Revisiting a model to predict pure triglyceride thermodynamic properties: parameter optimization and performance

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Abstract

In 1990, a well-known model to predict pure component properties of triglycerides was presented by Wesdorp in "Liquid-multiple solid phase equilibria in fats: theory and experiments" and has been shown to perform well despite making thermodynamically inconsistent predictions for certain test cases. In this study, the underlying parameter set is improved to deliver more physically consistent predictions, i.e., increasing melting point and enthalpy of fusion with increasing stability of the polymorphs, without deterioration of the primary model quality to describe the available experimental data. Interestingly, when a curated dataset containing only thermodynamically consistent data is compared to a broader dataset, it appears that the model's efficacy is highly dependent on the quantity of data, specifically the number of unsaturated triglycerides data. Quality and thermodynamic consistency of model predictions and the condition of a reliable description of monoacid triglycerides as a subset is discussed, addressing a potential interdependence.

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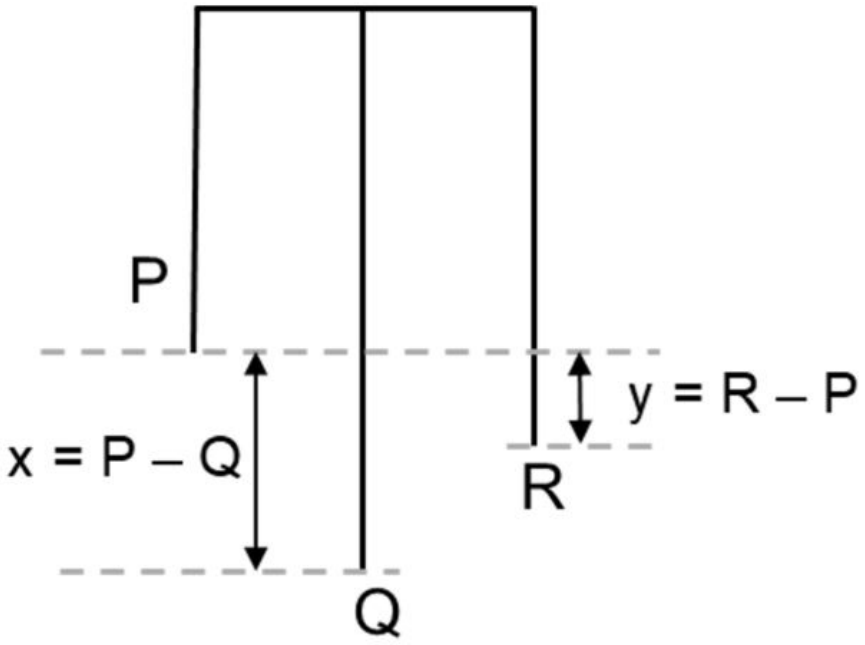

Predefined internal function variables

Defintion	Description	Defintion	Description	Defintion	Description
n_1	number of carbon atoms in FA_1	$P = \min(n_1,n_3)$	shortest outer chain length	n_{le}	number of linolenic chains
n_2	number of carbon atoms in FA_2	$Q = n_2$	middle chain length	n_{OO}	number of oleic-oleic pairs
n_3	number of carbon atoms in FA_3	$R = \max(n_1,n_3)$	longest outer chain length	n_{EE}	number of elaidic-elaidic pairs
$n = \sum n_i$	total carbon number	$x = Q - P$	chain length difference	n_{ll}	number of linoleic-linoleic pairs
u_1	number of double bonds in FA_1	$y = R - P$	chain length difference	n_{lele}	number of linolenic-linolenic pairs
u_2	number of double bonds in FA_2	n_O	number of oleic chains	n_{Ol}	number of oleic-linoleic pairs
u_3	number of double bonds in FA_3	n_E	number of elaidic chains	n_{Ole}	number of oleic-linolenic pairs
$u = \sum u_i$	total number of double bonds	n_l	number of linoleic chains	n_{lle}	number of linoleic-linolenic pairs

Saturated triglycerides

Predicting the enthalpy and entropy of fusion

$$\Delta H^{sat} = h\, n + h_0 + h_{xy}\, f_{xy} + h_{odd}\, f_{odd}\, f_\beta \quad [1]$$

$$\Delta S^{sat} = s\, n + s_0 + s_{xy}\, f_{xy} + s_{odd}\, f_{odd}\, f_\beta + R \ln 2\, f_{asym}\, f_\beta \quad [2]$$

$$f_{xy} = 2 - \exp\left(-\left(\frac{x - x_0}{k}\right)^2\right) - \exp\left(-\left(\frac{y}{k}\right)^2\right) \quad [3]$$

$$f_{odd} = \begin{cases} 1, \text{if } n_1 \text{ or } n_2 \text{ or } n_3 \text{ is odd numbered} \\ 0, \text{if } n_1 \text{ or } n_2 \text{ or } n_3 \text{ is even numbered} \end{cases} \quad [4]$$

$$f_{asym} = \begin{cases} 1, \text{if } y \neq 0 \\ 0 \text{ if } y = 0 \end{cases} \quad [5]$$

$$f_\beta = \begin{cases} 1, \text{if TAG is in } \beta \text{ polymorph} \\ 0, \text{if TAG is not in } \beta \text{ polymorph} \end{cases} \quad [6]$$

Parameter	Description
h, s	hydrocarbon chain contribution
h_0, s_0	end group contribution
h_{xy}, s_{xy}	contribution of differences in chain length
k, x_0	constant
h_{odd}, s_{odd}	odd chain contribution
A_0, B_0	end group contribution
A_{odd}, B_{odd}	odd chain contribution
A_x, A_{x^2}, A_{xy}, A_y, A_{y^2}, B_x, B_{x^2}, B_{xy}, B_y, B_{y^2}	fitting parameter

$$T_m^{sat} = \frac{\Delta H^{sat}}{\Delta S^{sat}} = \frac{h\, n + h_0'}{s\, n + s_0'} \quad [7]$$

$$h_0' = h_0 + h_{xy}\, f_{xy} + h_{odd}\, f_{odd}\, f_\beta \quad [8]$$

$$s_0' = s_0 + s_{xy}\, f_{xy} + s_{odd}\, f_{odd}\, f_\beta + R \ln 2\, f_{asym}\, f_\beta \quad [9]$$

Re-writing eq. [7] as Taylor series expansion around $\left(\frac{1}{n}\right)$:

$$T_m^{sat} = \frac{h}{s}\left(1 + \left(\frac{h_0'}{h} - \frac{s_0'}{s}\right)\frac{1}{n} - \frac{s_0'}{s}\left(\frac{h_0'}{h} - \frac{s_0'}{s}\right)\frac{1}{n^2} + \cdots\right) \quad [10]$$

Truncating the series and substituting for convenience results in eq. [11]

Predicting the melting point

$$T_m^{sat} = T_{inf}\left(1 + \frac{A^{sat}}{n} - \frac{A^{sat}\, B^{sat}}{n^2}\right) \quad [11]$$

1st approach

$$A^{sat} = A_0 + A_{odd} f_{odd} + A_x x + A_{x^2} x^2 + A_{xy} xy + A_y y + A_{y^2} y^2 \quad [12]$$

$$B^{sat} = B_0 + B_{odd} f_{odd} + B_x x + B_{x^2} x^2 + B_{xy} xy + B_y y + B_{y^2} y^2 \quad [13]$$

2nd approach

$$A^{sat} = \frac{\widehat{h_0}}{h} - \frac{\widehat{s_0}}{s} \quad [14] \qquad B^{sat} = \frac{\widehat{s_0}}{s} \quad [15]$$

$$\widehat{h_0} = h_0 + h_{xy}\, f_{xy} + h_{odd}\, f_{odd}\, f_\beta \quad [16]$$

$$\widehat{s_0} = s_0 + s_{xy}\, f_{xy} + s_{odd}\, f_{odd}\, f_\beta + R \ln 2\, f_\beta\, f_{asym} \quad [17]$$

Unsaturated triglycerides

Predicting the enthalpy of fusion

$$\Delta H^{unsat} = H^{sat} + h_O\, n_O + h_E\, n_E + h_l\, n_l \quad [18]$$

Predicting the melting point

$$A^{unsat} = A^{sat} + A_O\, n_O + A_E\, n_E + A_l\, n_l + A_{le}\, n_{le} + A_{OO}\, n_{OO} + A_{EE}\, n_{EE} + A_{ll}\, n_{ll} + A_{Ol}\, n_{Ol} + A_{Ole}\, n_{Ole} + A_{lle}\, n_{lle} \quad [19]$$

$$B^{unsat} = B^{sat} + B_O\, n_O + B_l\, n_l + B_{le}\, n_{le} \quad [20]$$

Parameter	Description
h_O	oleic chain contribution
h_E	elaidic chain contribution
h_l	linoleic chain contribution
A_O, A_E, A_l, A_{le}, B_O, B_l, B_{le}	correction parameter accounting for oleic, elaidic, linoleic and linolenic acid
A_{OO}, A_{EE}, A_{ll}, A_{lele}	interaction of the same unsaturated FA
A_{Ol}, A_{Ole}, A_{lle}	interaction of different unsaturated FA