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Binary mixtures of fatty acid ethyl esters: Solid-liquid equilibrium

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ABSTRACT

Biodiesel is a renewable fuel that is commonly used in diesel engines around the world mostly in blends with the conventional diesel. There are many studies concerning its production and its properties and a series of them confirms the biodiesel advantages when compared with conventional diesel in relation of the environmental impacts. In spite of many advances concerning the biodiesel production and properties its behavior at low temperatures is worst than the conventional diesel, and, unfortunately, low temperature property information concerning fatty acid ethyl esters (FAEE) and the biodiesel is still scarce for researchers. This paper presents nine solid-liquid phase diagrams of FAEE binary mixtures to complement the studies of FAEE phase diagram previously reported. All of the phase diagrams have been determined using differential scanning calorimetry (DSC) and also modelled using both the Predictive UNIQUAC and the ideal solution models. The results have been shown good correlation between experimental and modelled data.

1. Introduction

Biodiesel is a biofuel obtained from animal or vegetable oils and fats by a transesterification reaction employing short chain alcohols, for instance, ethanol or methanol. It is more environmentally friendly than conventional diesel because is produced from renewable resources, is less toxic, generates less gas emissions and it is biodegradable [1,2]. Considering the biodiesel properties compared with conventional diesel the former presents higher flash points, good lubricity [3] and similar specific gravity, heat of combustion and kinematic viscosity [4]. These characteristics enable the use of biodiesel and biodiesel blends with conventional diesel in diesel engines without changes.

Physicochemical properties like as vapour pressure [5,6], Flash point [7], densities and viscosities [8–11] and equilibrium data of biodiesel and its components, namely fatty acids methyl esters (FAME) or FAEE [12–14] have been determined with the objective to improve the biodiesel production and its use as energy source.

Unfortunately, the biodiesel properties at low temperatures do not favour their use in diesel engines, difficult its storage and transportation, and create a poor low temperature behavior in its blends with conventional diesel [15,16]. Problems due to nucleation and growing of solid crystals appear around 275 K in biodiesel while in conventional diesel they appear at around 260 K [4]. Some tests are used to characterize the biodiesel behavior at low temperatures in which most important are the cold filter plugging point (CFPP), pour point (PP) and cloud point (CP). The former is given at a temperature in which fuel filters and lines become plugged [17] (EN 116, IP-309, ASTM D-6371), the second is the lowest temperature that is possible to the fuel to be pumped or just to flow [4] (ASTM D-97, ASTM D-5949) and the last one, the CP, is a temperature determined for the crystals to become visible and to form a hazy or cloudy suspension [4] (EN 23015, ASTM D-2500).

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These properties are closely monitored to ensure the operation without problem in cold climates [4]. Beyond the cold flow properties the knowledge of biodiesel and its compounds behavior under low temperatures are interesting to development of purification and/or separation processes and equipment design [18], as well as the knowledge are necessary to help to looking for compounds that can be employed to improve this properties [19,20].

This work complements and completes the study of the solid-liquid phase diagrams for binary mixtures of FAEE [21–26]. In this article nine new binary mixtures were measured employing a Differential Scanning Calorimetry (DSC) and are presented for the first time in the literature. A discussion on the type of phase diagram presented by these systems and its relation with the differences in chain length and melting temperatures of the two mixture components is carried. Since most binary mixtures of FAEEs are simple eutectics the *liquidus* line of the mixtures was here modelled employing the predictive UNIQUAC model and an ideal solution model.

2. Experimental section

The binary samples were prepared using high purity FAEE (min 99%) supplied from Nu-Chek Prep, INC. and handled as received. Each mixture component was weighed on an analytical balance (±0.2 mg), melted in a nitrogen atmosphere under stirring and stored in a refrigerator until its use in MDSC 2920 calorimeter of TA Instruments. The calorimeter was calibrated through small amount of high-purified indium (99.99%), cyclohexane (min 99.9%) and naphthalene (min 99%). Indium purity validated by TA Instruments and cyclohexane and naphthalene were supplied by Merck. The calibration and analyses occurs in the temperature range between 200 K and 600 K using the TA Instruments refrigerated cooling system and according to a methodology described in previous studies [21,27].

The accuracy of the experimental melting point data was estimated at the repeated run basis and executed with the calibration substances and some chosen mixtures [27]. The deviation on the measured temperature is no higher than 0.3 K.

3. Modeling

The predictive UNIQUAC model was chosen to describe experimental *liquidus* lines. This approach was previously applied to diesels and crude oils [28,29], to fatty acids [30], fatty acid methyl esters [18], fatty acid ethyl esters [21,27,31]and for biodiesel behavior at low temperatures [32,33].

Equation (1) is a simplified form of the equation generally used to describe the solid-liquid equilibrium [27].

$$\ln\frac{x_i^s\gamma_i^s}{x_i^l\gamma_i^l} = \frac{\Delta_{fus,i}H_i}{RT_{fis,i}}\left(\frac{T_{fus,i}}{T}-1\right) \tag{1}$$

The liquid and solid phase activity coefficients (γ_i^l, γ_i^s) were described by means of UNIFAC model [34] and a new predictive UNIQUAC model version written as [29,35].

$$\frac{g^E}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{Z}{2}\sum_{i=1}^{n} q_i x_i \ln\left(\frac{\theta_i}{\Phi_i}\right) - \sum_{i=1}^{n} x_i q_i \ln\left[\sum_{j=1}^{n}\theta_j \exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{q_i RT}\right)\right] \tag{2}$$

with

$$\theta_i = x_i q_i \Big/ \sum_j x_j q_j \quad \text{and} \quad \Phi_i = x_i r_i \Big/ \sum_j x_j r_j \tag{3}$$

The predictive local composition concept [36] allows for estimation of the interaction energies (λ_{ij}) used by this model, without fitting to the experimental data. The pair interaction energies between two identical molecules are estimated from the enthalpy of sublimation of the pure crystalline component

$$\lambda_{ii} = -2/Z(\Delta_{sub}H_i - RT) \tag{4}$$

where Z is the coordination number ($Z = 10$). The enthalpies of sublimation ($\Delta_{sub}H = \Delta_{vap}H + \Delta_{fus}H$) are calculated at the melting temperature of the pure component.

The pair interaction energy between two non-identical molecules is given by

$$\lambda_{ij} = \lambda_{ji} = \lambda_{ii} \tag{5}$$

where i is the compound with the shorter alkyl chain of the pair ij.

As an alternative, a simpler approach for the description of the *liquidus* line measured in this study was also tested. It was assumed that the solid phase formed was essentially a pure fatty ester, and that the liquid phase was ideal. Based on these assumptions the relation between the composition of the mixture, x_i, and the melting/cloud point, T, was given by the classical solid-liquid equilibrium equation.

$$x_i^L = \exp\left[-\left(\frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T}-\frac{1}{T_{fus,i}}\right)\right)\right] \tag{6}$$

The models used to calculate the solid-liquid equilibrium are totally predictive employing just the property of pure components to estimate the behavior of each phase. These properties were correlated in a previous paper [33] and are presented in Table 1. To the fusion ($\Delta_{fus}H$) and vaporization enthalpies ($\Delta_{vap}H$) of FAEE the correlations are presented in Equations (7) and (8) [33] and the melting temperatures (T_{fus}) were got from the thermograms.

$$\Delta_{fus}H = 3.92C_n + 16.80 \tag{7}$$

$$\Delta_{vap}H = 4.9C_n + 9.0 \tag{8}$$

In Equations (7) and (8) the enthalpy units are kJ mol^{-1}. It was considered that the differences between the fusion enthalpy ($\Delta_{vap}H$) and vaporization enthalpy ($\Delta_{fus}H$) of FAEE may be the same as those observed for the methyl esters [33].

4. Results and discussion

Nine phase diagrams of FAEE binary mixtures are presented to complement previous studies [21–26]. Table 1 presents the experimental melting temperature data as well as the calculated melting enthalpy of each FAEE content in the binary mixtures [33]. In previous studies the phase diagrams of ethyl stearate with ethyl linoleate, ethyl oleate, ethyl palmitate, ethyl myristate, ethyl laurate, ethyl caprate and ethyl caprylate [21] and ethyl palmitate with ethyl linoleate, ethyl oleate, ethyl palmitate, ethyl myristate, ethyl laurate, ethyl caprate and ethyl caprylate [22] were presented performing a total of 13 binary systems. Recently Robustillo et al. studied some FAEE ternary systems formed by ethyl palmitate, ethyl myristate and ethyl laurate [23], ethyl stearate, ethyl palmitate and ethyl laurate [24], ethyl oleate, ethyl palmitate and ethyl laurate [25], and ethyl oleate, ethyl myristate and ethyl stearate [26]. In their studies the authors also discuss in detail the solid