

## 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%.

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### 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	$\varepsilon$	association energy
$S$	solvent selectivity	$\eta$	reduced fluid density
$a$	energy parameter in the physical term	$\rho$	mole density
$a_0, c_1$	parameters for calculating $a$	$\Delta$	association strength
$A_i$	site $A$ in molecule $i$		
$b$	co-volume		
$g$	simplified hard-sphere radial distribution function	<b>Subscripts</b>	
$k_{ij}$	binary interaction parameter	$c$	critical
$P$	vapor pressure	$i, j$	pure component indexes
$R$	gas constant	$r$	reduced
$T$	temperature		
$x$	mole fraction	<b>Superscripts</b>	
$w$	mass fraction	assoc.	association
$X_{Ai}$	fraction of molecule $i$ not bonded at site $A$	phys.	physical
$Z$	compressibility factor	calcd	calculated
		exptl	experimental
<b>Greek symbols</b>			
$\beta$	association volume		

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] satisfactorily 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  $\mu\text{m}$ , 30 m  $\times$  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  $\mu\text{L}$ , a model CTO-10ASVP column oven for precision temperature control even at sub-ambient temperatures, a single HPSEC Phenogel column (100  $\text{\AA}$ , 300 mm  $\times$  7.8 mm ID, 5 mm), a Phenogel column guard (30 mm  $\times$  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

The water content of both phases for all systems was determined by Karl Fischer titration using a model 701 Metrohm apparatus (Switzerland) equipped with a 5 mL burette. The Karl Fischer reagent used in the titration was from Merck (Germany).

## 2.2. Apparatus and procedures

The liquid–liquid equilibria data for the systems containing pure ethyl esters (palmitate/linoleate) + ethanol + water at temperatures between 298 and 333.15 K and technical grade ethyl oleate (oleate/linoleate/palmitate/stearate/laurate) + ethanol + water at 298.15 K were determined. The binodal curve for ethyl palmitate + ethanol + water system at 298.15 K was determined by the cloud-point method following the same procedure described by Lanza et al. [21]. The tie lines were determined using glass test tubes with screw caps (32 mL). Known quantities of each component were weighed on an analytical balance with a precision of 0.0001 g (Precisa, model XT220A, Sweden), and added directly to the glass test tubes. The corresponding ethyl ester, ethanol, and water mixtures were maintained under intensive agitation for 10 min at constant temperature and pressure using a test tube shaker (Phoenix, model AP 56). The ternary mixtures were then left at rest for 24 h in a thermostatic water bath at the desired temperature, until two separate, transparent liquid phases were clearly observed. At the end of the experiment, samples were taken separately from the upper and bottom phases using syringes containing previously weighed masses of acetonitrile or THF, so as to guarantee an immediate dilution of the samples and avoid further separation into two liquid phases at ambient temperature [22].

Samples from pure ethyl esters (linoleate/palmitate) + ethanol + water systems were analyzed by gas chromatography (GC). The detector and injector temperatures were 553 K and 523 K, respectively. The column oven was maintained at 313.15 K for 8 min and subsequently submitted to the following heating program: from 313.15 to 473.15 K at a rate of 20 K min<sup>-1</sup>, maintained at 473.15 K for 8 min; from 473.15 to 483.15 K at a rate of 10 K min<sup>-1</sup>, and finally maintained at 483.15 K for 2 min. The absolute pressure of the column was approximately 114 kPa; the carrier gas flowed at a rate of 1.6 mL min<sup>-1</sup>; the linear velocity was 34 cm s<sup>-1</sup> and the sample injection volume was 1.0 μL.

In the case of technical grade ethyl oleate + ethanol + water system, the samples from the two phases were analyzed by HPSEC method. The flow rate of the mobile phase was 1.2 ml/min. Sample injection volume was 50 μL, and all the analyses were carried out at 313.15 K.

The quantitative determination for all systems was carried out using calibration curves (external calibration) obtained by using standard solutions for each system component: ethyl linoleate, technical grade ethyl oleate, ethyl palmitate and ethanol. These compounds were diluted with acetonitrile in the concentration range from 0.05 to 150 mg/mL. The analyses for each tie-line were replicated at least three times and the values reported in the present work are the averages. The water mass fractions for all systems were determined at least three times using the Karl Fisher titration and the values reported are the averages.

The distribution coefficients and the solvent selectivity were calculated according to Eqs. (1) and (2), respectively, using the experimental compositions of both phases.

$$K_{d4} = \frac{w_4^{\text{WP}}}{w_4^{\text{EP}}} \quad (1)$$

$$S_{4/i} = \frac{K_{d4}}{K_{di}} \quad (2)$$

where  $K_{d4}$  is the distribution coefficient for ethanol,  $w_4$  is its mass fraction in the water (WP) or ester (EP) phases, respectively, and

$S_{4/i}$  stands for the solvent selectivity. The solvent selectivity reflects its effectiveness in separating ethanol from the ester phase ( $i = 1$  for ethyl linoleate, for instance).

## 2.3. Thermodynamic modeling

The modeling of polar and highly non-ideal systems in wide ranges of temperature and pressure requires the use of association equations of state that explicitly take into account specific interactions between like (self-association) and unlike (cross-association) molecules. One of these equations is the Cubic-Plus-Association (CPA) equation of state, [23,24] that combines a physical contribution from a cubic equation of state, in this work the Soave–Redlich–Kwong (SRK), with an association term accounting for intermolecular hydrogen bonding and solvation effects, [25–27] originally proposed by Wertheim and used in other association equations of state such as SAFT [28].

It can be expressed in terms of the compressibility factor as:

$$Z = Z^{\text{phys.}} + Z^{\text{assoc.}} \\ = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (3)$$

where  $a$  is the energy parameter,  $b$  the co-volume parameter,  $\rho$  is the molar density,  $g$  a simplified hard-sphere radial distribution function,  $X_{A_i}$  the mole fraction of sites  $A$  in component  $i$  not bonded at any other active sites, and  $x_i$  is the mole fraction of component  $i$ .

The pure component energy parameter,  $a$ , is obtained from a Soave-type temperature dependency:

$$a(T) = a_0 [1 + c_1 (1 - \sqrt{T_r})]^2 \quad (4)$$

where  $a_0$  and  $c_1$  are regressed (simultaneously with  $b$ ) from pure component vapor pressure and liquid density data.

When CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (5)$$

and

$$b = \sum_i x_i b_i \quad (6)$$

$X_{A_i}$  is related to the association strength  $\Delta^{A_i B_j}$  between sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (7)$$

where

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp \left( \frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (8)$$

where  $\varepsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$  are the association energy and the association volume, respectively.

The simplified radial distribution function,  $g(\rho)$  is given by [29]:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \text{where} \quad \eta = \frac{1}{4} b\rho \quad (9)$$

For non-associating components, such as esters, CPA has three pure component parameters in the cubic term ( $a_0$ ,  $c_1$  and  $b$ ) while for associating components, such as water and alcohols, it has two additional parameters in the association term ( $\varepsilon$  and  $\beta$ ). In both cases, the parameters are regressed simultaneously from the vapor

pressure and liquid density data. The objective function to be minimized is the following:

$$OF = \sum_i^{NP} \left( \frac{P_i^{\text{exptl}} - P_i^{\text{calcd}}}{P_i^{\text{exptl}}} \right)^2 + \sum_i^{NP} \left( \frac{\rho_i^{\text{exptl}} - \rho_i^{\text{calcd}}}{\rho_i^{\text{exptl}}} \right)^2 \quad (10)$$

For a binary mixture composed solely of non-associating compounds, the binary interaction parameter,  $k_{ij}$  (Eq. (5)), is the only adjustable parameter.

When CPA is used for mixtures containing two self-associating compounds, combining rules for the association term are required [30,31], and in this work, the Elliott Combining Rule (ECR) [31] was used:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (11)$$

Solvation can occur in some systems containing self-associating and non-self-associating compounds, as in the case of the ethyl ester + water or ethanol mixtures investigated in this work. For this type of system, the solvation phenomena is considered as a cross-association by the CPA EoS, proposed by Folas et al. [32] where the cross-association energy ( $\epsilon^{A_i B_j}$ ) is considered to be half the value of the association energy for the self-associating component, and the cross association volume ( $\beta^{A_i B_j}$ ) is left as an adjustable parameter, fitted to the equilibrium data. In these cases, the following objective function was minimized to estimate the parameters  $k_{ij}$  and  $\beta^{A_i B_j}$ :

$$OF = \sum_i^{NP} \left( \frac{x_i^{\text{calcd}} - x_i^{\text{exptl}}}{x_i^{\text{exptl}}} \right)^2 \quad (12)$$

where single phase or all phase data can be selected during optimization of the parameter.

The association term depends on the number and type of association sites. According to the nomenclature of Huang and Radosz [33] for alcohols, the two-site (2B) association scheme is applied, which proposes that hydrogen bonding occurs between the hydroxyl hydrogen and one of the lone pairs of electrons from the oxygen atom of another alcohol molecule. For the ester family, a single association site is considered that can cross-associate with self-associating molecules. For water, a four-site (4C) association scheme is adopted, considering that hydrogen bonding occurs between the two hydrogen atoms and the two lone pairs of electrons of the oxygen of the water molecule.

The average deviations (ADs) between the experimental compositions and those estimated by the CPA EoS were calculated according to Eq. (13).

$$AD = \sqrt{\frac{\sum_i^N \sum_n^R \left[ \left( w_{i,n}^{\text{WP,exptl}} - w_{i,n}^{\text{WP,calcd}} \right)^2 + \left( w_{i,n}^{\text{EP,exptl}} - w_{i,n}^{\text{EP,calcd}} \right)^2 \right]}{2 NR}} \quad (13)$$

where AD is the average deviation for each system,  $N$  is the total number of tie lines of the corresponding system,  $R$  is the total number of components ( $R = 3$ ),  $w$  is the mass fraction,  $i$  is the component, the subscript  $n$  stands for the tie line number and the superscripts exptl and calcd refer to the experimental and calculated compositions.

### 3. Results and discussion

Table 2 shows the experimental liquid–liquid equilibrium data for pure ethyl esters (ethyl linoleate and ethyl palmitate) + ethanol + water and mixture of ethyl esters (technical grade ethyl oleate) + ethanol + water systems, at several temperatures, in percentage by mass. The type A standard uncertainties [34] of the

equilibrium compositions ranged from (0.058 to 0.082)% by mass for ethyl esters, (0.059–0.637)% for ethanol and (0.0888–0.933)% for water, with the lowest values associated with the lowest mass percentages within the composition range investigated. On the basis of the total system mass and of the phase and overall compositions, the mass balances were checked according to the procedure suggested by Marcilla et al. [35] and recently applied to fatty systems by Follegatti-Romero et al. [16] According to this procedure, the masses of both liquid phases were calculated and checked against the total initial mass used in the experimental runs. The average results obtained for the mass balance deviations of each set of experimental data are shown in Table 3. In all cases, the values were lower than 0.40%, which indicates the good quality of the experimental data.

The distribution diagram for ethanol in the ethyl palmitate and in the technical grade ethyl oleate systems, at 298.15 K, is shown in Fig. 1. The ethanol mass fraction in the aqueous phase is much larger than in the ester phase, so that its distribution coefficient is, in most cases, above 4.46 for both systems (see Table 2) and above 3.3 for all systems. Considering that the ester mass fraction in the aqueous phase is usually low, the solvent selectivity is very high; always above 50 (see Table 1). These results are similar, as expected, to the ones previously obtained for ethyl laurate/myristate + ethanol + water systems [16], indicating that water washing of biodiesel is a very effective process for extracting residual ethanol from the ester phase generated at the end of the ethanolysis reaction, without losing any significant amount of FAEEs to the extract phase.

The CPA EoS was used to predict the experimental liquid–liquid equilibria data of the selected systems. The CPA EoS was previously used with success in the prediction of the LLE of other fatty acid ethyl esters ternary systems, such as ethyl laurate/myristate + ethanol + water [16] and canola oil ethylic biodiesel + ethanol + glycerol [18], using the same set of temperature independent binary interaction and cross-association parameters.

The first step to apply the CPA EoS to the prediction of the phase equilibria of multicomponent systems is the estimation of the CPA pure compound parameters, usually through a simultaneous regression of vapor pressure and liquid density data.

As esters being non-self-associating compounds there are only three pure compound parameters to be estimated, those of the physical term ( $a_0$ ,  $c_1$  and  $b$ ). With the recent appearance of experimental data for ethyl esters vapor pressures [36] and liquid densities [37] it was possible, in a previous work of ours [38], to estimate fatty acid ethyl esters CPA pure compound parameters. The critical temperatures for the fatty acid ethyl esters were calculated from the group contribution method of Nikitin et al. [39], that was previously assessed to be the best to compute this property for ethyl esters [40]. The parameters obtained are presented at Table 4 as well as liquid densities and vapor pressures deviations, which are inferior to 5% for both properties.

For ethanol, the five CPA pure parameters were previously established while performing a systematic study on the pure compound parameters for the n-alcohol family, from methanol to n-eicosanol, using the 2B association scheme [41]. These parameters were recently used for the description of the LLE of the system containing canola oil biodiesel, ethanol and glycerol [18] and of the VLE of fatty acid ester + ethanol systems at atmospheric pressure [42] and at near or supercritical conditions [43].

The five CPA pure compound parameters for water were previously established considering the 4C scheme for water [44], and were used to model the liquid–liquid equilibria data of ethyl laurate/ethyl myristate + ethanol + water systems and the phase equilibria of other water containing systems [17,24,45,46].

The remaining parameters to be obtained are the binary interaction parameters,  $k_{ij}$ 's, and the cross-association volumes,  $\beta_{ij}$ 's.

**Table 2**

Experimental liquid–liquid equilibria data for the ternary systems ethyl ester (i) + ethanol (4) + water (5) at temperatures between 298.15 and 333.15 K.

Ethyl ester (i)	T (K)	Overall composition			Water-rich phase			Ester-rich phase			$K_{d4}$ <sup>a</sup>	$S_{4/i}$ <sup>b</sup>	
		100 $w_i$	100 $w_4$	100 $w_5$	100 $w_i$	100 $w_4$	100 $w_5$	100 $w_i$	100 $w_4$	100 $w_5$			
Linoleate (1)	313.15	18.860	61.630	19.510	4.391	71.860	23.749	83.091	12.571	4.338	5.716	108.170	
		23.440	53.190	23.370	2.113	67.291	30.596	89.252	8.192	2.560	8.214	346.965	
		27.830	43.200	28.980	0.672	57.810	41.518	92.163	5.481	2.360	10.547	1446.540	
		36.810	26.260	36.930	0.312	39.514	60.174	94.530	3.181	2.320	12.422	3763.591	
		45.380	10.050	44.570	0.121	18.690	81.189	96.811	1.482	1.710	12.611	10090.215	
		51.360	0.000	48.640	0.081	0.000	99.919	99.220	0.000	0.800			
Oleate (2)	298.15	18.427	63.221	18.352	4.730	74.040	21.230	87.391	11.470	1.139	6.455	119.264	
		22.728	54.618	22.654	1.780	68.030	30.190	91.130	8.441	0.429	8.059	412.618	
		26.719	44.413	28.868	0.380	59.370	40.250	92.662	6.971	0.367	8.517	2076.778	
		36.223	29.109	34.668	0.200	44.520	55.280	95.801	4.030	0.169	11.047	5291.376	
		42.524	15.290	42.185	0.100	23.890	76.010	98.640	1.250	0.110	19.112	18852.077	
		51.412	0.000	48.588	0.050	0.000	99.950	99.280	0.000	0.720			
Palmitate (3)	298.15	15.290	68.960	15.750	7.100	74.140	18.760	81.680	16.600	1.720	4.466	51.381	
		20.020	59.960	20.020	2.568	71.252	26.180	87.227	11.743	1.030	6.068	206.098	
		25.130	49.800	25.070	0.770	63.560	35.670	90.665	8.631	0.704	7.364	867.105	
		30.053	39.964	29.983	0.172	55.538	44.290	93.524	6.012	0.464	9.238	5023.031	
		34.890	29.680	35.430	0.080	45.090	54.830	95.176	4.521	0.303	9.973	11865.422	
		40.520	19.840	39.640	0.045	31.535	68.420	96.598	3.122	0.280	10.101	21682.810	
		44.496	10.459	45.045	0.028	16.412	83.560	97.429	2.361	0.210			
		49.530	0.000	50.470	0.009	0.000	99.991	99.856	0.000	0.144			
		308.15	20.100	59.900	20.000	3.109	72.317	24.574	85.628	12.161	2.211	5.947	163.768
	25.201		49.702	25.097	0.902	65.230	33.868	91.768	7.419	0.813	8.793	894.753	
	25.302		42.701	31.997	0.303	56.105	43.592	94.118	5.375	0.507	10.438	3245.082	
	34.901		29.703	35.396	0.201	44.020	55.779	95.736	3.858	0.406	11.410	5434.658	
	40.503		19.820	39.677	0.093	31.385	68.522	96.913	2.720	0.367	11.537	12042.643	
	44.501		10.510	44.989	0.072	16.756	83.173	98.500	1.180	0.319	14.195	19510.167	
	333.15	25.140	49.770	25.090	1.705	63.070	35.225	75.221	19.000	5.779	3.319	146.448	
		30.040	39.950	30.010	0.472	54.187	45.341	81.944	14.021	4.035	3.865	670.952	
		34.900	29.680	35.420	0.112	43.025	56.862	85.644	11.090	3.266	3.880	2966.663	
		40.540	19.820	39.640	0.058	30.124	69.818	89.346	7.463	3.191	4.036	6217.937	
44.460		10.540	45.000	0.037	17.187	82.776	92.749	4.461	2.790	3.853	9657.737		
49.610		0.000	50.390	0.016	0.000	99.984	98.109	0.000	1.891				

<sup>a</sup>  $K_{d4}$  is the ethanol distribution coefficient according to Eq. (1).<sup>b</sup>  $S_{4/i}$  is the solvent selectivity according to Eq. (2).**Table 3**

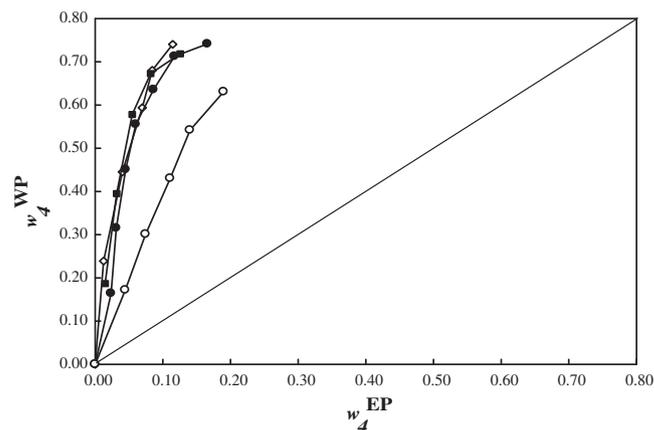
Deviations for the global mass balance of the phase compositions.

System	100 $\delta^a$
Ethyl linoleate + ethanol + water at 313.15 K	0.32
Technical grade ethyl oleate + ethanol + water at 298.15 K	0.29
Ethyl palmitate + ethanol + water at 298.15 K	0.39
Ethyl palmitate + ethanol + water at 308.15 K	0.25
Ethyl palmitate + ethanol + water at 333.15 K	0.18

<sup>a</sup> Relative deviation of the overall mass balance, calculated by  $\delta = \frac{1}{N} \sum_{n=1}^N |(m^{EP} + m^{WP} - m^{OS})/m^{OS}|$ , where  $m^{EP}$  is the calculated mass of the ester-rich phase,  $m^{WP}$  is the corresponding value of the water-rich phase,  $m^{OS}$  is the total mass of the system, and  $n$  is the tie line number.

Their values were computed using their transferability character, previously demonstrated [16,19].

Binary interaction parameters previously obtained from binary phase equilibria data were used in the prediction of the LLE of the ternary systems here measured. The possible subsystems comprise fatty acid ethyl ester + ethanol, fatty acid ethyl ester + water and ethanol + water mixtures. The binary interaction parameters,  $k_{ij}$ 's, between ethyl esters and ethanol were obtained from a linear correlation with the ethyl ester carbon number and the  $\beta_{ij}$  for this binary was fixed to 0.1. These correlations and the  $\beta_{ij}$  constant value were previously established by Oliveira et al. [42] when correlating isothermal vapor–liquid equilibria of ethanol + ester systems, with esters from 5 up to 19 carbons. A similar approach was also proposed by Oliveira et al. [17] for the  $k_{ij}$ 's and for the  $\beta_{ij}$ 's between fatty acids and water when modeling the water solubility in several fatty acid esters.



**Fig. 1.** Distribution diagram for: (–◇–), technical grade ethyl oleate + ethanol + water at 298.15 K; (–■–), ethyl linoleate + ethanol + water system at 313.15 K; (–●–), ethyl palmitate + ethanol + water at 298.15 K and (–○–) at 333.15 K.

In the case of the ethanol + water binary, the  $k_{ij}$  parameter was taken from the work by Follegatti-Romero et al. [16] who used a 4C scheme for correlating the corresponding liquid–liquid equilibria data. All parameters mentioned above are given in Table 5.

Having the CPA pure compound parameters, the binary interaction parameters and the cross-association volumes, it was then possible to predict the measured liquid–liquid equilibria. Technical

**Table 4**  
CPA pure compound parameters, critical temperatures and modeling results.

Compound	$T_c$ (K)	$a_0$ (J m <sup>3</sup> mol <sup>-2</sup> )	$c_1$	$b \times 10^5$ (m <sup>3</sup> mol <sup>-1</sup> )	$\varepsilon$ (J mol <sup>-1</sup> )	$\beta$	100 AAD <sup>d</sup>	
							$P$	$\rho$
Ethyl linoleate <sup>a</sup>	785.19	11.99	1.82	36.13	–	–	0.27	0.26
Ethyl oleate <sup>a</sup>	771.07	14.36	1.34	37.64	–	–	6.00	0.61
Ethyl palmitate <sup>a</sup>	766.41	9.82	2.12	33.80	–	–	0.37	0.17
Ethyl laurate <sup>a</sup>	719.13	7.00	1.92	26.12	–	–	4.29	0.33
Ethanol <sup>b</sup>	514.70	0.68	0.94	4.75	21,336	0.0190	0.35	0.51
Water <sup>c</sup>	647.30	0.12	0.67	1.45	16,655	0.0692	1.72	0.82

<sup>a</sup> Parameters taken from Follegatti-Romero et al. [38].

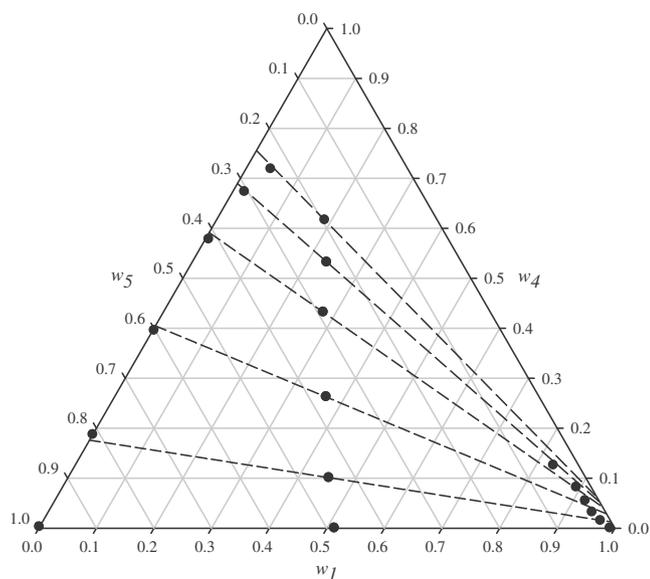
<sup>b</sup> Parameters taken from Oliveira et al. [41].

<sup>c</sup> Parameters taken from Oliveira et al. [44].

<sup>d</sup> AAD is calculated by:  $AAAD = \frac{1}{N} \sum_{i=1}^N |(\text{expt}_i - \text{calcd}_i) / \text{expt}_i|$ .

**Table 5**  
Binary interaction and cross-association parameters used to model the multicomponent systems LLE.

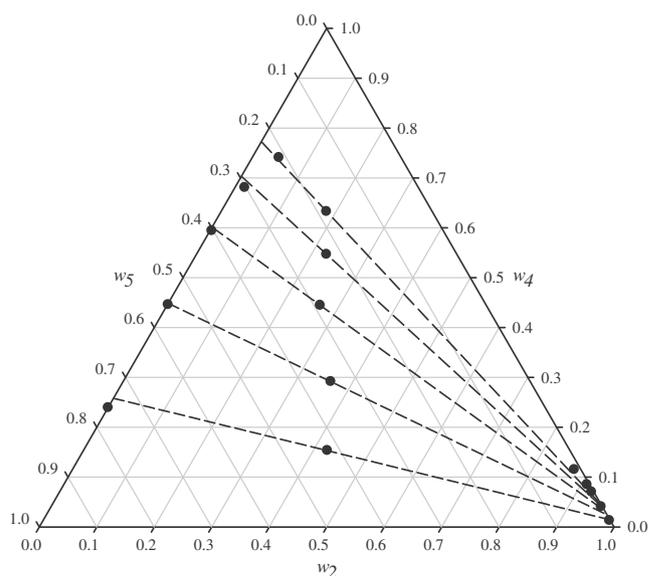
$k_{ij}$ (Unsaturated fatty acid ester/ethyl stearate + ethanol) [42]	–0.0260
$k_{ij}$ (Ethyl palmitate + ethanol) [42]	–0.0200
$k_{ij}$ (Ethyl laurate + ethanol) [42]	–0.0830
$k_{ij}$ (Unsaturated fatty acid ester/ethyl stearate + water) [17]	–0.0602
$k_{ij}$ (Ethyl palmitate + water) [17]	–0.0874
$k_{ij}$ (Ethyl laurate + water) [17]	–0.1720
$\beta_{ij}$ (Fatty acid ester + ethanol) [42]	0.1000
$\beta_{ij}$ (Fatty acid ester + water) [17]	0.2010
$k_{ij}$ (Ethanol + water) [16]	–0.1000



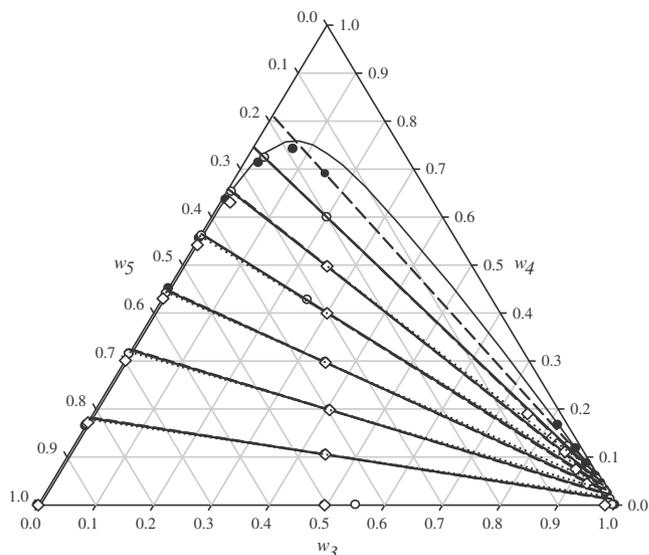
**Fig. 2.** Liquid–liquid equilibrium for the system ethyl linoleate (1) + ethanol (4) + water (5): experimental (●) and CPA results (–) at 313.15 K.

grade ethyl oleate + ethanol + water system was treated as a system of seven compounds, being the ethyl oleate considered as a mixture of five compounds according to its composition presented at Table 1: ethyl oleate, ethyl linoleate, ethyl palmitate, ethyl laurate, and ethyl stearate.

The CPA EoS prediction results of the phase diagrams measured in this work are reported in Figs. 2–4. Saturation curves and tie lines were properly predicted by the CPA EoS for all ternary and multicomponent systems in the selected temperature range, using temperature independent binary interaction and cross-association parameters correlated from binary phase equilibria data. A somewhat higher deviation can be observed in the region close to the plait point. Average deviations between



**Fig. 3.** Liquid–liquid equilibrium for the system ethyl oleate (2) + ethanol (4) + water (5): experimental (●) and CPA results (–) at 298.15 K.



**Fig. 4.** Liquid–liquid equilibrium for the system containing ethyl palmitate (3) + ethanol (4) + water (5): experimental (●), binodal curves (see Table S1) and CPA results (–) at 298.15 K, experimental (○) and CPA results (–) at 308.15 K and experimental (◇) and CPA results (···) at 333.15 K.

**Table 6**  
Average deviations (ADs) between the experimental and CPA EoS phase compositions.

System	100AD <sup>a</sup>
Technical grade ethyl oleate + ethanol + water at 298.15 K	2.41
Ethyl linoleate + ethanol + water at 313.15 K	2.77
Ethyl palmitate + ethanol + water at 298.15 K	3.20
Ethyl palmitate + ethanol + water at 308.15 K	1.79
Ethyl palmitate + ethanol + water at 333.15 K	5.28
Average global deviation	3.09

<sup>a</sup> Eq. (13).

the experimental and calculated compositions in both phases are shown in Table 6. Most deviations are within the range 2.41–5.28% and a global average deviation of 3.09% was obtained.

Considering the ethyl palmitate system for which LLE measurements were performed for three different temperatures, it was observed that the two-phase region suffers no significant change with temperature, as showed in Fig. 4 and previously observed for other similar systems [16]. In the same figure also is showed the binodal curve for the ethyl palmitate system, this curve indicate the two phase region at 298.15 K. (The experimental data used are presented in the Supporting information, Table S1.)

The modeling results here presented show that the CPA EoS is an useful predicting tool to be applied in the design and optimization of ethylic biodiesel washing units. The experimental results confirm that water washing is a very effective procedure for purifying biodiesel from polar contaminants, such as ethanol, glycerol and catalyst.

#### 4. Conclusions

As part of an ongoing work to characterize the LLE of fatty acid ethyl esters + ethanol + water, that have been overlooked by researchers, new experimental equilibrium data were measured in this work for ethyl linoleate/technical grade ethyl oleate/palmitate + ethanol + water systems at temperatures between 298.15 and 333.15 K.

High ethanol distribution coefficients and very high solvent selectivities show that water washing is a very effective alternative to remove ethanol from ester phase.

The experimental data were successfully predicted with the Cubic-Plus-Association equation of state (CPA EoS), using temperature independent and transferable binary interaction parameters, with global average deviations between the experimental data and the calculated compositions of only 3%.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2011.12.056.

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