



Solid–liquid equilibrium in ternary mixtures of ethyl laurate, ethyl palmitate and ethyl stearate



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ABSTRACT

Biodiesel is a substitute fuel for petroleum-based diesel obtained from vegetables, formed by fatty acid methyl or ethyl esters produced by transesterification reaction between fats or oils and alcohols. An experimental study of solid–liquid equilibrium of ternary mixtures of ethyl esters commonly present in biodiesel (ethyl laurate, ethyl palmitate and ethyl stearate) was carried out using differential scanning calorimetry. Experimental results show that no eutectic composition is observed for ternary systems, although binary systems formed by ethyl laurate and ethyl palmitate as well as ethyl laurate and ethyl stearate present eutectic points at $\geq 90\%$ (m/m) of ethyl laurate, indicating solid phase immiscibility. The system ethyl palmitate and ethyl stearate forms solid solutions for all compositions (miscible system). The experimental results were modeled using the Flory–Huggins equation for liquid phase and, when applicable, solid phase non-ideality, with good agreement.

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1. Introduction

Biodiesel is a mixture of mainly fatty acid alkyl esters obtained by transesterification of fatty acids and alcohol in alkaline medium, used as a less pollutant alternative for petroleum-based diesel. Although methanol is generally cheaper and the production technology using it is better known, the increasing production of ethanol from biomass sources makes biodiesel production from ethanol likely to become more important in the near future [1]. The feedstock biodiesel is made from, as well as the alcohol used during the process, determines its cold properties. At low temperatures, solid phases or a second liquid phase can be formed, which may hinder the use of this bio-fuel in some circumstances [2]. In this sense, it is very useful to know the composition of every ester that constitutes biodiesel and to predict solid–liquid equilibrium data in order to obtain a desired property [3] (e.g. cloud point, pour point, freezing point depression, etc.) and match the standards of biodiesel before approval for commercialization [4].

Fatty systems can present several types of solid–liquid phase behavior. In general, they can be classified as [5]:

- i) Systems with a *simple eutectic point*, wherein both components crystallize from the melt as pure phases, i.e. no solid solutions are formed [6]. In most cases, for fatty systems it can be further assumed that the two components are miscible in all proportions in the liquid phase.
- ii) Systems with *partial miscibility in the solid state*. Sometimes fatty mixtures may present partial solubility, forming a solid solution at the extremes of the phase diagrams.
- iii) Systems with *eutectic and peritectic reaction* (system with an incongruently melting compound) [7]. The peritectic point is typical of systems in which the two components e.g. A (liquid) and B (solid 1) form an intermediate compound C (solid 2) which will continue forming until one of the reactants is consumed. The formation of this compound occurs through a chemical reaction or physical association between the molecules forming the system [8].
- iv) Systems with a *complete series of solid solutions*, i.e. systems in which both solid and liquid phases show complete miscibility.

Concerning the thermodynamic modeling of such systems, regardless of the type of behavior and the approaches considered, thermodynamic models require the values of fusion properties of pure components forming the mixture as input to predict solid–liquid equilibrium phase diagrams. Unlike related vaporization parameters, these fusion properties are difficult to be correlated to the structure of the compound, being thus necessary

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

Chemical name	Source	Mass fraction purity ^a
Ethyl laurate	Sigma Aldrich	≥0.98
Ethyl palmitate	Sigma Aldrich	≥0.99
Ethyl stearate	Sigma Aldrich	≥0.99
Indium ^b	TA Instruments (calibration standard)	0.9999
Naphthalene ^b	Merck	≥0.99
Cyclohexane ^b	Merck	≥0.99
N-decane ^b	Sigma Aldrich	≥0.99

^a Purity as given by the supplier. No further purification method was used.

^b Compounds used only for calibrating the DSC apparatus.

to obtain them experimentally. A reason for this is the polymorphism phenomenon [9–11], i.e., the ability of some substances to exist in states with different atomic crystal structures. Each state, or thermodynamic phase, is stable under certain external conditions (temperature and pressure). In fatty compounds, differences in geometry – i.e. hydrocarbon chain packing and variations in the angle of tilt of the hydrocarbon chain packing – differentiate polymorphic forms. The polymorphism phenomenon depends on the molecular structure of the fatty compound and the processing conditions (temperature, pressure, rate of crystallization, impurities, and shear rate). It affects the physical properties (e.g. fusion temperature) [5,11,12] and crystallization behavior of the substance, including crystallization rate, crystal size, morphology, and total crystallinity [7,13].

The second factor which limits the prediction capability of thermodynamic models is the scarcity of experimental solid–liquid phase equilibrium data of fatty acid methyl or ethyl esters and related mixtures available in the literature. Some single compounds and binary mixtures have been analyzed by different authors [4,14–23]. Recently our team published experimental data of a ternary mixture composed by ethyl oleate, ethyl laurate and ethyl palmitate [3], which constitutes so far, to the best of our knowledge, the only experimental data set of ternary solid–liquid equilibrium for a fatty acid ethyl ester system.

In this work, an experimental study of solid–liquid equilibrium of the ternary mixture of ethyl laurate, ethyl palmitate and ethyl stearate, as well as their corresponding binary systems, was carried out using differential scanning calorimetry. In comparison to the previous work [3], the replacement of ethyl oleate (unsaturated) by ethyl stearate (saturated) considerably increases the melting point of the ternary mixture for concentrations of ethyl palmitate lower than 30%, in spite of both compounds having similar molecular weights. The binary system ethyl laurate and ethyl stearate is eutectic and the binary system ethyl palmitate and ethyl stearate forms solid solutions. The experimental results were appropriately correlated by the Flory–Huggins equation.

2. Experimental

2.1. Materials

Sources and purities of the fatty acid esters used in this work (ethyl laurate, ethyl palmitate and ethyl stearate) are presented in Table 1. The differential scanning calorimeter was calibrated using indium, naphthalene, cyclohexane and decane; sources and purities of these compounds are also presented in Table 1. The analyses were carried out in a MDSC 2920 model of TA Instruments, and 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 presented in the previous work [3]; briefly:

- (1) Samples of 2 and 5 mg of the mixture were weighted and placed in hermetic aluminum pans.
- (2) Each sample was heated to roughly 15 K above the highest pure component fusion 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 temperature of stable thermodynamic equilibrium (melting temperature) was considered to be the peak temperature, i.e., the temperature of the absolute maximum deviation from the baseline between two points on the phase change curve of the heating thermogram representing the heat capacity of solid and liquid before and after the thermal event, respectively. Changes in the trend of curve may also be observed on the same peak, which can be assigned to transitions corresponding to metastable states. The results were collected using the commercial software supplied by TA Instruments.

3. Modeling

Phase equilibrium was studied by means of a stability analysis according to Barbosa and Pessôa Filho [24]. According to this method, the *liquidus* line temperature corresponds to the beginning of the formation of a solid phase, for a certain liquid phase composition.

If no solid phase reaction occurs (i.e., if there is no formation of a peritectic compound), the resulting equations are those usually found in the modeling of solid–liquid equilibrium. The analysis of the *solidus* information for the systems studied herein showed that there is no formation of complexes in solid phase. Therefore, we considered only the possibilities that the solid phase is either a solid solution or a pure solid phase. In both cases, the solid–liquid equilibrium condition can be written as:

$$\ln \left(\frac{a_i^L}{a_i^S} \right) = - \frac{\Delta_{fus} H_i}{R} \left(\frac{1}{T} - \frac{1}{T_i^{fus}} \right) \quad i = A, B \quad (1)$$

As only mixtures of ethyl esters are considered, one can expect that the liquid phase behaves approximately as an ideal mixture. Therefore, the modeling was conducted either considering ideal behavior or considering that the liquid and (when applicable) solid phase non-ideality is given by the Flory–Huggins equation:

$$\ln(a_i^L) = 1 + \ln(\phi_i) - v_i \sum_j \frac{\phi_j}{v_j} + v_i \left(\sum_j \chi_{ij} \phi_j - \sum_j \sum_{k>j} \chi_{jk} \phi_j \phi_k \right) \quad (2)$$

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:

$$\phi_i = \frac{x_i v_i}{\sum_j x_j v_j} \quad (3)$$

and the summations are carried out over all compounds.

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