Solid–liquid equilibrium of binary and ternary mixtures containing ethyl oleate, ethyl myristate and ethyl stearate

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A B S T R A C T

Solid–liquid equilibrium for binary mixtures of ethyl oleate and ethyl myristate, ethyl oleate and ethyl stearate, and ethyl myristate and ethyl stearate was studied through differential scanning calorimetry. Experimental results confirmed the occurrence of polymorphism of ethyl oleate, ethyl myristate and ethyl stearate. Simple eutectic behavior was observed for systems containing the unsaturated ester ethyl oleate. However, the system formed by both saturated esters (ethyl myristate and ethyl stearate) presented a complex behavior, and not only eutectic transitions but also peritectic and metatectic transformations were observed. In addition, solid–liquid equilibrium for the ternary mixture formed by the esters mentioned was studied. A peritectic reaction was also manifested in the ternary system.

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1. Introduction

Biodiesel is a fuel constituted by alkyl esters of fatty acids, produced by the trans-esterification of vegetal oils and animal fats [1–6]. In recent years, it has become an attractive alternative to fuels derived from petroleum because it is a clean energy source, of high quality and economically sustainable. The future of this energy source is guaranteed if government legislation promotes biofuels through mandatory consumer laws, maintenance of tax incentives and subventions to produce oilseed crops such as soybean, rapeseed or sunflower with no impact on the food chain. The choice of waste cooking oil as a raw material for biodiesel production is also recognized to be an attractive and economic alternative to the use of vegetable oils [7].

However, the raw material for biodiesel production may limit the use of fuel at low temperatures for compression ignition engines. Biodiesel performance is strongly influenced by the crystallization of its components and by the high viscosity and poor cold flow properties at low temperatures, which can result in the plugging of fuel pipes and fuel filters and the impossibility of a normal fuel supply to the engine [8–11].

Numerous methods have been evaluated for improving the cold flow properties of biodiesel [12], the most relevant being winterizing [13], the addition of cold flow improvers [8,14], and the modification of the fatty ester composition [15]. The knowledge of conditions wherein solid formation occurs is necessary to establish preventive or remedial strategies; therefore, the reliable prediction of solid liquid equilibrium (SLE) by thermodynamic models is very important [16–22].

The values of the transition properties of pure components (melting temperature and the variations of enthalpy (ΔH_f) and heat capacity (C_p) on melting) are relevant in the thermodynamic modeling of solid–liquid equilibrium. Unlike vapor-related properties, these values are difficult to be correlated to the structure of the compound. The occurrence of polymorphisms in solid phase for organic compounds with a more complex structure such as triacylglycerols is common [23]. Polymorphism is the ability of a solid material to exist in more than one form or crystal structure with different properties, such as melting temperature and enthalpy.

Even for less complex compounds, such as esters of fatty acids, it was observed that the simple correlation between temperature and enthalpy of fusion of saturated esters with respect to the chain length leads to different equations for compounds with either odd or even number of carbons, although only linear chains were considered [19]. The fact that the melting temperature for ethyl esters is lower than the corresponding one to methyl esters shows that usual group contribution methods to determine phase change properties may fail.

Experimental data of three ternary systems formed by combination of ethyl laurate and ethyl palmitate with ethyl oleate [18], ethyl

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Table 1
Sources and purities of compounds used in the experiments.

Chemical name	Source	Mass fraction purity
Ethyl oleate	Sigma Aldrich	≥0.98
Ethyl myristate	Sigma Aldrich	≥0.99
Ethyl stearate	Sigma Aldrich	≥0.99
Indium[a]	TA Instruments (calibration standard)	0.9999
Naphthalene[a]	Merck	≥0.99
Cyclohexane[a]	Merck	≥0.99
N-decane[a]	Sigma Aldrich	≥0.99

[a] Compounds used only for calibrating the DSC apparatus.

stearate [24] and ethyl myristate [25] were recently published. Such results show that the SLE of ternary mixtures cannot be considered a simple extension of the SLE of binary mixtures.

This study is a continuation of these research works, and comprised the experimental determination and modeling of solid–liquid equilibria (SLE) of the binary systems (ethyl oleate + ethyl myristate, ethyl oleate + ethyl stearate, and ethyl myristate + ethyl stearate) through differential scanning calorimetry. The experimental results once again confirm the polymorphism of ethyl oleate, ethyl myristate and ethyl stearate. The solid liquid equilibrium for the ternary mixture formed by the esters mentioned was also studied. Peritectic reaction was manifested in binary system containing saturated esters and in the ternary system.

The experimental results were also successfully modeled considering an approach recently developed, for systems with immiscible solid phases and peritectic reactions, based on a stability analysis [26], using the Flory–Huggins equation to describe the liquid-phase non-ideality. The influence of the polymorphism phenomenon in model prediction was also evaluated: it affected the SLE prediction of the system ethyl myristate + ethyl stearate, in which a metatectic transition also takes place.

2. Experimental

2.1. Materials

Sources and purities of the fatty acid esters used in this work (ethyl oleate (1), ethyl myristate (2) and ethyl stearate (3), with molecular weights 310.51, 256.42 and 312.53 g mol^{-1}, respectively) are presented in Table 1. The differential scanning calorimeter (MDSC 2920 model of TA Instruments) was calibrated using indium, naphthalene, cyclohexane and n-decane; their purities and sources are also presented in Table 1. Masses were measured in a Sartorius balance.

2.2. Methods

The procedure for obtaining the temperature profile through Differential Scanning Calorimetry (DSC) was the same used in previous works [18,24,25]; briefly:

(1) Between 2 and 5 mg of the mixture were weighted and placed in hermetic aluminum pans.
(2) The sample was heated to approximately 15 K above the highest pure component melting temperature.
(3) The sample was cooled (at a cooling rate of 1 K min^{-1}) to approximately 25 K below the lowest pure component melting point and equilibrated at that temperature for 10 min.
(4) The sample was heated (at a heating rate of 1 K min^{-1}) until complete melting.

Nitrogen (99.99% purity) was fed at a rate of 50 mL min^{-1}. The transition temperature corresponding to the thermodynamically stable phase was considered to be the peak temperature, i.e., the temperature that corresponds to the absolute minimum of the heat flow in the heating thermogram. Local minimum points (corresponding to metastable phases) can also be observed. The results were collected using the commercial software supplied by TA Instruments.

2.3. Modeling

Phase equilibrium was studied by means of a stability analysis following the procedure previously developed by Barbosa and Pessôa Filho [26]. According to this method, the *liquidus* line temperature corresponds to the onset of the formation of a solid phase, for a certain liquid phase composition. It can thus be calculated through a stability analysis.

Assuming that the peritectic compound formed by the reaction between compounds i and j corresponds to a 1:1 compound, the *liquidus* line temperature T can be calculated through [26]:

$$\left(\frac{\Delta_{fus}G_i}{RT} + \ln(a_i^L)\right) + \left(\frac{\Delta_{fus}G_j}{RT} + \ln(a_j^L)\right) + \ln(K_{ij}) = 0 \quad (1)$$

wherein K_{ij} is the equilibrium constant of the peritectic reaction between i and j and its logarithm can be also written as a linear function of temperature:

$$\ln(K_{ij}) = -\frac{\Delta G_{ij}^0}{RT} = a + \frac{b}{T} \quad (2)$$

The liquid phase non-ideality was determined through the Flory–Huggins activity model:

$$\ln(a_i^L) = 1 + \ln(\phi_i) - v_i \sum_j \frac{\phi_j}{v_j} + v_i \left(\sum_j \chi_{ij}\phi_j - \sum_j \sum_{k>j} \chi_{jk}\phi_j\phi_k\right) \quad (3)$$

For eutectic systems (i.e., those with immiscibility in solid phase), the solid-phase activity was considered to be identical to 1.0. Volume fractions are calculated through:

$$\phi_i = \frac{x_i v_i}{\sum_j x_j v_j} \quad (4)$$

and the summations are carried out over all compounds.

3. Results and discussion

3.1. Experimental data

3.1.1. Pure compounds
Fig. 1 shows the heating thermograms of the ethyl esters we studied. In a previous work [18], no polymorphism was observed for ethyl oleate. However, in this work, another transition at 252.11 K located to the left of the main peak (254.29 K) was also observed during heating by further expanding the thermogram. Since it is a very low energy transition, it was initially ascribed to noise, and hence it was not considered before. An exothermic transition is also observed during heating. It may indicate that the cooling rate of 1 K min^{-1} is not low enough for this compound to uniformly crystallize. However, it may also indicate the existence of additional polymorphic forms.

As observed in previous work [25], polymorphism of ethyl myristate is manifested in heating thermograms (Fig. 1B) yielding transitions at the following heating temperatures: 286.9, 287.32