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Liquid–Liquid Equilibria in Ternary Mixtures of Methyl Oleate + Ethanol + Glycerol at Atmospheric Pressure

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Supporting Information

ABSTRACT: The knowledge and the ability to describe the phase equilibrium behavior of systems composed of transesterification products are very important in the optimization of biodiesel production and purification process. In this work, liquid–liquid equilibrium data have been measured for the ternary system methyl oleate + ethanol + glycerol, at temperatures between 303 and 333 K. This system has not been explored before. The experimental data measured were compared with analogous ternary systems showing an increasing of the solubility regarding the systems containing methanol. The isothermal experimental data have shown a good linear fit in an Othmer–Tobias plot. The group contribution with association GCA–EoS equation of state and the A-UNIFAC model were applied to represent the phase equilibria of this ternary system. The GCA–EoS model in particular, has shown a good predictive capability.

1. INTRODUCTION

Biodiesel has an important position among the alternatives to conventional petroleum based fuels due to various technical and economics factors: biodegradability, non–toxicity, renewability, lower emission of pollutants, and production from renewable resources.

The most currently used method of biodiesel production is the transesterification reaction of triglycerides from vegetable oils and animal fats using a basic homogeneous catalyst[1] with an excess of alcohol (methanol or ethanol) to form a mixture of fatty acid methyl esters or fatty acid ethyl ester respectively and glycerol.

The physical properties and intersolubility of the components are very important for the biodiesel production. In the transesterification reactions, reactants, alcohols, and oil are partially miscible.[2] Alkali catalyst exists in the alcohol phase. On the other hand, the formation of glycerol and fatty acid alkyl ester may change the distribution of reaction components in different phases. The reaction products are present in two separate liquid phases: a heavy one containing nearly all of the glycerol and a light one containing nearly all of the fatty acid ester used as biodiesel after purification. The separation of glycerol from the fatty phase in the product mixture is generally done by gravitation separation.[3] The solubility of glycerol in the product fatty acid alkyl ester directly influences the following purification of biodiesel. Unreacted alcohol distributes between these two liquid phases. The mutual solubility is also essential data for the alcohol recovery. Knowledge of the liquid–liquid equilibria in the biodiesel production process is fundamental during the transesterification reaction and during the recovery of the final products in order to provide the biodiesel with the quality levels required by the standards for marketing of alternative fuels.

Although there is a growing industrial interest in the separation processes associated in biodiesel production, there are few experimental data available on these systems reported in the open literature. Liquid–liquid equilibria of ternary systems composed of fatty acid methyl esters + methanol + glycerol[2–10] and fatty acid ethyl esters + ethanol + glycerol[11–15] have recently been the focus of several research works. Other systems of interest for the biodiesel industry are those formed by a fatty acid methyl ester + ethanol + glycerol but they are less studied. As mentioned before, while in the methyl route and ethyl route we obtain fatty acid methyl ester and ethyl ester respectively and glycerol; some researchers have obtained fatty acid methyl and ethyl esters using different mixtures of methanol and ethanol.[1,16,17] For example, Joshi et al.[16] have obtained fatty acid methyl and ethyl esters mixtures prepared from methanol/ethanol mixtures from soybean oil. The authors have found a faster formation of methyl esters than ethyl esters and have found a biodiesel with better fuel properties in comparison to fatty acid methyl ester. The aim of using a mixture of methanol and ethanol is to take the advantages of better solubility of oil in ethanol than methanol and better reactivity of methoxide ion than ethoxide to achieve the desired equilibrium.[16] In addition, as ethanol is also an attractive alternative biofuel and it is oxygenated, it provides the potential to reduce particulate emissions in compression-ignition engines. So, the mixture studied in this work is also useful in the study of ethanol/biodiesel[18,19] and ethanol/diesel/biodiesel[20–22] blends used as fuel of diesel engine. On the other hand, Sharma et al.[23] established that biodiesel can be

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separated from the glycerol through solvent extraction, like alcohols. In this sense, Mesquita et al.[24] have suggested a purification of biodiesel obtained by the methyl route using ethanol, to reduce operational problems due to the use of methanol.[11]

Regarding the kind of mixture studied, França et al.[25] have reported the binodal curve for the ternary systems castor oil biodiesel (obtained by the methyl route) + ethanol + glycerol at 298.15 and 333.15 K, while Carvallo[26] has shown the binodal curve for the methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol at 303.15 K. Mesquita et al.,[24] on the other hand, have measured the liquid–liquid equilibria (binodal curve and tie lines) for the ternary system soybean biodiesel + ethanol + glycerol at 293.15 and 323.15 K and sunflower biodiesel + ethanol + glycerol at 298.15 and 313.15 K. Both biodiesel were produced by using the methyl route. No more information was found available in the literature at this moment.

The traditional UNIFAC and its versions, UNIQUAC, NRTL model, Wilson activity coefficient model, GC–PPC–SAFT model, CPA EoS, and GCA–EoS have been applied in the thermodynamic modeling of these systems. A brief summary is presented in the Thermodynamic Modeling Section.

The main objectives of this work are to study the liquid–liquid equilibrium of the methyl oleate + ethanol + glycerol, to extend the information available of this kind of mixtures and to compare data with analogous systems. Binodal curves and tie line data were measured for this system at 303, 318, and 333 K. The group contribution with association equation of state GCA–EoS[27] and the UNIFAC with association A-UNIFAC[28] activity coefficient model have been applied to represent the experimental data.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The chemicals used for the experiments were glycerol (>99.5%, Biopack, Argentina), ethanol (>99.5%, Biopack, Argentina), and technical–grade methyl oleate (70%, Aldrich). To reduce the water content to negligible values, moderate temperature (353 K) was applied to the glycerol for several days, always immediately prior to their use. No further purification of ethanol and methyl oleate was carried out.

2.2. Saturation Curve of Methyl Oleate + Ethanol + Glycerol System. The binodal curve of methyl oleate + ethanol + glycerol ternary system was determined at 303, 318, and 333 K and atmospheric pressure by turbidimetric analysis using the titration method under isothermal conditions, following the procedure of Zhou et al.[2] The component titrated was added into the mixture by syringe. All weighing of the components were carried out in a Denver instrument APX–200 analytical balance with an uncertainty of $\pm 10^{-4}$ g.

A jacketed glass vessel of 70 mL volume with a magnetic stirrer was used to carry out the binodal curve experiments at atmospheric pressure. A water bath with recirculation provided with an electronic temperature controller was capable of maintaining the temperature constant in the cell within ±0.2 K.

While stirring with a mechanical agitator; the glycerol-rich phase was determined titrating with methyl oleate different mixtures of known weight of glycerol + ethanol, until the mixture changed from transparent to turbid. This point was considered as the saturation point of methyl oleate in the glycerol + ethanol mixture. On the other hand, the methyl oleate rich phase was determined titrating glycerol into methyl oleate + ethanol known mixture until the cloud point was visible. The data around the meeting point by the two branches of solubility curve, was obtained by titrating ethanol into methyl oleate + glycerol known mixture of given mass ratio to observe the point where the turbid mixture became transparent.

Knowing the weight of methyl oleate, glycerol, or ethanol (m_i) used in the titrations, the corresponding mass weight fraction w_i of the three components was calculated by the following equation:

$$w_i = \frac{m_i}{\sum_i m_i} \tag{1}$$

From w_i and the molecular weight of each component (MW_i), the molar fractions x_i of methyl oleate, ethanol, and glycerol were calculated by

$$x_i = \frac{w_i/\mathrm{MW}_i}{\sum_i w_i/\mathrm{MW}_i} \tag{2}$$

2.3. Tie Lines of the Methyl Oleate + Ethanol + Glycerol System. A jacketed glass vessel with two ports of 70 mL was used to carry out the LLE (liquid–liquid equilibria) experiments at 303, 318, and 333 K and atmospheric pressure. A similar equilibrium vessel was shown in the work of Peschke and Sandler.[29] The two immiscible components (methyl oleate and glycerol) were added into the vessel at a specific molar ratio, and different amounts of ethanol were added to obtain different global phase compositions for the measurement of a series of tie lines. According to the phase rule, the degrees of freedom are three when a ternary system is in equilibrium with two phases. At a given temperature and pressure, only one component can independently change its composition.

The mixture inside the vessel was stirred at a high speed under-well dispersed conditions for 60 min and allowed to settle between 8–12 h until both phases became clear. The construction of the cell allows samples to be obtained from the upper (methyl oleate) and lower (glycerol) phases without contamination resulting from penetrating the interface. Syringes with a needle were used to withdraw samples of around 200 mg through the white rubber septa of each port. Four samples of known weight were collected from each phase in order to check repeatability of the measured compositions.

The composition of ethanol in both liquid phases was determined by measuring the weight of ethanol evaporated from liquid samples placed 353 K for at least 12 h, until constant weight. The mass fraction of ethanol was obtained from the ratio between the weight of ethanol removed by evaporation and the initial weight of the sample. The glycerol and methyl oleate mass fractions were obtained from the binodal curves previously measured. The tie lines were obtained by plotting the data in the phase diagram and connecting the two points. This procedure was applied successfully in Oliveira et al.[11] and Liu et al.[12] The mutual solubility between glycerol and methyl oleate was estimated from the experimental mutual solubility of biodiesel–glycerol binary system reported by di Felice et al.[5] between 293–338 K.

The molar fractions x_i of methyl oleate, ethanol, and glycerol of each saturated liquid phase presented in Supporting Information were calculated according to the eq 2 from the mass fractions and the molecular weight of each component. The standard deviation of the ethanol composition was lower than 0.003 mol.

2.4. Experimental Results. Liquid–liquid equilibria of methyl oleate + ethanol + glycerol ternary system were measured at atmospheric pressure and 303, 318, and 333 K. The binodal curve and the tie line data are reported in the Supporting Information. The isothermal experimental data shows a good linear fit in an Othmer–Tobias plot[30] indicating the consistency of the experimental data as shown in Figure 1.

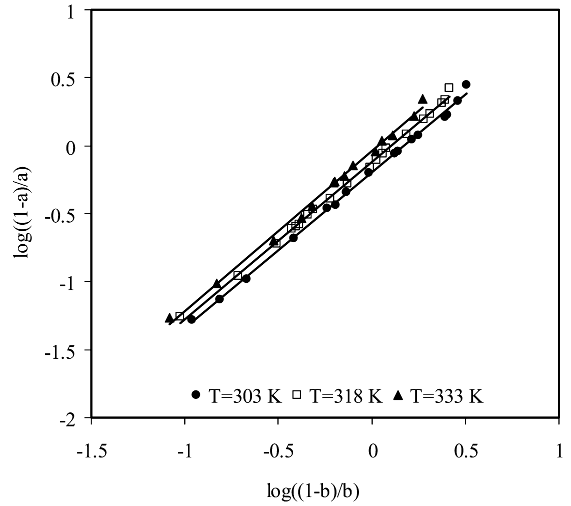

Figure 1. Othmer-Tobias plot: *a* is the mole fraction of methyl oleate in the methyl-oleate-rich phase, and *b* is the glycerol mole fraction in the glycerol-rich phase.

Our experimental data are in agreement with the tie lines reported by Mesquita et al.[24] for the soybean biodiesel + ethanol + glycerol at 293.15 and 323.15 K and sunflower biodiesel + ethanol + glycerol at the temperatures of 298.15 and 313.15 K. No more comparable data were found in the surveyed literature for fatty acid methyl ester + ethanol + glycerol.

Figure 2a compares the binodal curve for the methyl oleate + ethanol + glycerol with methyl oleate + methanol + glycerol[31] at 333 K and with ethyl oleate + ethanol + glycerol at 323 K.[13] Methyl oleate/alcohol and glycerol/alcohol are completely mutually soluble but glycerol/methyl oleate are nearly immiscible. The large region in the two-phase domain indicates high immiscibility between methyl oleate and glycerol even in the presence of alcohol. From this figure, it can be observed that the solubility is higher in the system containing ethanol. As discussed by Follegatti–Romero et al.,[13] the esters of long-chain fatty acids are nonpolar compounds and consequently ethanol (less polar) is more soluble in the fatty acid ester phase than methanol.

The tie lines show, a glycerol phase richer in ethanol than the methyl oleate phase. Since methanol or ethanol and glycerol have both 1:1 carbon to alcohol ratio, a high degree of hydrogen bonding is expected, therefore the alcohol will distribute predominantly in the glycerol phase.[10]

The distribution coefficients for ethanol in the methyl oleate + ethanol + glycerol system (this work) at 333 and ethyl oleate + ethanol +glycerol system at 323 K[13] and the methanol distribution coefficient in the methyl oleate + methanol + glycerol[10] system at 333K are presented in Figure 2b.

The distribution coefficient of alcohol (K_2) was defined as the relation between the alcohol (methanol or ethanol) mole fraction in the fatty acid and glycerol phases:

$$K_2 = \frac{x_{\text{alcohol}}^{\text{fatty acid}}}{x_{\text{alcohol}}^{\text{glycerol}}} \tag{3}$$

From this equation, lower distribution coefficients imply higher concentrations of alcohol in the glycerol phase and lower amounts of alcohol dissolved in fatty acid.

The distribution coefficient of alcohol values are inferior to 1 showing, as expected, that the glycerol phase is richer in alcohol than the methyl oleate phase. From the same results Mesquita et al.[24] have reported that the ethanol can be considered to be a good extractant for the separation of soybean or sunflower biodiesel (obtained by the methyl route) + glycerol mixtures.

The distribution coefficient for ethanol in the methyl oleate + ethanol + glycerol and ethyl oleate + ethanol + glycerol are higher than the methanol distribution coefficient in the methyl oleate + methanol + glycerol shown in Figure 2b. In the ethanol systems the mutual solubility among components (methyl oleate or ethyl oleate and glycerol) is higher than those in methanol systems. As mentioned before, the ethanol is more soluble in the methyl oleate than methanol.

Figures 3 and 4 show the temperature influence on the ternary phase diagrams of methyl oleate + ethanol + glycerol.

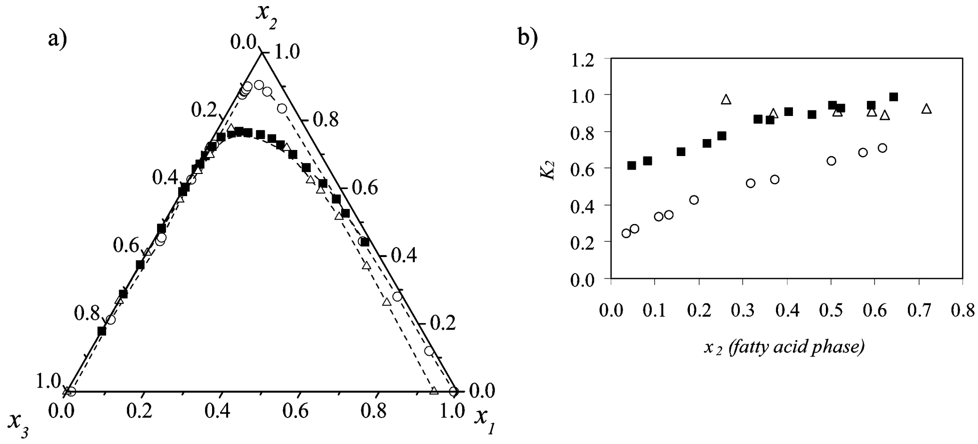

Figure 2. Comparison between the binodal curve (a) and experimental distribution coefficients of alcohol (b) in methyl oleate (1) + methanol (2) + glycerol (3) (refs 31 and 10, ○) at 333 K; methyl oleate (1) + ethanol (2) + glycerol (3) (this work, ■) at 333 K and ethyl oleate (1) + ethanol (2) + glycerol (3) (ref 13, Δ) at 323.15 K.

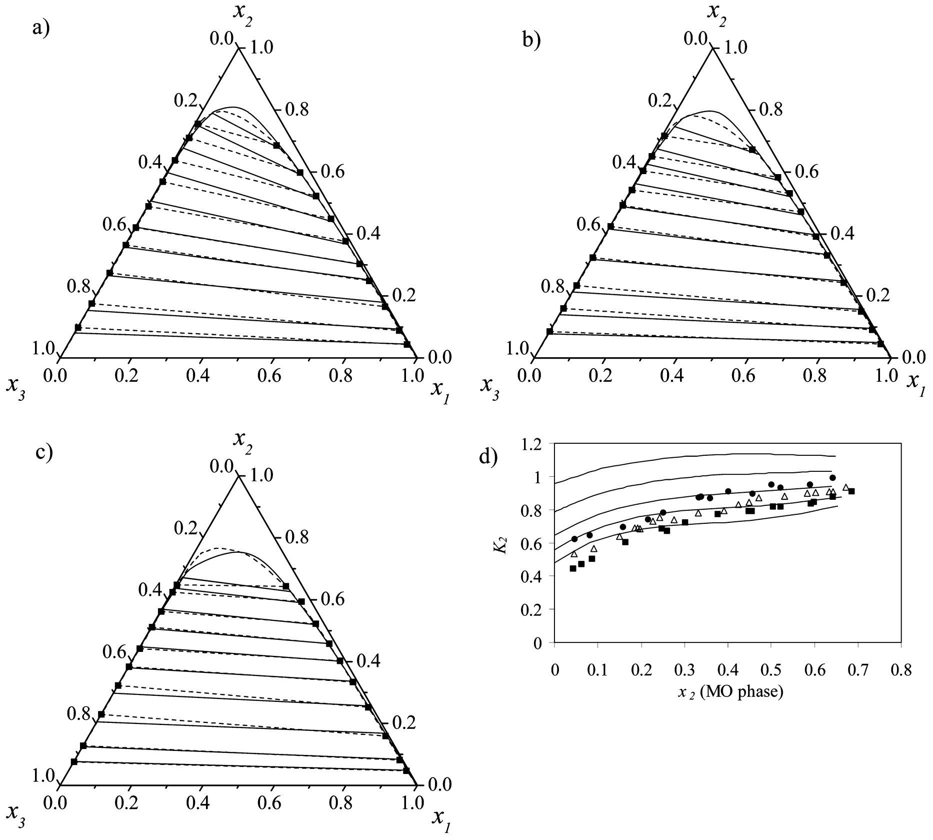

Figure 3. Comparison between GCA-EoS predicted (solid lines) and experimental tie lines and binodal curve (dashed lines/symbols) of the ternary system methyl oleate(1) + ethanol(2) + glycerol(3) at (a) 303 K, (b) 318 K, (c) 333 K. (d) Distribution coefficients of ethanol (K_2) at 303, 318, 333, 353, and 373 K: experimental (symbols) and GCA-EoS predictions (lines).

The solubility region increases with temperature. Similar results were found in the methyl oleate + methanol + glycerol[10] ternary system. The concentration of glycerol in the methyl ester phase is very low at the lower temperature. From the thermodynamic point of view, phase separation will be more effective, when the products are cooled. However, as discussed by Čerče et al.[4] transport properties have also to be considered in defining suitable conditions for phase separations.

Figures 3d and 4d represent the change of ethanol distribution coefficient with temperature and ethanol concentration in the ester phase in the methyl oleate + ethanol + glycerol ternary system. These figures show an increase of the distribution coefficient of ethanol with temperature.

3. THERMODYNAMIC MODELING SECTION

Regarding the thermodynamic modeling of alkyl ester + alcohols + glycerol, the traditional UNIFAC and its versions,[3,32,33] UNIQUAC,[25,33−35] NRTL model,[14,24,33−35] Wilson activity coefficient model,[5,6] GC−PPC−SAFT model,[9] CPA EoS,[11,13,36−38] GCA−EoS[10,39,40] have been applied.

Liquid−liquid experimental and UNIQUAC[41] and NRTL[42] correlations on methyl ester− glycerol binary systems and glycerol−methyl ester−methanol ternary systems have been presented by Korgitzsch.[34] Meanwhile, Kuramochi et al.[32] have made predictions of vapor−liquid and liquid−liquid equilibrium data using different UNIFAC[43,44] models. Chiu et al.[6] and Di Felice et al.[5] have studied the distribution coefficients of methanol between the biodiesel and glycerol phases. In both studies the experimental data were well correlated with the Wilson equation.[45] Negi et al.[3] have compared with agreement their experimental data on glycerol−methanol−methyl oleate with UNIFAC and UNIFAC−Dortmund predictions, while Zhang et al.[35] have applied UNIQUAC and NRTL activity coefficient models. Machado et al.[14] have measured the liquid−liquid equilibrium in the ternary castor oil biodiesel + ethanol + glycerol and have correlated with the NRTL model presenting goods results. Also Mesquita et al.[24] have applied the NRTL in the correlation of the biodiesel + glycerol + ethanol obtaining satisfactory results.

Lee et al.[33] have measured LLE data for the ternary systems of water + methanol + methyl esters at temperatures from 298 to 318 K and atmospheric pressure. The experimental data were correlated with the UNIFAC model and its modified versions including UNIFAC−LLE and UNIFAC−Dortmund, NRTL and UNIQUAC models. The UNIFAC, and its modified versions cannot reasonably predict the phase compositions of tie-lines, while the UNIQUAC model accurately correlates the LLE data for those investigated ternary systems. In addition França et al.[25] have obtained satisfactory results in correlation using UNIQUAC model for castor oil biodiesel + glycerol + alcohol system.

A group contribution method combined with a statistical associating fluid theory equation of state (GC-PPC-SAFT)[46] was able to predict with good quality the liquid−liquid diagram of the methanol + glycerol + methyl oleate ternary system reported by Barreau et al.[9]

Andreatta et al.[10] have measured LLE in the ternary system methyl oleate + methanol + glycerol in the range 313−393 K and 1−5 bar. The experimental data were predicted using the group contribution equation of state with association GCA−

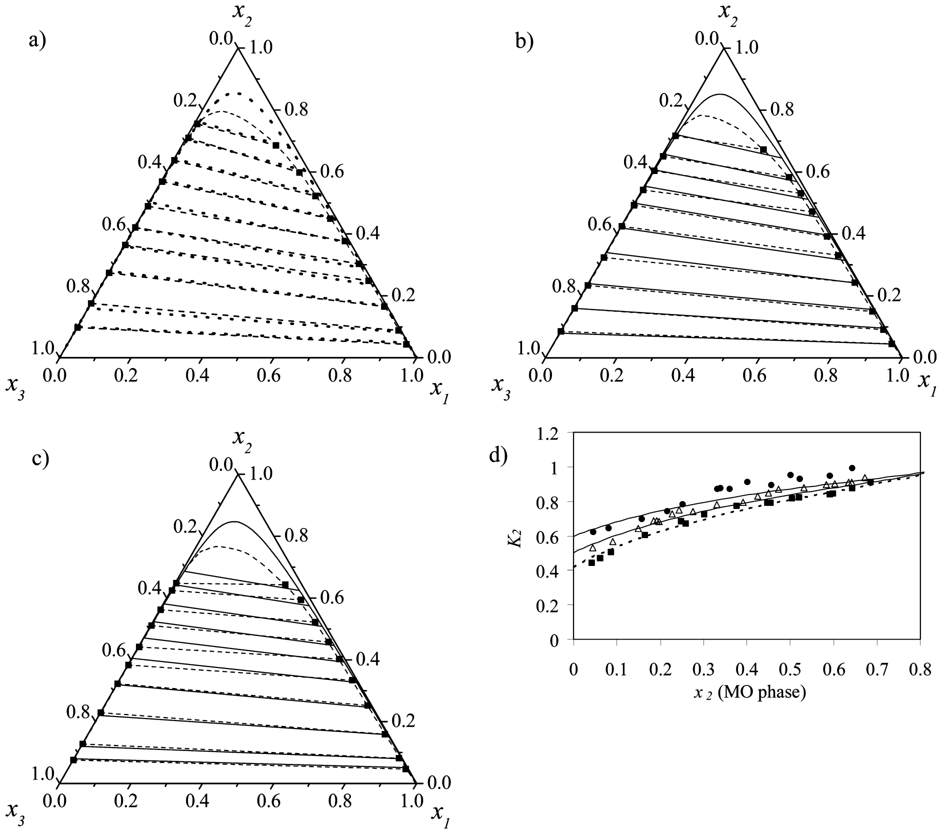

Figure 4. Comparison between A-UNIFAC correlated (dot lines)/predicted (solid lines) and experimental tie lines and binodal curve (dashed lines/symbols) of the ternary system methyl oleate(1) + ethanol(2) + glycerol(3) at (a) 303 K, (b) 318 K, (c) 333 K. (d) Distribution coefficient of ethanol (K_2): experimental (symbols) and A-UNIFAC correlations (dot lines)/predictions (solid lines).

EoS and A−UNIFAC activity coefficient model. The A-UNIFAC predictions of the partial liquid miscibility in the ternary system are reasonably good, though at lower temperatures this model erroneously predicts partial liquid miscibility between methanol and methyl oleate. The GCA−EoS model in particular shows a good predictive capability and has been used to predict phase equilibrium in the transesterification with supercritical alcohols.[10,40] Also, GCA−EoS equation was used satisfactory to model the phase behavior of biodiesel in binary mixtures with glycerol and alcohols and in ternary mixtures with glycerol and methanol.[39]

The experimental vapor−liquid equilibria of glycerol in binary mixtures with several alcohols from methanol to butanol were studied by Oliveira et al.[36] and the data were correlated with the CPA equation of state.[47] In the same work, they have compared the experimental ternary system methanol−glycerol−methyl oleate[3,10] with the CPA predictions. This model was also successfully applied in the predictions of the liquid−liquid equilibria for the canola oil biodiesel + ethanol + glycerol system at temperatures between 303 and 333 K[11] and ethyl esters + ethanol + glycerol at 323 and 353 K.[13] Furthermore the CPA has shown correct predictions in the vapor−liquid equilibria of ester + alcohols binary systems[37] and the predictions of near and supercritical alcohol + fatty acid ester and alcohol + glycerol systems, between 493−573 K and 2−12 MPa.[38]

In this work, the ternary system methyl oleate + ethanol + glycerol studied was modeled using the group contribution with association GCA−EoS equation of state and the A-UNIFAC model.

3.1. GCA−EoS Model.

The GCA−EoS model[27] is an extension to associating systems, of the GC−EOS equation of state originally proposed by Skjold−Jørgensen[48] for the calculation of gas solubilities in solvent mixtures. The GCA−EoS equation has three different contributions to the residual properties: repulsive, attractive, and associative. The Carnahan−Starling repulsive term uses the critical hard sphere diameter (d_c) to represent molecular size; the value of d_c is obtained from the critical properties and vapor pressure data of pure compounds. The group−contribution attractive term is a local composition, density−dependent NRTL expression. The characteristic parameters in this term are the surface energy (g_{ii}) of each functional group and the binary and nonrandom interaction parameters between different functional groups (k_{ij} and α_{ij}). Both, g_{ii} and k_{ij} can be temperature dependent. The group-contribution association term is based on Wertheim's theory[49] for fluids with highly directed attractive forces. Each associative functional group is characterized by the energy (ε) and volume (κ) of association between bonding sites. More details about the GCA−EoS equation can be found in earlier publications.[27]

The association effects in methyl oleate + ethanol + glycerol systems were described by three different associating groups, alcohol hydroxyl group (OH), glycerol hydroxyl group (OH^{gly}), and ester (CH_2COO) group, according to the procedure of Andreatta et al.[39] These authors have introduced an OH^{gly} associating group because the use of three OH groups to describe association in the glycerol molecule resulted in an overestimation of the self- and cross-association forces. The introduction of an OH^{gly} different from the alcohol (OH)

Table 1. GCA-EoS Pure-Group and Binary Interaction Parameters[a]

			pure-group parameters			
group	T_i*/ (K)	Q	g*	g'	g''	ref
CH_3	600.0	0.848	316910.00	−0.9274	0.0000	48
CH_2	600.0	0.540	356080.00	−0.8755	0.0000	48
CH_2COO	600.0	1.420	831400.00	−1.0930	0.0000	61
CH_3CH_2OH	**514.0**	**1.972**	**479952.59**	**-0.7454**	**0.1544**	this work
$C_3H_8O_3$	850.0	3.060	568125.90	−0.4833	0.0000	39

			binary interaction parameters			
group i	group j	k_{ij}	k'_{ij}	α_{ij}	α_{ji}	ref
CH_2COO	CH_3/CH_2	0.8690	0.000	0.00	0.00	61
CH_3CH_2OH	**CH_3**	**1.0100**	**0.093**	**0.00**	**0.00**	this work
	CH_2	**1.0400**	**0.062**	**0.00**	**2.00**	this work
	CH_2COO	**0.9900**	**-0.060**	**0.00**	**0.00**	this work
	$C_3H_8O_3$	**0.9390**	**0.000**	**0.00**	**0.00**	this work
$C_3H_8O_3$	CH_3/CH_2	0.9870	0.000	0.00	0.00	39
	CH_2COO	0.9052	0.000	0.00	0.00	39

[a] The units of the g parameters correspond to temperatures in Kelvin, volumes in $cm^3 \cdot mol^{-1}$, and a gas constant R = 82.05 cm^3 atm mol^{-1} K^{-1}.

group can be justified by the high degree of flexibility of glycerol; the presence of three hydroxyl groups can give rise to intra- and/or intermolecular hydrogen bonds.[50] From the point of view of association, ethanol, and glycerol molecules have one OH and three OH^{gly} groups, respectively. Each OH and OH^{gly} group is considered to have two associating sites: one electronegative O and one electropositive H. On the other hand, association in methyl ester is considered to take place through a single electron−donor site in the ester CH_2COO functional group. The ester associating group does not self-associate but can cross-associate with groups that have one electropositive site, such as the OH and OH^{gly} groups.

These mixtures present multiple associating sites and interactions, so a proper numerical approach was required for the mathematical solution of the phase equilibrium problem. Michelsen and Hendriks[51] and Tan et al.[52] have proposed procedures to obtain robust numerical solutions of these problems. Soria et al.[53] have explained in detail the application of these procedures in the GCA−EoS model.

For the quantification of dispersive forces (attractive term), ethanol and glycerol were described by the molecular groups CH_3CH_2OH and $C_3H_8O_3$, respectively. Methyl oleate (MO) was represented by one ester group (CH_2COO), two CH_3, and 15 CH_2 paraffin groups.

The critical diameters (d_c) of methyl oleate and glycerol were calculated from the critical properties while the critical diameter of ethanol was obtained from the critical properties and the corresponding vapor pressure of data set.

The (CH_3CH_2OH) characteristic temperature T* was set equal to 514 K, the critical temperature of ethanol[48] and the surface parameter q was calculated from van der Waals surface area, according to Bondi.[54]

The pure-group energy parameters of ethanol were determined by fitting vapor pressure data of pure ethanol. The GCA−EoS equation was able to reproduce the vapor pressures[55] of this compound with an average deviation of 0.38% in the range of temperatures 290−510 K. The binary interaction parameters between ethanol (CH_3CH_2OH) and paraffin groups (CH_3/CH_2) were obtained by fitting experimental vapor−liquid equilibrium data of ethanol−alkanes (pentane, hexane, heptane, octane) at temperatures between 293 and 318 K and pressures between 0.06 and 0.7 bar[56,57] and infinite dilution activity coefficients (γ^{∞}) of ethanol + alkanes (pentane, hexane, heptane, octane) at temperatures between 283−354 K and atmospheric pressure.[58]

The binary interaction parameters ethanol and ester (CH_2COO) groups were obtained by fitting experimental vapor−liquid equilibrium data on the binary fatty acid methyl ester (methyl laurate, methyl myristate, methyl oleate) + ethanol at 1 bar.[37] The interaction parameters ethanol−glycerol were obtained by adjusting vapor−liquid equilibrium data between both components in the range 0.2−88 bar and 320−573 K.[36,59,60] Good results were obtained in the correlation procedure.

Table 1 reports the complete set of pure-group and binary interaction parameters while Table 2 presents the association parameters required for predicting the phase behavior of ternary mixtures between methyl oleate, ethanol, and glycerol. The numbers in bold correspond to the new parameters obtained in this work. The remaining parameters were taken from elsewhere.[39,48,61]

Table 2. Energy (ε/k) and Volume (κ) of Association in the GCA-EoS Model[a]

	ε/k (K)	κ (cm^3/mol)
self-association OH	2700.0	0.8621
self-association OH^{gly}	2480.0	0.7350
cross-association OH−CH_2COO	2105.3	0.9916
cross-association OH^{gly}−CH_2COO	2200.0	0.9100
cross-association OH−OH^{gly}	2660.0	0.7986

[a] The parameters were taken from Andreatta et al.[39]

Figure 3 compares GCA−EoS predictions with the experimental data measured in this work for the ternary system methyl oleate + ethanol + glycerol. The model gives a very adequate representation of liquid−liquid equilibria. In addition, using the predictive capacity of this model, Figure 3d shows the distribution coefficients of ethanol at 353 and 373 K.

The standard deviation in the prediction of methanol distribution coefficients is 9.5%. The mean and maximum absolute differences between the experimental and calculated molar fractions of methyl oleate in the glycerol phase are 0.001 and 0.009, respectively. The same differences for the molar

Table 3. GCA-EoS Binary Interaction Parameters between Alcohols with Ester and Glycerol

group *i*	group *j*	k_{ij}	k'_{ij}	α_{ij}	α_{ji}	ref
$C_3H_8O_3$	CH_3OH	1.040	0.00	0.00	0.00	39
	CH_3CH_2OH	0.939	0.00	0.00	0.00	this work
CH_2COO	CH_3OH	1.000	0.00	0.00	0.00	61
	CH_3CH_2OH	0.990	−0.06	0.00	0.00	this work

fraction of glycerol in the methyl oleate phase are 0.004 and 0.012, respectively. Table 3 compares the GCA–EoS binary interaction parameters between methanol and ethanol with ester and glycerol used in this work for the system methyl oleate + ethanol + glycerol and those reported before for the methyl oleate + methanol + glycerol[39] system. Both alcohols were descripted by molecular groups, and their binary interaction parameters with ester and glycerol were obtained from the respective binary system. As we can see from this Table, the parameters present smalls differences between them due to the parametrization procedure.

3.2. A-UNIFAC Model. Mengarelli et al.[28] have presented a modified UNIFAC model that takes into account association effects. This A-UNIFAC model adds a group contribution association term to the original UNIFAC combinatorial and residual expressions.[43] As in the GCA–EoS equation, this association term is based on Wertheim's theory for fluids with highly directed attractive forces[49] and it follows the group contribution approach proposed by Gros et al.[27]

The same procedure applied by Soria et al.[53] in the GCA–EoS model to calculate the phase equilibrium of systems with multiple associating groups was applied in the A-UNIFAC model.

In this model, the association effects in the ternary system methyl oleate + ethanol + glycerol are represented by different associating functional groups described before for the GCA–EoS model. The scarce experimental information of phase equilibrium glycerol–alkanes avoided the estimation for a new associative "glycerol hydroxyl group" (OH^{gly}). In this sense, just one reference of activity coefficients at infinite dilution of alkanes in glycerol[62] was found and it was not sufficient to estimate the association and residual parameters from this unique data set. So, the association effects in methyl oleate + ethanol + glycerol were described by two different associating groups: alcohol hydroxyl group (OH) and ester (CCOO) group according the procedure of Andreatta et al.[10] used to represent the liquid–liquid equilibria of methyl oleate + methanol + glycerol ternary system.

From the point of view of association, ethanol and glycerol molecules have one and three OH groups, respectively. Each OH group is considered to associate through one electronegative O and one electropositive H bonding site. On the other hand, association in methyl ester is considered to take place through a single electron–donor site in the ester CH_2COO functional group.

Table 4 reports the values of the oxidril (OH) and ester (CCOO) self- and cross-association parameters for the A-UNIFAC model while Table 5 reports the residual group interaction parameters. Again, the numbers in bold are the new parameters determined in this work. The remaining parameters were taken from elsewhere.[10,63,64]

The group composition of each compound is the same as the one adopted in the GCA–EoS equation. Table 6 shows the A-UNIFAC group volume (R_k) and surface area (Q_k) parameters used in the mixture studied.

Table 4. Energy ε/k and Volume κ Association Parameters for the A-UNIFAC Model[a]

	ε/k (K)	κ
self-association OH	3125.0	0.0062
cross-association OH–CCOO	1975.0	0.0710

[a] The parameters were taken from Ferreira et al.[63]

Table 5. Residual Group Interaction Parameters $a_{m,n}$ (K) for the A-UNIFAC Model

m	*n*			
	CH_2	$\mathbf{CH_3CH_2OH}$	$C_3H_8O_3$	CCOO
CH_2	0.00	**125.90**[a]	101.50[c]	232.10[b]
$\mathbf{CH_3CH_2OH}$	**-52.06**[a]	0.00	**-17.10**[a]	**-15.50**[a]
$C_3H_8O_3$	−51.20[c]	**60.00**[a]	0.00	886.30[c]
CCOO	114.80[b]	**8.40**[a]	20.00[c]	0.00

[a] The parameters were taken from this work. [b] The parameters were taken from Gmehling et al.[64] [c] The parameters were taken from Andreatta et al.[10]

Table 6. A-UNIFAC Group Volume (R_k) and Surface Area (Q_k) Parameters[a]

k	R_k	Q_k
CH_3	0.9011	0.848
CH_2	0.6744	0.540
ethanol	**2.1055**	**1.972**
glycerol	3.3856	3.060
CH_2COO	1.6764	1.420

[a] The bold numbers were obtained in this work while the remainder were taken from Gmehling et al.[64]

The binary interaction parameters between ethanol (CH_3CH_2OH) and paraffin groups (CH_2) were obtained by fitting experimental vapor–liquid equilibrium data of ethanol–alkanes (pentane, hexane, heptane, octane, isooctane) in the range 293–318 K and 0.06 and 0.7 bar[56,57] and infinite dilution activity coefficients (γ^{∞}) of ethanol + alkanes (pentane, hexane, heptane, octane) at temperatures between 283–354 K.[58]

The ethanol–ester (CH_3CH_2OH/CCOO) and ethanol–glycerol ($CH_3CH_2OH/C_3H_8O_3$) residual interaction parameters were obtained by fitting experimental liquid–liquid equilibrium data of methyl oleate + ethanol + glycerol at 303 K and atmospheric pressure reported in this work.

The predictive capability of the A-UNIFAC model was evaluated by calculating the liquid–liquid equilibria of methyl oleate + ethanol + glycerol at 318 and 333 K. The correlation and predictions results are shown in Figure 4. The A-UNIFAC model is able to give a good representation of liquid–liquid equilibria.

The standard deviation in the prediction of ethanol distribution coefficients is 3.93%. The mean and maximum differences between the experimental and calculated mole fractions of methyl oleate in the glycerol phase are 0.001 and

0.002, respectively. The same differences for the mole fraction of glycerol in the methyl oleate phase are 0.013 and 0.036, respectively.

Table 7 compares the A-UNIFAC residual group interaction parameters between methanol and ethanol with ester and glycerol used in this work for the system methyl oleate + ethanol + glycerol and those reported before for the system methyl oleate + methanol + glycerol.[10] Like GCA−EoS model, methanol and ethanol were descripted by molecular groups. However, in this work the residual interaction parameters ethanol−ester and ethanol−glycerol were obtained by fitting experimental LLE of methyl oleate + ethanol + glycerol at 303 K while in the previous work[10] the residual interaction parameters were obtained by fitting isothermal vapor−liquid equilibrium data on the respective binary systems. This procedure was not possible to follow in this work due the impossibility of the A-UNIFAC to predict the methyl oleate + ethanol + glycerol ternary system from the parameters obtained in the correlation of the respective binary systems. Therefore, the parameters between ester and glycerol with the corresponding alcohols present a high difference between them.

Table 7. A-UNIFAC Residual Group Interaction Parameters $a_{m,n}$ between Alcohols with Ester and Glycerol

m	n	a_{mn}	a_{nm}	ref
$C_3H_8O_3$	CH_3OH	−273.60	417.40	10
	CH_3CH_2OH	60.00	−17.10	this work
CCOO	CH_3OH	18.49	200.20	10
	CH_3CH_2OH	8.40	−15.50	this work

4. CONCLUSIONS

New measurements for liquid−liquid equilibria of methyl oleate + ethanol + glycerol have been presented in this work at 303, 318, and 333 K and atmospheric pressure. The isothermal experimental data have shown a good linear fit in an Othmer−Tobias plot.

Some remarks are important at the moment to choose the best model to design the purification of biodiesel: (a) the mixtures involved in this kind of mixture present polar compounds with strong associative interactions increasing the complexity of these systems and hindering the use of conventional thermodynamic models, therefore, an important factor to take into account is the ability of the model to describe the association effects present in the mixture; (b) group contribution models have an advantage over molecular models: a large number of compounds and mixtures can be represented with a reduced number of functional groups; (c) the ability to predict the phase behavior in situations in which no experimental data are available.

In this work, the GCA−EoS and A-UNIFAC group contribution thermodynamic models that take into account association effects were used to represent correctly the experimental information. While GCA−EoS model can predict all the isotherms studied, the A-UNIFAC model only shows predictive capability at 318 and 333 K.

GCA−EoS has shown capability to model conditions over wide ranges of temperature and pressure up to 30 MPa,[48] therefore, this model can be applied to explore the operating conditions in the reactor and the downstream separation train of low- and high-pressure biodiesel production plants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Solubility and tie line data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Madras, G.; Kolluru, C.; Kumar, R. Synthesis of Biodiesel in Supercritical Fluids. *Fuel* **2004**, *83*, 2029.

(2) Zhou, H.; Lu, H.; Liang, B. Solubility of Multicomponent Systems in the Biodiesel Production by Transesterification of Jatropha Curcas L. Oil with Methanol. *J. Chem. Eng. Data* **2006**, *51*, 1130.

(3) Negi, D. S.; 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.

(4) Čerče, T.; Peter, S.; Weidner, E. Biodiesel-Transesterification of Biological Oils with Liquid Catalysts: Thermodynamic Properties of Oil-Methanol-Amine Mixtures. *Ind. Eng. Chem. Res.* **2005**, *44*, 9535.

(5) 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.

(6) Chiu, C.-W.; Goff, M. J.; Suppes, G. J. Distribution of Methanol and Catalysts between Biodiesel and Glycerin Phases. *AIChE J.* **2005**, *51*, 1274.

(7) Ma, F.; Clements, L. D.; Hanna, M. A. Biodiesel Fuel from Animal Fat. Ancillary Studies on Transesterification of Beef Tallow. *Ind. Eng. Chem. Res.* **1998**, *37*, 3768.

(8) Csernica, S. N.; Hsu, J. T. Reverse-Phase Ternary Phase Diagram, Tie Lines, and Plait Point for Commercial Biodiesel−Glycerol−Methanol. *Ind. Eng. Chem. Res.* **2010**, *50*, 1012.

(9) Barreau, A.; Brunella, I.; de Hemptinne, J. C.; 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.

(10) Andreatta, A. E.; Casás, L. M.; Hegel, P.; Bottini, S. B.; Brignole, E. A. Phase Equilibria in Ternary Mixtures of Methyl Oleate, Glycerol, and Methanol. *Ind. Eng. Chem. Res.* **2008**, *47*, 5157.

(11) Oliveira, M. B.; Barbedo, S.; Soletti, J. I.; Carvalho, S. H. V.; Queimada, A. J.; Coutinho, J. A. P. Liquid−Liquid Equilibria for the Canola Oil Biodiesel + Ethanol + Glycerol System. *Fuel* **2011**, *90*, 2738.

(12) Liu, X.; Piao, X.; Wang, Y.; Zhu, S. Liquid−Liquid Equilibrium for Systems of (Fatty Acid Ethyl Esters + Ethanol + Soybean Oil and Fatty Acid Ethyl Esters + Ethanol + Glycerol). *J. Chem. Eng. Data* **2008**, *53*, 359.

(13) Follegatti-Romero, L. A.; Oliveira, M. B.; Batista, F. R. M.; Batista, E. A. C.; Coutinho, J. A. P.; Meirelles, A. J. A. Liquid−Liquid Equilibria for Ternary Systems Containing Ethyl Esters, Ethanol, and Glycerol at 323.15 and 353.15 K. *Fuel* **2012**, *94*, 386.

(14) Machado, A. B.; Ardila, Y. C.; de Oliveira, L. H.; Aznar, M.n.; Wolf Maciel, M. R. Liquid−Liquid Equilibrium Study in Ternary Castor Oil Biodiesel + Ethanol + Glycerol and Quaternary Castor Oil

Biodiesel + Ethanol + Glycerol + NaOH Systems at (298.2 and 333.2) K. *J. Chem. Eng. Data* **2011**, *56*, 2196.

(15) Ardila, Y. C.; Pinto, G. M. F.; Machado, A. B.; Wolf Maciel, M. R. Experimental Determination of Binodal Curves and Study of the Temperature in Systems Involved in the Production of Biodiesel with Ethanol. *J. Chem. Eng. Data* **2010**, *55*, 4592.

(16) Joshi, H.; Moser, B. R.; Toler, J.; Walker, T. Preparation and Fuel Properties of Mixtures of Soybean Oil Methyl and Ethyl Esters. *Biomass Bioenergy* **2010**, *34*, 14.

(17) Kumar, D.; Kumar, G.; Johari, R.; Kumar, P. Fast, Easy Ethanomethanolysis of Jatropha Curcus Oil for Biodiesel Production Due to the Better Solubility of Oil with Ethanol in Reaction Mixture Assisted by Ultrasonication. *Ultrason. Sonochem.* **2012**, *19*, 816.

(18) Guo, Y.; Wei, H.; Yang, F.; Li, D.; Fang, W.; Lin, R. Study on Volatility and Flash Point of the Pseudo-binary Mixtures of Sunflowerseed-Based Biodiesel+Ethanol. *J. Hazard. Mater.* **2009**, *167*, 625.

(19) Zhu, L.; Cheung, C. S.; Zhang, W. G.; Huang, Z. Combustion, Performance and Emission Characteristics of a DI Diesel Engine Fueled with Ethanol−Biodiesel Blends. *Fuel* **2011**, *90*, 1743.

(20) Shi, X.; Yu, Y.; He, H.; Shuai, S.; Wang, J.; Li, R. Emission Characteristics Using Methyl Soyate−Ethanol−Diesel Fuel Blends on a Diesel Engine. *Fuel* **2005**, *84*, 1543.

(21) Chotwichien, A.; Luengnaruemitchai, A.; Jai-In, S. Utilization of Palm Oil Alkyl Esters as an Additive in Ethanol−Diesel and Butanol−Diesel Blends. *Fuel* **2009**, *88*, 1618.

(22) Park, S. H.; Kim, S. H.; Lee, C. S. Mixing Stability and Spray Behavior Characteristics of Diesel−Ethanol−Methyl Ester Blended Fuels in a Common-Rail Diesel Injection System. *Energy Fuels* **2009**, *23*, 5228.

(23) Sharma, Y. C.; Singh, B.; Upadhyay, S. N. Advancements in Development and Characterization of Biodiesel: A Review. *Fuel* **2008**, *87*, 2355.

(24) Mesquita, F. M. R.; Feitosa, F. X.; Sombra, N. E.; de Santiago-Aguiar, R. S.; de Sant'Ana, H. B. Liquid−Liquid Equilibrium for Ternary Mixtures of Biodiesel (Soybean or Sunflower) + Glycerol + Ethanol at Different Temperatures. *J. Chem. Eng. Data* **2011**, *56*, 4061.

(25) França, B. B.; Pinto, F. M.; Pessoa, F. L. P.; Uller, A. M. C. Liquid−Liquid Equilibria for Castor Oil Biodiesel + Glycerol + Alcohol. *J. Chem. Eng. Data* **2008**, *54*, 2359.

(26) Carvalho, S. *Equilíbrio Líquido−Líquido na Produção de Biodiesel.* Master Dissertation, Aveiro University, Portugal, 2007.

(27) Gros, H. P.; Bottini, S.; Brignole, E. A. A Group Contribution Equation of State for Associating Mixtures. *Fluid Phase Equilib.* **1996**, *116*, 537.

(28) Mengarelli, A. C.; Brignole, E. A.; Bottini, S. B. Activity Coefficients of Associating Mixtures by Group Contribution. *Fluid Phase Equilib.* **1999**, *163*, 195.

(29) Peschke, N.; Sandler, S. I. Liquid−Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 1. *J. Chem. Eng. Data* **1995**, *40*, 315.

(30) Othmer, D.; Tobias, P. Liquid−Liquid Extraction Data—The Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693.

(31) Andreatta, A. E. *Equilibrio entre Fases en el Procesamiento de Productos Naturales Renovables*. Ph.D. Thesis, Universidad Nacional del Sur, Argentine, 2008.

(32) Kuramochi, H.; Maeda, K.; Kato, S.; Osako, M.; Nakamura, K.; Sakai, S.-i. Application of UNIFAC Models for Prediction of Vapor−Liquid and Liquid−Liquid Equilibria Relevant to Separation and Purification Processes of Crude Biodiesel Fuel. *Fuel* **2009**, *88*, 1472.

(33) Lee, M.-J.; Lo, Y.-C.; Lin, H.-M. Liquid−Liquid Equilibria for Mixtures Containing Water, Methanol, Fatty Acid Methyl Esters, and Glycerol. *Fluid Phase Equilib.* **2010**, *299*, 180.

(34) Korgitzsch, F. M. *Study of Phase Equilibria as a Fundament for the Refinement of Vegetable and Animal Fats and Oils*. Ph.D. Thesis, Technical University of Berlin, Germany, 1993.

(35) Zhang, Y.; Dubé, M. A.; McLean, D. D.; Kates, M. Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment. *Bioresour. Technol.* **2003**, *89*, 1.

(36) Oliveira, M. B.; Teles, A. R. R.; Queimada, A. J.; Coutinho, J. A. P. Phase Equilibria of Glycerol Containing Systems and Their Description with the Cubic-Plus-Association (CPA) Equation of State. *Fluid Phase Equilib.* **2009**, *280*, 22.

(37) Oliveira, M. B.; Miguel, S. I.; Queimada, A.n.J.; Coutinho, J.o.A.P. Phase Equilibria of Ester + Alcohol Systems and Their Description with the Cubic-Plus-Association Equation of State. *Ind. Eng. Chem. Res.* **2010**, *49*, 3452.

(38) Oliveira, M. B.; Queimada, A. J.; Coutinho, J. A. P. Prediction of Near and Supercritical Fatty Acid Ester+Alcohol Systems with the CPA-EoS. *J. Supercrit. Fluids* **2010**, *52*, 241.

(39) Andreatta, A. E.; Lugo, R.; de Hemptinne, J.-C.; Brignole, E. A.; Bottini, S. B. Phase Equilibria Modeling of Biodiesel Related Mixtures Using the GCA-EoS Model. *Fluid Phase Equilib.* **2010**, *296*, 75.

(40) Hegel, P.; Andreatta, A.; Pereda, S.; Bottini, S.; Brignole, E. A. High Pressure Phase Equilibria of Supercritical Slcohols with Triglycerides, Fatty Esters and Cosolvents. *Fluid Phase Equilib.* **2008**, *266*, 31.

(41) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116.

(42) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135.

(43) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086.

(44) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC: A Group Contribution Method*; Elsevier Scientific Pub. Co.: Michigan, 1977.

(45) Wilson, G. M. Vapor−Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127.

(46) Tamouza, S.; Passarello, J. P.; Tobaly, P.; de Hemptinne, J. C. Group Contribution Method with SAFT EOS Aplied to Vapor Liquid Equilibria of Various Hydrocarbon Series. *Fluid Phase Equilib.* **2004**, *222−223*, 67.

(47) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An Equation of State for Associating Fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310.

(48) Skjold-Jørgensen, S. Gas Solubility Calculations. II. Application of a New Group-Contribution Equation of State. *Fluid Phase Equilib.* **1984**, *16*, 317.

(49) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations. *J. Stat. Phys.* **1984**, *35*, 35.

(50) Chelli, R.; Gervasio, F. L.; Gellini, C.; Procacci, P.; Cardini, G.; Schettino, V. Density Functional Calculation of Structural and Vibrational Properties of Glycerol. *J. Phys. Chem. A.* **2000**, *104*, 5351.

(51) Michelsen, M. L.; Hendriks, E. M. Physical Properties from Association Models. *Fluid Phase Equilib.* **2001**, *180*, 165.

(52) Tan, S. P.; Adidharma, H.; Radosz, M. Generalized Procedure for Estimating the Fractions of Nonbonded Associating Molecules and Their Derivatives in Thermodynamic Perturbation Theory. *Ind. Eng. Chem. Res.* **2003**, *43*, 203.

(53) Soria, T. M.; Andreatta, A. E.; Pereda, S.; Bottini, S. B. Thermodynamic Modeling of Phase Equilibria in Biorefineries. *Fluid Phase Equilib.* **2011**, *302*, 1.

(54) Bondi, A. A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley: New York, 1968.

(55) *Design Institute for Physical Properties, BYU-DIPPR, Project 801 Evaluated Process Design Data*. American Institute of Chemical Engineers: New York, 2003.

(56) Gmehling, J.; Onken, U.; Arlt, W. Organic hydroxy compounds: alcohols. *Vapor Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol. I, 2c; Dechema: Frankfurt, Germany, 1982; Supplement 1.

(57) Gmehling, J.; Onken, U. Organic hydroxy compounds: alcohols. *Vapor Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol. I, 2a; Dechema: Frankfurt, Germany, 1977.

(58) Cori, L.; Delogu, P. Infinite Dilution Activity Coefficients of Ethanol-*n*-Alkanes Mixtures. *Fluid Phase Equilib.* **1986**, *27*, 103.

(59) Shimoyama, Y.; Abeta, T.; Zhao, L.; Iwai, Y. Measurement and Calculation of Vapor−Liquid Equilibria for Methanol + Glycerol and Ethanol + Glycerol Systems at 493−573 K. *Fluid Phase Equilib.* **2009**, *284*, 64.

(60) Coelho, R.; dos Santos, P. G.; Mafra, M. R.; Cardozo-Filho, L.; Corazza, M. L. (Vapor + Liquid) Equilibrium for the Binary Systems {Water + Glycerol} and {Ethanol + Glycerol, Ethyl Stearate, and Ethyl Palmitate} at Low Pressures. *J. Chem. Thermodyn.* **2011**, *43*, 1870.

(61) Ferreira, O.; Macedo, E. A.; Brignole, E. A. Application of the GCA−EoS Model to the Supercritical Processing of Fatty Oil Derivatives. *J. Food Eng.* **2005**, *70*, 579.

(62) Ge, M.-L.; Ma, J.-L.; Wu, C.-G. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in Glycerol Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2010**, *55*, 1714.

(63) Ferreira, O.; Macedo, E. A.; Bottini, S. B. Extension of the A-UNIFAC Model to Mixtures of Cross- and Self-Associating Compounds. *Fluid Phase Equilib.* **2005**, *227*, 165.

(64) Gmehling, J.; Rasmussen, P.; Fredenslund, A. Vapor−Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118.

Table A. Binodal curves for the system methyl oleate (1) + ethanol (2) + glycerol (3)

T=303 K		T=318 K		T= 333 K	
x_1	x_2	x_1	x_2	x_1	x_2
0.616	0.372	0.639	0.347	0.541	0.441
0.481	0.501	0.427	0.550	0.451	0.526
0.398	0.577	0.354	0.613	0.406	0.568
0.320	0.642	0.307	0.650	0.349	0.614
0.284	0.672	0.272	0.674	0.283	0.661
0.205	0.727	0.227	0.705	0.229	0.700
0.153	0.759	0.199	0.723	0.183	0.728
0.075	0.793	0.168	0.741	0.152	0.746
0.038	0.793	0.118	0.763	0.117	0.758
0.018	0.780	0.086	0.774	0.082	0.764
0.010	0.760	0.048	0.783	0.057	0.768
0.006	0.724	0.033	0.779	0.041	0.762
0.005	0.689	0.025	0.770	0.020	0.751
0.003	0.654	0.011	0.751	0.011	0.723
0.003	0.622	0.007	0.731	0.007	0.696
0.003	0.553	0.005	0.674	0.006	0.671
0.003	0.501	0.003	0.625	0.003	0.656
0.002	0.362	0.003	0.562	0.002	0.603
0.002	0.243	0.002	0.484	0.002	0.590
0.001	0.148	0.002	0.396	0.002	0.482
0.001	0.065	0.002	0.351	0.001	0.374
0.001	0.038	0.002	0.220	0.001	0.288
0.001	0.018	0.002	0.134	0.001	0.178

Table B. Experimental LLE data of the system methyl oleate(1) + ethanol(2) + glycerol(3) at 303, 318 and 333 K.

Glycerol phase			Fatty phase		
x_1	x_2	x_3	x_1	x_2	x_3
T= 303 K					
0.010	0.758	0.232	0.263	0.686	0.051
0.008	0.735	0.257	0.320	0.643	0.037
0.006	0.710	0.284	0.373	0.598	0.029
0.005	0.707	0.288	0.381	0.592	0.027
0.003	0.637	0.360	0.458	0.522	0.020
0.003	0.618	0.379	0.476	0.506	0.018
0.003	0.577	0.420	0.527	0.457	0.016
0.003	0.569	0.428	0.536	0.449	0.015
0.003	0.489	0.508	0.611	0.377	0.012
0.002	0.420	0.578	0.687	0.303	0.010
0.002	0.388	0.610	0.731	0.260	0.009
0.002	0.364	0.634	0.743	0.249	0.008
0.002	0.274	0.724	0.828	0.165	0.007
0.001	0.175	0.824	0.907	0.088	0.005
0.001	0.133	0.866	0.934	0.062	0.004
0.001	0.098	0.901	0.953	0.043	0.004
T= 318 K					
0.006	0.717	0.277	0.274	0.672	0.054
0.006	0.706	0.288	0.317	0.642	0.041
0.006	0.697	0.297	0.327	0.635	0.038
0.005	0.667	0.328	0.368	0.602	0.030
0.004	0.651	0.345	0.389	0.583	0.028
0.003	0.604	0.393	0.448	0.530	0.022
0.003	0.542	0.455	0.509	0.472	0.019
0.003	0.532	0.465	0.532	0.449	0.019
0.002	0.512	0.486	0.558	0.425	0.017
0.002	0.492	0.506	0.593	0.391	0.016
0.002	0.424	0.574	0.655	0.331	0.014
0.002	0.372	0.626	0.712	0.276	0.012
0.002	0.324	0.674	0.746	0.244	0.010
0.002	0.312	0.686	0.762	0.228	0.010
0.002	0.289	0.709	0.793	0.198	0.009
0.002	0.280	0.718	0.798	0.193	0.009
0.002	0.270	0.728	0.806	0.186	0.008
0.002	0.234	0.764	0.842	0.150	0.008
0.002	0.160	0.838	0.903	0.091	0.006
0.001	0.085	0.914	0.950	0.045	0.005

Cont. Table B

Glycerol phase			Fatty phase		
x_1	x_2	x_3	x_1	x_2	x_3
T= 333 K					
0.003	0.648	0.349	0.311	0.643	0.046
0.003	0.624	0.373	0.375	0.591	0.034
0.002	0.562	0.436	0.455	0.522	0.023
0.002	0.528	0.470	0.477	0.502	0.021
0.002	0.511	0.487	0.524	0.457	0.019
0.002	0.442	0.556	0.581	0.402	0.017
0.002	0.415	0.583	0.625	0.360	0.015
0.001	0.388	0.611	0.647	0.339	0.014
0.001	0.384	0.615	0.653	0.333	0.014
0.001	0.323	0.676	0.736	0.252	0.012
0.001	0.294	0.705	0.772	0.217	0.011
0.001	0.229	0.770	0.832	0.159	0.009
0.001	0.128	0.871	0.912	0.082	0.006
0.001	0.076	0.923	0.948	0.047	0.005