $CH_3(CH_2)_{10}COOH$
Calculated earlier, from Joback's method (11):

$$Pc = 19.22 \text{ bar} = 19.22 \times 10^5 \text{ N/m}^2$$
$$Vc = 731.5 \text{ cm}^3\text{/mol} = 731.5 \times 10^{-6} \text{ m}^3\text{/mol}$$

and from Fedor's method:

$$Tc = 756.21 \text{ K}$$

Putting the values into the equation gives:

$$\omega = 1/0.08 \{0.291 - [(Pc\ Vc)/(RTc)]\}$$
$$= 1/0.08 \{0.291 - [(19.22 \times 10^5 \times 731.5 \times 10^{-6})/(8.314 \times 756.21)]\}$$
$$\omega = 0.8422$$

III. Sample Calculation for Specific Heat Capacity of Fatty Acids

For acid, lauric acid, $CH_3(CH_2)_{10}COOH$

$$\left\{1.45 + 0.45\left(1 - \frac{T}{756.21}\right)^{-1} + 0.2106\left[17.11 + 25.2\left(1 - \frac{T}{756.21}\right)^{1/3}\left(\frac{T}{756.21}\right)^{-1}\right]\right\}$$
$$\left\{\left[+1.742\left(1 - \frac{T}{756.21}\right)^{-1}\right]\right\} \times 8.314 + C_p^o \times 4.187$$

For T = 150°C = 150 + 273.15 = 423.15 K

(i) Calculation of C_p° (11):

C_p° (T = 150°C)
$= 5.9592 + (26.9695 \times 10^{-2} \times T) - (1.5379 \times 10^{-4} \times T^2)$
$+ (0.033981 \times 10^{-6} \times T^3)$
C_p° (T = 150°C) = 95.11828 cal/mol K

(ii) Calculation of C_p, using Rowlinson-Bondi equation:

C_p (T = 150°C) = 515.6697 J/mol K

Mw = 200 kg/kmol
C_p (F.A.)(T = 150°C) = 2.5783 J/g K

IV. Sample Calculation for Specific Heat Capacity of Triacylglycerol

An example for PPO is illustrated.
First, the C_p (F.A.) is calculated.
Using Kay's rule the following values are calculated:

$$Tc, \text{mix} = \Sigma x_i T_{ci}$$
$$= 806.39 \text{ K}$$
$$\text{Mw, mix} = 264 \text{ kg/kmol}$$
$$\omega(\text{mix}) = 1.1342$$

The mole fractions of the fatty acids are as follows: for *P*, $x_i = 2/3$ and for O, $x_i = 1/3$.
The values are calculated at $T = 100°C = 373.15$ K.

$C_p°$ is calculated using Rihani and Doraisamy (11) method.
$C_p° = 116.9788$ cal/mol K = 489.7903 J/mol K
$C_p°$(F.A.) is calculated using Rowlinson-Bondi equation, Equation 1:

$$C_p°(\text{F.A.})\ (T = 100°C) = 661.1512 \text{ J/mol K} = 2.5044 \text{ J/g K}$$

PPO, which has Mw = 832 kg/kmol, is an unsaturated mixed triglyceride.

$$F_c = -0.3328 - 0.0001\ |850 - \text{Mw}| = -0.3310 \text{ J/g K}$$

Therefore,

$$C_{p(\text{est.})}\ (T = 100°C) = C_p\ (\text{F.A.}) + F_c = 2.5044 - 0.3310 = 2.1734 \text{ J/g K}$$

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