Liquid–liquid equilibria for ternary systems containing ethyl esters, ethanol and glycerol at 323.15 and 353.15 K

Luis A. Follegatti-Romero [a], Mariana B. Oliveira [b], Fabio R.M. Batista [a], Eduardo A.C. Batista [a], João A.P. Coutinho [b], Antonio J.A. Meirelles [a,*]

[a] ExTrAE, Laboratory of Extraction, Applied Thermodynamics and Equilibria, Department of Food Engineering, Faculty of Food Engineering, University of Campinas – UNICAMP, 13083-862, Campinas, SP, Brazil
[b] CICECO, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

ABSTRACT

The knowledge and the capacity to describe the phase equilibria of systems composed by transesterification products are very important for an adequate design and operation of biodiesel production and purification facilities. Despite their importance for the production of ethylic biodiesel, fatty acid ethyl ester + ethanol + glycerol systems have been, up to now, object of less attention than the corresponding systems formed during biodiesel production using methanol.

In this work, new experimental measurements were performed for the liquid–liquid equilibria of the systems ethyl linoleate/ethyl oleate/ethyl palmitate/ethyl laurate + ethanol + glycerol at 323.15 and 333.15 K. It is shown that the Cubic-Plus-Association Equation of State (CPA EoS) can successfully predict the new experimental data with global average deviations inferior to 6%.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel is at the front line of the new energy solutions to the environmental, political and economical problems related to the use of petroleum based fuels [1]. It can be mixed in all proportions with regular diesel with no motor changes, it is easy to store and transport, has a more favorable combustion profile, it is biodegradable, non-toxic and provides lower emissions profiles [2,3]. Biodiesel consists on a blend of fatty acid esters that are industrially produced through the transesterification of a vegetable oil or a fat with an alcohol, usually using a basic catalyst to increase the reaction speed and yield [2].

Methanol is the most commonly used alcohol considering its low price and chemical advantages in the process [3,4], although alternatively other alcohols may be used in the esterification route [5,6]. In fact, bearing in mind that methanol is mainly obtained from non-renewable sources such as natural gas or coal, methylic biodiesel production and use is not completely carbon neutral concerning environmental problems [7,8]. Biodiesel produced from ethanol is entirely based on renewable agricultural sources, has a superior dissolving capability, lower toxicity, higher heat content, higher cetane index and lower cloud and pour points [5,9,10]. Considering these advantages, its use is a quite promising route in the case of biodiesel production in Brazil, where ethanol is produced in large quantities from sugar cane [11].

The transesterification reaction occurs in a multiphase reactor where the oil reacts with ethanol to produce fatty acid ethyl esters and glycerol [12]. The initial ethanol–vegetable oil two phase reactive mixture [13] changes into an ethanol–glycerol–fatty acid ethyl ester (biodiesel) partially miscible system. Due to the restricted solubilities between FAEEs and glycerol, the current of products leaving the reactor is a biphasic stream composed of the glycerol rich phase and ethyl esters rich phase. The unreacted ethanol is distributed between these two phases [14].

Understanding and predicting the products distribution between the immiscible phases in a broad range of thermodynamics conditions is required to properly evaluate operating conditions of existing or new ethylic biodiesel production and purification processes. Operation costs can be reduced and biodiesel quality assured, subsequently increasing the industrial feasibility of the process and biodiesel acceptance among consumers. Liquid–liquid equilibria of ternary systems composed of fatty acid esters (usually fatty acid methyl esters), glycerol and alcohols have recently been the focus of several research works. Csernica et al. [15] experimentally determined the LLE data for a commercial biodiesel + glycerol + methanol system. Negi et al. [16] and Andreatta et al. [17]

* Corresponding author. Tel.: +55 19 3521 4037; fax: +55 19 3521 4027.
E-mail address: tomze@fea.unicamp.br (A.J.A. Meirelles).

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
1	ethyl linoleate
2	ethyl oleate
3	ethyl palmitate
4	ethyl laurate
5	ethanol
6	glycerol

Superscripts

assoc.	association
phys.	physical
calcd	calculated
exptl	experimental

---

measured the LLE of the methyl oleate + glycerol + methanol system and compared the experimental data with predictions from different UNIQUAC models and the Association Group Contribution Equation of State (GCA EoS). Two versions of the UNIFAC model were also used by Tizvar et al. [18] to predict their experimental results for the LLE of the system methyl oleate + glycerol + methanol + hexane. And finally, França et al. [19] and Machado et al. [20] measured the LLE of the castor oil methyl ester biodiesel + glycerol + methanol/ethanol systems at 298.15 and 333.15 K and compared the experimental data with predictions from the UNIQUAC and the NRTL models, respectively.

Fatty acid ethyl esters containing systems have been much less studied. Up to now, LLE data have only been presented for the soybean oil ethylic biodiesel + ethanol + glycerol [21] and for the canola oil based ethyl ester biodiesel + ethanol + glycerol [22] systems.

An alternative to the usually applied activity coefficient models to predict systems with polar compounds with strong associative interactions found at the biodiesel production and purification processes is the use of association equations of state. Recently, Barreau et al. [23] used the Group Contribution Statistical Associating Fluid Theory (SAFT) to describe the measured LLE data for the methyl oleate + glycerol + methanol system.

A much simpler and reliable alternative was recently proposed by Coutinho and co-workers [24–30] using the Cubic-Plus-Association Equation of State (CPA EoS). The CPA EoS was applied to describe the LLE of the above mentioned multicomponent systems showing a similar, if not even better, performance than the group contribution methods referred above, using no more than two, transferable and temperature independent binary interaction parameters [27].

The objective of this work was to increase the available liquid–liquid equilibria data for systems containing fatty acid ethyl esters, ethanol and glycerol of interest for the production of ethylic biodiesel, in particular the equilibria data for systems containing ethyl linoleate/ethyl oleate/ethyl palmitate/ethyl laurate + ethanol + glycerol at 323.15 and 353.15 K.

The excellent extrapolation and predictive performance of the CPA EoS was also used here to predict the measured LLE data, using binary interaction parameters previously established from binary phase equilibria data.

2. Experimental section

2.1. Materials

Ethyl palmitate and ethyl laurate used in this work were purchased from Tecnosyn (Cajamar/SP, Brazil), and their mass purities were 99.5%, and 99.3%, respectively. Ethyl oleate and ethyl linoleate used were purchased from Sigma Aldrich, with mass purities of 77.5% and 97%, respectively. The purities of all fatty acid ethyl esters were determined by Gas Chromatography. In case of the technical grade ethyl oleate the main contaminant was ethyl linoleate. The solvents used were anhydrous ethanol from Merck, with a mass purity of 99.9%, and tetrahydrofuran (THF) from Tedia, with a mass purity of 99.8%. The glycerol used was purchased from Merck, with mass purity of 99.5%.

Ethyl esters, ethanol and glycerol 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.

2.2. Apparatus and procedures

The liquid–liquid equilibria data for the systems containing ethyl linoleate/ethyl oleate/ethyl palmitate/ethyl laurate + ethanol + glycerol were determined at 323.15 and 353.15 ± 0.1 K. Tie lines were determined using glass test tubes with screw caps (32 and 10 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 mixture of ethyl ester, ethanol and glycerol was maintained under intensive agitation for 10 min at constant temperature and pressure using a test tube shaker (Phoenix, model AP 56). The ternary mixture was 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 and diluted immediately with THF to guarantee an immediate dilution of the samples and avoid further separation into two liquid phases at ambient temperature. It was used the same procedure described in a previous work by Follegatti-Romero et al. [31].

Samples from the two phases were analyzed by liquid chromatography (HPLC). The quantitative determination was carried out using calibration curves (external calibration) obtained using standard solutions for each system component: ethyl esters, ethanol, and glycerol. These compounds were diluted with THF in the concentration range from 0.5 to 100 mg/mL. The experimental data for each tie-line were replicated at least three times and the values reported in the present work are the average ones. The mass fractions of ethyl esters, ethanol and glycerol were determined from the areas of the corresponding HPSEC chromatographic peaks, adjusted by the response factors obtained by previous calibration.

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

$$K_{d5} = \frac{w_5^{GP}}{w_5^{EP}} \tag{1}$$

$$S_{5/i} = \frac{K_{d5}}{K_{di}} \tag{2}$$

where K_{d5} is the distribution coefficient for ethanol, w_5 is its mass fraction in the glycerol (GP) or ester (EP) phases, respectively, and $S_{5/i}$ stands for the solvent selectivity. Note that glycerol can be considered as a solvent able to extract ethanol from the ester phase and, in this way, the solvent selectivity reflects its effectiveness in recovering ethanol from the lipophilic phase ($i = 1$–4 for ethyl esters).

2.3. Thermodynamic modeling

The Cubic-Plus-Association Equation of State (CPA-EoS) was used to predict the experimental data for the systems containing fatty acid ethyl ester + ethanol + glycerol at 323.15 and 333.15 K.

The CPA-EoS takes into account specific interactions between like (self-association) and unlike (cross-association) molecules [32–34]. It 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, [35,36] originally proposed by Wertheim for fluids with highly directed attractive forces and used in other association equations of state such as SAFT [37].

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

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

where a is the energy parameter, b the co-volume parameter, ρ is the molar density, g a simplified hard-sphere radial distribution function, X_{Ai} the mole fraction of pure component i not bonded at site A, and x_i is the mole fraction of component i.

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

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

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:

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

and

$$b = \sum_i x_i b_i \tag{6}$$

X_{Ai} is related to the association strength Δ^{AiBj} between sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{Ai} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{Bj}\Delta^{A_iB_j}} \tag{7}$$

where

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

where ε^{AiBj} and β^{AiBj} are the association energy and the association volume, respectively.

The simplified radial distribution function, $g(\rho)$, is given by [38]:

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

For non-associating components, such as ethyl esters, CPA has three pure component parameters in the cubic term (a_0, c_1 and b), while for associating components, such as glycerol and ethanol, it has two additional parameters in the association term (ε and β). In both cases, the parameters were regressed simultaneously from the vapor pressure and liquid density data found in the literature. The objective function to be minimized is the following:

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

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 [39,40], and in this work the Elliott Combining Rule (ECR) [40] was used:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \tag{11}$$

Solvation can occur in some systems containing self-associating and non-self-associating compounds, as in the case of the ester + glycerol or ester + ethanol mixtures investigated in this work. For this type of systems, the solvation phenomena is considered as a cross-association by the CPA EoS, where the cross-association energy (ε^{AiBj}) is considered to be half the value of the association energy for the self-associating component and the cross association volume (β^{AiBj}) is left as an adjustable parameter, fitted to the equilibria data. This approach, proposed by Folas et al. [41], was successfully applied to model the phase equilibria of the ethyl laurate/ethyl myristate + ethanol + water system [31] and of multicomponent systems involving fatty acid esters, alcohols and glycerol [27,30].

In these cases, the following objective function was minimized to estimate the parameters k_{ij} and β^{AiBj}:

$$OF = \sum_{i}^{NP} \left(\frac{x_i^{calcd} - x_i^{exptl}}{x_i^{exptl}} \right)^2 \tag{12}$$

where single phase or all phase data can be selected during the parameter optimization. The association term depends on the number and type of association sites. According to the nomenclature of Huang and Radosz [42] 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 glycerol, a new association scheme previously proposed for glycerol, the $3 \times 2B$ scheme, is applied [28].

The average deviations (AD) between the experimental compositions and those estimated by the CPA EoS were calculated according to the following equation:

$$AD = \sqrt{\frac{\sum_{n}^{N} \sum_{i}^{R} \left[\left(w_{i,n}^{GP,exptl} - w_{i,n}^{GP,calcd} \right)^2 + \left(w_{i,n}^{EP,exptl} - w_{i,n}^{EP,calcd} \right)^2 \right]}{2 \, NR}} \tag{13}$$

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 in the glycerol (GP) or ester phases (EP), respectively, i is the component, the subscript n

Table 1
Experimental liquid–liquid equilibria data for the ternary systems containing ethyl ester (i) + anhydrous ethanol (5) + glycerol (6) at 323.15 and 353.15 ± 0.1 K.

Ethyl ester (i)	T/K	Overall composition			Glycerol-rich phase			Ester-rich phase			K_{d5}[a]	$S_{5/i}$[b]
		100 w_i	100 w_5	100 w_6	100 w_i	100 w_5	100 w_6	100 w_i	100 w_5	100 w_6		
Linoleate (1)	323.15	27.483	45.309	27.208	9.936	54.765	35.299	72.285	24.316	3.399	2.25	16.385
		25.813	41.583	32.604	7.155	50.205	42.640	74.970	21.352	3.678	2.35	24.637
		32.158	33.227	34.615	3.564	44.020	52.416	82.498	15.243	2.259	2.89	66.848
		36.702	24.976	38.322	1.540	34.771	63.689	86.552	11.819	1.629	2.94	165.346
		20.501	20.502	58.997	1.123	23.494	75.383	90.790	7.786	1.424	3.02	243.950
		20.613	13.927	65.460	0.970	15.511	83.519	94.234	4.647	1.119	3.34	324.267
		22.360	0.000	77.640	0.900	0.000	99.100	99.200	0.000	0.800		
	353.15	18.650	47.149	34.201	12.597	50.377	37.026	66.197	27.077	6.726	1.86	9.777
		16.563	41.919	41.518	7.639	46.268	46.093	74.647	21.620	3.733	2.14	20.912
		15.600	37.952	46.448	4.663	41.977	53.360	78.431	18.562	3.007	2.26	38.037
		17.271	28.658	54.071	1.469	33.044	65.487	82.944	15.127	1.929	2.18	123.340
		20.322	21.198	58.480	1.228	23.469	75.303	89.617	8.711	1.672	2.69	196.616
		20.904	12.712	66.384	1.092	15.492	83.416	93.158	5.326	1.516	2.91	248.144
		26.471	0.000	73.529	0.970	0.000	99.030	99.101	0.000	0.899		
Oleate (2)	323.15	23.895	52.256	23.849	16.171	56.170	27.659	61.097	31.992	6.911	1.76	6.634
		29.577	40.816	29.607	8.713	50.359	40.928	73.713	21.801	4.486	2.31	19.542
		31.981	35.881	32.138	5.489	46.320	48.191	77.313	19.210	3.477	2.41	33.963
		35.524	29.041	35.435	2.835	38.716	58.449	83.052	14.437	2.511	2.68	78.562
		41.474	17.048	41.478	0.576	25.640	73.784	89.422	8.406	2.172	3.05	473.533
		44.727	10.542	44.731	0.252	15.447	84.301	92.794	5.232	1.974	2.95	1087.166
		37.681	0.000	62.319	0.190	0.000	99.810	98.161	0.000	1.839		
	353.15	29.577	40.526	29.897	9.219	47.900	42.881	69.551	24.936	5.513	1.92	14.492
		34.124	31.384	34.492	3.762	42.254	53.984	79.830	17.532	2.638	2.41	51.143
		39.271	21.590	39.140	2.521	30.898	66.581	85.889	11.972	2.139	2.58	87.928
		41.531	17.990	40.479	1.886	24.325	73.789	88.400	9.630	1.970	2.53	118.396
		44.317	11.510	44.173	0.900	14.600	84.500	91.891	6.335	1.774	2.30	235.308
		28.996	0.000	71.004	0.320	0.000	99.680	98.027	0.000	1.973		
Palmitate (3)	323.15	24.958	49.842	25.200	12.350	55.910	31.740	57.058	32.496	10.446	1.72	7.949
		28.544	42.076	29.380	5.852	51.753	42.395	73.558	21.545	4.897	2.40	30.194
		34.244	31.200	34.556	2.323	41.218	56.459	80.684	16.306	3.010	2.53	87.797
		39.341	21.007	39.652	1.384	28.931	69.685	88.353	10.635	1.012	2.72	173.665
		43.000	13.733	43.267	0.592	21.123	78.285	92.431	7.261	0.308	2.91	454.208
		45.690	8.616	45.694	0.299	12.961	86.740	94.761	5.013	0.226	2.59	819.406
		54.967	0.000	45.033	0.174	0.000	99.826	99.947	0.000	0.053		
	353.15	31.087	37.493	31.420	6.510	47.480	46.010	74.236	20.437	5.327	2.32	26.493
		34.325	32.040	33.635	4.707	42.686	52.607	77.302	18.281	4.417	2.33	38.347
		38.156	24.250	37.594	1.202	33.092	65.706	81.289	15.720	2.991	2.11	142.363
		40.452	18.784	40.764	0.794	24.802	74.404	85.124	12.753	2.123	1.94	208.500
		44.317	11.414	44.269	0.322	14.096	85.582	92.123	7.438	0.439	1.90	542.191
		66.466	0.000	33.534	0.190	0.000	99.810	99.919	0.000	0.081		
Laurate (4)	323.15	29.750	40.540	29.710	7.345	46.431	46.224	58.317	33.686	7.997	1.38	10.944
		34.696	30.646	34.658	2.625	38.388	58.987	72.829	23.709	3.462	1.62	44.922
		39.341	21.557	39.102	1.282	28.699	70.019	83.601	14.846	1.553	1.93	126.061
		43.603	12.752	43.645	0.876	15.434	83.690	91.651	7.824	0.525	1.97	206.387
		64.251	0.000	35.749	0.280	0.000	99.720	99.972	0.000	0.028		
	353.15	32.014	36.841	31.145	10.984	42.193	46.823	58.393	31.852	9.755	1.32	7.042
		34.504	30.895	34.601	3.806	37.925	58.269	71.053	24.273	4.674	1.56	29.169
		38.131	23.819	38.050	1.278	29.904	68.818	77.561	19.873	2.566	1.50	91.323
		41.184	17.265	41.551	0.893	20.283	78.824	84.710	13.855	1.435	1.46	138.870
		44.780	10.027	45.193	0.525	11.786	87.689	91.601	7.640	0.759	1.54	269.162
		56.267	0.000	43.733	0.649	0.000	99.351	99.871	0.000	0.129		

[a] K_{d5} is the ethanol distribution coefficient according to Eq. (1).
[b] $S_{5/i}$ is the solvent selectivity according to Eq. (2).

stands for the tie line number and the superscripts exptl and calcd refer to the experimental and calculated compositions.

3. Results and discussion

Liquid–liquid equilibria data at atmospheric pressure for the ethyl linoleate/ethyl oleate/ethyl palmitate/ethyl laurate + ethanol + glycerol systems at 323.15 and 353.15 K are presented at Table 1. The accuracy and precision of the experimental data were evaluated through Type A uncertainty, calculated by the standard deviations of the analytical measurements [43]. The uncertainties of the equilibria compositions ranged from (0.05 to 0.88)% by mass for ethyl esters, (0.03 to 0.37)% for ethanol and (0.02 to 0.33)% for glycerol, with the lowest figures associated with the lowest mass fractions within the composition range investigated.

Based on the total system mass and on the phase and overall compositions, mass balances were checked according to the procedure suggested by Marcilla et al. [44] and recently applied to systems containing ethyl esters by Follegatti-Romero et al. [31]. According to this procedure, the mass of both liquid phases was calculated and checked against the total initial mass used in the experimental runs. Average results obtained for the mass balance deviations of each set of experimental data are shown in Table 2. In all cases, values were lower than 0.30%, indicating the good quality of the measured data. The equilibrium data were tested using the Othmer-Tobias and Hand correlations [45,46]. Regression coefficients higher than 0.965 were obtained for all the sets of data measured in the present work, confirming their consistency.

Ethanol distribution coefficients (Table 1) were calculated as the ratio of the ethanol mass fraction in the glycerol rich phase to the ethanol mass fraction in the ethyl ester rich phase (Eq. (1)). Distribution coefficient values were superior to 1.3 showing, as expected, that the glycerol phase is richer in ethanol than the ethyl ester phase.

The distribution diagram for ethanol in the ethyl oleate + ethanol + glycerol system (this work) is presented in Fig. 1 along with the methanol distribution diagram in the methyl oleate + methanol + glycerol system [17]. Methanol distribution coefficients are higher, meaning that in ethanol containing systems the mutual solubility among components (ethyl esters and glycerol) is higher than those in methanol systems. That can be explained taking into account that esters of long-chain fatty acids are non-polar compounds and consequently ethanol (less polar) is more soluble in the fatty acid ester phase than methanol. This fact was already emphasized by Zhou and Boocock [47] in their study about the alcohol distribution between the glycerol and ester rich phases during the transesterification reaction with ethanol and methanol. These authors observed that 42.0% of the alcohol was in the ester rich phase at the end of methanolysis but this percentage increased
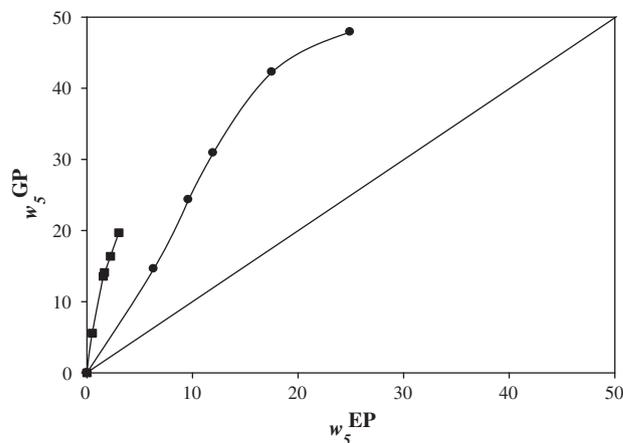
Table 2
Deviations (δ) for the global mass balance of the phase compositions.

System	100 δ^a
Ethyl linoleate + ethanol + glycerol at 323.15 K	0.19
Ethyl linoleate + ethanol + glycerol at 353.15 K	0.25
Ethyl oleate + ethanol + glycerol at 323.15 K	0.12
Ethyl oleate + ethanol + glycerol at 353.15 K	0.27
Ethyl palmitate + ethanol + glycerol at 323.15 K	0.19
Ethyl palmitate + ethanol + glycerol at 353.15 K	0.16
Ethyl laurate + ethanol + + glycerol at 323.15 K	0.18
Ethyl laurate + ethanol + glycerol at 353.15 K	0.16
Average global deviation	0.19

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

Fig. 1. Distribution diagram for ethyl oleate (2) + ethanol (5) + glycerol (6) (–●–, this work) and for methyl oleate + methanol + glycerol (–■–, Andreatta et al. [17]) at 353.15 K.

to 75.4% in case of ethanolysis. Glycerol selectivity was high and in most cases above 100. However, it decreases with increasing ethanol mass fraction (see Table 1). This occurs because higher amounts of ethanol enhance the mutual solubility of the glycerol and ester rich phases.

The CPA EoS was used to predict the experimental liquid–liquid equilibria data. The CPA EoS was previously used with success for the description of the LLE of biodiesel multicomponent systems such as ethyl laurate/myristate + ethanol + water [31], methyl stearate/methyl myristate + ethanol + glycerol, methyl oleate/ methyl myristate + methanol + glycerol [27] and canola oil ethylic biodiesel + ethanol + glycerol [22], using the same temperature independent binary interaction and cross-association parameters.

To apply the CPA EoS to model the phase equilibria of multicomponent systems, the CPA pure compound parameters (a_0, c_1 and b) are first estimated, usually, trough a simultaneous regression of vapor pressure and liquid density data. In this way, CPA EoS parameters for several esters families were proposed in a previous work [30] where it was also shown that the parameters a_0, c_1 and b follow a linear trend with the ester carbon number. Consequently, correlations to compute these parameters were proposed enabling to estimate them for new compounds when liquid density and vapor pressure data are not available. These correlations were already applied to compute fatty acid esters CPA pure compound parameters enabling to properly predict, for instance, the near and supercritical VLE of fatty acid ester + alcohol systems [25,26].

With the recent appearance of experimental data for ethyl esters vapor pressures [48] and liquid densities [49] it was also possible to estimate esters CPA pure compound parameters by a simultaneous regression of these pure component data. Critical temperatures (T_c) for fatty acid ethyl esters were determined from the group contribution method of Nikitin et al. [50], that was previously assessed to be the best one to compute this property for ethyl esters [51]. Thus, two set of CPA pure compound parameters for esters were considered in the present work, a first set based on the regression of vapor pressure and liquid density data and a second one estimated from literature correlations. Both sets were used in the LLE prediction. The parameters obtained with the two referred approaches are presented at Table 3 as well as the liquid densities and vapor pressures deviations.

The five CPA pure parameters for ethanol 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 [52]. The CPA pure parameters for glycerol were previously established considering

Table 3
CPA pure compound parameters, modeling results and critical temperatures.

Compound	T_c (K)	a_0 (J m^3 mol^{-2})	c_1	$B \times 10^5$ (m^3 mol^{-1})	ε (J mol^{-1})	β	100 AAD[c]	
							P	ρ
Ethyl linoleate[a]	785.19	11.99	1.82	36.13	–	–	0.27	0.26
Ethyl oleate[a]	771.07	14.36	1.34	37.64	–	–	6.00	0.61
Ethyl palmitate[a]	766.41	9.82	2.12	33.80	–	–	0.37	0.17
Ethyl laurate[a]	719.13	7.00	1.92	26.12	–	–	4.29	0.33
Ethyl linoleate[b]	785.19	12.09	1.75	37.17	–	–	38.05	3.58
Ethyl oleate[b]	771.07	12.09	1.75	37.17	–	–	44.06	0.28
Ethyl palmitate[b]	766.41	10.80	1.65	33.37	–	–	39.00	0.55
Ethyl laurate[b]	719.13	8.23	1.45	25.93	–	–	1.03	14.44
Ethanol	514.70	0.68	0.94	4.75	21336	0.0190	0.35	0.51
Glycerol	766.10	1.21	1.06	6.96	19622	0.009	0.77	1.49

[a] Parameters calculated from vapor pressure and density data.
[b] Parameters calculated using linear correlations with the ester carbon number.
[c] AAD is calculated by $\mathbf{AAD} = \frac{1}{N}\sum_{i=1}^{Np}|(\text{exptl}_i - \text{calcd}_i)/\text{exptl}_i|$.

Table 4
Binary interaction and cross-association parameters used to model ternary systems LLE.

k_{ij} (unsaturated fatty acid ester + ethanol)	−0.026
k_{ij} (ethyl palmitate + ethanol)	−0.020
k_{ij} (ethyl laurate + ethanol)	−0.083
k_{ij} (fatty acid ester + glycerol)	0.129
β_{ij} (fatty acid ester + ethanol)	0.10
β_{ij} (fatty acid ester + glycerol)	0.100
k_{ij} (ethanol + glycerol)	0.060

the 3 × 2B scheme, and used for modeling the phase equilibria of several glycerol + alcohol and glycerol + water systems [28].

The remaining parameters to be obtained are the binary interaction parameters, k_{ij}, and the cross-association volumes, β_{ij}. In the same way as performed when predicting the LLE of multicomponent systems composed of fatty acid methyl esters + methanol + glycerol [27], and taking advantage of the transferability of the CPA parameters, binary interaction parameters for the binary subsystems were obtained from binary equilibria data. The possible subsystems comprise fatty acid ethyl ester + glycerol, glycerol + ethanol and fatty acid ethyl ester + ethanol mixtures. The binary interaction parameter, k_{ij}, between ethyl esters and ethanol were obtained from a linear correlation with the ethyl ester carbon number and the β_{ij} for this binary was fixed to 0.1. These correlations and the constant value were previously established by Oliveira et al. [26] when correlating isothermal vapor–liquid equilibria of ethanol + ester systems, with esters from 5 up to 19 carbons, at atmospheric pressure and at temperatures ranging from 339 to 440 K. For fatty acid ester + glycerol mixtures, the binary interaction parameter (k_{ij}) and the cross-association volume (β_{ij}) were fixed in 0.129 and 0.1, respectively, for all systems studied. These values were fitted from mutual solubility data of the methyl dodecanoate + glycerol system, at atmospheric pressure and at temperatures ranging from 370 to 438 K and already applied for modeling other biodiesel multicomponent systems [27]. In the case of the ethanol + glycerol binary, the k_{ij} parameter was taken from the work by Oliveira et al. [28] who used a 3 × 2B scheme for correlating the corresponding vapor–liquid equilibria data, at atmospheric pressure and at temperatures ranging from 363 to 453 K. All parameters mentioned above are given in Table 4. Note that all required binary interaction parameters and cross-association volumes were taken from the literature and no readjustment was performed in this case.

Having the CPA pure compounds parameters, the binary interaction parameters and the cross-association volumes, it was then possible to predict the measured multicomponent phase equilibria. A slightly better LLE prediction was obtained when using pure
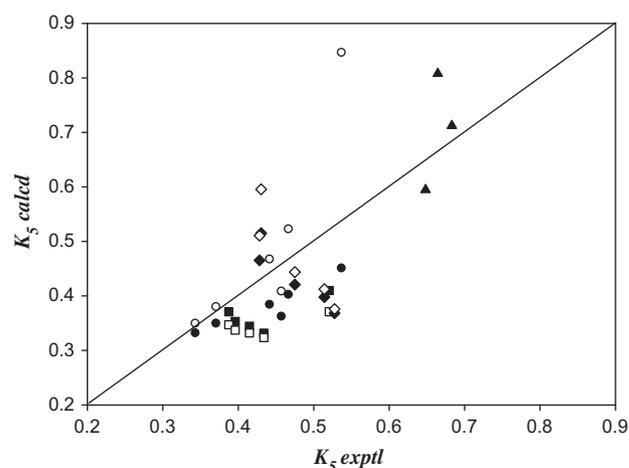

Fig. 2. Ethanol distribution coefficient from the CPA EoS versus the experimental ethanol distribution coefficient for the systems ethyl ester (i) + ethanol (5) + glycerol (6) at 323.15 K: ●○, ethyl linoleate; ■□, ethyl oleate; ♦◇, ethyl palmitate; ▲, ethyl laurate. Full symbols represent CPA EoS results using CPA pure parameters for esters computed from ester carbon number correlations and the empty symbols represent the CPA EoS results using pure parameters for esters calculated from density and vapor pressure data.

Table 5
Average deviations (AD) between the experimental and CPA phase compositions.

System	100AD[a]	100AD[b]
Ethyl linoleate + ethanol + glycerol at 323.15 K	4.18	2.94
Ethyl linoleate + ethanol + glycerol at 353.15 K	3.81	5.35
Ethyl oleate + ethanol + glycerol at 323.15 K	6.45	7.29
Ethyl oleate + ethanol + glycerol at 353.15 K	3.11	3.48
Ethyl palmitate + ethanol + glycerol at 323.15 K	3.91	9.60
Ethyl palmitate + ethanol + glycerol at 353.15 K	2.71	3.14
Ethyl laurate + ethanol + + glycerol at 323.15 K	12.48	9.11
Ethyl laurate + ethanol + glycerol at 353.15 K	10.41	10.45
Average global deviation	5.88	6.42

[a] Using CPA pure compound parameters for esters computed from ester carbon number correlations.
[b] Using CPA pure compound parameters for esters computed from vapor pressure and liquid density data correlation.

parameters estimated from the ester carbon number correlations proposed in the literature, as shown in Fig. 2, where the predicted and experimental ethanol distribution coefficients are plotted. The average deviations between the experimental and calculated compositions in both phases are shown in Table 5. Deviations are within the range 2.71–12.48% and a global average deviation of 5.88%
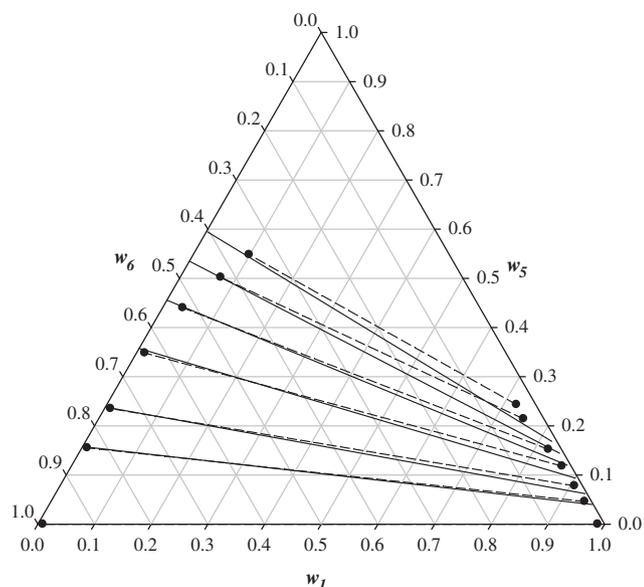
Fig. 3. Liquid–liquid equilibria for the system containing ethyl linoleate (1) + ethanol (5) + glycerol (6) at 323.15 K. Experimental (● and – – –) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).
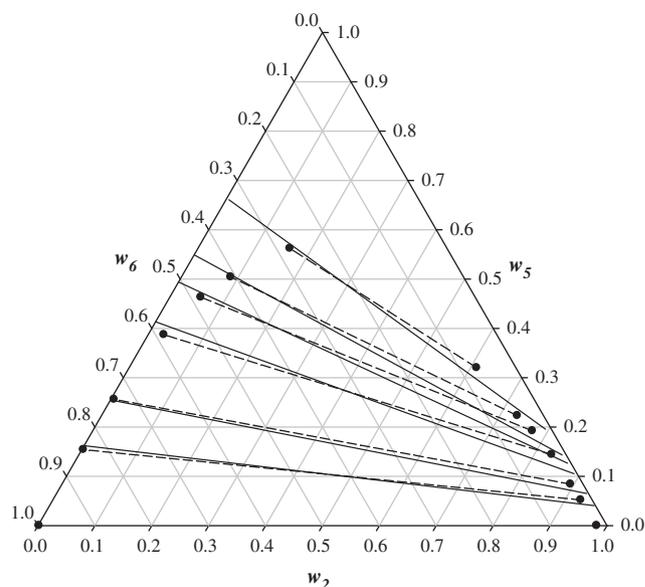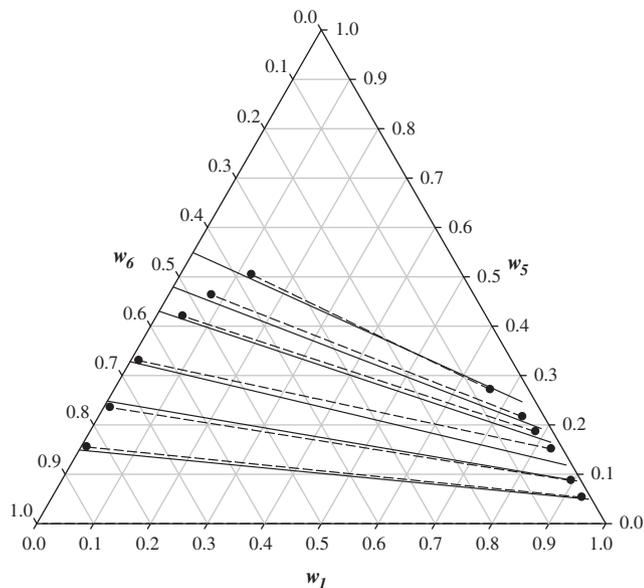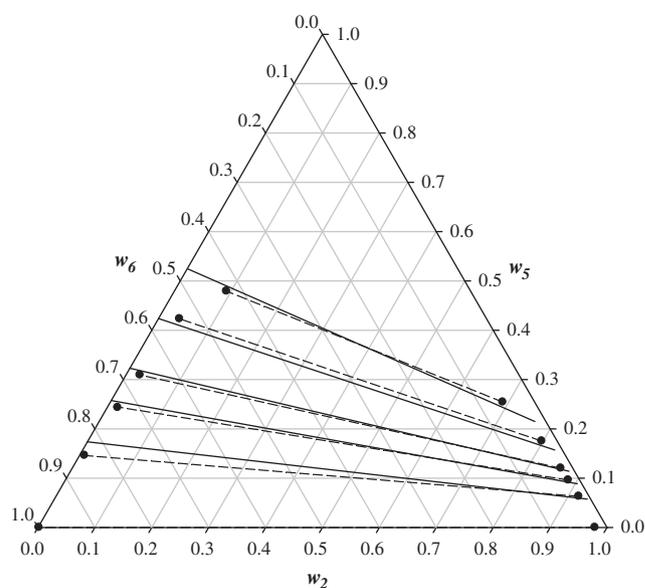

Fig. 5. Liquid–liquid equilibria for the system containing ethyl oleate (2) + ethanol (5) + glycerol (6) at 323.15 K. Experimental (● and – – –) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).

Fig. 4. Liquid–liquid equilibria for the system containing ethyl linoleate (1) + ethanol (5) + glycerol (6) at 353.15 K. Experimental (● and – – –) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).

Fig. 6. Liquid–liquid equilibria for the system containing ethyl oleate (2) + ethanol (5) + glycerol (6) at 353.15 K. Experimental (● and – – –) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).

was obtained using pure parameters obtained from the ester carbon number correlations. In the case of pure parameters based on the regression of vapor pressure and liquid density data, the deviations were slightly higher.

Figs. 3–8 shows the experimental and predicted tie-lines for ethyl linoleate, oleate and palmitate ternary systems in the selected temperature range The predicted tie-lines given in these figures were calculated using the pure parameters determined from the ester carbon number correlations proposed in the literature. As can be observed in these figures, the deviations between experimental and calculated values are larger in the region close to the plait point. Similar average deviation between the experimental

and calculated compositions by CPA EoS were recently reported by Follegatti-Romero et al. [28] for fatty systems containing ethyl esters, ethanol and water.

Transesterification reaction is strongly influenced by molar ratio of alcohol to vegetable oil. In fact, this is a reversible reaction, requiring an excess of ethanol for enhancing the oil conversion. For this reason a 6:1 ethanol/oil molar ratio is generally considered the most appropriate. In the case of this molar ratio, the following approximate overall composition is usually obtained at the end of the ethanolysis reaction, if one assumes the complete oil conversion: 80 mass% of biodiesel, 12 mass% of excess ethanol and 8 mass% of glycerol. This composition indicates that the lower part
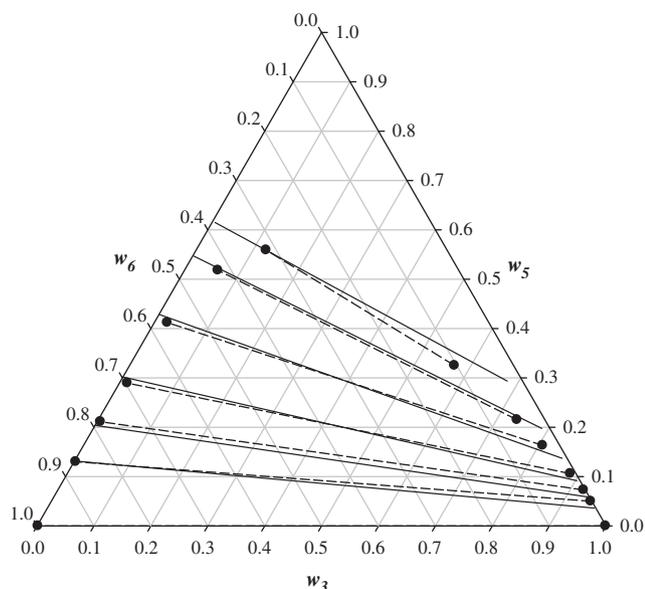
Fig. 7. Liquid–liquid equilibria for the system containing ethyl palmitate (3) + ethanol (5) + glycerol (6) at 323.15 K. Experimental (● and –––) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).
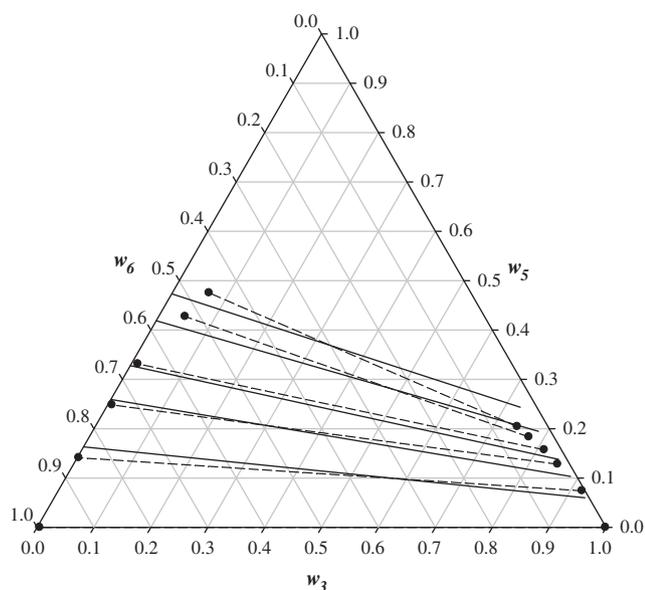

Fig. 8. Liquid–liquid equilibria for the system containing ethyl palmitate (3) + ethanol (5) + glycerol (6) at 353.15 K. Experimental (● and –––) and CPA EoS results using CPA pure compound parameters for esters computed from ester carbon number correlations (—).

of the phase splitting region in the phase equilibrium diagrams is the most important one for designing the separation process of ethylic biodiesel. This part is exactly the region particularly well described by the CPA Equation of State.

Once again, and following previous works [24,27,31], the results here presented show the very good predictive capability of the CPA EoS and the transferability of its binary parameters obtained from binary phase equilibria data, to predict phase equilibria of multicomponent systems of relevance for biodiesel production processes.

4. Conclusions

New measurements for the liquid–liquid equilibria data were carried out in this work for the ethyl linoleate/ethyl oleate/ethyl palmitate/ethyl laurate + ethanol + glycerol systems at 323.15 and 353.15 K.

The experimental data were successfully predicted with the Cubic-Plus-Association Equation of State (CPA EoS). Two approaches were used to estimate esters CPA pure compound parameters and the LLE results were taken into account for the selection of the most adequate set.

Global average deviations below 6% were obtained, using temperature independent interaction parameters previously correlated from binary data.

Acknowledgments

References

[1] Shahid EM, Jamal Y. A review of biodiesel as vehicular fuel. Renew Sust Energ Rev 2008;12:2484–94.
[2] Ma FR, Hanna MA. Biodiesel production: a review. Bioresource Technol 1999;70:1–15.
[3] Van Gerpen J. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.
[4] Marjanovic AV, Stamenkovic OS, Todorovic ZB, Lazic ML, Veljkovic VB. Kinetics of the base-catalyzed sunflower oil ethanolysis. Fuel 2010;89:665–71.
[5] Foglia TA, Nelson LA, Dunn RO, Marmer WN. Low-temperature properties of alkyl esters of tallow and grease. J Am Oil Chem Soc 1997;74:951–5.
[6] Moser BR. Biodiesel production, properties, and feedstocks. In Vitro Cell Dev-Pl 2009;45:229–66.
[7] Jones JC. On the use of ethanol in the processing of biodiesel fuels. Fuel 2010;89:1183.
[8] Jones JC. On the processing of biodiesel fuels. Fuel 2009;88:583.
[9] Boros L, Batista MLS, Vaz RV, Figueiredo BR, Fernandes VFS, Costa MC, et al. Crystallization behavior of mixtures of fatty acid ethyl esters with ethyl stearate. Energy Fuel 2009;23:4625–9.
[10] Knothe G, Dunn RO. A comprehensive evaluation of the melting points of fatty acids, esters determined by differential scanning calorimetry. J Am Oil Chem Soc 2009;86:843–56.
[11] Meneghetti SMP, Meneghetti MR, Wolf CR, Silva EC, Lima GES, Silva LD, et al. Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis. Energy Fuel 2006;20:2262–5.
[12] Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production costs. Bioresource Technol 2006;97:671–8.
[13] Follegatti-Romero LA, Lanza M, Da Silva CAS, Batista EAC, Meirelles AJA. Mutual Solubility of Pseudobinary Systems Containing Vegetable Oils and Anhydrous Ethanol from (298.15 to 333.15) K. J Chem Eng Data 2010;55:2750–6.
[14] Di Felice R, De Faveri D, De Andreis P, Ottonello P. Component distribution between light and heavy phases in biodiesel processes. Ind Eng Chem Res 2008;47:7862–7.
[15] Csernica SN, Hsu JT. Reverse-phase ternary phase diagram, tie lines, and plait point for commercial biodiesel–glycerol–methanol. Ind Eng Chem Res 2010;50:1012–6.
[16] Negi DS, Sobotka F, Kimmel T, Wozny G, Schomäcker R. Liquid–liquid phase equilibrium in glycerol–methanol–methyl oleate and glycerol–monoolein–methyl oleate ternary systems. Ind Eng Chem Res 2006;45:3693–6.
[17] Andreatta AE, Casás LM, Hegel P, Bottini SB, Brignole EA. Phase equilibria in ternary mixtures of methyl oleate, glycerol, and methanol. Ind Eng Chem Res 2008;47:5157–64.
[18] Tizvar R, McLean DD, Kates M, Dube MA. Liquid–liquid equilibria of the methyl oleate–glycerol–hexane–methanol system. Ind Eng Chem Res 2008;47:443–50.
[19] Franca BB, Pinto FM, Pessoa FLP, Uller AMC. Liquid–liquid equilibria for castor oil biodiesel plus glycerol plus alcohol. J Chem Eng Data 2009;54:2359–64.
[20] Machado AB, Ardila YC, de Oliveira LH, Aznar Mn, Wolf Maciel MR. Liquid–liquid equilibrium study in ternary castor oil biodiesel + ethanol + glycerol. J Chem Eng Data 2011;56:2196–201.
[21] Liu XJ, Piao XL, Wang YJ, Zhu SL. Liquid-liquid equilibrium for systems of fatty acid ethyl esters plus ethanol plus soybean oil and fatty acid ethyl esters plus ethanol plus glycerol. J Chem Eng Data 2008;53:359–62.

[22] Oliveira MB, Barbedo S, Soletti JI, Carvalho SHV, Queimada AJ, Coutinho JAP. Liquid–liquid equilibria for the canola oil biodiesel + ethanol + glycerol system. Fuel 2011;90:2738–45.

[23] Barreau A, Brunella I, De Hemptinne JC, Coupard V, Canet X, Rivollet F. Measurements of liquid–liquid equilibria for a methanol + glycerol + methyl oleate system and prediction using group contribution statistical associating fluid theory. Ind Eng Chem Res 2010;49:5800–7.

[24] Oliveira MB, Ribeiro V, Queimada AJ, Coutinho JAP. Modeling phase equilibria relevant to biodiesel production: a comparison of g(E) Models, Cubic EoS, EoS-g(E) and Association EoS. Ind Eng Chem Res 2011;50:2348–58.

[25] Oliveira MB, Queimada AJ, Coutinho JAP. Prediction of near and supercritical fatty acid ester plus alcohol systems with the CPA EoS. J Supercrit Fluid 2010;52:241–8.

[26] Oliveira MB, Miguel SI, Queimada AJ, Coutinho JAP. Phase equilibria of ester plus alcohol systems and their description with the Cubic-Plus-Association Equation of State. Ind Eng Chem Res 2010;49:3452–8.

[27] Oliveira MB, Queimada AJ, Coutinho JAP. Modeling of biodiesel multicomponent systems with the Cubic-Plus-Association (CPA) Equation of State. Ind Eng Chem Res 2010;49:1419–27.

[28] Oliveira MB, Teles ARR, Queimada AJ, Coutinho JAP. Phase equilibria of glycerol containing systems and their description with the Cubic-Plus-Association (CPA) Equation of State. Fluid Phase Equilibr 2009;280:22–9.

[29] Oliveira MB, Pratas MJ, Marrucho IM, Queimada AJ, Coutinho JAP. Description of the mutual solubilities of fatty acids and water with the CPA EoS. Aiche J 2009;55:1604–13.

[30] Oliveira MB, Varanda FR, Marrucho IM, Queimada AJ, Coutinho JAP. Prediction of water solubility in biodiesel with the CPA equation of state. Ind Eng Chem Res 2008;47:4278–85.

[31] Follegatti-Romero LA, Lanza M, Batista FRM, Batista EAC, Oliveira MB, Coutinho JoAP, et al. Ind Eng Chem Res 2010;49:12613–9.

[32] Oliveira MB, Coutinho JAP, Queimada AJ. Mutual solubilities of hydrocarbons and water with the CPA EoS. Fluid Phase Equilibr 2007;258:58–66.

[33] Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part 1. Pure compounds and self-associating systems. Ind Eng Chem Res 2006;45:4855–68.

[34] Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part 2. Cross-associating and multicomponent systems. Ind Eng Chem Res 2006;45:4869–78.

[35] Michelsen ML, Hendriks EM. Physical properties from association models. Fluid Phase Equilibr 2001;180:165–74.

[36] Wu JZ, Prausnitz JM. Phase equilibria for systems containing hydrocarbons, water, and salt: an extended Peng–Robinson equation of state. Ind Eng Chem Res 1998;37:1634–43.

[37] Muller EA, Gubbins KE. Molecular-based equations of state for associating fluids: a review of SAFT and related approaches. Ind Eng Chem Res 2001;40:2193–211.

[38] Kontogeorgis GM, Yakoumis IV, Meijer H, Hendriks E, Moorwood T. Multicomponent phase equilibrium calculations for water–methanol–alkane mixtures. Fluid Phase Equilibr 1999;160:201–9.

[39] Voutsas EC, Yakoumis IV, Tassios DP. Prediction of phase equilibria in water/alcohol/alkane systems. Fluid Phase Equilibr 1999;160:151–63.

[40] Folas GK, Gabrielsen J, Michelsen ML, Stenby EH, Kontogeorgis GM. Application of the cubic-plus-association (CPA) equation of state to cross-associating systems. Ind Eng Chem Res 2005;44:3823–33.

[41] Folas GK, Kontogeorgis GM, Michelsen ML, Stenby EH. Application of the cubic-plus-association (CPA) equation of state to complex mixtures with aromatic hydrocarbons. Ind Eng Chem Res 2006;45:1527–38.

[42] Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules. Ind Eng Chem Res 1990;29:2284–94.

[43] B.N. Taylor, C.E. Kuyatt, Guidelines for the evaluation and expression of uncertainty in NIST measurement results technical note 1297 for NIST. Gaithersburg: MD; 1994.

[44] Marcilla A, Ruiz F, García AN. Liquid–liquid–solid equilibria of the quaternary system water–ethanol–acetone–sodium chloride at 25 °C. Fluid Phase Equilibr 1995;112:273–89.

[45] Othmer DF, Tobias PE. Liquid–liquid extraction data – toluene and acetaldehyde systems. Ind Eng Chem 1942;34:690–2.

[46] Brandani V, Chianese A, Rossi M. Ternary liquid–liquid equilibrium data for the water–ethanol–benzene system. J Chem Eng Data 1985;30:27–9.

[47] Zhou WY, Boocock DGB. Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil. J Am Oil Chem Soc 2006;83:1047–52.

[48] Silva LYA, Falleiro RMM, Meirelles AJA, Krähenbühl MA. Determination of the vapor pressure of ethyl esters by differential scanning calorimetry. J Chem Thermodynam 2011;43:943–7.

[49] Pratas MJ, Freitas S, Oliveira MB, Monteiro SC, Lima AS, Coutinho JAP. Densities and viscosities of fatty acid methyl and ethyl esters. J Chem Eng Data 2010;55:3983–90.

[50] Nikitin ED, Pavlov PA, Bogatishcheva NS. Critical properties of long-chain sunbstances from the hypothesis of functional self-similarity. Fluid Phase Equilibr 2005;235:1–6.

[51] Lopes JCA, Boros L, Krahenbuhl MA, Meirelles AJA, Daridon JL, Pauly J, et al. Prediction of cloud points of biodiesel. Energy Fuel 2008;22:747–52.

[52] Oliveira MB, Marrucho IM, Coutinho JAP, Queimada AJ. Surface tension of chain molecules through a combination of the gradient theory with the CPA EoS. Fluid Phase Equilibr 2008;267:83–91.