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Liquid−Liquid Equilibria for Castor Oil Biodiesel + Glycerol + Alcohol[†]

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Phase equilibrium behavior of the system castor oil biodiesel + glycerol + methanol was studied to provide experimental data for the optimization of the separation downstream processes. Measurements of solubility were carried out for the ternary systems containing biodiesel derived from castor + glycerol + methanol at 298.15 K and + ethanol at (298.15 and 333.15) K. An increase of the system mutual solubility was observed with temperature. Binodal curves were determined by the cloud point using the titration method under isothermal conditions. The tie-lines for biodiesel + glycerol + methanol at 298.15 K were indirectly measured by analyzing the mixture density. The Othmer−Tobias correlation was used to ascertain the consistency of tie-line data. The results were correlated with the UNIQUAC model satisfactorily.

Introduction

The production of biofuels by vegetable or fatty oil increases continuously. Although crude vegetable oils can be used directly to replace diesel fuel, its high viscosity limits their application.[1] An alternative to correct this problem is to react the oil with an alcohol through a transesterification reaction, producing esters, which have viscosities similar to diesel, and glycerol as byproducts.

The sulfur content of commercial diesel fuels causes a decrease in its lubricity, causing possible damage to the engine and fuel injection systems.[2] Biodiesel can be used as an additive in diesel fuel increasing lubricity.[3] Castor oil has shown a better performance as an additive with more effective lubricity than oils that do not contain any hydroxylated fatty acids.[4] The hypothesis was that the hydroxylated fatty acids of ricinoleic acid in castor oil, which represent approximately 90 % of oil composition,[3,5] give it better performance as a lubricity enhancer than other common vegetable oil esters.[5]

According to Scholz and Silva,[6] castor oil is an undemanding oil plant, which grows very well in tropical conditions and provides high oil yields, but it does require a large amount of hand labor. It is therefore a suitable crop for the small-scale farming structures in the northeast of Brazil. Besides the use as an additive in diesel fuel, castor oil is highly valuable for industrial purposes due to this chemical composition.

The purity level of the biodiesel has strong effects on its fuel properties.[7] Therefore, the refining step of the products obtained by transesterification reaction is extremely important. After completion of the reaction, the mixture forms two phases for most vegetable oils used as raw material and can be separated by decantation. However, depending on the reaction conditions, the products obtained by transesterification of castor oil do not form two liquids phases.

Phase equilibrium of ternary systems with biodiesel, glycerol, and alcohol was previously studied. Negi et al.[8] investigated the phase equilibria of the glycerol + methanol + methyl oleate system at (333.15 and 408.15) K and compared the experimental data with predictions by the UNIFAC model. Zhou et al.[9] measured the solubility of the ternary system *Jotropha curcas* biodiesel + glycerol + methanol at different temperatures. Glycerol showed low solubility in the biodiesel phase. The solubility was considered temperature insensible. Additionally, Komers et al.[10] carried out experiments with the ternary mixture biodiesel from rapeseed oil + methanol + glycerol in the temperature range of (295 to 298.15) K using water contents of ≤ 0.025 % and 1 % under ambient pressure.

The main objective of this work is to study the liquid−liquid equilibrium of ternary systems containing castor oil biodiesel, glycerol, and alcohol. Binodal curves were determined experimentally using two types of alcohol, methanol at 298.15 K, and ethanol at (298.15 and 333.15) K. Tie line data were measures for the system containing methanol at 298.15 K. Results were correlated through the UNIQUAC model, with estimation of new binary interaction parameters.

Experimental Section

Materials. Alcohols and glycerol used in the experiments were obtained from Vetec Química with purity of 99.5 %. Distillated water was used for preliminary measurements. The castor oil was supplied by Aboissa Óleos Vegetais and has the composition present in Table 1, according to data provided by the company. Biodiesel was prepared in the laboratory by transesterification of castor oil with methanol with basic catalyst at 298.15 K and atmospheric pressure. The product mixture was washed with water twice and with acetic acid solution to remove residual humidity. Finally, the biodiesel was heated until 379.15 K to remove any remaining alcohol. The final water content was 0.531 % for castor oil biodiesel, determined by Karl Fisher analysis.

A glass equilibrium cell shown in Figure 1, with two partitions (inner partition for the sample and outer for water circulation), was used for the measurements. The cell temperature was controlled by a thermostatic bath with an uncertainty of about ± 0.1 °C. A thermometer was used for monitoring the cell

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Table 1. Fatty Acid Composition for Castor Oil

fatty acids		
structure	common name	composition (%)
$CH_3(CH_2)_{14}COOH$	C16:0 (palmitic)	0.74
$CH_3(CH_2)_{16}COOH$	C18:0 (stearic)	0.92
$CH_3(CH_2)_7CHCH(CH_2)_7COOH$	C18:1 (oleic)	2.71
$CH_3(CH_2)_5CHOHCH_2CHCH(CH_2)_7COOH$	C18:1,OH (ricinoleic)	89.87
$CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_7COOH$	C18:2 (linoleic)	4.31
$CH_3(CH_2CHCH)_3(CH_2)_7COOH$	C18:3 (linolenic)	0.32
$CH_3CH_2CHCH(CH_2)_2CHOHCH_2CHCH(CH_2)_7COOH$	C18:2,OH (densipolic)	0.93

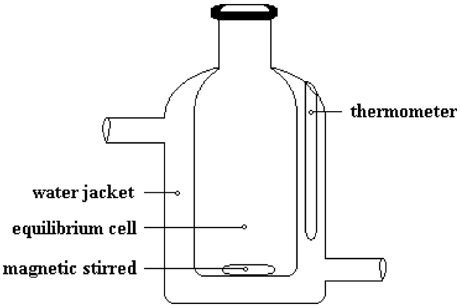

Figure 1. Equilibrium cell used for measurements.

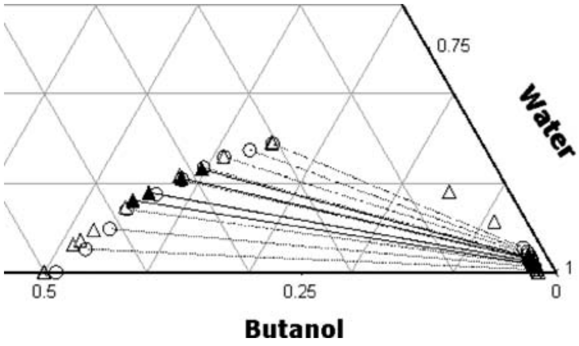

Figure 2. Measured solubility (Δ) of butanol + propanol + water and ▲, experimental and ○, literature[12] tie-line data at 298.15 K.

Table 2. Binodal Curves for Systems Containing Castor Oil Biodiesel (1), Glycerol (2), and Alcohol (3)

w_1	w_2	w_3
biodiesel + glycerol + methanol at 298.15 K		
0.2918	0.2987	0.4097
0.4126	0.2213	0.3661
0.5401	0.1400	0.3199
0.6327	0.0962	0.2710
0.7857	0.0433	0.1708
0.8899	0.0152	0.0950
0.1478	0.3846	0.4676
0.0022	0.5987	0.3991
0.0017	0.6988	0.2994
0.0010	0.7993	0.1997
biodiesel + glycerol + ethanol at 298.15 K		
0.2974	0.3044	0.3981
0.4046	0.2129	0.3825
0.5276	0.1275	0.3449
0.6270	0.0808	0.2923
0.7926	0.0224	0.1850
0.1581	0.4547	0.3872
0.0534	0.5772	0.3694
0.0199	0.6887	0.2915
0.0037	0.7970	0.1993
biodiesel + glycerol + ethanol at 333.15 K		
0.3150	0.3151	0.3699
0.7819	0.0544	0.1651
0.6372	0.1113	0.2514
0.5485	0.1480	0.3035
0.4275	0.2368	0.3357
0.2045	0.4415	0.3541
0.0855	0.5634	0.3511
0.0269	0.6847	0.2884
0.0144	0.7915	0.1941

temperature. Density measurements were made using an Anton Paar DMA 4500 densimeter.

Procedure. Binodal curves were determined by the cloud point using the titration method under isothermal conditions, with density measurements. Mixtures with different concentrations of biodiesel and glycerol were prepared and stirred by a magnetic agitator, while homogeneous mixtures of glycerol + alcohol (glycerol-enriched phase) or biodiesel + alcohol (biodiesel-enriched phase) were titrated with a buret. The point when the mixture changed from turbid to transparent was considered to be a binodal curve point. The volumes were used to calculate the component mass fraction. Samples of transparent mixtures were collected for density analysis. In this way, an expression for the density as a function of mass fraction is obtained according to Maduro and Aznar.[11] The expressions for the density are functions of the mass fraction of each component and not of the three components.

The mixture of castor oil biodiesel, methanol, and glycerol was put inside the equilibrium cell, under 1 h intensive agitation with a magnetic stirrer, at constant temperature and pressure. After that, the ternary mixture was keep at rest for 30 h until two separate transparent liquid phases were observed clearly. One phase was enriched biodiesel and the other enriched glycerol. When the equilibrium was achieved, a sample was taken from both the biodiesel-enriched phase (upper) and the glycerol-enriched phase (lower) for density measurements. The mass fraction of castor oil biodiesel, glycerol, and methanol in the samples of the two phases was determined from the density calibration equations for each component. All experiments of binodal and tie-line data were replicated three times.

To check the accuracy and validate the experimental procedure, the solubility of the previous ternary system butanol + propanol + water at 298.15 K was measured, and the results were compared with those obtained from the literature.[12]

As can be seen in Figure 2, binodal and tie-line data show satisfactory reproducibility. The previous system validates experi-

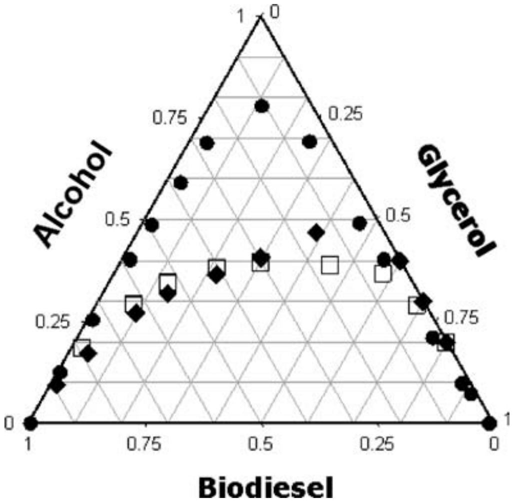

Figure 3. Phase diagram of castor oil biodiesel + glycerol + ◆, methanol; + □, ethanol at 298.15 K. ●, *Jatropha curcas* biodiesel at 298.15 K.[9]

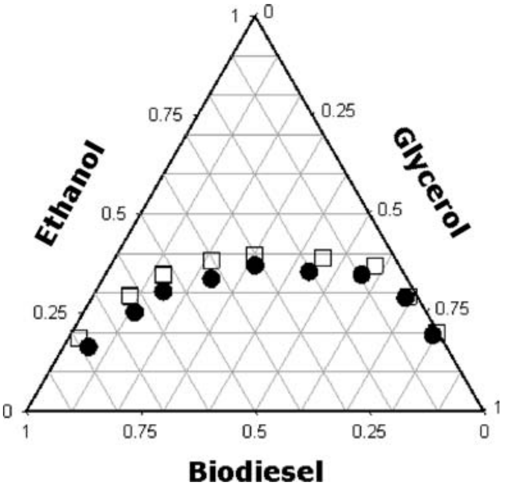

Figure 4. Phase diagram of biodiesel + glycerol + ethanol at □, 298.15 K and ●, 333.15 K.

mental procedures to determine the binodal curve with the cloud point method and tie lines using density calibration curves.

Results and Discussion

The binodal curve for the systems castor oil biodiesel + glycerol + methanol at 298.15 K and + ethanol at (298.15 and 333.15) K are shown in Table 2 and represented in Figures 3 and 4.

It can be observed in Figure 3 that biodiesel has greater solubility in the glycerol-enriched phase in the system containing ethanol at 298.15 K. The analysis of the ternary phase diagram for *Jatropha curcas* biodiesel shows lower solubility compared to castor oil biodiesel, glycerol, and methanol. This can be explained due to the fact that castor oil biodiesel is composed by 90 % methyl ricinoleate. This ester has a hydroxyl group and forms hydrogen bonds with alcohol and glycerol, increasing the system mutual solubility.

Comparing the systems with ethanol at (298.15 and 333.15) K in Figure 4, it can be observed that the solubility increases with temperature. Despite these variations, they are not significant enough to determine phase behavior of the systems. The alcohol concentration is the main factor that affects biodiesel product solubility.

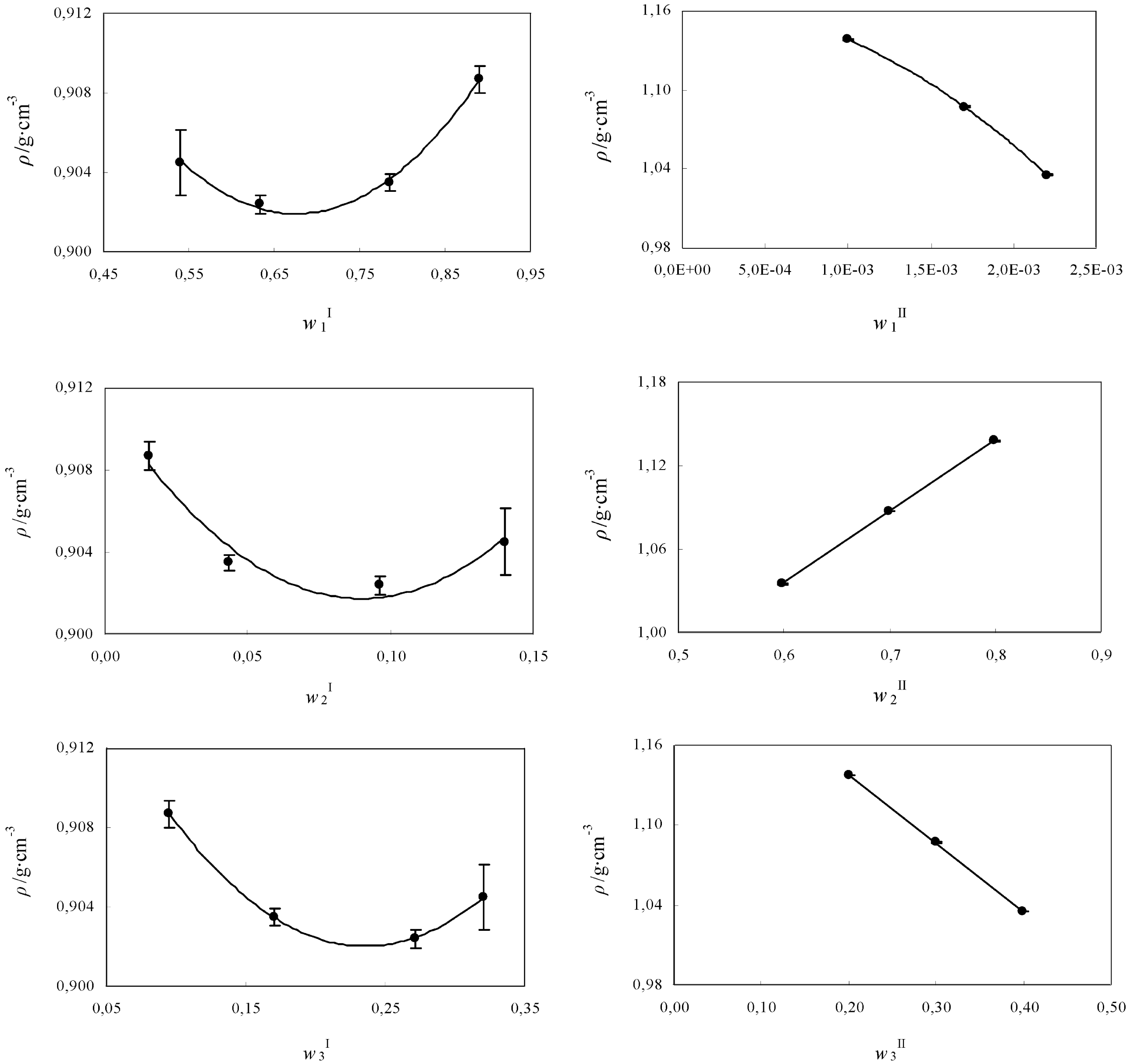

Figure 5. Calibration curves for the ternary system biodiesel (1), glycerol (2), and methanol (3) at 298.15 K.

Table 3. Ternary LLE Data for the System Castor Oil Biodiesel (1) + Glycerol (2) + Methanol (3) at 298.15 K

overall composition			biodiesel phase			glycerol phase		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.375	0.375	0.250	0.8057	0.0433	0.1546	0.0021	0.5893	0.4085
0.400	0.400	0.200	0.8839	0.0155	0.1024	0.0015	0.7286	0.2698
0.350	0.350	0.300	0.9235	0.0014	0.0763	0.0012	0.7829	0.2159
0.360	0.360	0.280	0.8432	0.0299	0.1294	0.0018	0.6554	0.3425
0.420	0.420	0.160	0.8158	0.0397	0.1478	0.0020	0.6188	0.3790
0.385	0.385	0.230	0.8562	0.0266	0.1232	0.0018	0.6732	0.3247
0.410	0.410	0.180	0.9085	0.0067	0.0861	0.0011	0.7446	0.2539

The second-order polynomial equations for the density of the biodiesel, glycerol, and methanol system as a function of component mass fractions ($d = f(w_i)$) gave the calibration curves shown in Figure 5, where ρ is the ternary mixture density; w_i^{I} indicates the mass fraction of component i in the biodiesel phase; and w_i^{II} indicates the mass fraction of component i in the glycerol phase. These curves were obtained through density measurements during binodal curve experiments.

The tie-line data for the system castor oil biodiesel + glycerol + methanol are presented in Table 3. The composition of equilibrium phases cross global composition, as can be seen in Figure 6. The consistency of the tie-line data was ascertained by applying the Othmer−Tobias correlation.[13]

The calibration curves of density versus mass fraction of each component were used to determine component mass fractions for the tie lines. The range of validation was restricted to the range of measurements.

The solubility of glycerol in the biodiesel phase is slightly greater than that of biodiesel in the glycerol phase, unlike the behavior found from Zhou et al.[9] for *Jatropha curcas* biodiesel.

Othmer and Tobias[13] formulate an equation that reproduced the tie lines in a straight line from a plot of $((1 - a)/a)$ against $((1 - a)/a)$, where in this case, a is the mole fraction of biodiesel in the biodiesel phase and b is the mole fraction of glycerol in the glycerol phase. Figure 7 shows a good linear fit with the Othmer−Tobias correlation, indicating the consistency of the experimental data.

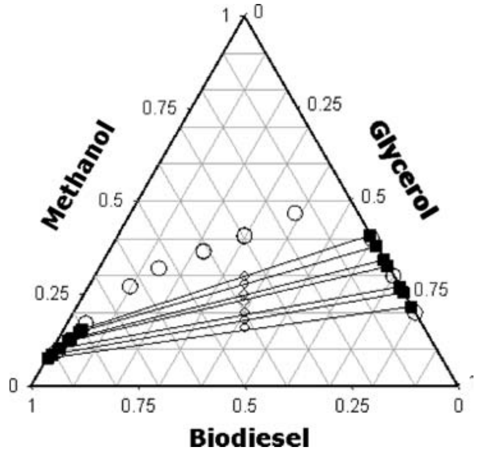

Figure 6. Tie lines for the system biodiesel + glycerol + methanol at 298.15 K: ○, binodal; ◇, global composition; and ■, tie line.

Thermodynamic Model

Activity coefficient based models can be used to correlate experimental and calculated liquid equilibrium data. For nonideal systems at low temperature and ambient pressure, the UNIQUAC model was recommended.[14]

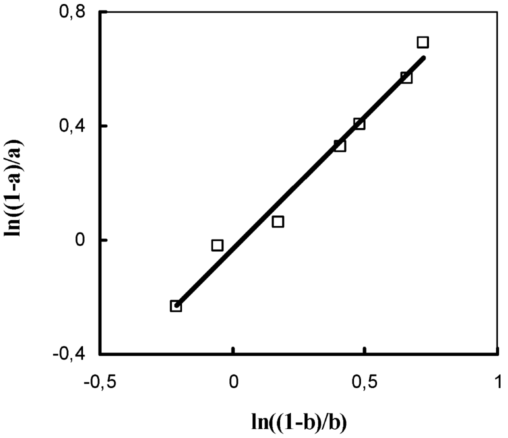

Figure 7. Othmer−Tobias plot[13] for the experimental data from the biodiesel + glycerol + methanol system at 298.15 K.

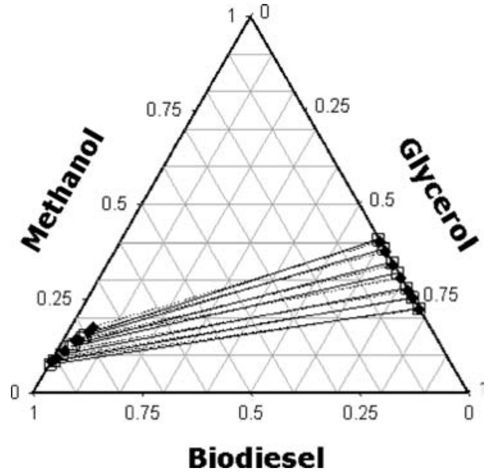

Figure 8. Tie-line for the system biodiesel + glycerol + methanol at 298.15 K. □, experimental and ◆, calculated via UNIQUAC.

Table 4. Parameters r_i' and q_i' for the Studied System

compound	r_i'	q_i'
biodiesel	13.461	11.351
glycerol	4.795	4.908
methanol	1.901	2.048

Table 5. UNIQUAC Interaction Parameters for Castor Oil Biodiesel (1) + Glycerol (2) + Methanol (3) at 298 K and 1 atm

pair $i-j$	$A_{ij}[K]$	$A_{ji}[K]$
1−2	4585.70	2219.00
1−3	−300.11	5953.38
2−3	−432.55	4816.01

The algorithm proposed by Prauznits et al.[15] was used to estimate UNIQUAC binary interaction parameters, with the Symplex method, through the objective function described by eq 1 as shown in Sorensen et al.[16] Figure 8 shows a comparison of the experimental data with the calculations of UNIQUAC.

$$F = \sum_{k}^{D} \sum_{j}^{M} \sum_{i}^{N-1} \{(w_{ijk}^{\mathrm{I,exp}} - w_{ijk}^{\mathrm{I,calc}})^2 + (w_{ijk}^{\mathrm{II,exp}} - w_{ijk}^{\mathrm{II,calc}})^2\} \quad (1)$$

where D is the number of data sets; N and M are the number of components and tie lines in each data set; w is the mass fraction of the components; the superscripts I and II refer to the two liquid phases in equilibrium; and the superscripts exp and calc refer to the experimental and calculated values of the liquid-phase concentrations.

Table 6. Model Deviations for the Components on the Biodiesel and Glycerol Phase

	rmsd	AAD
	Biodiesel Phase	
w_1	3.28E-2	3.23E-2
w_2	4.20E-3	2.92E-3
w_3	3.01E-2	2.94E-2
	Glycerol Phase	
w_1	3.27E-5	3.20E-5
w_2	9.72E-3	7.89E-3
w_3	2.03E-2	1.86E-2
Global (·100)	1.73	1.52

The system was treated as pseudoternary, with biodiesel represented by methyl ricinoleate, the major component of castor oil biodiesel. The molecular volume and surface area parameters r_i' and q_i' were calculated via UNIFAC LLE[17] and presented in Table 4.

The tie-line data obtained experimentally present a good agreement with calculated mass fraction for the two phases at equilibrium. Table 5 presents the binary interaction parameters estimated with experimental data for the system containing biodiesel, glycerol, and methanol at 298.15 K.

A comparison between the experimental and calculated composition of each component of two phases at equilibrium was made with the parameters estimated by the UNIQUAC model. The root-mean-square deviation (rmsd) and average absolute deviation (AAD) were calculated according to eqs 2 and 3, respectively, and are shown in Table 6.

$$\text{rmsd} = \sqrt{\frac{1}{N}\sum_i (w_i^{\text{exp}} - w_i^{\text{calc}})^2} \qquad (2)$$

$$\text{AAD} = \frac{1}{N}\sum_i |w_i^{\text{exp}} - w_i^{\text{calc}}| \qquad (3)$$

where w_i is the mass fraction of the components and N is the number of tie lines.

The results are satisfactory, with a good correlation. The UNIQUAC model is able to correlate the data, with a global rmsd of 1.73 % and an AAD of 1.52 %.

Conclusions

The experimental procedure used in this work is simple and allows determining liquid−liquid equilibrium data from density analysis only, showing accurate results.

The solubility of glycerol and alcohol in castor oil biodiesel gives more difficulty during separation and purification steps. Biodiesel solubility in the glycerol-enriched phase is slightly higher for the ternary mixture containing ethanol compared to methanol, and the system mutual solubility increases with temperature. The liquid−liquid equilibrium occurs for lower alcohol concentrations.

The knowledge of phase equilibrium for the systems studied is important to optimize biodiesel purification, as well as thermodynamic modeling to simulate the behavior. The UNIQUAC model can represent the experimental data for liquid equilibrium of nonideal mixtures satisfactorily.

Appendix

The standard deviations for experimental points of binodal curve and tie-line data were calculated considering the replicates and equipment errors. The values are presented in Tables 7 and 8.

Table 7. Standard Deviations for Binodal Curves of Ternary Systems

w_1	w_2	w_3
	Biodiesel + Glycerol + Methanol at 298.15 K	
3.41E-03	2.16E-03	3.14E-03
1.40E-03	2.75E-03	1.44E-03
1.02E-03	1.31E-03	2.45E-04
8.73E-04	1.05E-03	2.56E-04
1.07E-03	8.16E-04	1.98E-04
1.71E-03	1.75E-03	6.47E-04
3.27E-03	9.51E-03	7.25E-04
3.97E-04	2.65E-04	1.49E-04
6.25E-04	5.47E-04	1.34E-04
3.09E-04	3.68E-04	9.43E-05
	Biodiesel + Glycerol + Ethanol at 298.15 K	
3.53E-03	1.54E-03	2.28E-03
3.24E-04	5.76E-04	4.78E-04
1.34E-03	1.58E-03	2.03E-03
8.66E-04	9.47E-04	4.57E-04
7.85E-04	6.37E-04	1.41E-04
3.27E-04	8.16E-04	2.45E-04
9.39E-04	5.72E-04	3.68E-04
4.08E-04	3.68E-04	4.71E-04
2.05E-04	2.45E-04	4.72E-04
	Biodiesel + Glycerol + Ethanol at 333.15 K	
4.71E-04	1.63E-04	1.25E-04
4.08E-04	3.27E-04	2.00E-03
6.13E-04	5.72E-04	4.71E-04
1.14E-03	1.35E-03	1.63E-04
3.27E-04	5.31E-04	2.05E-04
2.87E-04	4.72E-04	2.45E-04
8.27E-03	3.58E-03	4.72E-03
6.76E-03	9.51E-04	5.32E-04
1.37E-03	1.53E-04	5.48E-04

Table 8. Standard Deviations of Tie Lines for the System Castor Oil Biodiesel + Glycerol + Methanol at 298.15 K

biodiesel phase			glycerol phase		
w_1	w_2	w_3	w_1	w_2	w_3
3.93E-03	1.47E-03	2.80E-03	9.47E-07	3.05E-04	3.05E-04
9.19E-03	3.44E-03	6.40E-03	1.03E-06	2.48E-04	2.44E-04
1.90E-03	7.08E-04	1.31E-03	3.61E-06	7.22E-04	7.11E-04
2.55E-03	9.56E-04	1.79E-03	6.56E-07	1.91E-04	1.89E-04
1.88E-03	7.03E-04	1.33E-03	8.83E-07	2.84E-04	2.84E-04
8.01E-04	2.99E-04	5.60E-04	3.03E-06	8.75E-04	8.69E-04
5.15E-04	1.94E-04	3.58E-04	8.65E-07	2.05E-04	2.01E-04

Supporting Information Available:

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

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