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Experimental data and thermodynamic modeling of solid-liquid equilibrium of binary systems containing representative compounds of biodiesel and fossil fuels: Ethyl esters and *n*-hexadecane

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ABSTRACT

In this work, solid-liquid equilibrium data of binary mixtures formed by n-hexadecane, a representative compound of fossil fuels, and ethyl esters present in ethylic biodiesel (ethyl oleate, ethyl laurate, ethyl palmitate, ethyl myristate and ethyl stearate) were determined through differential scanning calorimetry (DSC). Equilibrium data were thermodynamically modeled using the UNIFAC-Dortmund model for liquid-phase nonideality, considering experimentally obtained transition properties (melting temperatures and enthalpies). The complex phase behavior of these systems may have unexpected impacts on the performance of blends of biodiesel and fossil fuels at low temperatures.

1. Introduction

About 25% of worldwide anthropogenic emissions of carbon dioxide come from burning fossil fuels for transportation [1]. These fossil fuels are mainly obtained from petroleum, such as gasoline and conventional diesel (for land and ship transport), and kerosene and jet fuel (for air transport). An alternative to reduce these emissions is the use of biofuels, such as biodiesel, mixed with fossil fuels. However, biodiesel performance is unsatisfactory at low temperatures [2–5] due to the formation of solid phases that can block fuel filters and pipelines, resulting in flow assurance problems and eventual engine damage, and worsening a problem that may also occur with conventional diesel. Thus, besides all aspects related to the combustion itself, the study and understanding of solid–liquid equilibrium of the compounds involved is necessary before any attempt of mixing biodiesel with fossil fuels.

Biodiesel composition depends on the source of fatty acids (biomass) and on the alcohol used in the esterification reaction (methanol or ethanol). Many sources of fatty acids contain high melting temperature compounds, such as stearic acid (C18:0), and medium melting temperature compounds, such as oleic acid (C18:1) and linoleic acid (C18:2). Some fatty acids, such as lauric acid (C12:0) and myristic acid (C14:0), are found in high proportions in coconut oil, while palmitic acid (C16:0) is abundant in palm oil [6]. These fatty acids are converted into the corresponding methyl or ethyl fatty esters, which constitute the biodiesel.

From the point of view of the intended application, ethyl esters may be preferred to methyl esters, as the melting temperature of an ethyl ester is lower than that of the methyl ester with the same fatty acid chain.

Experimental solid–liquid equilibrium (SLE) data of pure ethyl esters and of mixtures containing these compounds are comparatively scarce in literature. Experimental data of pure fatty acid methyl esters (DSC) [4], of binary mixtures of ethyl and methyl esters [7–10] and of ternary mixtures of ethyl esters [11–14] were published only recently. Other published sets of experimental data include mixtures of ethyl esters and naphthenic hydrocarbons [15], aromatic hydrocarbons [16–17] and linear alkanes [18–19].

Recently, Moura-Nickel et al. [20] presented experimental *liquidus* temperature data of binary and ternary mixtures formed by either ethyl palmitate or ethyl stearate with n-hexadecane. However, no detailed information was provided about the solid phase. Chabane et al. [21] also published experimental SLE data of the system formed by ethyl myristate and n-hexadecane.

The objective of this work is to determine experimental solid–liquid equilibrium phase diagrams of binary mixtures containing an ethyl ester (ethyl oleate, ethyl laurate, ethyl myristate, ethyl palmitate or

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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 laurate	Sigma Aldrich	≥0.98
Ethyl myristate	Sigma Aldrich	≥0.99
Ethyl palmitate	Sigma Aldrich	≥0.99
Ethyl stearate	Sigma Aldrich	≥0.99
n-hexadecane	Sigma Aldrich	≥0.99
n-decane[a]	Sigma Aldrich	≥0.99
Indium[a,b]	Perkin Elmer	0.9999
Cyclohexane[a]	Merck	≥0.99

[a] – Compounds used only for calibrating the DSC apparatus.
[b] – Calibration standard.

ethyl stearate, compounds commonly found in ethylic biodiesel [6]) and n-hexadecane, a linear paraffin typical the alkane fraction present in conventional diesel and in aviation fuel [22]. All systems were analyzed through differential scanning calorimetry (DSC), with the simultaneous determination of the *liquidus* line (i.e., the temperature of the onset of solid phase formation from a liquid phase with definite composition) and of other transitions in solid phase. This technique has been extensively used to analyze similar mixtures [23]. To the best of our knowledge, no experimental data set for the binary systems containing ethyl oleate or ethyl laurate and n-hexadecane has been reported in literature. The solid–liquid equilibrium was modeled considering different descriptions of the liquid-phase – viz., ideal mixture and UNIFAC-Dortmund [24–25] – and considering different polymorphs in the solid phase. Simple eutectic behavior was considered in all modeling scenarios.

2. Experimental section

2.1. Materials

Sources and purities of the compounds used in this work – ethyl oleate (1), ethyl laurate (2), ethyl myristate (3), ethyl palmitate (4), ethyl stearate (5) and n-hexadecane (6) – are presented in Table 1. Experiments were conducted in a differential scanning calorimeter model DSC 8500 (PerkinElmer) calibrated using indium, cyclohexane and n-decane; The purities and sources of compounds used to calibrate the apparatus are also presented in Table 1. Masses were measured in a Sartorius balance with 220 g weighing capacity and 0.1 mg readability.

2.2. Methods

The experimental procedure to obtain the enthalpy-temperature profile through Differential Scanning Calorimetry (DSC) was analogous to that used in previous works [11–15,19]. In summary, it consists of cycles of heating, cooling and heating. Heating ramps were limited by approximately 15 K above the highest pure component melting temperature. Cooling ramps were limited by approximately 25 K below the lowest pure component melting temperature. Heating and cooling ramp rates were 1.0 K min^{-1}. Samples were equilibrated for 5 min between cooling and heating ramps. High purity nitrogen (99.99%) was fed at a rate of 50 mL min^{-1}.

The phase transition peak apex, located in the intersection of the tangents to the peak slopes, identifies the corresponding transition temperature [15,19]. For partially superimposed peaks, phase transition temperatures were taken as the temperature of the absolute minimum of the heat flow in the heating thermogram, or obtained through the mathematical deconvolution of the corresponding curves.

3. Modeling

Following previous works, the *liquidus* line temperature was

Table 2
Fusion properties of polymorphs of the studied compounds as determined by DSC and/or estimated from heating thermograms. Melting temperatures (T_f) and enthalpies (ΔH_f) obtained at atmospheric (uncontrolled) pressure 0.1 MPa.[a]

Compound	Formula	Polymorph	Type	Method A			Method B		
				T_f/K	ΔH_t/kJ·mol^{-1}	$\Delta H_{f\ total}$/kJ·mol^{-1} [d,e]	T_f/K	ΔH_t/kJ·mol^{-1}	$\Delta H_{f\ total}$/kJ·mol^{-1} [d,e]
Ethyl oleate (EO)	$C_{20}H_{38}O_2$	EO-1	Metastable	251.98	2.12	2.12	–	–	–
		EO-2	Stable	254.00	47.41	49.53	–	–	
Ethyl laurate (EL)[c]	$C_{14}H_{22}O_2$	EL-1	Metastable	272.56	25.18	25.18	272.23	23.73	23.73
		EL-2	Metastable	272.66	11.2	36.38	272.66	10.54	34.27
		EL-3	Stable	273.00	2.56	38.94	272.95	4.00	38.27
Ethyl myristate (EM)	$C_{16}H_{32}O_2$	EM-1	Metastable	286.96	21.25	21.25	286.50	15.71	15.71
		EM-2	Metastable	287.23	10.65	31.90	286.65	10.65	26.36
		EM-3	Stable	287.42	13.65	45.55	287.50	18.79	45.15
Ethyl palmitate (EP)[c]	$C_{18}H_{36}O_2$	EP-1	Metastable	294.27[b]	0.34	0.34	–	–	–
		EP-2	Stable	297.65	53.83	54.17	–	–	
Ethyl stearate (ES)	$C_{20}H_{40}O_2$	ES-1	Metastable	302.72	0.20	0.20	–	–	–
		ES-2	Metastable	303.49	0.40	0.60	–	–	–
		ES-3	Metastable	304.86	1.85	2.45	–	–	–
		ES-4	Stable	307.35	56.73	59.18	–	–	–
n-hexadecane (HD)	$C_{16}H_{34}$	HD-1	Metastable	291.62	6.68	6.68	291.93	24.32	24.32
		HD-2	Metastable	292.46	31.57	38.25	292.39	18.24	42.56
		HD-3	Stable	292.64	12.39	50.64	292.70	7.65	50.21

[a] – Standard uncertainty u is u(T) ≈ 0.3 K. u(T) was calculated by considering several analyses of the same sample.
[b] – Exothermic peak, which indicates a non-equilibrium transformation.
[c] – Results from Robustillo et al. [15,19].
[d] – Cumulative values, i.e., the transition enthalpy values of the metastable polymorphs at lower temperatures is added to determine the melting enthalpy of each polymorph.
[e] – The relative experimental uncertainty on melting enthalpy data is u(H)/H ≈ 0.03.