



Binary solid–liquid equilibrium systems containing fatty acids, fatty alcohols and trilaurin by differential scanning calorimetry



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ABSTRACT

Solid–liquid phase diagrams of six binary mixtures composed by trilaurin plus fatty acids (myristic acid, palmitic acid and stearic acid) and trilaurin plus fatty alcohols (1-tetradecanol, 1-hexadecanol and 1-octadecanol) were studied by differential scanning calorimetry (DSC) and some mixtures by optical microscopy. The experimental data showed that all the studied systems present an eutectic point. Trilaurin + 1-tetradecanol and trilaurin + 1-hexadecanol systems exhibited a partial formation of solid solution. Experimental data were used to adjust the parameters of the three-suffix Margules and NRTL models and the results showed that these models can appropriately describe the liquidus lines of above mentioned systems.

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1. Introduction

The knowledge of the physical properties of fatty compounds is an important tool for their implementation in a food matrix [1]. In general, oils and fats are composed of a complex mixture of triacylglycerols (TAGs) (usually > 95% of their total composition), which tends to determine a large part of their physicochemical properties. Beyond of the triacylglycerols, oils and fats present minor constituents in their compositions, such as diacylglycerols, monoacylglycerols, free fatty acids and fatty alcohols as well as phospholipids, sterol esters (tocopherols and tocotrienols), and vitamins [2].

Solid–liquid equilibrium (SLE) studies of mixtures containing triacylglycerols (TAGs), fatty acids and fatty alcohol have been the subject of interest of many researchers [3–9] due to their presence in a variety of systems such as complex lipid mixtures used in food, chemical and pharmaceutical industries as surfactant and structuring agents for emulsification with the ability of forming gel, for example. Moreover recent studies have been considered this kind of substances as phase change materials (PCMs) for thermal storage

processes [10,11].

Experimental determination of SLE phase diagrams of fatty mixtures is often accomplished by differential scanning calorimetry (DSC) technique which is widely used as simple, faster and reliable technique to determine temperatures and enthalpies of phase transitions and heat capacities of solid and liquid phases. It also provides information about polymorphic transformations and data to estimate solid fat contents [8,12,13]. All of these analyses need small samples [13–16]. Although this technique is not an absolute way to measure equilibrium data because the measurements are not performed in a thermal equilibrium but in a quasi-equilibrium condition, it is a usual practice to report equilibrium phase diagrams measured by DSC [5,8,14,16–22].

This study aims to analyze the SLE behavior of the following binary mixtures: trilaurin (1) + myristic acid (2), + palmitic acid (3), + stearic acid (4), + 1-tetradecanol (5), + 1-hexadecanol (6) and + 1-octadecanol (7) employing DSC technique. Some thermal transitions were evaluated with the aid of an optical microscopy coupled with a temperature controller. The liquidus lines of the studied systems were adjusted using three suffixes Margules and NRTL models.

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2. Experimental

2.1. Materials

Highly pure components were used in this study without further purification (Table 1). The equipment calibration was performed using indium (≥ 0.999 M fraction, CAS number 7440-74-6, certificated by PerkinElmer, USA), decane (≥ 0.99 M fraction, CAS number 124-18-5), from Fluka Analytical (Germany) and cyclohexane (≥ 0.999 M fraction, CAS number 110-82-7), from Sigma-Aldrich (USA), at heating rate of 1 K min^{-1} .

2.2. Preparation of binary mixture samples

The samples were prepared by mixing known amounts of each substance to cover the entire range of the phase diagram in steps of 0.1 of the molar fraction as described in a previous study [23]. For this set of binary systems, the uncertainty of compositions, obtained by error propagation from values of the weighed masses, was estimated as not higher than 4×10^{-4} (in molar fractions).

2.3. Differential scanning calorimetry

The experimental data were performed on a Differential Scanning Calorimeter (DSC 8500 PerkinElmer, USA) equipped with a cooling system and operated within the temperature range from 248 K to 360 K. High-purity nitrogen (99.99%) was used as purge gas. Experimental data were characterized at local room pressure $p = 94.6 \pm 0.1 \text{ kPa}$. A detailed description of the experimental procedure in which the samples were submitted in the DSC equipment was presented in the previous study [20].

2.4. Optical microscopy

Optical microscopy (Leica DM 2700 M, China) coupled with a temperature controller (Linkam LTS 420, United Kingdom) was used to evaluate the behavior of the solid–liquid transition of some mixtures. Each sample was submitted to a heating rate of 0.1 K min^{-1} until the sample melting. The images were acquired at each 0.1 K with a magnification of 20 times.

2.5. SLE thermodynamics

As described in detail in our previous study [23], it was adopted three-suffix Margules and NRTL models to describe the liquidus lines. The thermodynamic models are used in Eq. (1), proposed by Prausnitz et al. [24], in which was not considered solid–solid phase transitions and the molar heat capacities of pure components. The solid phase was considered as a pure solid component ($x_i^S \gamma_i^S = 1$), which represents that both components in solid phase are completely immiscible.

Table 1
Sources and purities of standard compounds used this study.

Chemical name	Source	CAS number	Mass fraction purity ^a
Trilaurin	Nu-Chek	538-24-9	>0.99
Myristic acid	Sigma–Aldrich (USA)	544-63-8	>0.99
Palmitic acid	Nu-Chek	57-10-3	>0.99
Stearic acid	Nu-Chek	57-11-4	>0.99
1-Tetradecanol	Sigma–Aldrich (USA)	112-72-1	>0.984
1-Hexadecanol	Aldrich (Germany)	36653-82-4	>0.99
1-Octadecanol	Aldrich (Germany)	112-92-5	>0.99

^a As reported by the supplier.

$$\ln \frac{1}{x_i^L \gamma_i^L} = \frac{\Delta_{\text{fus},i} H}{RT_{m,i}} \left(\frac{T_{m,i}}{T} - 1 \right) \quad (1)$$

where (x_i^L) is the molar fraction of component i in the liquid (L) phase, (γ_i^L), the activity coefficient of component i in the liquid phase, ($\Delta_{\text{fus},i} H$) is the enthalpy of fusion at the melting temperature of the compound i , ($T_{m,i}$) is the melting temperature of the compound i , (T) is the calculated temperature, and (R) is the universal gas constant.

Eq. (2) was used to verify the root mean square deviation (RMSD) between the temperature calculated by three-suffix Margules or NRTL models and the observed ones.

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^N (T_i^{\text{exp}} - T_i^{\text{cal}})^2}{N}} \quad (2)$$

where (N) is the number of experimental measurements, (T^{exp}) is the experimental temperature and (T^{cal}) is the calculated temperature.

3. Results and discussion

The thermal properties of pure components obtained in this study and those reported in literature are presented in Table 2. The experimental standard deviations are indicated in parenthesis. The average relative deviation (ARD) of the melting temperatures and the molar enthalpies of fusion of pure components measured in this work ($T_{i,\text{this work}}$) and data found in literature ($T_{i,\text{literature}}$) were calculated according to Equation (3), where (N) is the number of observations. The ARD for melting temperatures was equal to 0.14%, confirming that there is a good agreement between these experimental data and those found in literature. The ARD for the molar enthalpy of fusion was equal to 7.80%. Although this value is not as small as the value found for the melting temperatures, it can be considered a good result, since only comparing the literature data of molar enthalpies of fusion, it is possible to note a significant difference between them (9.95%), particularly for myristic acid, 1-tetradecanol and 1-hexadecanol. The data of myristic acid and 1-tetradecanol can be found in our previous study [23].

$$\text{ARD} = \left(\frac{1}{N} \sum_{i=1}^N \frac{|T_{i,\text{this work}} - T_{i,\text{literature}}|}{T_{i,\text{this work}}} \right) \times 100 \quad (3)$$

Differential thermal curves of pure fatty alcohols, 1-hexadecanol and 1-octadecanol, and fatty acids, palmitic acid and stearic acid, present overlapping peaks with a light inflection very close the melting temperature suggesting the occurrence of a solid–solid transition (Table 2) [17,22,37]. The same behavior was also observed for the myristic acid and 1-tetradecanol in previous work [23]. The overlapping peaks occurs due to the proximity in the values of temperature of each thermal event and can be an indication that polymorphic transitions occur during the melting process of these compounds [38–40]. Once the thermal events are very close, the determination of the enthalpy of each transition observed does not lead to an accurate and reliable value [5,41].

Differential thermal curves of trilaurin, in turn, presents two peaks, the first one, an exothermic peak with temperature equal to 295.42 K, and the second one, an endothermic peak, with temperature equal to 319.67 K, represents the full sample melting.

SLE data obtained in this study for system composed of trilaurin plus fatty acid and trilaurin plus fatty alcohol are presented in Tables 3–8. All the phase diagrams were plotted in a way that

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