

# SOLID-LIQUID EQUILIBRIUM OF TRIOLEIN WITH FATTY ALCOHOLS

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**Abstract** - Triacylglycerols and fatty alcohols are used in the formulation of cosmetic, pharmaceutical and food products. Although information about the phase transitions of these compounds and their mixtures is frequently required for design and optimization of processes and product formulation involving these substances, these data are still scarce in the literature. In the present study, the solid-liquid phase diagrams of two binary systems composed of triolein + 1-hexadecanol and triolein + 1-octadecanol were evaluated by differential scanning calorimetry (DSC) and optical microscopy. The experimental data were compared with predicted data by solving the phase equilibrium equations using an algorithm implemented in MATLAB. The liquid-phase activity coefficients were calculated using the Margules equation (two- and three-suffix) and the UNIFAC model (original and modified Dortmund model). The approaches used for calculating system equilibrium allowed an accurate prediction of the *liquidus* line with low deviations from the experimental data.

**Keywords:** Triolein; Fatty alcohol; Solid-liquid equilibrium; Differential scanning calorimetry; Modeling; UNIFAC.

## INTRODUCTION

Fats and oils are multicomponent systems composed of a mixture of triacylglycerols (TAGs) and minor components, such as free fatty acids and nutraceuticals. Under thermal treatment, triacylglycerols are responsible for the formation of a crystalline network and, consequently, particular microstructures that influence the sensorial, rheological and thermodynamic profiles of food and chemical products (Bruin, 1999; O'Brien, 2004). Within the food and chemical industry, there is a clear trend towards the development of new ways of structuring these systems, such as the utilization of surfactants and co-surfactants. In particular, fatty alcohols have been evaluated as gelling and surfactant agents in food, chemical and pharmaceutical oil-based

products (Egan *et al.*, 1984; Kreutzer, 1984; Daniel and Rajasekharan, 2003). Therefore, the study of the phase equilibrium of these compounds is a powerful tool for process and product design.

The differential scanning calorimetry technique (DSC) is often used for the experimental determination of solid-liquid equilibrium (SLE). Some data on solid-liquid transitions of fatty mixtures, phase diagrams and pure component properties using this technique, including TAGs, fatty acids, esters and alcohols, can be found in the literature (Wesdorp, 1990; Costa *et al.*, 2007, 2009, 2010a, 2010b, 2011; Carareto *et al.*, 2011). The phase transition behavior can be modeled by solving a system of equations based on the conditions of thermodynamic equilibrium (Wesdorp, 1990; Dos Santos *et al.*, 2011). Several approaches for this

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procedure can be found in the literature; the majority is based on evaluation of the activity coefficients of the compounds in the equilibrium phases (Wesdorp, 1990; Slaughter and Doherty, 1995; Coutinho *et al.*, 1998). The activity coefficients in the solid-liquid equilibrium can be estimated with adjustable models such as the Margules equation or with predictive methods such as the group-contribution UNIFAC model (Fredenslund *et al.*, 1975; Gmehling *et al.*, 1978; Chiavone Filho and Rasmussen, 2000; Coutinho *et al.*, 2001), both based on the calculation of excess Gibbs free energy.

Binary solid-liquid equilibrium data on systems composed of mixtures of triacylglycerols, mixtures of fatty alcohols or mixtures of these components with other fatty compounds are available in the literature, but data on systems composed of triacylglycerols + fatty alcohols are still scarce. In the present work, solid-liquid equilibrium data on two fatty mixtures, triolein + 1-octadecanol and triolein + 1-hexadecanol, were measured by differential scanning calorimetry (DSC), evaluated with optical microscopy and modeled by resolution of the thermodynamic equilibrium equations using the two- and three-suffix Margules equations, the original UNIFAC (Fredenslund *et al.*, 1975) and the modified UNIFAC-Dortmund model (Gmehling *et al.*, 1993) for calculation of the liquid-phase activity coefficient. An optimization algorithm was implemented in MATLAB for prediction of the melting point.

### Thermodynamic Framework

The solid-liquid equilibrium of each component in a binary or two-phase system is represented by Equation (1), as discussed by Prausnitz *et al.* (1986).

$$\frac{x_i^L \gamma_i^L}{x_i^S \gamma_i^S} = \exp \left[ \frac{\Delta h_{if}}{R} \left( \frac{1}{T_{if}} - \frac{1}{T} \right) \right] \quad (1)$$

where  $x_i^L$  and  $x_i^S$  are the mole fractions of component  $i$  in the liquid (L) and solid (S) phases,  $\gamma_i^L$  and  $\gamma_i^S$  are the activity coefficients of component  $i$  in the same phases,  $\Delta h_{if}$  is the enthalpy,  $T_{if}$  is the melting temperature of pure component  $i$  and  $T$  is the temperature of the system. The Margules equation and the group-contribution UNIFAC model are often used for calculation of  $\gamma_i$ . Using the two-suffix Margules equation for a binary mixture, the  $\gamma$  of component 1 is given by Equations (2) and (3). Using the three-suffix Margules equation, the  $\gamma$  of

the components in a binary mixture are calculated using Equations (4) and (5) (Reid *et al.*, 1987).

$$RT \ln \gamma_1 = Ax_2^2 \quad (2)$$

$$RT \ln \gamma_2 = Ax_1^2 \quad (3)$$

$$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Ax_2^3 \quad (4)$$

$$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Ax_1^3 \quad (5)$$

where  $A$  and  $B$  are adjustable parameters and  $R$  is the ideal-gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). According to the UNIFAC model (Equations (6) to (17)) (Fredenslund *et al.*, 1975), the activity coefficient can be written as the sum of a combinatorial contribution  $\gamma_i^C$ , which accounts for the effects of size and shape, and a residual contribution  $\gamma_i^R$ , which accounts for interactions among groups.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (6)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (7)$$

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k + \ln \Gamma_k^{(i)}) \quad (8)$$

$$l_i = 5(r_i - q_i) - (r_i - 1) \quad (9)$$

$$\phi_i = \frac{r_i x_i}{\sum_j x_j r_j} \quad (10)$$

$$\theta_i = \frac{q_i x_i}{\sum_j x_j q_j} \quad (11)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (12)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (13)$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (14)$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (15)$$

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \quad (16)$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \quad (17)$$

where  $\phi_i$  is the volume fraction of molecule  $i$ ,  $\theta_i$  is the area fraction of molecule  $i$ ,  $r_i$  is the molecular volume parameter,  $q_i$  is the surface area parameter,  $v_k^i$  is the number of  $k$ -type groups in molecule  $i$ ,  $\Gamma_k$  is the activity coefficient of group  $k$  in the mixture composition,  $\Gamma_k^{(i)}$  is the activity coefficient of group  $k$  for a group composition corresponding to pure component  $i$ ,  $\Theta_i$  is the surface area fraction of component  $i$  in the mixture,  $X_m$  is the group mole fraction of group  $m$ ,  $\psi_{nm}$  is the Boltzmann factor,  $R_k$  and  $Q_k$  are the structural parameters for the groups and  $a_{nm}$  is the temperature-dependent group-interaction parameter (Reid *et al.*, 1987).  $T$  is the temperature (K). In this work, in addition to the original UNIFAC model, the modified UNIFAC-Dortmund model (Gmehling *et al.*, 1993) was also used. In this model, the combinatorial term  $\gamma_i^C$  (Equation (18)) was empirically changed to make it possible to deal with compounds that are very different in size. Also, the Boltzmann factor  $\psi_{nm}$  (Equation (20)) of the residual term is temperature-dependent, with three new group-interaction parameters,  $a_{nm}$ ,  $b_{nm}$  and  $c_{nm}$ .

$$\ln \gamma_i^C = 1 - \frac{\phi_i'}{x_i} + \ln \frac{\phi_i'}{x_i} - 5q_i \left(1 - \frac{\phi_i}{\theta_i} + \ln \frac{\phi_i}{\theta_i}\right) \quad (18)$$

$$\phi_i' = \frac{x_i r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \quad (19)$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \quad (20)$$

For systems that show only a eutectic transition and whose components are immiscible in the solid phase, it is possible to assume that the solid phase is composed of a pure component, so Equation (21) becomes valid.

$$x_i^S \gamma_i^S = 1 \quad (21)$$

With these considerations, a system of equations can be constructed for prediction of the melting point using: i) the equation expressing the equilibrium condition for each component (Equation (1)), ii) a

model for calculation of the activity coefficients of the liquid phase (Equations (2) to (20)) and iii) the global molar balance of the system.

## MATERIALS AND METHODS

Triolein (C<sub>57</sub>H<sub>104</sub>O<sub>6</sub>), 1-octadecanol (C<sub>18</sub>H<sub>38</sub>O) and 1-hexadecanol (C<sub>16</sub>H<sub>34</sub>O) with purity greater than 99% by mass were supplied by Sigma-Aldrich (USA). Samples (1 g) of triolein + 1-octadecanol and triolein + 1-hexadecanol were prepared gravimetrically in amber flasks using an analytical balance (Precisa Gravimetrics AG, Dietkon) with a precision of 2×10<sup>-4</sup> g and a mole fraction of component 1 from 0.0 to 1.0. The samples were pretreated on Thermoprep (Metrohm, Herisau) by heating in a nitrogen atmosphere to 15 K above the highest melting point of the components. The mixtures were then allowed to cool to room temperature and kept in a freezer at 273.15 K until DSC analysis.

### Differential Scanning Calorimetry (DSC)

SLE of pure triolein, fatty alcohols and their mixtures were characterized by DSC using a DSC8500 calorimeter (PerkinElmer, Waltham) that was equipped with a refrigerated cooling system, which in this work operated between 223 and 343 K using nitrogen as a purge gas. Indium (certificated by PerkinElmer, Waltham) and cyclohexane (C<sub>6</sub>H<sub>12</sub>) (Merk, USA), both with 0.99 molar fraction, had previously been used as primary standards to calibrate the melting temperature and heat flow at a heating rate of 1 K·min<sup>-1</sup>. Samples (2-5 mg) of each mixture, triolein + 1-hexadecanol and triolein+ 1-octadecanol, were weighed in a microanalytical balance AD6 (PerkinElmer, Waltham) with a precision of 2×10<sup>-6</sup> g and put in sealed aluminum pans. In order to erase previous thermal histories related to the effects of polymorphism, a pretreatment was carried out based on the methodology described by Costa *et al.* (2007). For this purpose, each sample was kept at a temperature of 15 K above the highest melting point of the components. After 20 min at this temperature, the samples were cooled to 40 K below the lowest melting point of the components at a cooling rate of 1 K·min<sup>-1</sup> and allowed to remain at this temperature for 20 min. After this pretreatment, each sample was analyzed in a heating run at a heating rate of 1 K·min<sup>-1</sup>. Measurements were evaluated using PerkinElmer (Waltham) analysis software. The temperatures of the thermal transitions were the peak top temperatures

and the enthalpies were calculated from the area of the corresponding peaks.

### Optical Microscopy

In order to evaluate the behavior of the solid:liquid fraction of the systems as a function of the concentration of the components, as well as the assumption of solid phase immiscibility, both systems were analyzed at 298.15 K by optical microscopy using a Carl Zeiss model Scope A1 microscope (Zeiss, Germany). Samples of each mixture of both systems were heated from storage temperature (above 273.15 K) to 298.15 K on a Thermoprep (Metrohm, Herisau). The images obtained were taken with magnifications of 10× and 40×.

### Modeling Procedure

SLE modeling was carried out according to the previous thermodynamic approach. The binary parameters  $A$  and  $B$  of the Margules equations were numerically adjusted by an algorithm implemented in MATLAB 7.0, and based on the calculation of the melting temperatures by Equation (1), rewritten as a function of  $T$ , and by Equations (2) to (5) as the  $\gamma_i^L$  model. The one-variable optimization problem (using the two-suffix Margules equation) was implemented using a parabolic interpolation method (MATLAB function *fminbnd*). The two-variable optimization problem (using the three-suffix Margules equation) was carried out using a sequential quadratic programming method (MATLAB function *fmincon*). In both cases, the objective function was the root mean square deviation (RMSD) (Equation (22)) between the experimental temperature ( $T_{\text{exp}}$ ) and the calculated one ( $T_{\text{calc}}$ ).

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^n (T_{\text{exp}} - T_{\text{calc}})_i^2}{n}} \quad (22)$$

In the case of the UNIFAC or the UNIFAC-Dortmund model for calculation of  $\gamma_i^L$ , equilibrium Equation (1) cannot be rewritten as a function of  $T$ , and thus an optimization algorithm was implemented in MATLAB 7.0 using sequential quadratic programming (MATLAB function *fmincon*) for the calculation of the melting temperature of the mixtures. In this case, the objective function was the square of the absolute deviation between the experimental temperature ( $T_{\text{exp}}$ ) and the calculated one ( $T_{\text{calc}}$ ) (Equations (23) and (24)) for a composition

$x_i^L$ . The routine was repeated for  $0 < x_i^L < 1$  and the first iteration started with a melting temperature sufficiently close to that of the optimal solution, taken as the melting point of pure component 1 or 2.

$$F_{\text{obj}} = (T_{\text{exp}} - T_{\text{calc}})_i^2 \quad (23)$$

$$T_{\text{calc}} = \frac{\Delta h_{\text{if}} T_{\text{if}}}{\Delta h_{\text{if}} - RT_{\text{if}} \ln x_i^L \gamma_i^L} \quad (24)$$

For modeling, the pure component properties (temperature and enthalpy of fusion) were taken from the experimental data in this work. Also, data from the literature (Wesdorp, 1990; Ventolà *et al.*, 2004; Nichols *et al.*, 2006) was used for evaluation of the significance of these properties for modeling accuracy. Accounting for the immiscibility in the solid phase, the procedure described above was applied along the entire composition range for calculating the mixtures' melting points, assuming that either the light or the heavy component represents the pure solid phase. Therefore, two temperatures were obtained, with the equilibrium temperature (*liquidus* line) being the higher. This is the usual procedure for estimating equilibrium temperatures in a simple eutectic mixture, so the left-hand curve corresponds to a solid phase composed of the pure heavy component and the right-hand curve to a solid phase of the pure light component and the predicted eutectic mixture occurs exactly at their intersection.

## RESULTS AND DISCUSSION

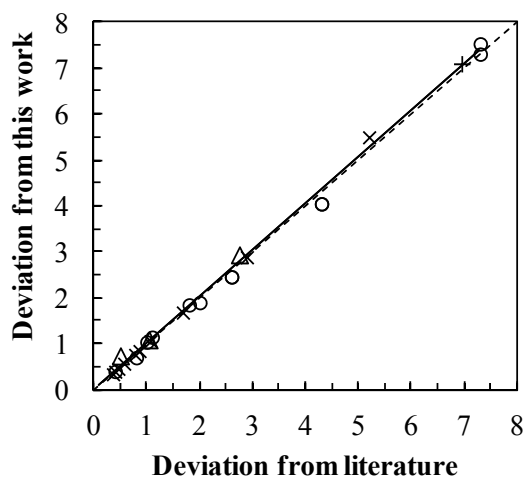
### Performance of the Algorithm

To evaluate the performance of the algorithm, solid-liquid equilibrium data on fatty mixtures and other organic binaries from the literature were modeled. The deviations obtained were compared with data from the literature (Table 1) and plotted for evaluation (Figure 1). The agreement between the data from the literature and the data in this study was good since the fitted curve (continuous line in Figure 1) determined by linear regression shows only a slight deviation from the straight diagonal line. Apart from differences in numerical procedures, the observed deviations are probably due to differences in pure component properties, which have an important effect on the results of the equilibrium estimation, as will be discussed below.

**Table 1: Deviation<sup>a</sup> data from the literature (lit.) and from the algorithm proposed in this work**

System	Margules two-suffix		Margules three-suffix		UNIFAC		UNIFAC – Dortmund		Ideal	
	lit.	this work	lit.	this work	lit	this work	lit	this work	lit.	this work
palmitic acid + tristearin <sup>b</sup>	0.36	0.34	0.16	0.14	-	-	0.46	0.46	-	-
trilinolein + stearic acid <sup>b</sup>	1.07	1.06	1.02	0.94	-	-	5.20	5.92	-	-
capric acid + palmitic acid <sup>b</sup>	0.86	0.84	0.56	0.57	-	-	2.89	2.89	-	-
capric acid + stearic acid <sup>b</sup>	0.78	0.76	0.67	0.67	-	-	1.68	1.68	-	-
triolein + tripalmitin <sup>b</sup>	0.40	0.39	0.10	0.10	-	-	0.57	0.57	-	-
1-octanol + 1-dodecanol <sup>c</sup>	2.00	1.90	1.80	1.85	-	-	2.60	2.58	2.60	2.46
1-dodecanol + 1-octadecanol <sup>c</sup>	1.00	1.04	0.40	0.40	-	-	4.30	3.94	4.30	4.05
1-decanol + 1-hexadecanol <sup>c</sup>	1.10	1.15	0.80	0.70	-	-	7.30	7.31	7.30	7.53
2-aminobenzoic acid + benzoic acid <sup>d</sup>	-	-	-	-	6.95	7.10	-	-	-	-
tetrachloromethane + 2-dodecanone <sup>e</sup>	-	-	-	-	2.75	2.94	-	-	-	-
tetrachloromethane + 2-undecanone <sup>e</sup>	-	-	-	-	1.04	1.09	-	-	-	-
indane + dodecane <sup>e</sup>	-	-	-	-	0.50	0.74	-	-	-	-

<sup>a</sup> RMSD (Equation (22)) data from <sup>b</sup>Boros (2005), <sup>c</sup>Carareto *et al.* (2011), <sup>d</sup>Huang and Chen (2000) and average of the absolute deviations  $\sum_i^n |T_{\text{calc}} - T_{\text{exp}}|_i / n$  from <sup>e</sup>Jakob *et al.* (1995).



**Figure 1:** Deviation (this work) versus deviation from the literature (data from Table 2): (○) Carareto *et al.*, (2011), (×) Boros (2005), (+) Huang and Chen (2000) and (Δ) Jakob *et al.* (1995). Dashed line represents the straight diagonal line and the continuous line is the curve fitted with the data ( $y = 1.0123x - 0.017$ ,  $r^2 = 0.9966$ ). Number of observations = 31.

### Experimental and Predicted Solid-Liquid Equilibrium Data

The reproducibility of the data was checked by performing three repeat runs for the calibration standard (indium) and for the pure components (triolein, 1-hexadecanol and 1-octadecanol). The standard deviation of the melting point data obtained was 0.13 K. This deviation was assumed to be the uncertainty of all of the melting points measured in this work. Also, these experimental data were

compared with experimental data obtained from the literature (Ferguson and Lutton, 1947; Kolp and Lutton, 1951; Wesdorp, 1990; Rolemberg, 2002; Ventolà *et al.*, 2004; Carareto *et al.*, 2011; National Bureau of Standards, 2011). The average relative deviations (ARDs) (%) of the melting data measured in this work ( $T^{\text{work}}$ ) in relation to data found in the literature ( $T^{\text{lit}}$ ) were calculated according to Equation (25), where  $n$  is the number of observations. The agreement between both sets of data was good, since the ARD was 0.14%.

$$\text{ARD (\%)} = \left( \sum_i^n \frac{|T_i^{\text{lit}} - T_i^{\text{work}}| 100}{T_i^{\text{lit}}} \right) \frac{1}{n} \quad (25)$$

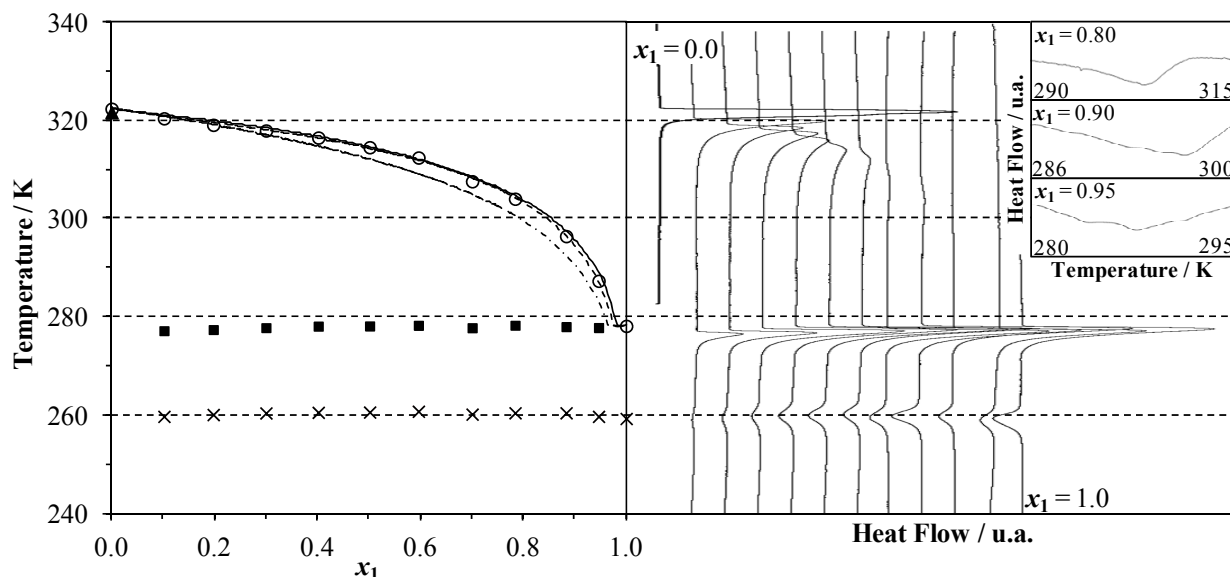
The thermograms obtained with DSC runs and the phase diagrams of the two binary systems evaluated, (1) triolein + (2) 1-hexadecanol and (1) triolein + (2) 1-octadecanol, are presented in Figures 2 and 3. Figures 2 and 3 also show results for modeling with the ideal assumption, using the adjustable three-suffix Margules equation and the predictive UNIFAC-Dortmund model for  $\gamma_i^L$  calculation. In addition, the experimental data related to the thermogram analysis are presented in Tables 2 and 3.

For pure 1-hexadecanol and 1-octadecanol two overlapping peaks could be seen in the region very close to the melting temperature, as observed by other authors (Ventolà *et al.*, 2004; Carareto *et al.*, 2011). In fact, fatty alcohols have rotator forms during crystallization processes ( $T_{\text{FA rotator form}}$ , Tables 2 and 3) that are structurally different but with very similar thermodynamic properties (Ventolà *et al.*, 2004). Despite the fact that the melting temperatures of these rotator forms could easily be found on the thermograms, the proximity of their values makes determination of the enthalpy of each of these pure component forms difficult.

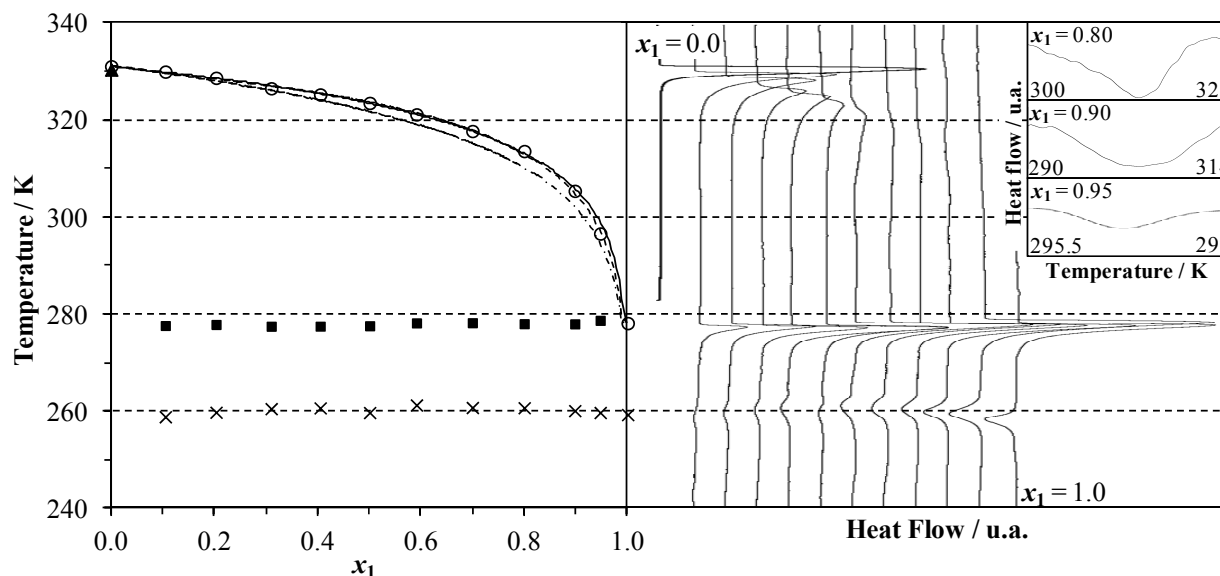
For pure triolein two well-defined peaks and a

third mild peak at a lower temperature were observed. In fact, TAGs usually have three polymorphic forms, known as alpha, beta-prime and beta, with differences in the crystal lattice packing, temperatures and heats of fusion (Wesdorp, 1990; Rolemberg, 2002; Costa, 2008). According to Fergusson and Lutton (1947), triolein also has these three polymorphic forms, melting at 241.15 K, 260.15 K and 278.65 K, respectively, and these values are very similar to the temperatures found in this work (Tables 2 and 3).

The thermograms of the mixtures of triolein and 1-hexadecanol or 1-octadecanol clearly showed three well-defined peaks, which were also observed by other authors for fatty mixtures with triacylglycerols (Costa *et al.*, 2010a, 2010b, 2011). The thermal transition at the highest temperature is related to the solid-liquid equilibrium temperature of the mixture. The transition at the lowest temperature is close to the solid-solid transition of the triolein beta-prime polymorphic form, and thus is probably related to this transition. The last one ( $T_{\text{trans}}$ , Tables 2 and 3) is a transition temperature close to the triolein melting point, which will be discussed below. The transition related to the alpha polymorphic form of triolein, the polymorphic form with the lowest transition temperature, was not well identified in the thermograms of the mixtures and is not shown in Figures 2 and 3.



**Figure 2:** Solid-liquid phase diagram (temperature in Kelvin and mole fraction) and thermograms for the triolein (1) + 1-hexadecanol (2) system. Symbols for phase diagrams: (○) experimental melting point, (■) transition near triolein melting point, (×) solid-solid triolein beta-prime transition and data modeled by (---) the three-suffix Margules equation, (—) the UNIFAC-Dortmund model and (- · -) the ideal assumption. In detail, magnification of the thermograms close to the melting temperature for  $x_1 > 0.7$ .



**Figure 3:** Solid-liquid phase diagram (temperature in Kelvin and mole fraction) and thermograms for the triolein (1) + 1-octadecanol (2) system. Symbols for phase diagrams: ( $\circ$ ) experimental melting point, ( $\blacksquare$ ) transition near triolein melting point, ( $\times$ ) solid-solid triolein beta-prime transition and data modeled by (- - -) the three-suffix Margules equation (—) the UNIFAC-Dortmund model and (- · -) the ideal assumption. In detail, magnification of the thermograms close to the melting temperature for  $x_1 > 0.7$ .

**Table 2:** Experimental solid-liquid equilibrium data (K) for triolein (1) + 1-hexadecanol (2). (Experimental error =  $\pm 0.13$  K)

$x_{\text{triolein}}$	$T_{\text{fusion}}$	$T_{\text{FA rotator form}}$	$T_{\text{trans}}$	$T_{\beta\text{'melting}}$
0.0000	322.34	321.62		
0.1018	320.40		277.18	259.74
0.1975	319.07		277.41	260.12
0.3000	317.92		277.80	260.44
0.4017	316.48		278.10	260.56
0.5014	314.51		278.15	260.62
0.5963	312.42		278.28	260.78
0.7006	307.58		277.78	260.20
0.7840	304.03		278.29	260.47
0.8833	296.43		278.00	260.47
0.9463	287.33		277.82	259.74
1.0000	278.16			259.31

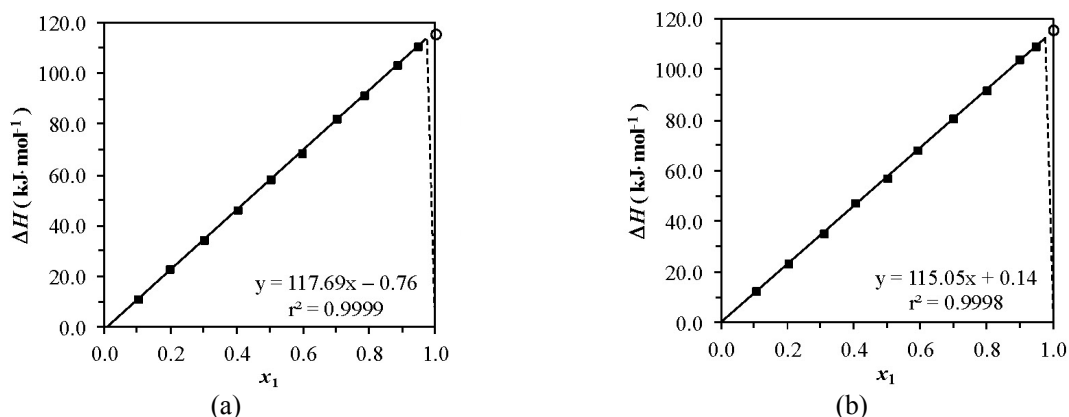
**Table 3:** Experimental solid-liquid equilibrium data (K) for triolein (1) + 1-octadecanol (2). (Experimental error =  $\pm 0.13$  K)

$x_{\text{triolein}}$	$T_{\text{fusion}}$	$T_{\text{FA rotator form}}$	$T_{\text{trans}}$	$T_{\beta\text{'melting}}$
0.0000	331.04	330.35		
0.1048	329.93		277.65	258.87
0.2030	328.66		277.87	259.80
0.3097	326.50		277.51	260.53
0.4046	325.23		277.52	260.69
0.5004	323.49		277.61	259.73
0.5910	321.13		278.19	261.29
0.6993	317.70		278.24	260.77
0.7996	313.58		278.03	260.72
0.8975	305.38		278.00	260.13
0.9467	296.60		278.72	259.74
1.0000	278.16			259.31

Figure 4 contains the Tammann plots of the mixtures, showing the enthalpy variation of the observed invariant transitions as a function of triolein molar concentration. In general, the polymorphic transitions and the eutectic reaction, which separates the solid-liquid region from the solid-solid, are the most common invariant thermal events of mixtures of triacylglycerols and fatty compounds. The Tammann plot allows a better determination of the eutectic point, since enthalpy increases as the mixture concentration approximates the eutectic composition, where the enthalpy should begin to decrease. In several cases, the increase in the difference between melting temperatures of pure components increases the proximity of the eutectic point to the melting temperature of the pure lighter component (Levine, 2002). The linear regression (with  $r^2 > 0.99$ ) of the Tammann curves for the transition close to the triolein melting point (Figure 4) shows that, for  $x = 1$ , the enthalpy variation is very close to the corresponding value for pure triolein. This means that this invariant thermal event may correspond to a eutectic reaction with a composition very close to that of pure triolein, making it virtually impossible to differentiate the

eutectic composition from pure triolein. In agreement with this observation, triolein + 1-octadecanol and triolein + 1-hexadecanol modeled phase diagrams had eutectic points higher than 0.99 and 0.98 triolein mole fraction, respectively, for all  $\gamma_i^L$  models.

The binary parameters ( $\text{J}\cdot\text{mol}^{-1}$ ) for both Margules equations and the deviations between calculated and experimental data for each modeling approach are shown in Table 4. It can easily be observed that the *liquidus* line was well described by all models, since the average absolute deviation was always less than 0.7 K. The Margules parameter values obtained were very similar to those found in the literature for binary fatty mixtures with TAGs and for systems with fatty alcohols (Costa *et al.*, 2010a, 2011; Carareto *et al.*, 2011). The ideal assumption shows the highest deviations, indicating that the systems of triolein + 1-hexadecanol and triolein + 1-octadecanol are slightly nonideal. In fact, the activity coefficients calculated by all the models were higher than 1 for both systems and the highest values were obtained for the most accurate model, the three-suffix Margules equation. In this case the values were close to 2 when  $x_i^L$  was close to 0.



**Figure 4:** Tammann plots of (a) triolein (1) + 1-hexadecanol (2) and (b) triolein (1) + 1-octadecanol (2). (—) Linear regression for data on (■) transition close to the triolein melting point, (○) pure triolein transition and (---) hypothetical plot with a eutectic point.

**Table 4:** Adjusted parameters (*A* and *B*) and mean absolute deviations<sup>a</sup>  $\sigma$  of the predicted data from the experimental data (in Kelvin).

Model		triolein +1-hexadecanol	triolein +1-octadecanol	Average
Two-suffix Margules	<i>A</i>	1065.77	855.15	0.56
	$\sigma$	0.53	0.60	
Three-suffix Margules	<i>A</i>	1186.79	1026.36	0.33
	<i>B</i>	-396.02	-507.89	
	$\sigma$	0.32	0.34	
UNIFAC	$\sigma$	0.45	0.42	0.43
UNIFAC-Dortmund	$\sigma$	0.68	0.47	0.57
Ideal	$\sigma$	2.31	1.78	2.04

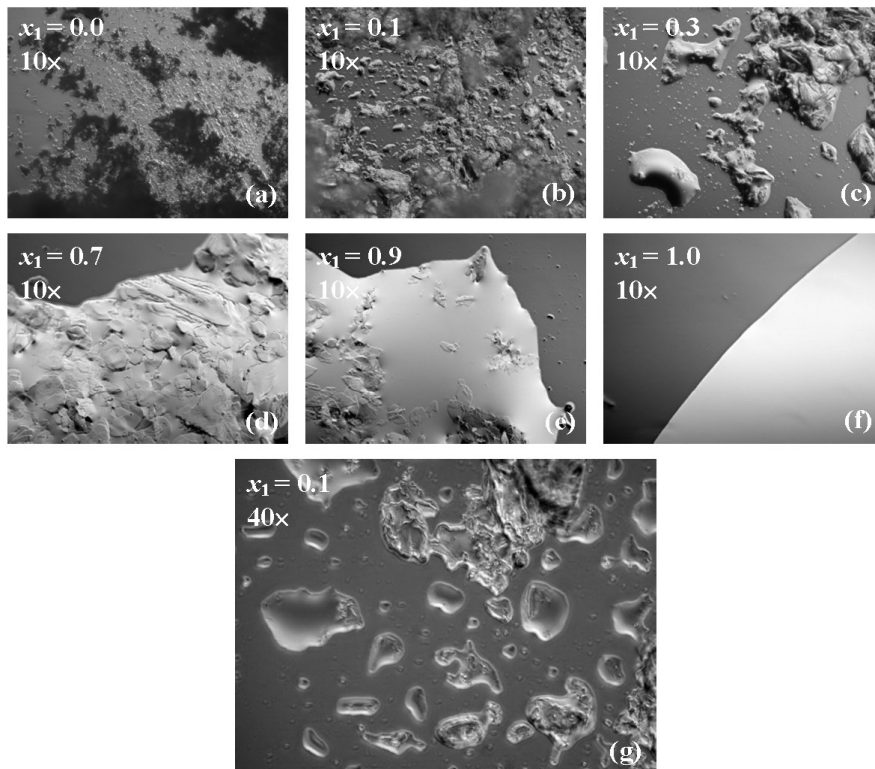
$$\sigma = \frac{\sum_{i=1}^n |T_i^{\text{exp}} - T_i^{\text{pred}}|}{n}$$



Solid phase immiscibility is usually assumed for the purpose of modeling fatty systems (Wesdorp, 1990; Rolemberg, 2002; Costa *et al.*, 2007). Nevertheless, several fatty mixtures have regions of solid solution close to the pure component composition on the phase diagram (Costa *et al.*, 2009, 2011; Carareto *et al.*, 2011). In order to check the immiscibility assumption and thus comprehend the behavior of the solid:liquid fraction in the solid-liquid biphasic region (under the *liquidus* line), optical micrographs of both systems were taken at 298.15 K. Some of the images of the binary mixture of triolein (1) + 1-octadecanol (2) are shown in Figure 5. Firstly, it was clearly observed that increasing the concentration of triolein decreased the solid fraction, in agreement with the lever rule (Figures 5(a) to 5(f)). Since the melting points of the pure saturated fatty alcohols 1-hexadecanol and 1-octadecanol are higher than that of triolein, in this region of the phase diagram the solid fraction of the system is probably composed only of pure fatty alcohol. Secondly, the micrograph of the system with a triolein mole fraction of 0.1 at a magnification of 40× (Figure 5(g)) clearly shows that there is a liquid fraction even at this relatively low concentration. Thus, there is probably no solid solution at the concentration close to the pure heavy

component ( $x_1 = 0.0$ ). Tammann plots of both systems also corroborate this probability, since enthalpy values tend to zero at  $x_1 = 0.0$ . Both observations validate our modeling approach.

Finally, the influence of pure component properties on the accuracy of the modeling approach was investigated. Component properties taken from the literature (Wesdorp, 1990; Ventolà *et al.*, 2004; Nichols *et al.*, 2006) as well as the values obtained in this work are presented in Table 5. The values from the literature were also used with the modeling procedure presented above. In the case of the pure component properties taken from the literature, the global average absolute deviation between the calculated and the experimental results, including the ideal solution assumption, was 0.90 K, while for the pure component properties obtained in this work the deviation was 0.79 K. Firstly, the differences in the pure compounds' experimental values observed in Table 5 can probably be attributed to differences between the experimental method used in the literature and in this work (different heating and cooling rates and isothermal conditions). In addition, the effects of polymorphism could produce peaks that overlap or are too close, which disrupts the determination of enthalpy, especially for fatty alcohols, as discussed previously.



**Figure 5:** Optical micrographs of samples of triolein (1) + 1-octadecanol (2) with magnifications of 10× ((a) to (f)) and 40× (g) at 298.15 K.

**Table 5: Pure fatty components properties from the literature (lit.) and in this work.**

Component	Temperature (K)		Enthalpy (kJ mol <sup>-1</sup> )	
	lit.	this work	lit.	this work
Triolein	277.95 <sup>a</sup>	278.15	100.000 <sup>a</sup>	115.560
1-hexadecanol	321.60 <sup>b</sup>	322.34	58.400 <sup>c</sup>	56.591
1-octadecanol	330.30 <sup>b</sup>	331.04	69.600 <sup>c</sup>	65.642

<sup>a</sup>Wesdorp (1990), <sup>b</sup>Ventola *et al.* (2004), <sup>c</sup>Nichols *et al.* (2006).

In case of the interactions parameters and the corresponding liquid phase activity coefficients obtained by using literature's pure compounds properties, an increasing of the positive deviations was observed with values slightly higher than 2 when  $x_i^L$  was close to 0 for three-suffix Margules equation, also the most accurate model in this case. In fact, these results were very close to the  $\gamma_i^L$  values observed in this work, as previously discussed. Nonetheless, this discussion highlights the fact that pure component properties are very important for a reliable modeling approach, being very significant for the solid-liquid equilibrium calculation.

### CONCLUSIONS

In the present work the solid-liquid phase diagrams for the binary mixtures of triolein + 1-hexadecanol and triolein + 1-octadecanol were measured using differential scanning calorimetry. Both diagrams exhibited three well-defined transitions: the mixture melting temperature, the solid-liquid transition related to the melting of triolein or of a triolein-rich eutectic mixture and a solid-solid transition related to the triolein beta-prime polymorph. The two- and three-suffix Margules equations and the group-contribution UNIFAC and UNIFAC-Dortmund models were accurate for estimating the activity coefficients of the liquid phase and provided a melting point of the fatty mixtures evaluated with a global mean absolute deviation of 0.47 K. Micrographs showed that the assumption of solid phase immiscibility was valid for the systems investigated. The present work also showed that pure component properties are very important for developing a reliable modeling approach.

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