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Liquid–liquid equilibria for ethyl esters + ethanol + water systems: Experimental measurements and CPA EoS modeling

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ABSTRACT

The knowledge and the capacity to describe the liquid–liquid equilibria of systems composed of fatty acid ethyl esters, ethanol and water are crucial for an adequate design of the biodiesel washing units found in the ethylic biodiesel production processes. Since limited data is available for systems of this kind, in this work measurements were carried out for fatty acid ethyl esters + ethanol + water systems containing some of the fatty acid ethyl esters most commonly found in biodiesels: ethyl linoleate + ethanol + water at 313.15 K, technical grade ethyl oleate + ethanol + water at 298.15 K and ethyl palmitate + ethanol + water at 298.15, 308.15 and 333.15 K. The experimental data were predicted with the Cubic-Plus-Association equation of state (CPA EoS). Using temperature independent interaction parameters, obtained from binary data, this equation of state was able to provide a very good prediction of the phase diagrams of the studied systems, with average global deviations of only 3.09%.

1. Introduction

Biodiesel production has received considerable attention in recent years since it is a renewable, biodegradable and non-toxic fuel. It also produces insignificant amounts of carbon dioxide or sulfur, decreasing greenhouse gases pollution [1]. Methanol has been the most commonly used alcohol to produce biodiesel. However, ethanol has received special attention in the last decade, since it is derived from renewable agricultural sources providing a reliable alternative for countries producing this alcohol in considerable quantities, such as Brazil does from sugar cane [2]. Moreover, and in contrast to what happens with biodiesel produced from methanol, ethanolic biodiesel is carbon neutral, has a higher energy density, lower pour and cloud points [3,4] and better storage properties [5].

Ethylic biodiesel, a blend of fatty acid ethyl esters (FAEEs), is produced by the transesterification (ethanolysis) reaction of a vegetable oil with an excess of ethanol, in the presence of a catalyst to increase reaction speed and yield [6]. Depending on the raw material used, this biofuel can contain more or less unsaturated fatty acids ethyl esters on its composition. For example, ethyl oleate and ethyl linoleate are the main products from soybean oil and ethyl palmitate from palm oil [7]. Among the raw materials, the oleaginous seeds with high oil content (soybean, sunflower and rapeseed seeds) have gained much attention as renewable raw materials for biodiesel production due to their relatively high yield [8,9].

After the transesterification reaction the produced ethylic biodiesel is separated from the by-product glycerol, usually by settling, and the resultant fatty acid ethyl ester stream is purified in order to fulfill quality conditions established by international standards [10]. One of the purification steps consists on the biodiesel washing with water to remove the excess of catalyst, ethanol and glycerol, which drastically reduce biodiesel quality [11,12]. The process of washing biodiesel involves mixing it with water, typically at temperatures ranging from 313.15 to 333.15 K and, subsequently, two liquid phases are formed: a water-rich phase and an ester-rich one [13].

Understanding and predicting the products distribution between the immiscible phases formed during the biodiesel washing process, in a wide temperature range, is therefore required to properly optimize operating conditions for economical and efficient ethylic biodiesel purification and alcohol recuperation processes.

Several works have been presented concerning the LLE of systems found in the biodiesel washing units, but few of them were devoted to fatty acid ethyl esters and ethanol containing systems. Di Felice et al. [14] measured the LLE of the biodiesel + water + methanol system and modeled the experimental data with the Wilson activity coefficient model. Kuramochi et al. [15] measured the LLE of the rapeseed oil methyl ester biodiesel + water pseudobinary

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Nomenclature

K_d	distribution coefficient
S	solvent selectivity
a	energy parameter in the physical term
a_0, c_1	parameters for calculating a
A_i	site A in molecule i
b	co-volume
g	simplified hard-sphere radial distribution function
k_{ij}	binary interaction parameter
P	vapor pressure
R	gas constant
T	temperature
x	mole fraction
w	mass fraction
X_{Ai}	fraction of molecule i not bonded at site A
Z	compressibility factor

Greek symbols

β	association volume
ε	association energy
η	reduced fluid density
ρ	mole density
Δ	association strength

Subscripts

c	critical
i,j	pure component indexes
r	reduced

Superscripts

assoc.	association
phys.	physical
calcd	calculated
exptl	experimental

system and of the rapeseed oil methyl ester biodiesel + water + methanol pseudoternary system at 298.15 and 318.15 K, and compared the data with predictions from several UNIFAC models. The few available literature data concerning the LLE of ternary systems containing fatty acid ethyl esters and ethanol are restricted to systems with water [16].

An alternative to the activity coefficient models to predict these complex polar mixtures is the use of the Cubic-Plus-Association equation of state (CPA EoS), which explicitly takes into account specific interactions between like (self-association) and unlike (cross-association) molecules. Oliveira et al. [17] satisfactory correlated the water solubility in different biodiesels and, taking advantage of the transferability of the CPA EoS temperature independent binary interaction parameters. The same authors also predicted the LLE data for several fatty acid esters + methanol/ethanol + glycerol/water systems [18–20] with better results than the group contribution models referred above.

Having in a previous work experimentally determined the LLE data for the ethyl laurate/ethyl myristate + ethanol + water systems at 298.15, 313.15, and 333.15 K, and compared the experimental results with predictions from the CPA EoS [16], in this work we intend to continue the characterization of the LLE for systems of interest for the ethylic biodiesel washing processes. LLE measurements were carried out for the ethyl linoleate + ethanol + water system at 313.15, for the technical grade ethyl oleate + ethanol + water system at 298.15 K and for the ethyl palmitate + ethanol + water system at 298.15, 308.15 and 333.15 K, and the CPA EoS was used to predict the measured experimental data.

2. Experimental section

2.1 Materials

Ethyl palmitate was purchased from Tecnosyn (Cajamar/SP, Brazil), and its mass purity was 99.2%. Ethyl linoleate (99.2% purity) and technical grade ethyl oleate (ethyl ester mixture) were purchased from Sigma Aldrich. Purities of all fatty acid ethyl esters were determined by gas chromatography. The technical grade ethyl oleate composition was also determined by gas chromatography and it is showed in Table 1. The solvents used were anhydrous ethanol from Merck (Germany), with a mass purity of 99.9%, acetonitrile from Vetec (Brazil), with a mass purity of 99.8%, and Tetrahydrofuran (THF) from Tedia, with a mass purity of 99.8%.

For the fatty acid ethyl esters quantification different gas and liquid chromatographic analyses were used depending on the system. Thus, for systems involving pure ethyl ester it was used the gas chromatography and for the ethyl ester mixture it was used the High Pressure Size Exclusion Chromatography (HPSEC).

Quantification of the ethyl palmitate/ethyl linoleate and ethanol systems was carried out in a Shimadzu (GC-17A) capillary gas chromatograph system with programmable pneumatics and a flame ionization detector (FID). A DB-WAX capillary column (0.25 μm, 30 m × 0.25 mm i.d) from J&W Scientific (Rancho Cordoba, CA, USA) was used, and the carrier gas was helium from White Martins (Brazil), with a mass purity of 99.9%.

In the case of technical grade ethyl oleate, the quantification was carried out in a Shimadzu VP series HPLC equipped with two LC-10ADVP solvent delivery units for binary gradient elution, a model RID10A differential refractometer, an automatic injector with an injection volume of 20 μL, a model CTO-10ASVP column oven for precision temperature control even at sub-ambient temperatures, a single HPSEC Phenogel column (100 Å, 300 mm × 7.8 mm ID, 5 mm), a Phenogel column guard (30 mm × 4.6 mm), a model SCL-10AVP system controller and LC-Solution 2.1 software for remote management.

Table 1
Technical grade ethyl oleate composition.

Ethyl ester	% Mass
Ethyl caprylate	0.02
Ethyl caprate	0.03
Ethyl laurate	2.30
Ethyl myristate	0.17
Ethyl pentadecanoate	0.02
Ethyl palmitate	8.80
Ethyl palmitoleate	0.03
Ethyl heptadecanoate	0.09
Ethyl cis-heptadec-9-enoate	0.04
Ethyl stearate	1.89
Ethyl elaidate	0.73
Ethyl oleate	74.10
Ethyl trans, trans-9,12-octadecadienoate	0.56
Ethyl linoleate	10.60
Ethyl all-trans-octadeca-9,12,15-trienoate	0.14
Ethyl arachidate	0.18
Ethyl eicosanoate	0.30