



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

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ABSTRACT

Biodiesel is a liquid mixture of fatty acid esters obtained through the reaction between fats or oils and alcohols. At low temperatures, the esters that constitute biodiesel tend to crystallize, which may be particularly critical for the biodiesel produced from ethanol, process little used or studied, although promising, since ethanol can also be obtained from biomass sources. In this work, an experimental study of solid–liquid equilibrium of ternary mixtures of ethyl oleate, ethyl laurate and ethyl palmitate 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 oleate and ethyl laurate as well as ethyl laurate and ethyl palmitate present eutectic points at approximately 80% M ethyl oleate and 90% M ethyl laurate, respectively, indicating immiscibility in solid phase. The difference between the melting points in the case of the system ethyl oleate and ethyl palmitate causes ethyl oleate to act primarily as a solvent, being thus difficult to observe the eutectic point for this binary. Such results show that the solid–liquid phase equilibrium of these ternary mixtures cannot be seen as a simple extension of the solid–liquid equilibrium of the binary mixtures. The experimental results were also modeled considering that the liquid phase can be described by the Flory–Huggins activity model, with excellent agreement.

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1. Introduction

Biodiesel is essentially a mixture of fatty acid alkyl ester components obtained by reaction between fats or oils and alcohol in an alkaline medium, the production of which has been stimulated in recent years due to economic reasons and environmental legislation [1]. There are a wide variety of raw materials containing the glycerides necessary for the production of biodiesel, such as rapeseed, soy, palm and canola oils or animal fat. The cost of the raw materials, which could be directed to the food industry or for direct consumption instead of biodiesel production, is the main limitation to a more widespread use of biodiesel [2]. The use of waste oil or cheap and non-edible oils and fats can help minimize this problem, but the formulation of a biodiesel must conform to a number of standards before approval for commercialization. At low temperatures, solid phases or a second liquid phase can be formed, and this may, in some cases, be an impediment to the use of biodiesel [3]. This fact may be particularly critical in the biodiesel produced from

ethyl alcohol, process little used or studied, albeit promising, since ethanol can also be obtained from biomass sources.

Several factors can impact biodiesel phase behavior and consequently cold temperature operability and handling. One of them is the type of feedstock used in production and the alcohol from which it is formed, which determines the biodiesel composition. Most sources have more appreciable quantities of stearic (C18:0), oleic (C18:1) and linoleic (C18:2) acids; coconut, with a predominance of lauric acid (C12:0) and myristic (C14:0), as well as palm, with a predominance of palmitic acid (C16:0), are exceptions [4]. Each fatty acid is indicated by the number of carbons and the number of double bonds, so C18:1 indicates a fatty acid with 18 carbon atoms and one double bond.

Biodiesel with a high concentration of saturated fatty acids esters, in spite of its better combustion properties, has a worse behavior at low temperatures due to the tendency of esters to crystallize [3]. In addition, biodiesel with a higher saturated fatty ester content undergoes wax crystal formation and begins to gel at significantly higher temperatures than those containing higher amounts of unsaturated fatty esters. Moreover, the longer the carbon chains in the biodiesel, the worse the low-temperature properties [5].

Biodiesel behavior under low-temperature conditions is specified by cold properties. The basic ones are the cloud point (CP)

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List of symbols*Latin letters*

a_i^L	activity of compound i in liquid phase
$\Delta_{fus}C_{P_i}$	change in the constant pressure heat capacity in the fusion of compound i ($J mol^{-1} K^{-1}$)
$\Delta_{fus}H_i$	enthalpy of fusion of compound i ($J mol^{-1}$)
f_i^L	fugacity of pure compound i in liquid phase (Pa)
f_i^S	fugacity of pure compound i in solid phase (Pa)
R	gas constant ($8.314 J mol^{-1} K^{-1}$)
T	temperature (K)
T_{f_i}	fusion temperature of compound i (K)
T_e	eutectic temperature (K)
T_t	solid phase transition temperature (K)
v_i	molar volume of pure liquid compound i
x_i	molar fraction of compound i in liquid phase
z_i	molar fraction of compound i in solid phase

Greek letters

ϕ_i	volume fraction of compound i
γ_i^L	activity coefficient of compound i in liquid phase
γ_i^S	activity coefficient of compound i in solid phase
χ_{ij}	Flory Huggins interaction parameter between compounds i and j

and the pour point (PP). Generally, the cloud point corresponds to the onset temperature at which dissolved n -paraffins are no longer completely soluble in a fuel, precipitating as a second phase and giving the fluid a cloudy appearance [6–9]; for biodiesel, the molecules that may aggregate and are susceptible to form crystals are the fatty acid alkyl esters. The pour point is the handling temperature at which a fuel stops flowing. It is reached when the precipitated solids have a visible size ($\sim 0.5 \mu m$) and the subsequent cooling accelerates their growth and form a larger structure [6,10,11]. Biodiesel has cloud and pour points between 15 and 25 °C higher than those of conventional diesel [12]. Conventional diesel causes problems of wax precipitation only when the ambient temperature is below the cloud point or pour point, which is not a common situation [10,13].

Both CP and PP can be easily measured in laboratory. Nevertheless, such properties do not predict temperature limits at which operability problems may be expected to occur in real tanks and fuel systems after prolonged exposure [14]. Consequently, laboratory-scale tests such as the cold filter plugging point (CFPP) or the low temperature flow test (LTFT), whose results can be correlated with field data, are used. They correspond to the lowest temperature at which solids plug a filter through which chilled fuel is pumped; the differences between them are the cooling rates and filters used.

The importance of cold properties mentioned above highlight the relevance of studying the solid–liquid equilibrium (SLE) of biodiesel and its components to understand biodiesel behavior at low temperatures. Concerning the thermodynamic modeling of these mixtures, there are several factors that hinder solid–liquid equilibrium phase prediction. One of them is the existence of the polymorphism phenomenon [15], i.e., the existence of two or more crystalline forms of a same compound, with different melting points [16]. This phenomenon is caused by a change in the sequence of packing of the greater carbon number chain in a particular direction. This change is only noticeable in a 3D arrangement of unit cells and takes place only when the interaction energy between different layers is weak enough to promote the change [17]. The second factor is the scarcity of experimental solid–liquid phase equilibrium data of mixtures of fatty acid methyl or ethyl esters found in the literature, which are necessary to check the reliability of

Table 1

Fatty acid esters found in the literature whose experimental (solid + liquid) equilibrium data were determined.

Author	Systems studied
Francis and Piper [19]	Even and odd carbon content fatty acids, methyl and ethyl esters from C ₁₂ to C ₄₆ (carbon content of acid)
Lutton and Hugenberg [20]	MeC16:0 + MeC18:0 EtC16:0 + EtC18:0
Dörfler and Pietschmann [21]	MeC15:0 + MeC16:0 MeC15:0 + MeC17:0 MeC15:0 + MeC19:0
Lockemann and Schlünder [22]	MeC14:0 + MeC16:0
Imahara et al. [4]	MeC12:0 + MeC16:0 MeC14:0 + MeC16:0 MeC16:0 + MeC18:0 MeC16:0 + MeC18:1 MeC16:0 + MeC18:2 MeC18:0 + MeC18:1 MeC18:0 + MeC18:2 MeC18:1 + MeC18:2 MeC16:0 + MeC18:0 + MeC18:1 + MeC18:2
Lopes et al. [23]	EtC12:0 + EtC14:0 EtC12:0 + EtC16:0 EtC12:0 + EtC18:0
Knothe and Dunn [24]	Melting points of pure methyl and ethyl esters
Boros et al. [25]	EtC18:0 + EtC8:0 EtC18:0 + EtC10:0 EtC18:0 + EtC12:0 EtC18:0 + EtC14:0 EtC18:0 + EtC16:0 EtC18:0 + EtC18:1 EtC18:0 + EtC18:2
Coutinho et al. [26]	Commercial biodiesel sample: MeC16:0 + MeC18:0 + MeC18:1 + MeC18:2
Costa et al. [27]	MeC14:0 + MeC16:0 MeC14:0 + MeC18:0 MeC16:0 + MeC18:0
Costa et al. [28]	EtC16:0 + EtC8:0 EtC16:0 + EtC10:0 EtC16:0 + EtC12:0 EtC16:0 + EtC14:0 EtC16:0 + EtC18:1 EtC16:0 + EtC18:2

thermodynamic models. Some authors have analyzed single pure compounds and binary mixtures, but no phase diagrams of ternary systems of ethyl or methyl esters have been obtained; generally, experimental data of SLE of ternary systems are scarce in literature—a few ones are analyzed in Slaughter and Doherty [18]. Table 1 summarizes the related works found so far in the literature [4,19–28]. In this table, the prefix “Me” indicates the methyl ester of the considered acid, and the prefix “Et”, the ethyl ester.

In this work, an experimental study of solid–liquid equilibrium of ternary mixtures of ethyl oleate, ethyl laurate and ethyl palmitate was carried out using differential scanning calorimetry, which has been shown to be an adequate tool for investigating solid–liquid phase transitions [29]. Although the onset of solid phase formation (i.e., the *liquidus* line) is relatively straightforward to obtain, the treatment of ternary mixtures is still an open question in the literature and the correct interpretation of experimental data has some uncertainties and complexity by the possibility of formation of several solid phases and the occurrence of eutectic and peritectic transitions. The results obtained were also correlated using the Flory–Huggins equation.

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