Estimating thermodynamic properties of pure triglyceride systems using the Triglyceride Property Calculator: Mathematical Details

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The underlying semi-empirical model, herein referred to as the Wesdorp model, for predicting thermodynamic properties of pure TAGs was originally developed in [1] and presented with improvements in [2] and further analysis in [3]. In this section, we present a summarized representation of the Wesdorp model, with a focus on features of importance to the numerical calculator.

For convenience of description, we illustrate a simple sketch of a triglyceride (TAG) as Figure 1. As shown, there are three hydrocarbon chains attached to a glycerol head group. The length, level of saturation, and interaction between these hydrocarbon chains (referred to as R_1, R_2, and R_3 in Figure 1) allow us to describe the TAG by defined attributes. These attributes are subsequently used to predict the thermodynamic properties of the TAG.
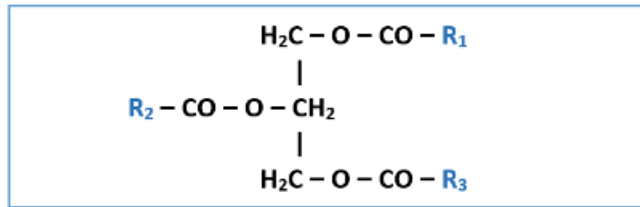

Figure 1: Triglyceride stencil used for mathematical model description.

2.1.1 Defining TAG attributes

TAGs can be discussed in terms of molecular composition using three letter acronyms. For example, tristearin is referred to as SSS. For a given three letter description, we define the following TAG attributes:

n_1 = number of carbons in R_1,

n_2 = number of carbons in R_2,

n_3 = number of carbons in R_3,

u_1 = number of double bonds in R_1,

u_2 = number of double bonds in R_2,

u_3 = number of double bonds in R_3,

where R_1 through R_3 are as referenced in Figure 1, and values for n_1 through u_3 can be found through Table 1. The Wesdorp model requires the total number of carbons (n) and total number of double bonds (u), computed as follows:

$$n = n_1 + n_2 + n_3,$$

$$u = u_1 + u_2 + u_3.$$

From these primary attributes, many secondary and tertiary attributes can be defined. To classify families of TAGs, we compute the differences in length of fatty acid chains. We define three lengths, the length of the shortest side chain (1 or 3 position) fatty acid in the TAG as P, the length of the middle side chain (position 2) fatty acid in the TAG as Q, and the length of the longest side chain (1 or 3 position) fatty acid in the TAG as R. Using computational syntax and the primary length attributes n_1 through n_3, we can define lengths P, Q, and R as:

$$P = \min(n_1, n_3),$$

$$Q = n_2,$$

$$R = \max(n_1, n_3).$$

Subsequently, we can define the difference in chain lengths of the 3 fatty acid side chains using:

$$x = Q - P, \text{ and}$$

$$y = R - P.$$

When describing unsaturated TAGs, the enthalpy of fusion and melting temperature are modified by the presence of particular unsaturated fatty acid chains: (i) oleic acid, (ii) elaidic acid, (iii) linoleic acid, and (iv) linolenic acid. We can thus define the following variables:

$$n_O = \text{number of oleic chains in the TAG,}$$

$$n_E = \text{number of elaidic chains in the TAG,}$$

$$n_J = \text{number of linoleic chains in the TAG,}$$

$$n_N = \text{number of linolenic chains in the TAG.}$$

We also define the number of pairs of unsaturated fatty acids as follows:

$$n_{OO} = \text{number of oleic} - \text{oleic pairs,}$$
$$n_{EE} = \text{number of elaidic} - \text{elaidic pairs,}$$
$$n_{JJ} = \text{number of linoleic} - \text{linoleic pairs,}$$
$$n_{NN} = \text{number of linolenic} - \text{linolenic pairs,}$$
$$n_{OJ} = \text{number of oleic} - \text{linoleic pairs,}$$
$$n_{ON} = \text{number of oleic} - \text{linolenic pairs,}$$
$$n_{JN} = \text{number of linoleic} - \text{linolenic pairs.}$$

Using computational syntax, these pairs can be calculated as:

$$n_{OO} = \max(0, n_O - 1),$$
$$n_{EE} = \max(0, n_E - 1),$$
$$n_{JJ} = \max(0, n_J - 1),$$
$$n_{NN} = \max(0, n_N - 1),$$
$$n_{OJ} = \max(0, n_O + n_J - 1),$$
$$n_{ON} = \max(0, n_O + n_J - 1),$$
$$n_{JN} = \max(0, n_J + n_N - 1),$$

where the MAX function is used to maintain non-negativity during calculations in cases where any or all of the unsaturated fatty acids combinations are not present in the TAG. Using these attributes, the enthalpies of fusion and melting temperature of pure TAGs can be calculated.

Table 1: Symbols used in description of Triglyceride composition. Columns "nC" and "nU" describing the number of carbons and number of double bounds, respectively, in the fatty acid chain.

Symbol	Fatty Acid	nC	nU	Symbol	Fatty Acid	nC	nU
U	Butyric	4	0	G	Lignoceric	24	0
K	Caproic	6	0	F	Ceric	26	0
R	Caprylic	8	0	T	Palmitoleic	16	1
C	Capric	10	0	O	Oleic	18	1
L	Lauric	12	0	J	Linoleic	18	2
M	Myristic	14	0	N	Linolenic	18	3
P	Palmitic	16	0	D	Elaidic	18	1
S	Stearic	18	0	E	Erucic	22	1
A	Arachidic	20	0	H	Arachidonic	20	4
B	Behinic	22	0	#	# (odd chain)	#	0

2.1.2 Predicting properties of saturated TAGs

In [2], the authors describe the enthalpy and entropy of fusion for saturated TAGs using:

$$(2)\ \Delta H_f^{sat} = hn + h_o + h_{xy} f_{xy} + h_{odd} f_{odd} \cdot f_\beta,$$

$$(3)\ \Delta S_f^{sat} = sn + s_o + s_{xy} f_{xy} + s_{odd} f_{odd} \cdot f_\beta + Rln2 \cdot f_{asym} \cdot f_\beta,$$

where h and s are the enthalpy and entropy contributions, respectively, of the total carbon number in the TAG, h_o and s_o are the contributions due to the glycerol head group, h_{xy} and s_{xy} are the contributions due to difference in chain length between fatty acid chains, h_{odd} and s_{odd} are the contributions due to an odd number of total carbons in the fatty acids, R is the universal gas constant, and functions $f_{xy}, f_{odd}, f_{asym}$ and f_β are defined as:

$$(4)\ f_{xy} = 2 - \exp\left(-\left(\frac{x-x_o}{k_x}\right)^2\right) - \exp\left(-\left(\frac{y}{k_y}\right)^2\right),$$

$$(5)\ f_{odd} = \begin{cases} 1, & \text{if } n_1 \text{ or } n_2 \text{ or } n_3 \text{ is an odd number,} \\ 0, & \text{if all fatty acid chains are even,} \end{cases}$$

$$(6)\ f_{asym} = \begin{cases} 1, & \text{if } y \neq 0, \\ 0, & \text{if } R_1 = R_3, \end{cases}$$

$$(7)\ f_\beta = \begin{cases} 1, & \text{if TAG is } \beta \text{ polymorph,} \\ 0, & \text{if not } \beta \text{ polymorph,} \end{cases}$$

where parameters x_o, k_x and k_y are used for data fitting. The melting point of a TAG can be defined as:

$$(8)\ T_f = \frac{\Delta H}{\Delta S},$$

and so for a saturated TAG, based on the descriptions of enthalpy and entropy described in Equations 2 and 3:

(9) $T_f^{sat} = \frac{\Delta H_f^{sat}}{\Delta S_f^{sat}} = \frac{hn + h_o + h_{xy}f_{xy} + h_{odd}f_{odd}f_\beta}{sn + s_o + s_{xy}f_{xy} + s_{odd}f_{odd}f_\beta + Rln2 \cdot f_{asym}f_\beta} = \frac{hn + h_o'}{sn + s_o'}$,

where

(10) $h_o' = h_o + h_{xy}f_{xy} + h_{odd}f_{odd}f_\beta$,

(11) $s_o' = s_o + s_{xy}f_{xy} + s_{odd}f_{odd}f_\beta + Rln2 \cdot f_{asym}f_\beta$.

Equation 9 can be re-written as a series, which will prove valuable in describing unsaturated TAGs, following a Taylor series expansion around $\left(\frac{1}{n}\right)$ resulting in:

(12) $T_f^{sat} = \frac{h}{s}\left(1 + \left(\frac{h_o'}{h} - \frac{s_o'}{s}\right)\frac{1}{n} - \frac{s_o'}{s}\left(\frac{h_o'}{h} - \frac{s_o'}{s}\right)\frac{1}{n^2} + \cdots \right)$.

Cutting off the series to carry second order errors and making substitutions for convenience, we can re-write Equation 12 as:

(13) $T_f^{sat} \cong T_\infty\left(1 + \frac{A_s}{n} - \frac{A_s B_s}{n^2}\right)$,

where

(14) $T_\infty = \frac{h}{s}$,

(15) $A_s = \frac{h_o'}{h} - \frac{s_o'}{s}$,

(16) $B_s = \frac{s_o'}{s}$.

Thus, with appropriate parameters, the enthalpy of fusion and melting point and of a saturated TAG can be estimated using Equations 2 and 13, and their dependencies (Equations 10, 11, 14, 15, and 16). During initial model fitting, the authors of [2] observed that Taylor series coefficients A_s and B_s were best described as a functions of chain length differences x and y, thus introducing the following Taylor series parameters:

(17) $T_\infty = T_{\infty,e}$,

(18) $A_s = A_o + A_{odd}f_{odd} + A_x x + A_{x^2}x^2 + A_{xy}xy + A_y y + A_{y^2}y^2$,

(19) $B_s = B_o + B_{odd}f_{odd} + B_x x + B_{x^2}x^2 + B_{xy}xy + B_y y + B_{y^2}y^2$,

where parameters of the form C_i are fitted using experimental data. For completeness, the current implementation of the TPC estimates two melting temperatures, one using Equations 13-16, and the other using Equations 13, 17-19. The melting temperature estimated using Equations 13-16 is indicated with an "[a]" on the user interface, and the temperature estimated using Equations 13, 17-19 is indicated with a "[b]". For ease of discussion, we refer to the varied implementations by these indication letters: Model A and Model B. Please see Section 2.1.4 for a description of the software and user interface.

2.1.3 Predicting properties of unsaturated TAGs

In [2], it assumed that the thermodynamic properties of an unsaturated TAG can be estimated using the thermodynamic properties of the equivalent saturated system (based on number of carbons and difference in chain length) and corrected for using the number of unsaturated chains (full chains, not double bonds) in the TAG. The

work done for predicting unsaturated TAGs is far less developed than is for saturated TAGs. To summarize, the enthalpy of fusion for an unsaturated TAG is estimated using:

(20) $\Delta H_f^{unsat} = \Delta H_f^{sat} + \hat{h}_O n_O + \hat{h}_E n_E + \hat{h}_J n_J,$

where $\hat{h}_O$, $\hat{h}_E$, $\hat{h}_J$ are the contribution to enthalpy due to oleic, elaidic and linoleic acids, respectively, and the melting point of an unsaturated TAG is estimated using:

(21) $T_f^{unsat} = T_\infty \left(1 + \frac{A_u}{n} - \frac{A_u B_u}{n^2} \right),$

where

(22) $A_u = A_s + \hat{A}_O n_O + \hat{A}_E n_E + \hat{A}_J n_J + \hat{A}_N n_N + \hat{A}_{OO} n_{OO} + \hat{A}_{EE} n_{EE} + \hat{A}_{JJ} n_{JJ} + \hat{A}_{NN} n_{NN} + \hat{A}_{OJ} n_{OJ} + \hat{A}_{ON} n_{ON} + \hat{A}_{JN} n_{JN},$

(23) $B_u = B_s + \hat{B}_O n_O + \hat{B}_J n_J + \hat{B}_N n_N,$

and parameters of the form $\hat{C}_i$ and $\hat{C}_{ij}$ are fitting parameters describing the contribution of unsaturated tags indexed by i and unsaturated pairs by i, j. The parameters T_∞, A_s and B_s are defined as in Equations 14-16 or 17-19. The previously described system of equations relies on the estimation of 28 parameters to estimate using Model A, and 42 to estimate using Model B. These parameters were determined using experimentally collected data and a least squares regression by the authors of [2]. The authors of [3] challenged some of the published coefficient estimates and presented edited values. Further investigation has now made clear that many parameters in both [5] and [3] can be further improved, and so we present the best known parameters as Table 2. Continued collection of pure triglyceride enthalpies and melting points is being undertaken to improve the quality of parameter estimates.

Table 2: Parameters used for model predictions. Adapted and corrected from Wesdorp et. al (2012) and Liu (2014). Unit "nC" indicates number of carbons. For example, the units for parameter (h) are kilojoules per mole per number of carbons in the TAG. Units "nX" indicate the number of molecule X. For example, the units of (A_O) are inverse number of Oleic chains. Similarly, units "nXY" indicate the number of pairs of molecules X and Y. For example, the units of (A_{OJ}) are inverse number of Oleic-Linoleic pairs. Parameter values in parenthesis indicate those that were guessed due to inadequate data for fitting.

#	Parameter	Units	α – modification	β' - modification	β – modification
1	h_o	kJ/mol	-31.95	-35.86	-17.16
2	h	$kJ/mol \cdot nC$	2.7	3.86	3.89
3	s_o	$J/K \cdot mol$	-19.09	-39.59	31.04
4	s	$J/K \cdot mol \cdot nC$	6.79	10.13	9.83
5	h_{xy}	kJ/mol	-13.28	-19.35	-22.29
6	s_{xy}	$J/K \cdot mol$	-36.7	-52.51	-64.58
7	$k_x = k_y = k$	nC	4.39	1.99	2.88
8	x_o	nC	1.25	2.46	0.77
9	$T_{\infty,e}$	K	401.15	401.15	401.15
10	h_{odd}	kJ/mol	-	-	2.29
11	s_{odd}	J/mol	-	-	-
12	A_o	$1/nC$	-9.058	-8.454	-8.048
13	A_{odd}	$1/nC$	-0.196	-0.308	-0.019
14	A_x	$1/nC$	0.003	-0.104	0.074
15	A_{x^2}	$1/nC$	-0.062	-0.019	-0.035
16	A_{xy}	$1/nC$	0.115	0.074	0.008
17	A_y	$1/nC$	-0.453	-0.497	-0.404
18	A_{y^2}	$1/nC$	-0.006	0.012	0.011
19	B_o	$1/nC$	-4.484	-0.265	2.670
20	B_{odd}	$1/nC$	-0.003	0.005	0.008
21	B_x	$1/nC$	-0.001	0.550	-0.317
22	B_{x^2}	$1/nC$	0.149	0.074	0.086
23	B_{xy}	$1/nC$	-0.366	-0.341	0.041
24	B_y	$1/nC$	1.412	2.342	0.550
25	B_{y^2}	$1/nC$	-0.002	-0.136	9e-4
26	$\hat{A}_O$	$1/nO$	-3.46	-2.2	-2.93
27	$\hat{A}_E$	$1/nE$	-1.38	-1.34	-1.68
28	$\hat{A}_J$	$1/nJ$	-3.35	-2.51	-4.69
29	$\hat{A}_N$	$1/nN$	-4.2	-2.23	-5.18
30	$\hat{A}_{OO}$	$1/nOO$	-0.01	0.27	0.89
31	$\hat{A}_{EE}$	$1/nEE$	0.01	0.04	0.4
32	$\hat{A}_{JJ}$	$1/nJJ$	-3.68	0.55	1.21
33	$\hat{A}_{NN}$	$1/nNN$	-0.98	1.51	1.38
34	$\hat{A}_{OJ}$	$1/nOJ$	0.53	-1	0.71
35	$\hat{A}_{ON}$	$1/nON$	0.83	0.76	0.69
36	$\hat{A}_{JN}$	$1/nJN$	-2.97	1.12	0.73
37	$\hat{B}_O$	$1/nO$	0	-4.3	-3.7
38	$\hat{B}_J$	$1/nJ$	5.4	-7.8	-1.5
39	$\hat{B}_N$	$1/nN$	2.6	-13.7	-1.8
40	$\hat{h}_O$	$kJ/mol \cdot nO$	-31.7	-28.3	-30.2
41	$\hat{h}_E$	$kJ/mol \cdot nE$	-11.7	(-15.9)	-15.9
42	$\hat{h}_J$	$kJ/mol \cdot nJ$	(-37.7)	(-37.7)	-37.7

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