JOURNAL OF CHEMICAL & ENGINEERING DATA

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Liquid−Liquid Equilibrium for Ternary Mixtures of Biodiesel (Soybean or Sunflower) + Glycerol + Ethanol at Different Temperatures

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Supporting Information

ABSTRACT: Biodiesel has many advantages because it is a biodegradable, nontoxic fuel and its production results in less particulate matter. For this reason it has been studied in many fields of science as a substitute for mineral fuels. Short chain alcohols such as ethanol have been used for extraction of soybean and sunflower biodiesel in the literature. The present paper reports liquid−liquid equilibrium data for systems containing soybean biodiesel + glycerol + ethanol at (293.15 and 323.15) K and sunflower biodiesel + glycerol + ethanol at (298.15 and 313.15) K. Binodal curves were obtained by the cloud-point method, while tie-line compositions were obtained by density measurements. The values of distribution coefficients and selectivities indicate that the ethanol is a good solvent for the extraction of soybean biodiesel and sunflower biodiesel from glycerol. The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer−Tobias equation. The experimental data were correlated by the nonrandom two-liquid (NRTL) model, using the simplex minimization method with a composition-based objective function. The results found in this work were considered satisfactory, by analyzing statistical parameters using root-mean-square deviations.

1. INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats.[1] Its production by vegetable or fatty oil increases continuously. In addition to being an alternative to diesel fuel, one of the most promising applications for biodiesel is its use as a diesel fuel lubricity agent. It was observed by Kulkarni and Dalai[2] that, with a 1 % biodiesel addition to ultra low sulfur diesel, the lubricity of the fuel was increased by 60 %.

In Brazil, the most important raw material sources used for the production of biodiesel are soybean seeds (77.13 %), followed by bovine fat (17.07 %) and cotton seeds (4.62 %) (data from the last Bulletin of the Brazilian Regulatory Agency; Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, ANP).[3] The most significant method of biodiesel production is the transesterification reaction using a basic homogeneous catalyst. In this is process, vegetable oil is added to a monohydroxyl alcohol (ethanol or methanol) in the presence of a basic homogeneous catalyst to form a mixture of ethyl or methyl esters and glycerol. Biodiesel can be separated from the glycerol through solvent extraction, like alcohols.[4] It should be noticed that the purification procedure is extremely important, once it can determine the final specification of the product. Experimental data of the multicomponent liquid−liquid equilibrium are essential for the design, operation, and optimization of the extraction process.

Liquid−liquid equilibrium (LLE) data for ternary systems containing oil, acid, and alcohols have been recently presented in the literature.[5−10] Nevertheless, biodiesel + glycerol + alcohol data are still scarce.[11−21] França et al.[11] determined liquid−liquid equilibrium data for castor oil biodiesel + glycerol + alcohol (methanol and ethanol) at (298.15 and 333.15) K; Negi et al.[12] 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.[13] measured the solubility of the ternary system of *Jotropha curcas* biodiesel + glycerol + methanol at different temperatures; Komers et al.[14] studied ternary mixture biodiesel from rapeseed oil + methanol + glycerol in the temperature range of (295 to 298.15) K using water content of 0.025 % and 1 % under ambient pressure. This study reports experimental LLE data for soybean biodiesel + glycerol + ethanol at (293.15 and 323.15) K and sunflower biodiesel + glycerol + ethanol at the temperatures of (298.15 and

Table 1. Fatty Acid Methyl Ester (FAME) Profile of Soybean and Sunflower Oil

fatty acid		M[a] g·mol^{-1}	mass fraction % soybean oil	mass fraction % sunflower oil
palmitic	C 16:0[b]	256.43	11.32	7.1
stearic	C 18:0	284.49	3.13	4.8
oleic	C 18:1	282.47	23.87	22.6
linoleic	C 18:2	280.45	54.94	65.5
linolenic	C 18:3	278.44	4.94	
behenic	C 22:0	340.59	1.80	

[a] M = molar mass. [b] In Cx:y, x = number of carbons and y = number of double bonds.

Received: May 20, 2011
Accepted: September 27, 2011
Published: October 13, 2011

dx.doi.org/10.1021/je200340x | J. Chem. Eng. Data 2011, 56, 4061–4067

Table 2. Binodal Curves of Systems Containing Glycerol, Ethanol, and Soybean or Sunflower Biodiesel

Glycerol (1) + Ethanol (2) + Soybean Biodiesel (3)			
w_1	w_2	w_3	density ($g \cdot cm^{-3}$)
293.15 K			
0.0152	0.0000	0.9848	0.8856
0.0170	0.1774	0.8056	0.8712
0.0142	0.0888	0.8970	0.8774
0.0434	0.2777	0.6789	0.8687
0.0673	0.3500	0.5827	0.8680
0.0850	0.3975	0.5175	0.8683
0.1093	0.4494	0.4413	0.8704
0.9883	0.0000	0.0117	1.2184
0.6171	0.3617	0.0212	1.1311
0.4899	0.4900	0.0201	1.0863
0.6955	0.2905	0.0140	0.9847
0.7694	0.2066	0.0240	1.0469
0.9097	0.0625	0.0278	1.2608
323.15 K			
0.0129	0.0000	0.9871	0.8639
0.0411	0.1205	0.8384	0.8567
0.0379	0.1794	0.7827	0.8569
0.0434	0.2378	0.7188	0.8508
0.0749	0.3098	0.6153	0.8552
0.1139	0.3927	0.4934	0.8709
0.9828	0.0000	0.0172	1.2390
0.8901	0.0739	0.0360	1.1987
0.8331	0.1190	0.0479	1.1650
0.6605	0.2967	0.0428	1.0686
0.5535	0.4160	0.0305	1.0022

Glycerol (1) + Ethanol (2) + Sunflower Biodiesel (3)			
w_1	w_2	w_3	density ($g \cdot cm^{-3}$)
298.15 K			
0.0277	0.0645	0.9078	0.8745
0.0186	0.1218	0.8596	0.8699
0.0250	0.1558	0.8192	0.8669
0.0402	0.2457	0.7141	0.8633
0.0533	0.2994	0.6473	0.8609
0.8986	0.0562	0.0452	1.2154
0.8295	0.1059	0.0646	1.1853
0.8212	0.1290	0.0498	1.1731
0.7767	0.1757	0.0476	1.1407
0.7179	0.2373	0.0448	1.1071
0.6761	0.2969	0.0270	1.0756
313.15 K			
0.0228	0.0663	0.9109	0.8629
0.0195	0.1241	0.8564	0.8596
0.0265	0.1922	0.7813	0.8545
0.0407	0.2415	0.7178	0.8533
0.0373	0.3015	0.6612	0.8511
0.9031	0.0626	0.0343	1.2082
0.8568	0.1214	0.0218	1.1758
0.7807	0.1888	0.0305	1.1324
0.7254	0.2439	0.0307	1.1040
0.6726	0.3093	0.0181	1.0733

313.15) K with the objective to study the solubility between components of systems. It should be noticed that the biodiesel used in this work was produced by using the methyl route, as it has been indicated in the literature that this route produces biodiesel at a high conversion rate.[2] Nevertheless, in this work we suggested a purification process using ethanol, to reduce operational problems due to the use of methanol.[18] The data were correlated by the nonrandom two-liquid (NRTL) model.[22]

2. EXPERIMENTAL SECTION

2.1. Chemicals. Glycerol (Synth, ≥ 99 %, water content: 241 ppm), methanol (Synth, ≥ 99.8 %, water content: 32 ppm), ethanol (Synth, ≥ 99.8 %, water content: 173 ppm), oleic acid (Synth, ≥ 99.8 %, water content: 538 ppm), soybean oil refined (Liza), sunflower oil refined (Liza), and colza oil refined (Purilev) were used in this work. It is important to note that these chemicals have been used without further purification.

Biodiesel samples used in this work were obtained by alkaline catalyzed using 0.8 % of potassium methoxide for the soybean system and 0.6 % for the sunflower system. The transesterification reactions were carried out using methanol as transesterificant alcohol, without any pretreatment to the feedstocks due to their lower acidity number, as described by Nogueira Jr. et al.[23]

After production, a biodiesel sample was characterized following laboratory procedures and standards indicated by the Brazilian Regulatory Agency (ANP).[3] The compositions of the esters were analyzed by gas chromatography (GC) using a Varian CP-3800 gas chromatograph system equipped with a flame ionization detector (FID; $T_{\text{detector}} = 523.15$ K) and automated split injector ($T_{\text{injection}} = 473.15$ K). The column was a CP WAX 52CB 30 m × 0.25 mm × 0.05 μm DB ($T_{\text{column}} = 483.15$ K). The fatty acid methyl ester (FAME) profile of soybean and sunflower oil is given in Table 1.

2.2. Apparatus and Procedures. Experiments were carried out in equilibrium cells, such as described by Santiago and Aznar.[24] The cell temperature was regulated by a thermostatic bath (Tecnal TE-184), accurate to ± 0.01 K. A thermometer was used for monitoring the cell temperature. The overall mixture was prepared directly inside the cell, and the components were weighed on an analytical balance (Shimadzu, accurate to 0.0001 g). The ternary mixture was vigorously agitated with a magnetic stirrer (Fisatom 752A) for 3 h, at constant temperature, to allow intimate contact between the phases; the equilibrium was achieved by letting the mixture rest for 14 h, until two separate transparent liquid phases were observed clearly. The upper phase was enriched biodiesel, and the lower phase was enriched glycerol. Separate samples of both phases were collected and analyzed.

The mass fraction of soybean biodiesel, sunflower biodiesel, glycerol, and ethanol 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 twice. Density measurements were made using a digital viscodensimeter (Anton Paar SVM 3000, uncertainty for the ± 0.0005 $g \cdot cm^{-3}$

Table 3. Ternary LLE Data for System Glycerol (1) + Ethanol (2) + Soybean or Sunflower Biodiesel (3), Distribution Coefficients of Glycerol (β_1) and Ethanol (β_2), and Selectivity (S) at Different Temperatures

Glycerol (1) + Ethanol (2) + Soybean Biodiesel (3)											
overall composition			biodiesel-rich phase			glycerin-rich phase			β_1	β_2	S
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	(w_1^{II}/w_1^{I})	(w_2^{II}/w_2^{I})	(β_2/β_1)
293.15 K											
0.4665	0.0393	0.4942	0.0148	0.0239	0.9613	0.9269	0.0542	0.0189	0.02	0.44	27.73
0.4457	0.1066	0.4477	0.0199	0.0522	0.9279	0.8285	0.1506	0.0209	0.02	0.35	14.40
0.4080	0.1768	0.4152	0.0261	0.0861	0.8878	0.7338	0.2444	0.0218	0.04	0.35	9.92
0.3702	0.2492	0.3806	0.0373	0.1497	0.8130	0.6500	0.3284	0.0216	0.06	0.46	7.96
0.3272	0.3437	0.3291	0.0419	0.1774	0.7807	0.5247	0.4563	0.0190	0.08	0.39	4.87
323.15 K											
0.4760	0.0577	0.4663	0.0205	0.0204	0.9591	0.8797	0.0816	0.0387	0.02	0.25	10.76
0.4445	0.1220	0.4335	0.0278	0.0389	0.9333	0.7793	0.1963	0.0244	0.04	0.20	5.55
0.4110	0.1957	0.3933	0.0391	0.0644	0.8965	0.6811	0.2965	0.0224	0.06	0.22	3.79
0.3635	0.2579	0.3786	0.0632	0.1043	0.8325	0.6105	0.3791	0.0104	0.10	0.28	2.65
0.3269	0.3234	0.3497	0.0761	0.1161	0.8078	0.5446	0.4285	0.0269	0.14	0.27	1.94

Glycerol (1) + Ethanol (2) + Sunflower Biodiesel (3)											
overall composition			biodiesel phase			glycerol phase			β_1	β_2	S
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	(w_1^{II}/w_1^{I})	(w_2^{II}/w_2^{I})	(β_2/β_1)
298.15 K											
0.4904	0.0431	0.4665	0.0175	0.0329	0.9496	0.9073	0.0498	0.0429	0.02	0.66	34.28
0.4665	0.0663	0.4672	0.0171	0.0412	0.9417	0.8674	0.0845	0.0481	0.02	0.49	24.61
0.4423	0.1039	0.4538	0.0164	0.0592	0.9244	0.8219	0.1276	0.0505	0.02	0.46	23.33
0.4391	0.1354	0.4255	0.0159	0.0693	0.9148	0.7797	0.1710	0.0493	0.02	0.41	19.83
0.4118	0.1799	0.4083	0.0143	0.1079	0.8778	0.7281	0.2295	0.0424	0.02	0.47	23.95
0.3994	0.2099	0.3907	0.0140	0.1158	0.8702	0.6930	0.2730	0.0340	0.02	0.42	21.03
313.15 K											
0.4864	0.0352	0.4784	0.0188	0.0072	0.9740	0.9184	0.0529	0.0287	0.02	0.14	6.66
0.4752	0.0642	0.4606	0.0199	0.0272	0.9529	0.8791	0.0925	0.0284	0.02	0.29	12.91
0.4774	0.0993	0.4233	0.0212	0.0477	0.9311	0.8375	0.1349	0.0276	0.03	0.35	14.00
0.4279	0.1344	0.4377	0.0228	0.0737	0.9035	0.7934	0.1803	0.0263	0.03	0.41	14.25
0.4117	0.1717	0.4166	0.0240	0.0929	0.8831	0.7431	0.2327	0.0242	0.03	0.40	12.34
0.3996	0.2066	0.3938	0.0249	0.1061	0.8690	0.6933	0.2856	0.0211	0.04	0.37	10.34

mass fraction). The uncertainty in mole fractions reported on this work is estimated to be less than $\pm 1.8 \cdot 10^{-3}$.

Solubility measurements along with tie-lines data of oleic acid + ethanol + colza oil system at 293.15 K were used to validate the experimental methodology, by comparing our data with those obtained from the literature,[9] as illustrated in the Supporting Information (SI, Figure S1). It could be observed that the methodology is reliable, presenting a satisfactory reproducibility.

Solubility (binodal) curves at different temperatures were determined by cloud-point method using the titration procedure under isothermal conditions, with density measurements, as described above. For the biodiesel-enriched phase, mixtures of biodiesel + ethanol have been prepared at various concentrations. However, for the glycerol-enriched phase, glycerol + ethanol mixtures have been prepared. These mixtures were titrated with a third component (glycerol in the biodiesel-enriched phase or biodiesel in the glycerol-enriched phase) under stirring using a magnetic stirrer (Fisatom 752A). This third component was added until it has been observed a transition phase on the ternary mixtures (change from transparent to turbid). The cloud point was considered to be a binodal curve point. For the mixture biodiesel + ethanol, the third component added was glycerol, with a uncertainty of the drop estimated to be ± 0.005 g. For glycerol + ethanol, titration was carried out with biodiesel, and the uncertainty of the drop was ± 0.0009 g. The mixture was weighed again to determine the mass of the third component. Samples of approximately 5 mL were collected for carrying out the density analysis. In this way, a simple second degree polynomial expression for density was obtained of each component.

2.3. Parameter Estimation. The NRTL model was used to adjust interaction parameters of the systems: soybean or sunflower biodiesel + ethanol + glycerol experimental equilibrium data.

The estimation of the interaction parameters was performed by using a flash liquid−liquid calculation implemented in the Fortran code TML-LLE 2.0;[25,26] the procedure is based on the Simplex method proposed by Nelder and Mead,[27] and consists in

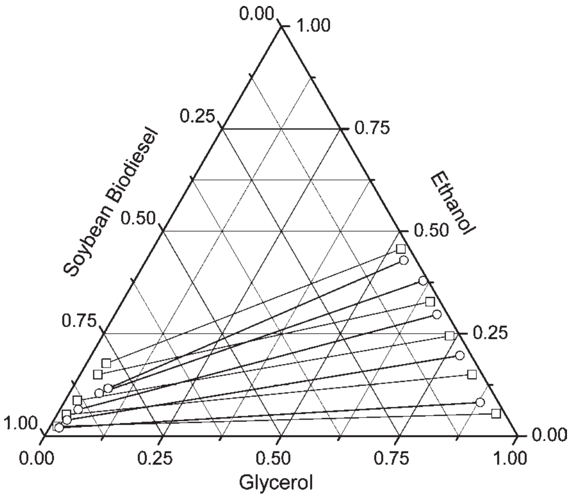

Figure 1. Phase diagram for the soybean biodiesel + glycerol + ethanol system at □, 293.15 K and ○, 323.15 K.

the minimization of a concentration-based objective function, F[28] defined by:

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

Here, D is the number of data sets, N and M are the number of components and tie-lines in each data set, respectively; the superscripts I and II refer to the two liquid phases in equilibrium, while the superscripts exp and calc refer to the experimental and calculated values of the liquid-phase concentration.

With the interaction parameters estimated by the procedure above, comparisons between the experimental and the calculated composition of each component in each of the two phases were made through root-mean-square (rms) deviation, given by:

$$\delta x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N}(x_{ij}^{\mathrm{I,\,exp}} - x_{ij}^{\mathrm{I,\,calc}})^2 + (x_{ij}^{\mathrm{II,\,exp}} - x_{ij}^{\mathrm{II,\,calc}})^2}{2MN}} \qquad (2)$$

In the present work, the experimental data measured for the model systems were used to adjust the NRTL interaction parameters between glycerol (1) + ethanol (2) + soybean or sunflower biodiesel (3).

3. RESULTS AND DISCUSSION

The binodal curve and the density of the system glycerol (1) + ethanol (2) + soybean biodiesel (3) at (293.15 and 323.15) K and glycerol (1) + ethanol (2) + sunflower biodiesel (3) at (298.15 and 313.15) K are shown in Table 2. The experimental liquid—liquid equilibrium data (tie-lines) for the systems in study are presented in Table 3. The phase diagrams for the systems in study are shown in Figures 1 and 2. It can be observed that, as expected, the size of the two-phase region decreases by increasing temperature. The slopes of the lines show that ethanol prefers the glycerol-rich phase than the biodiesel-rich phase. This phenomena indicates that ethanol can be considered as a good extractant for soybean biodiesel and sunflower biodiesel. The large region in the two-phase domain indicates high immiscibility between biodiesel and glycerol even in the present of ethanol.

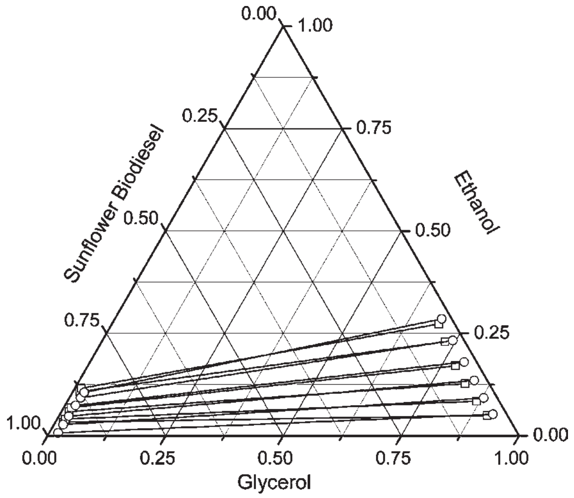

Figure 2. Phase diagram for the sunflower biodiesel + glycerol + ethanol system at □, 298.15 K and ○, 313.15 K.

Table 4. Othmer—Tobias Equation Constants (A and B) and the Correlation Factor (R^2) for the (Soybean or Sunflower Biodiesel + Ethanol + Glycerol) Ternary System

T	Othmer—Tobias correlation		
K	A	B	R^2
	Soybean Biodiesel + Ethanol + Glycerol		
293.15	1.35269	−0.93665	0.98
323.15	1.80376	−1.05969	0.98
	Sunflower Biodiesel + Ethanol + Glycerol		
298.15	1.26562	−0.96479	0.97
313.15	0.44761	−1.69985	0.91

The consistency of the tie-line data was ascertained by applying the Othmer—Tobias correlation:[29]

$$\ln\left(\frac{1 - w_2^{\mathrm{II}}}{w_2^{\mathrm{II}}}\right) = A + B\ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \qquad (3)$$

where $w_2{}^{\mathrm{II}}$ and $w_1{}^{\mathrm{I}}$ stand for the mass fraction of ethanol in biodiesel-rich phase and the mass fraction of glycerol liquid in glycerol-rich phase, respectively.

The Othmer—Tobias plots for the studied systems are shown in the SI, Figures S2 and S3, and the parameters and the regression coefficient R^2 are presented in Table 4. The linearity of the Othmer—Tobias plot indicates the degree of consistency of the data. It can be seen that the regression coefficient is approximately 1, which indicates a good degree of consistency of the experimental data.

Equally important for the selection of the extraction solvent are coefficient distribution and selectivity analysis. The ability of ethanol to separate soybean or sunflower biodiesel + glycerol mixtures can be also calculated by using the distribution coefficient (β) and selectivity (S):[30]

$$\beta_{\mathrm{glycerol}} = \beta_1 = \frac{(w_{\mathrm{glycerol}})_{\mathrm{biodiesel-rich\ phase}}}{(w_{\mathrm{glycerol}})_{\mathrm{glycerol-rich\ phase}}} = \frac{w_1^{\mathrm{II}}}{w_1^{\mathrm{I}}} \qquad (4)$$

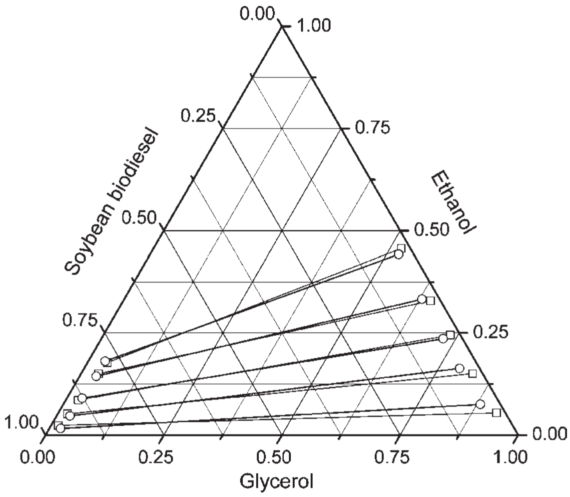

Figure 3. System of soybean biodiesel + glycerol + ethanol system at 293.15 K: □, experimental; ○, NRTL.

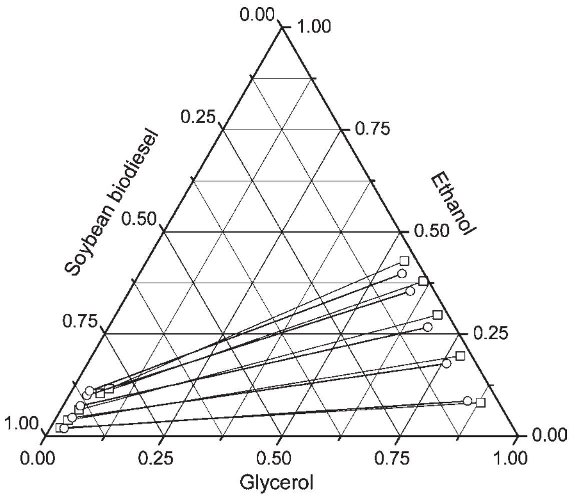

Figure 4. System of soybean biodiesel + glycerol + ethanol system at 323.15 K: □, experimental; ○, NRTL.

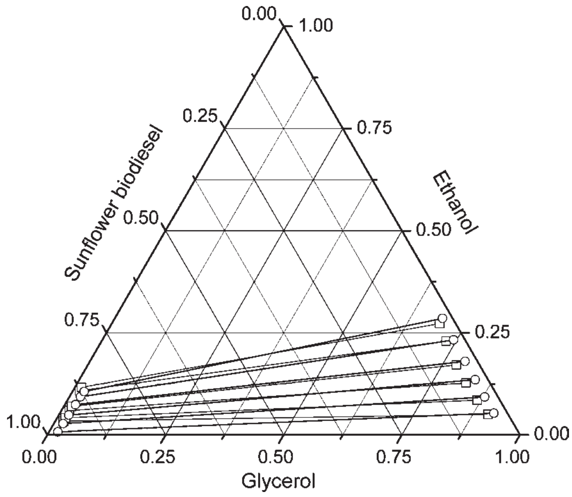

Figure 5. System of sunflower biodiesel + glycerol + ethanol system at 298.15 K: □, experimental; ○, NRTL.

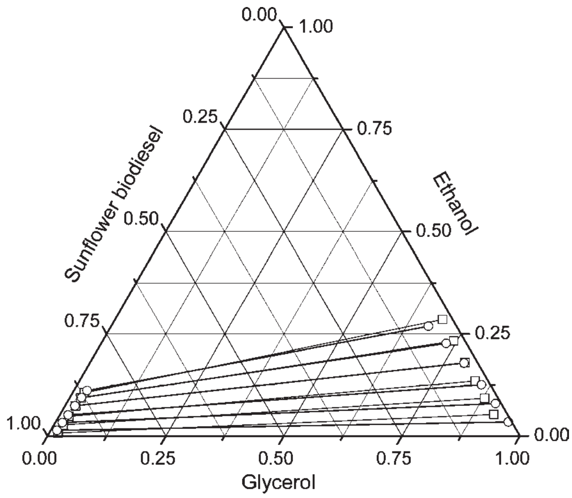

Figure 6. System of sunflower biodiesel + glycerol + ethanol system at 313.15 K: □, experimental; ○, NRTL.

$$\beta_{\text{ethanol}} = \beta_2 = \frac{(w_{\text{ethanol}})_{\text{biodiesel-rich phase}}}{(w_{\text{ethanol}})_{\text{glycerol-rich phase}}} = \frac{w_2^{\text{II}}}{w_2^{\text{I}}} \tag{5}$$

$$S = \frac{\beta_{\text{ethanol}}}{\beta_{\text{glycerol}}} = \frac{\beta_2}{\beta_1} \tag{6}$$

Table 3 shows the distribution coefficients and selectivity. The distribution coefficients are shown in the SI, Figures S4 and S5, while the selectivity is shown in the SI, Figures S6 and S7. It can be observed that the values obtained from selectivity has been larger than 1. It indicates that soybean or sunflower biodiesel extraction is possible by using ethanol.

From solubility data along with selectivity and distribution coefficients it can be seen that the use and recovery of ethanol can be possible for the separation unit operation of liquid−liquid extraction.

Table 5. NRTL Interaction Parameters between Glycerol + Ethanol + Soybean or Sunflower Biodiesel

	NRTL		
pair *ij*	A_{ij}/K	A_{ji}/K	α_{ij}
glycerol−ethanol	16.06	565.76	0.2
glycerol−soybean biodiesel	1004.20	393.48	0.2
ethanol−soybean biodiesel	7054.70	567.04	0.2
glycerol−sunflower biodiesel	1619.70	543.11	0.2
ethanol−sunflower biodiesel	817.08	−122.10	0.2

Figures 3 to 6 show the experimental data points and the tie lines fitted by using NRTL model for the systems studied. These figures indicate that the thermodynamic model used was able to describe with accuracy the phase compositions for the system investigated.

The adjusted parameters of NRTL model are shown in Table 5. The deviations between experimental and calculated compositions in both phases were calculated according to eq 2

Table 6. Mean Deviations in Phase Compositions of Soybean and Sunflower Biodiesel + Glycerol + Ethanol

system	T/K	NRTL Δw (%)
soybean biodiesel + glycerol + ethanol	293.15	1.8
soybean biodiesel + glycerol + ethanol	323.15	2.5
sunflower biodiesel + glycerol + ethanol	298.15	1.4
sunflower biodiesel + glycerol + ethanol	313.15	1.6
Global Deviation of the Correlation		1.9

and are shown in Table 6. It is important to mention that the thermodynamic model studied in this work was able to correlate our experimental data, with global rms deviations for NRTL model of 1.9 % for the systems studied.

4. CONCLUSIONS

Experimental liquid−liquid equilibrium data, both binodal curves and tie-lines, were determined for the ternary systems soybean biodiesel + glycerol + ethanol at (293.15 and 323.15) K and sunflower biodiesel + ethanol + glycerol at (298.15 and 313.15) K, using density measurements. Consistency, coefficient distribution, and selectivity analyses were performed. The consistency of the tie-lines was ascertained by applying the Othmer−Tobias correlation. The distribution coefficients and selectivities show that ethanol could be a good extraction solvent for the separation of soybean or sunflower biodiesel + glycerol mixtures. The NRTL model was used to correlate the activity coefficient, by using the Simplex method and a concentration-based objective function. The results are satisfactory, with root-mean-square deviations between calculated and experimental compositions in both equilibrium phases about 1.9 % for the systems studied.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures containing the measured solubility, Othmer−Tobias plots, plots of the distribution coefficient, and experimental separation factor, S. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

The financial support by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) and FUNCAP (Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico) is gratefully acknowledged. The authors also thank the technical support from GPSA (Grupo de Pesquisa em Separações por Adsorção) and from the LADP (Laboratório de Análise e Desenvolvimento de Processos) from Universidade Federal do Ceará.

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