

Phase Equilibria in Ternary Mixtures of Methyl Oleate, Glycerol, and Methanol

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Transesterification reactions are common in the production of some important chemicals, such as biodiesel and mono- and diglycerides. Knowledge of the phase equilibrium conditions of the reactive mixture is essential to explore possible operating conditions for the reactor and the downstream separation process. In this work, liquid–liquid and vapor–liquid–liquid equilibrium data have been measured for the ternary system methyl oleate–methanol–glycerol, at temperatures between 313 and 393 K. The group contribution with association equation of state (GCA-EOS) and the A-UNIFAC model were applied to represent the phase equilibria of this ternary system. Self-association in glycerol and methanol and cross-association with methyl esters were taken into account.

1. Introduction

The production of biofuels from renewable material is becoming attractive due to the high prices of fossil fuels, the decline of fuel reserves, and the general concern about environmental issues.

Biodiesel is produced by transesterification of triglycerides from oils and fats with an excess of alcohol (generally methanol). A catalyst is generally added to accelerate the reaction. Alkaline-based,¹ acid-based,² homogeneous, or heterogeneous catalysts are employed. The use of enzymes³ and solid or liquid amines⁴ as well as catalyst-free supercritical transesterification processes⁵ has also been investigated.

During transesterification at atmospheric pressure via the conventional catalyzed process, the initial alcohol–triglyceride two-phase reactive mixture changes into an alcohol–glycerol–fatty ester partially miscible system. There are two separate liquid phases at the end of the reaction. The lower phase is rich in glycerol and the upper phase contains the fatty acid ester (generally fatty acid methyl ester, FAME), which is used as biodiesel after purification. Unreacted alcohol (generally methanol) distributes between these two liquid phases. Depending on the process and the raw material, the final reactive mixture may also contain intermediate products, catalyst, water, and soap.

Knowledge of the phase equilibrium condition of the ternary system FAME + glycerol + methanol is obviously necessary for the simulation and optimization of the reactor and the downstream separation train. Only recently a number of experimental results on the phase behavior of biodiesel production processes have been reported in the literature.^{4,6–8} Moreover, some of these data^{7,8} show discrepancies in the values of the distribution coefficients of methanol between the glycerol and fatty phases.

Regarding the thermodynamic modeling of these systems, the traditional UNIFAC, UNIFAC-Dortmund, UNIQUAC, and NRTL activity coefficient models have been applied.^{7,9}

In the present work experimental data of liquid–liquid and vapor–liquid–liquid equilibria of the methyl oleate–methanol–

glycerol system from 313 to 393 K are presented. Taking into account the presence of hydrogen bonding species, two associating models have been applied to represent the experimental data: the group contribution with association equation of state (GCA-EOS)¹⁰ and the UNIFAC with association (A-UNIFAC)¹¹ activity coefficient model.

2. Experimental Section

2.1. Materials and Analytical Methods. The chemicals used for the experiments were glycerol (>99.0% GC, Sigma-Aldrich), methanol (>99.8% GC, Riedel-de Haën), and technical-grade methyl oleate (70%, Aldrich). No further purification of these products was carried out.

The composition of methanol in both liquid phases was determined by measuring the weight of methanol evaporated from liquid samples placed in a vacuum oven at 0.98 bar and 333 K for at least 12 h, until constant weight. After evaporation of methanol, the remaining compounds (glycerol and methyl oleate) were analyzed by gas chromatography (GC) following the AOCS Cd11b-91 official method. Pyridine (99.5%, Sintorgan) was used as solvent, bis(trimethylsilyl)trifluoroacetamide (BSTFA) (98.6%, Supelco) and trimethylchlorosilane (TMCS) (>97%, Aldrich) were the silylating agents, and tetradecane (>99%, Aldrich) was the internal standard. Silylation was applied to glycerol, to facilitate GC analysis.

The chromatographic analyses were carried out in a Varian (3400 CX) gas chromatograph, with a DB5-HT column (J & W, 15 m length, 0.32 mm internal diameter, and 0.1 μ m film thickness) and a flame ionization detector. The carrier gas was hydrogen (99.9%, AGA).

2.2. Experimental Setup and Procedure. A jacketed glass vessel of 70 mL volume with a magnetic stirrer was used to carry out the liquid–liquid equilibrium (LLE) experiments at atmospheric pressure. The two immiscible components (glycerol and methyl oleate) were added into the vessel at a specific molar ratio, and different amounts of the third component (methanol) were added to obtain different global phase compositions for the measurement of a series of tie lines. A thermostat (Cole Parmer, Model 1268-20) with an electronic temperature controller maintained the temperature in the cell constant within ± 0.2 K. The mixture inside the vessel was stirred at a high speed under well-dispersed conditions for 150 min and allowed to

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Table 1. Experimental LLE Data of the System Methyl Oleate (1)–Methanol (2)–Glycerol (3) at 313 and 333 K

glycerol phase			fatty phase		
X_1	X_2	X_3	X_1	X_2	X_3
$T = 313 \text{ K}$					
0.010	0.105	0.885	0.981	0.019	0.000
0.007	0.123	0.871	0.978	0.022	0.000
0.001	0.138	0.861	0.973	0.027	0.000
0.010	0.145	0.846	0.971	0.029	0.000
0.002	0.317	0.681	0.925	0.075	0.000
0.002	0.521	0.477	0.798	0.202	0.000
0.009	0.667	0.324	0.684	0.316	0.000
0.001	0.724	0.275	0.646	0.354	0.000
0.002	0.822	0.176	0.567	0.433	0.000
0.011	0.845	0.144	0.550	0.450	0.000
0.013	0.879	0.108	0.474	0.523	0.003
$T = 333 \text{ K}$					
0.002	0.142	0.856	0.959	0.035	0.007
0.010	0.203	0.787	0.944	0.054	0.002
0.011	0.327	0.662	0.884	0.109	0.008
0.007	0.386	0.608	0.859	0.133	0.007
0.006	0.447	0.547	0.812	0.181	0.007
0.008	0.617	0.376	0.669	0.319	0.012
0.002	0.701	0.297	0.606	0.374	0.020
0.004	0.789	0.207	0.481	0.502	0.017
0.006	0.836	0.157	0.409	0.573	0.017
0.010	0.871	0.119	0.361	0.618	0.021

settle for at least 5 h until both phases became clear. Sampling of the lower (glycerol) and upper (methyl oleate) phases was conducted through the side and upper ports of the equilibrium vessel, respectively. GC syringes (Hamilton) were used to withdraw samples of around 200 μL through the white rubber septa of each port.

At 353, 373, and 393 K, the experimental work was carried out in a high-pressure, constant-volume equilibrium cell (35 mL volume) with maximum operating pressure and temperature of 15 MPa and 420 K, respectively. The cell has a magnetic stirrer and two windows for visual observation of the cell contents. A platinum resistance thermometer measures the temperature, and a proportional controller keeps it constant within $\pm 0.2 \text{ K}$. The cell thermostat is made of a solid aluminum jacket, 12 mm thick, electrically heated. Three 1/16 in. stainless steel sampling lines allow withdrawing of samples of the different phases.¹² Following a procedure similar to the liquid–liquid equilibrium measurements at atmospheric pressure, mixtures of glycerol and methyl oleate with increasing amounts of methanol were fed into the equilibrium cell. After application of vacuum to eliminate air from the cell, each mixture was stirred during 4–6 h and left to stand for at least 16 h to attain equilibrium. Then, samples of about 200 μL were withdrawn from the upper and lower liquid phases, through the corresponding capillary lines and on–off valves. The vapor phase was not sampled. Taking into account the low vapor pressures of glycerol and methyl oleate in the range of temperatures studied, the vapor phase was considered to be pure methanol.

2.3. Analysis. Four samples of known weight were collected from each phase in order to check the repeatability of the measured compositions. The mass fraction of methanol was obtained from the ratio between the weight of methanol removed by vacuum evaporation and the initial weight of the sample. After methanol evaporation, the samples were diluted in pyridine (pyridine to sample ratio equal to 20:1 by volume) for determination of methyl oleate and glycerol mass fractions by the AOCS Cd11b-91 norm. Samples of 100 μL were silylated with 200 μL BSTFA and 100 μL TMCS; 100 μL of a solution of tetradecane in pyridine of known composition was added as internal standard. The vial with the reaction mixture and the internal standard was closed and shaken vigorously. Then the

mixture was heated at 343 K for approximately 20 min and 5 μL of this mixture was injected into the GC column. The detector and injector temperatures were 653 and 593 K, respectively. The initial column temperature was 323 K, and it was held at this value for 3 min before it was raised to 333 K at a rate of 2 K/min. The column was then heated to 523 K at a rate of 10 K/min.

The mass fractions of glycerol and methyl oleate in the sample were determined from the areas of the corresponding GC chromatographic peaks, adjusted by the response factors obtained by previous calibration. From these values and knowing the weight fraction of methanol and the molecular weight of each component, the molar fractions x_i of methyl oleate, methanol, and glycerol in each sample were calculated. The molar fractions reported in Tables 1 and 2 are the mean values obtained from the analysis of four samples taken from each saturated liquid phase. The standard deviation of these values was less than 0.3 mol %.

2.4. Experimental Results. Liquid–liquid equilibria at atmospheric pressure for methyl oleate–methanol–glycerol

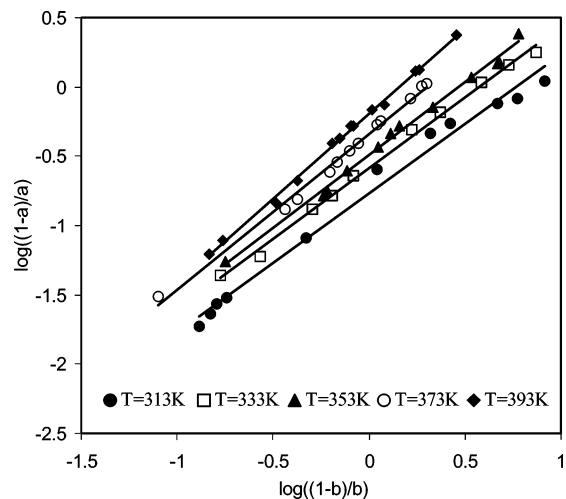


Figure 1. Othmer–Tobias plot. a is the mole fraction of methyl oleate in the methyl oleate rich phase, and b is the glycerol mole fraction in the glycerol rich phase.

Table 2. Experimental LLE and VLLE Data of the System Methyl Oleate (1)–Methanol (2)–Glycerol (3) at 353, 373, and 393 K

glycerol phase			fatty phase			<i>P</i> (bar)
<i>X</i> ₁	<i>X</i> ₂	<i>X</i> ₃	<i>X</i> ₁	<i>X</i> ₂	<i>X</i> ₃	
<i>T</i> = 353 K						
LLE						
0.005	0.147	0.848	0.948	0.045	0.007	
0.008	0.357	0.635	0.860	0.137	0.003	
0.008	0.371	0.621	0.850	0.147	0.003	
0.006	0.431	0.564	0.799	0.197	0.004	
0.009	0.518	0.473	0.730	0.267	0.004	
VLLE						
0.007	0.556	0.437	0.684	0.310	0.006	1.31
0.009	0.582	0.409	0.658	0.336	0.006	1.33
0.013	0.669	0.319	0.582	0.411	0.007	1.38
0.012	0.762	0.227	0.459	0.521	0.019	1.44
0.011	0.813	0.176	0.404	0.575	0.021	1.47
0.012	0.814	0.174	0.393	0.585	0.022	1.47
0.012	0.846	0.142	0.292	0.665	0.043	1.50
<i>T</i> = 373 K						
LLE						
0.000	0.074	0.926	0.970	0.026	0.004	
0.000	0.268	0.732	0.885	0.111	0.004	
0.001	0.295	0.703	0.866	0.130	0.004	
VLLE						
0.004	0.379	0.617	0.804	0.192	0.004	1.57
0.004	0.400	0.596	0.778	0.217	0.005	1.68
0.004	0.437	0.559	0.745	0.248	0.007	1.82
0.004	0.463	0.533	0.717	0.280	0.003	1.95
0.005	0.518	0.477	0.652	0.340	0.008	2.18
0.005	0.529	0.465	0.640	0.351	0.009	2.22
0.005	0.616	0.378	0.547	0.440	0.013	2.49
0.008	0.645	0.348	0.495	0.481	0.025	2.57
0.010	0.655	0.335	0.484	0.490	0.026	2.59
<i>T</i> = 393 K						
LLE						
0.009	0.119	0.872	0.941	0.054	0.004	
0.003	0.144	0.853	0.928	0.067	0.004	
VLLE						
0.010	0.237	0.753	0.874	0.121	0.005	1.77
0.003	0.295	0.702	0.826	0.164	0.010	2.17
0.006	0.386	0.609	0.720	0.267	0.013	3.05
0.003	0.409	0.588	0.700	0.285	0.015	3.19
0.002	0.443	0.556	0.656	0.326	0.018	3.50
0.010	0.443	0.547	0.659	0.327	0.014	3.50
0.002	0.507	0.491	0.594	0.389	0.017	3.92
0.002	0.544	0.454	0.574	0.409	0.017	4.05
0.006	0.629	0.365	0.436	0.517	0.047	4.65
0.002	0.644	0.354	0.430	0.525	0.044	4.70
0.008	0.733	0.259	0.296	0.624	0.080	5.12

system were measured at 313 and 333 K. The tie line data are reported in Table 1. Table 2, on the other hand, gives the liquid–liquid and vapor–liquid–liquid equilibrium conditions obtained at 353, 373, and 393 K. As mentioned before, in the vapor–liquid–liquid equilibrium (VLLE) data the vapor phase is assumed to be pure methanol.

Our experimental data are in agreement with the information reported in the literature at 293,⁴ 333,⁷ and 348 K.⁶ All these data show discrepancies with the values of the distribution coefficient of methanol between glycerol and fatty phases reported by Zhou et al.⁸ On the other hand, the isothermal experimental data of Tables 1 and 2 show a good linear fit in an Othmer–Tobias plot¹³ as shown in Figure 1.

According to the phase rule, at a given temperature and pressure, the compositions of the three-phase vapor–liquid–liquid boundary are fixed. Therefore, keeping the temperature constant and increasing the pressure, we can follow the evolution of the VLLE region up to the point where complete liquid miscibility is achieved. In this way, the binodal curve of the

saturated liquid phases can be drawn on a ternary diagram, where each tie line corresponds to a different pressure.

Figures 2 and 3 shows the effect of temperature on the ternary phase diagrams of this system. The immiscibility region decreases with increasing temperature. The concentration of glycerol in the methyl ester phase is very low at the lower temperature. Higher purities of the glycerol and methyl oleate products can be reached by separations at low temperature. However, as discussed by Čerče et al.,⁴ the faster phase separation achieved at higher temperatures can prevail over the better purities obtained at low temperatures.

The tie lines show, as expected, that the glycerol phase is richer in methanol than the fatty phase. Figures 2f and 3f depict the change of methanol distribution coefficient (*K*₂) with temperature and methanol concentration in the ester phase. The distribution coefficient was defined as the ratio between the methanol mole fraction in the methyl oleate (FAME) and glycerol (GLY) phases:

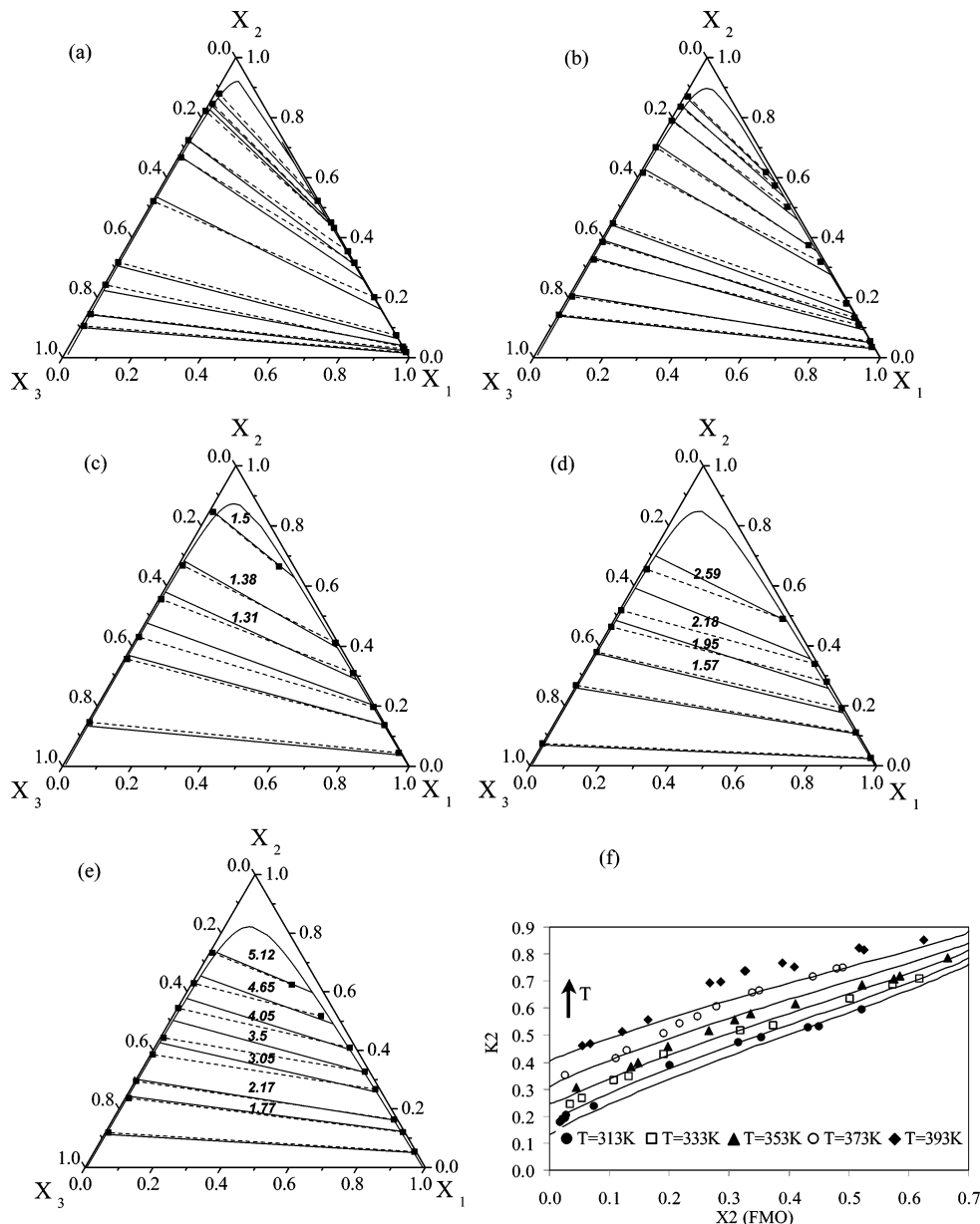


Figure 2. Comparison between GCA-EOS predicted (solid lines) and experimental (dashed lines) tie lines of the ternary system methyl oleate (1)–methanol (2)–glycerol (3) at (a) 313, (b) 333, (c) 353, (d) 373, and (e) 393 K. (f) Distribution coefficients of methanol (K_2): experimental (symbols) and GCA-EOS predictions (lines).

$$K_2 = \frac{x_{\text{MeOH}}^{\text{FAME}}}{x_{\text{MeOH}}^{\text{GLY}}} \quad (1)$$

According to this definition, lower distribution coefficients imply higher concentrations of methanol in the glycerol phase and lower amounts of methanol dissolved in methyl oleate. Since methanol and glycerol both have a 1:1 carbon to alcohol ratio, a high degree of hydrogen bonding is expected. This means that methanol will distribute predominantly in the glycerol phase, as supported by the experimental information. The experimental results also show that the distribution coefficient of methanol increases with temperature. This is also expected, as association effects will decrease with temperature.

3. Thermodynamic Modeling

3.1. GCA-EOS. The GCA-EOS model¹⁰ is an extension to associating systems, of the GC-EOS equation of state originally proposed by Skjold-Jørgensen¹⁴ 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 theory¹⁵ 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.

Methanol and glycerol molecules have, respectively, one and three hydrogen bonding hydroxyl groups. Each OH group is considered to associate through one electronegative O and one

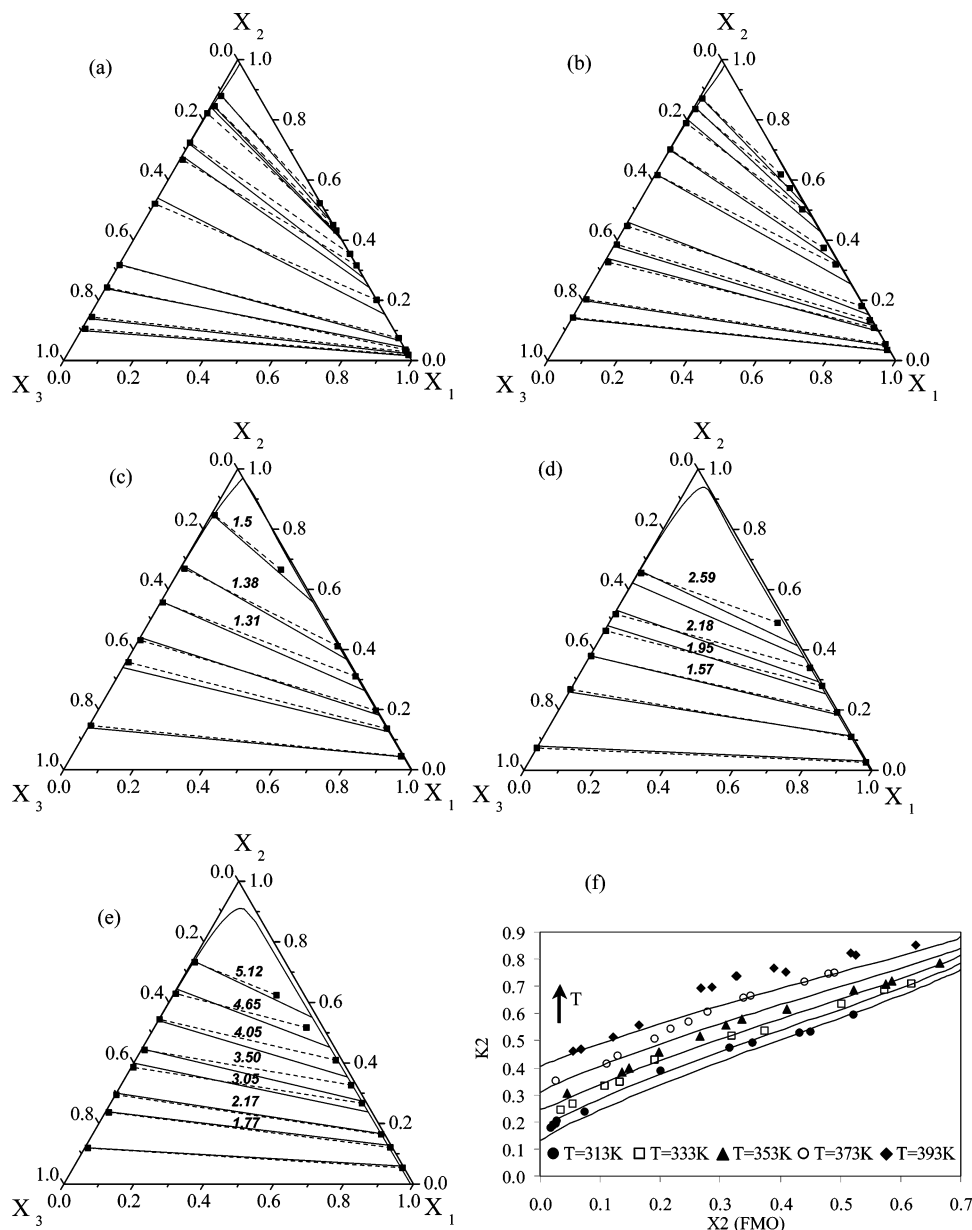


Figure 3. Comparison between A-UNIFAC predicted (solid lines) and experimental (dashed lines) tie lines of the ternary system methyl oleate (1)–methanol (2)–glycerol (3) at (a) 313, (b) 333, (c) 353, (d) 373, and (e) 393 K. (f) Distribution coefficient of methanol (K_2): experimental (symbols) and A-UNIFAC predictions (lines).

electropositive H bonding sites. 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. This associating group does not self-associate (i.e., self-association parameters are equal to zero) but can cross-associate with groups that have one electropositive site, such as the OH group.¹⁶

For the quantification of dispersive forces (attractive term), methanol and glycerol were described by the molecular groups CH_3OH and $\text{C}_3\text{H}_8\text{O}_3$, respectively. Methyl oleate, on the other hand, was represented by the following group composition: 1 ester group (COOCH_2) + 1 olefin group ($\text{CH}=\text{CH}$) + 15 paraffin groups ($2\text{CH}_3 + 13\text{CH}_2$).

Tables 3 and 4 report the complete set of pure-group and binary interaction parameters required for predicting the phase behavior of binary and ternary mixtures between methyl oleate, methanol, and glycerol. Entries in italics correspond to new parameters determined in this work. The remaining parameters were taken from previous work.^{16–18}

Table 3. Energy ϵ/k and Volume κ Association Parameters for the GCA-EOS Model

	ϵ/k (K)	κ (cm^3/mol)
self-association OH	2700.0	0.8621
cross-association OH–CCOO	2105.3	0.9916

The surface energy parameters (g) of $\text{C}_3\text{H}_8\text{O}_3$ were determined by adjusting the vapor pressures of pure glycerol¹⁹ in the range between 340 and 800 K. Following Skjold-Jørgensen's approach,¹⁴ the characteristic temperature T^* of this group was set equal to the estimated critical temperature of glycerol.¹⁹ The values of q in Table 4 represent the normalized van der Waals surface areas.

The binary interaction parameters between CH_3OH and $\text{C}_3\text{H}_8\text{O}_3$ were obtained by fitting isothermal vapor–liquid equilibrium data on the binary methanol–glycerol.⁶ The binary interaction parameters between CH_3OH and the paraffin CH_3 and CH_2 groups were determined by fitting experimental vapor–liquid equilibrium data on binary mixtures of methanol with

Table 4. GCA-EOS Pure-Group and Binary Interaction Parameters

Pure-Group Parameters					
group	Ti^*	q	g^{**}	g'	g''
CH ₃	600.0	0.848	316 910.0	-0.9274	0.00
CH ₂	600.0	0.540	356 080.0	-0.8755	0.00
COOCH ₂	600.0	1.42	831 400.0	-1.0930	0.00
CH ₃ OH	512.6	1.432	816 116.0	-0.3877	0.00
C ₃ H ₈ O ₃	850.0	3.060	510 302.3	-0.3190	0.00
Binary Interaction Parameters					
group <i>l</i>	group <i>j</i>	k_{ij}	k'_{ij}	α_{ij}	α_{ji}
CH ₃ OH	CH ₃	0.9760	0.00	0.00	0.00
	CH ₂	1.0000	0.00	0.00	0.00
	C ₃ H ₈ O ₃	1.0400	0.00	0.00	0.00
	COOCH ₂	1.0000	0.00	0.00	0.0
C ₃ H ₈ O ₃	COOCH ₂	1.0174	0.00	0.00	0.00
	CH ₃ /CH ₂	1.0900	-0.02	0.00	0.00
	COOCH ₂	0.869	0.00	0.00	0.00

Table 5. Energy ϵ/k and Volume κ Association Parameters for the A-UNIFAC Model

	ϵ/k (K)	κ
self-association OH	3125.0	0.0062
cross-association OH-CCOO	1975.0	0.071

acetates (methyl, ethyl, butyl)²⁰ and alcohols (1-butanol, 1-pentanol)²¹ in the ranges 0.17–1 bar and 298–396 K. The interactions of glycerol (C₃H₈O₃)–ester (COOCH₂) and glycerol (C₃H₈O₃)–paraffins (CH₃/CH₂) were calculated by adjusting methyl oleate–methanol–glycerol ternary data at 333 K. Taking into account the low concentration of the olefin group (CH=CH) in the methyl oleate molecule, the interaction parameters for this functional group were set equal to those of the paraffin groups.

Figure 2 compares GCA-EOS predictions with the experimental data measured in this work. From these figures it can be concluded that the GCA-EOS is able to give reasonably good predictions of the liquid–liquid and vapor–liquid–liquid equilibria of the methyl oleate–methanol–glycerol system in all the ranges of temperatures and pressures studied.

The standard deviation in the prediction of methanol distribution coefficients was 7.82%. The mean and maximum differences between the experimental and calculated mole fractions of methyl oleate in the glycerol phase are 0.004 and 0.012, respectively. The same differences for the mole fraction of glycerol in the methyl oleate phase are 0.006 and 0.047, respectively.

3.2. A-UNIFAC. Mengarelli et al.¹¹ have proposed 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.²² As in the GCA-EOS equation, this association term is based on Wertheim's theory for fluids with highly directed attractive forces,¹⁵ and it follows the group-contribution approach proposed by Gros et al.¹⁰

Association effects in the ternary system methyl oleate + methanol + glycerol are represented by the same associating functional groups already described for the GCA-EOS model. Also, the group composition of each compound is the same as the one adopted in the GCA-EOS equation.

Table 5 reports the values of the hydroxyl (OH) and ester (CCOO) self- and cross-association parameters for the A-UNIFAC model, and Table 6 lists the residual group interaction parameters. Again, the entries in italics correspond to new parameters determined in this work. The remaining parameters were taken from elsewhere.^{23–25}

Table 6. Residual Group Interaction Parameters $a_{m,n}$ (K) for the A-UNIFAC Model

m	n			
	CH ₂	C ₃ H ₈ O ₃	CH ₃ OH	CCOO
CH ₂	0.0	101.5	122.7	232.1
C ₃ H ₈ O ₃	-51.2	0.0	-273.6	886.3
CH ₃ OH	-19.78	417.4	0.0	200.2
CCOO	114.8	20.0	18.49	0.0

The residual interaction parameters between CH₃OH and C₃H₈O₃ were obtained by fitting isothermal vapor–liquid equilibrium data on the binary system methanol–glycerol.⁶ The glycerol/paraffin (C₃H₈O₃/CH₂) and glycerol/ester (C₃H₈O₃/CCOO) interaction parameters were calculated by fitting experimental data on liquid–liquid equilibrium and infinite dilution activity coefficients of the binary systems dodecanoic acid methyl ester–glycerol and hexanoic acid methyl ester–glycerol between 320 and 438 K.²⁶

Figure 3 compares experimental data with liquid–liquid equilibrium predictions by the A-UNIFAC model. Predictions of the partial liquid miscibility in the ternary system are reasonably good, though at the lower temperatures (313 and 353 K) this model erroneously predicts partial liquid miscibility between methanol and methyl oleate. The standard deviation in the prediction of methanol distribution coefficients was 8.91%. The mean and maximum differences between the experimental and calculated mole fractions of methyl oleate in the glycerol phase are 0.005 and 0.011, respectively. The same differences for the mole fraction of glycerol in the methyl oleate phase are 0.007 and 0.065, respectively.

4. VLLE Phase Boundaries

The GCA-EOS model was used to predict the vapor–liquid–liquid equilibrium scenario of the ternary system methyl oleate + methanol + glycerol in a wider range of temperatures and pressures than those measured experimentally. Figure 4 shows, for a series of isotherms, the curves pressure vs methanol mole fraction in the saturated liquid phases. For each isotherm, the solid and dashed lines give, respectively, the molar fraction of methanol in the methyl oleate and glycerol phases at different pressures. The point of intersection of these two lines represents the plait point at the given temperature. It should be noticed that, at temperatures above 453 K, the distribution coefficient of methanol defined by eq 1 starts to be greater than 1; i.e., the molar fraction of methanol in the methyl oleate phase is higher than that in the glycerol phase. However, in terms of weight fractions, the glycerol phase is always richer in methanol than

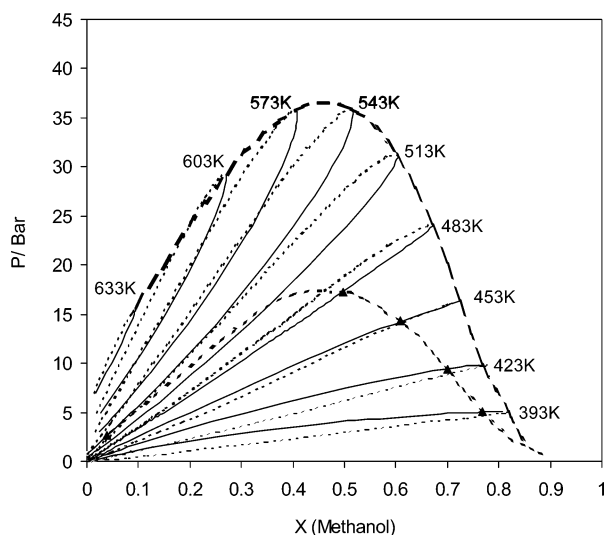


Figure 4. VLE boundaries. Solid line (—), methanol mole fraction in the liquid methyl oleate phase; dotted line (···), methanol mole fraction in the liquid glycerol phase; external dashed line (---), plait point locus; internal dotted line and triangular symbols (···▲···), locus of the partial liquid miscibility limits for mixtures having 1:3 molar ratio of glycerol to methyl oleate.

the methyl oleate phase. This is due to the difference in molecular weight between the fatty and glycerol phases.

It is interesting to notice that the plait point locus goes through a maximum in pressure. At the lower temperatures the glycerol/methyl oleate mutual solubility is very low and high concentrations of methanol are required to achieve complete miscibility in the liquid phase. At these temperatures the plait point pressure increases with temperature due to the increase of methanol vapor pressure. However, as the temperature rises, the glycerol/methyl oleate mutual solubility increases (in particular, the solubility of glycerol in the methyl oleate phase becomes higher) and lower amounts of methanol are required to reach complete liquid miscibility. Hence, the plait point pressure decreases. The GCA-EOS predicts a maximum plait point pressure of 36 bar. This means that, for all temperatures, the ternary system methyl oleate + methanol + glycerol will show complete liquid miscibility above this pressure. This information is valuable for the design of noncatalytic supercritical methanol biodiesel reactors.

Figure 4 also shows the miscibility limits for a ternary mixture having a glycerol to methyl oleate molar ratio equal to 1:3, i.e., the stoichiometric ratio between the reaction products in the transesterification of triglycerides. The highest temperature at which these mixtures can present partial liquid miscibility is 546 K. At higher temperatures the solubility of glycerol in methyl oleate is greater than 0.25 in molar fraction; hence the liquid phase will be completely miscible even without any methanol.

5. Conclusions

Phase equilibrium data of the system methyl oleate–methanol–glycerol have been measured at temperatures between 313 and 393 K and pressures up to 0.6 MPa. Good agreement was found with previous experimental data from the literature. The GCA-EOS and A-UNIFAC thermodynamic models were used to represent the data. The GCA-EOS model, in particular, shows a good predictive capability. Hence, it can be applied to explore the operating conditions in the reactor and the downstream separation train of biodiesel production plants.

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