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Solid–liquid equilibrium of binary and ternary systems formed by ethyl laurate, ethyl palmitate and n-decane: Experimental data and thermodynamic modeling

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ABSTRACT

The solid–liquid equilibrium phase diagrams of binary and ternary mixtures formed by n-decane and the fatty acid ethyl esters ethyl laurate and ethyl palmitate were studied through differential scanning calorimetry (DSC). Phase change properties of polymorphs were obtained by resolving the thermograms into the corresponding overlapping peaks through a fitting analysis with a Gaussian function. The binary systems show immiscibility in solid phase. The system formed by ethyl laurate and n-decane presents two peritectic transformations, which were also observed in the ternary phase diagram. Equilibrium data were thermodynamically modeled using different models for liquid phase non-ideality and considering different polymorphs in solid phase. The results of modeling are in good agreement with the eutectic behavior of the system formed by ethyl palmitate and n-decane. However, higher discrepancies were observed if no peritectic behavior for the binary system formed by ethyl laurate and n-decane is considered. The results obtained in this work constitute another step forward to enhance the understanding and description of the complex behavior of biodiesel/diesel mixtures at low temperatures.

1. Introduction

The use of pure biodiesel at low temperatures is limited by the crystallization of its components, which affects cold–flow properties [1–3] and may lead to flow assurance problems and damage of engines. Thus, the use of blends of biodiesel and conventional hydrocarbon-based diesel has become increasingly common. The sources of biomass, along with the alcohol used in the production process, determine the composition of the biodiesel. High melting temperature compounds, such as stearic acid (C18:0), or medium melting temperature compounds, such as oleic acid (C18:1) and linoleic acid (C18:2), occur in appreciable amounts in most sources. Other acids such as lauric acid (C12:0) and myristic acid (C14:0) are found in large proportions in coconut oil, while palmitic acid (C16:0) is the main component of palm oil [4]. The formulation, transport and storage of diesel/biodiesel blends can be improved if the solid liquid equilibrium (SLE) of these blends is known. However, experimental equilibrium data of such mixtures is still scarce. Concerning pure compounds, Knothe and Dunn [2] conducted an extensive evaluation of melting points of fatty acids and esters, summarized the experimental data available in literature and published new data obtained by differential scanning calorimetry (DSC). Phase diagrams of some binary mixtures of fatty acid methyl and ethyl esters are presented in Lockemann and Schlünder [5], Boros et al. [6] and Costa et al. [7,8]. Robustillo et al. [9–12] presented *liquidus* lines of ternary systems formed by several ethyl esters (ethyl laurate, ethyl palmitate, ethyl oleate, ethyl myristate and ethyl stearate). Mixtures of biodiesel were analyzed by Imahara et al. [4] and Coutinho et al. [13]. Kouakou et al. [14] and Carareto et al. [15] studied the influence of pressure in pure methyl esters and binary mixtures of ethyl esters, respectively. However, only a few solid liquid phase diagrams of mixtures of fatty acid esters and

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Table 1
Sources and properties of the pure compounds used in the experiments.

Chemical name	Source	Mass fraction purity	Formula	Molar mass/g·mol^{-1}	$T_{f,\,Lit}$/K[c]	Functional groups					v_i
						$-CH_3$	$-CH_2$	c$-CH_2$	c$-CH$	$-CH_2COO$	
Ethyl laurate (EL)	Sigma Aldrich	≥0.98	$C_{14}H_{22}O_2$	228.4		2	10	0	0	1	8.860
Ethyl palmitate (EP)	Sigma Aldrich	≥0.99	$C_{18}H_{36}O_2$	284.5		2	14	0	0	1	11.390
N-decane (DE)	Sigma Aldrich	≥0.99	$C_{10}H_{22}$	142.3	243.51 [26]	2	8	0	0	0	6.325
Indium[a]	Mettler Toledo[b]	0.9999	In	114.82	429.75						
Naphthalene[a]	Merck	≥0.99	$C_{10}H_8$	128.17	353.35 [27]						
Cyclohexane[a]	Merck	≥0.99	C_6H_{12}	84.16	279.81 [27]						

[a] Compounds used only for calibrating the DSC apparatus.
[b] Calibration standard.
[c] Literature onset melting temperature.

components of conventional diesel have been obtained. The exceptions are the works by Collinet and Gmehling [16], where mixtures of ethyl myristate and p-xylene were studied, and the works of Benziane et al. [17,18], where solid–liquid equilibrium of fatty acid methyl esters with heavy alkanes and aromatics were studied. Recently, we have studied the solid–liquid equilibrium behavior of binary and ternary mixtures of ethyl esters and a naphthenic compound (dodecylcyclohexane) [19]. To the best of our knowledge, no work was found in the literature studying the solid–liquid phase behavior of ethyl esters and light alkanes.

This work comprises the experimental determination of solid–liquid equilibrium (SLE) of binary and ternary mixtures of ethyl laurate and ethyl palmitate, two ethyl esters commonly found in biodiesel [4], and n-decane, a low molecular weight paraffin present in conventional diesel [20]. Mixtures were analyzed by differential scanning calorimetry (DSC), which allows the simultaneous determination of both the *liquidus* and the *solidus* lines. Properties of polymorphs of ethyl laurate and ethyl palmitate were formerly obtained [19] by integration of corresponding heating thermograms following a method previously proposed by Canotilho et al. [21]. The polymorphism of n-decane is also addressed. The solid–liquid equilibrium was described by considering different models for the liquid phase behavior (ideal mixture, Flory–Huggins [22] and UNIFAC-Dortmund [23–25]), and considering different polymorphs in the solid phase. To the best of our knowledge, no other experimental data set for the binary systems containing these ethyl esters and n-decane, as well as for the corresponding ternary systems, was reported in literature.

2. Experimental section

2.1. Materials

Sources and purities of the compounds used in this work – n-decane (1), ethyl laurate (2) and ethyl palmitate (3) – are presented in Table 1. The differential scanning calorimeter (model DSC 822e, Mettler Toledo) was calibrated using indium, naphthalene, cyclohexane and n-decane. Their properties are also presented in Table 1. Literature onset melting temperatures for calibration were obtained from Refs. [26,27]. Masses were measured in a Sartorius balance with 220 g weighing capacity and 0.1 mg readability.

2.2. Methods

The procedure to obtain the temperature profile through Differential Scanning Calorimetry (DSC) was similar as used in previous works [9–12,19] and comprises the following steps:

(1) A sample was weighed (between 2 and 5 mg) and placed in hermetic aluminum pans inside the DSC furnace.
(2) This 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 5 min.

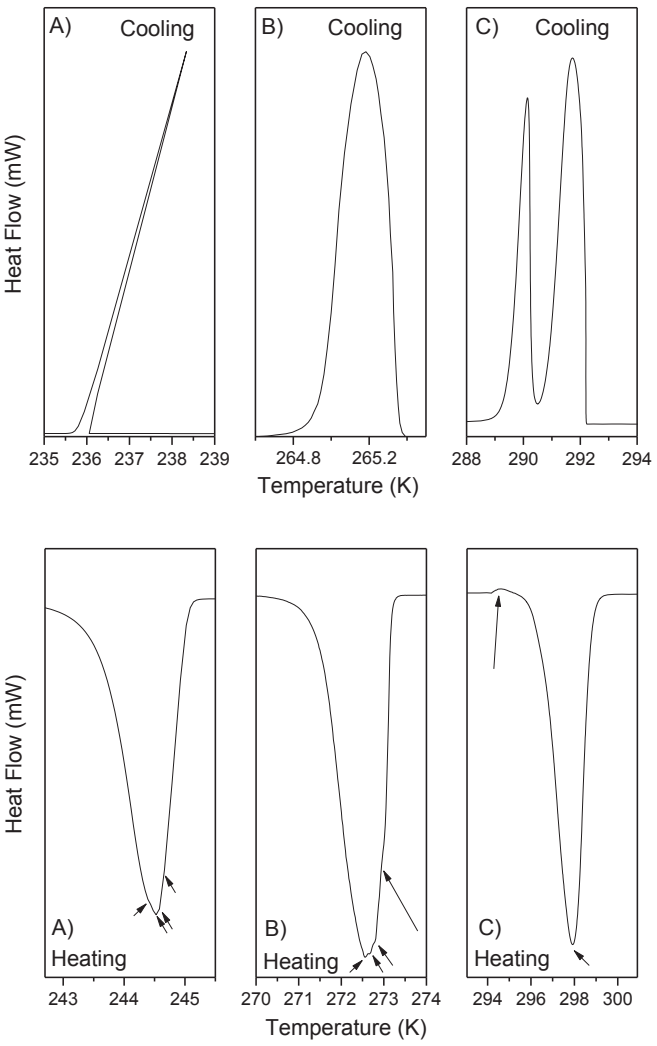

Fig. 1. Thermograms of the compounds studied in this work: A) n-decane (1); B) ethyl laurate (2); C) ethyl palmitate (3).

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