Fluid Phase Equilibria 361 (2014) 188–199

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

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

Maria Dolores Robustillo[a], Deise Fernanda Barbosa[a], Antonio José de Almeida Meirelles[b], Pedro de Alcântara Pessôa Filho[a],*

[a] Department of Chemical Engineering, Engineering School, University of São Paulo (USP), Caixa Postal 61548, 05424-970 São Paulo, SP, Brazil
[b] Department of Food Engineering (DEA), School of Food Engineering (FEA), University of Campinas (UNICAMP), Campinas, SP, Brazil

ARTICLE INFO

Article history:
Received 25 April 2013
Received in revised form 7 October 2013
Accepted 13 October 2013
Available online 21 October 2013

Keywords:
Solid–liquid equilibrium
Ethyl esters
Liquidus line

ABSTRACT

An experimental study into the solid–liquid equilibrium of ternary mixtures of ethyl laurate, ethyl palmitate and ethyl myristate, commonly present in biodiesel, is presented. Experimental results reveal the polymorphism of ethyl myristate and show the existence of a peritectic-type reaction in binary systems containing such compound, as well as in the ternary system. A probable metatectic reaction was also found for the binary system ethyl laurate and ethyl myristate. The experimental results were modeled considering an approach recently developed for systems with immiscible solid phases and peritectic reactions.

1. Introduction

While the widespread use of non-renewable fuels increases, high crude oil prices and the effect of the CO_2 released on the climate make it necessary to investigate ways to reduce the social and economic impact. Biodiesel, defined by ASTM as “a fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats” [1], has been proposed as a sustainable and appropriate alternative. Nevertheless, the formulation of biodiesel mixtures must meet several specifications. There are a number of technical problems that must be resolved before it becomes a more attractive alternative than petroleum diesel, especially at low-temperature conditions [2].

Natural wax esters contained in biodiesel are typically esters of long-chain fatty acids and long-chain alcohols [3]. Wax esters crystallization begins at higher temperatures in biodiesel and its blends, causing them to gel sooner than paraffin wax of conventional fossil fuels. This crystallization leads to operational difficulties, since the new solid structures formed may quickly stop fuel lines and fuel filters and, consequently, engine starving due to reduced fuel flow. The difference in crystallization temperatures for wax esters or analogous paraffin waxes is probably attributed to the strength of C═O covalent bond present in the structure of wax esters [4], which is greater than that of the C—C bond, the most abundant in both types of waxes.

As mentioned in previous works [5–7], the most relevant specification parameters affecting the flow through fuel filters are the cloud point, the pour point and the cold filter plugging point, which are related to physicochemical properties (mainly the chain length and the degree of unsaturation) and solid–liquid transitions. Biodiesel with the highest temperature points will show the poorest performance [1]. In general, the longer is the carbon chain and the lower is the degree of unsaturation, the higher is the melting point. Such properties are strongly influenced by both the feedstock and the alcohol used in the biofuel production process. Some of the most common raw materials used for biodiesel production contain fatty acids such as palmitic, lauric, myristic, oleic and stearic, among others [1].

From the facts mentioned above, the knowledge of solid–liquid equilibrium of biodiesel is important to assure and to improve its pumpability. Such knowledge allows the selection of raw materials for biodiesel production, the preparation of suitable blends of biodiesel and conventional diesel, and the selection of flow improvers formulated to reduce the pour point, preventing or modifying wax crystallization. In addition, the study of solid–liquid equilibrium itself is relevant in order to establish the criteria to be used in the purification and separation processes of fatty compounds [8] such as fatty acids, fatty alcohols or fatty esters, which can be used in lubricants, cosmetics, linoleum, printing inks, candles and polishes [3].

There are several factors that hinder thermodynamic modeling of the solid-equilibrium of mixtures of fatty compounds. Among them, one can mention the scarcity of experimental data to check the reliability of thermodynamic models and the possible existence

---

* Corresponding author. Tel.: +55 11 3091 1106; fax: +55 11 3091 2284.
E-mail address: pedro.pessoa@poli.usp.br (P.d.A. Pessôa Filho).

0378-3812/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2013.10.024

of polymorphisms or invariant points in the phase diagram. These invariant points include eutectic, peritectic or metatectic reactions and transformations [8], which are responsible for the shape of the liquidus line of each system.

Several works presenting experimental data of solid–liquid equilibrium of fatty mixtures can be found in the literature [9–17], but none of them deal with ternary systems of fatty acid esters. Exceptions are two recent works by the same authors [7,18], wherein some of the most common binary and ternary systems of fatty ethyl esters contained in biodiesel formulations obtained by ethanol route were studied by means of differential scanning calorimetry. In these works, ethyl oleate [7] or ethyl stearate [18] were added to binary mixtures of ethyl laurate and ethyl palmitate, yielding eutectic type ternary systems with partially miscible solid solutions in both cases. The results of these investigations showed that the solid–liquid phase equilibrium of the ternary mixtures cannot be seen as a simple extension of the solid–liquid equilibrium of the binary mixtures, and it may have unexpected impacts on the behavior of biodiesel at low temperatures. It must be stressed that fatty mixtures may generate systems presenting peritectic [19,20] or inverse peritectic reactions and transformations [21–23]. The peritectic reaction corresponds to the reaction between a liquid phase and another compound in the primary solid phase, generating a secondary solid phase on cooling [20] at the interface between the melt and the primary solid phase. Although there may be subtle differences between peritectic reactions and transformations [24], in this paper both terms are used as synonyms to describe the global peritectic phenomenon. The same considerations are extended for other phenomena such as eutectic, inverse peritectic, etc.

Inverse peritectic reactions, which are some sometimes called “metatectic”, “inverse melting” or “catatectic”, are related to systems wherein one or the two constituents present polymorphisms. In this work, different types of inverse peritectic reactions were observed; they are called either metatectic (when the transformed solid phase is a primary one) or inverse peritectic (when the transformed solid phase is a secondary one).

As a continuation of previous works [7,18], we report herein the results of a similar investigation on the addition of ethyl myristate to the binary mixture formed by ethyl laurate and ethyl palmitate. The melting temperature (*liquidus* line) and solid-phase transitions were determined. The experimental results were also correlated through an appropriate approach recently presented by Barbosa and Pessôa Filho [25], suitable for systems wherein a solid-phase complex is formed.

2. Experimental

2.1. Materials

Sources and purities of the fatty acid esters used in this work (ethyl laurate, ethyl palmitate and ethyl myristate) are presented in Table 1. The differential scanning calorimeter was calibrated using indium, naphthalene, cyclohexane and *n*-decane; their purities and sources are also presented in Table 1. No further purification was carried out. The analyses were carried out in a MDSC 2920 model of TA Instruments, and masses were measured in a Sartorius balance.

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

Chemical name	Source	Mass fraction purity
Ethyl laurate	Sigma Aldrich	≥0.98
Ethyl palmitate	Sigma Aldrich	≥0.99
Ethyl myristate	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.

2.2. Methods

The procedure for obtaining the temperature profile through Differential Scanning Calorimetry (DSC) was the same used in previous works [7,18]; 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 temperature of stable thermodynamic equilibrium (melting temperature) was considered to be the peak temperature, i.e., the temperature that corresponds to the point of maximum deviation from the baseline between two points of the phase change curve in the heating thermogram. The results were collected using the commercial software supplied by TA Instruments.

3. Modeling

Phase equilibrium for eutectic and peritectic type systems was studied by means of a procedure previously developed by Barbosa and Pessôa Filho [25]. 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 [25]:

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

wherein $\Delta_{\text{fus}}G$ is the Gibbs energy change on fusion, a_i^L is the activity of compound i in liquid phase, R is the gas constant and 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 (T):

$$\ln(K_{ij})=-\frac{\Delta G^0}{RT}=-\frac{\Delta H^0}{R}\left[\frac{1}{T}\right]+\frac{\Delta S^0}{R}=\frac{b}{T}+a \quad (2)$$

wherein ΔH^0 and ΔS^0 are the standard enthalpy and entropy associated to the peritectic reaction, respectively. Parameters a and b from Eq. (2) are adjustable parameters, obtained from the best fit for $\ln(K_{ij})$ versus T^{-1}. The liquid phase non-ideality was calculated through the Flory–Huggins activity model:

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

wherein χ_{ij} is the Flory Huggins interaction parameter for the interaction between compounds i and j and v_i is the molar volume of pure liquid compound i.