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LIQUID-LIQUID EQUILIBRIUM OF SYSTEMS COMPOSED OF SOYBEAN OIL + MONOACYLGLYCEROLS + DIACYLGLYCEROLS + ETHYL OLEATE + OLEIC ACID + ETHANOL AT 303.15 AND 318.15 K

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Abstract - Steady increase in prices of petroleum-based fuels and growing environmental concerns are boosting attention to alternative fuels. In this context, biodiesel has drawn attention as an alternative fuel, especially as a substitute to traditional diesel. Biodiesel is commonly produced from triacylglycerols and alcohol through transesterification reaction. Knowledge of equilibrium phase distribution of key components in transesterification systems is essential for a better understanding of the reaction pathway and for guiding the design and optimization of reactors and the products separation. This study reports experimental results and thermodynamic modeling of the liquid-liquid equilibrium of systems composed of soybean oil + monoacylglycerols + diacylglycerols + ethyl oleate + oleic acid + ethanol at 303.15 and 318.15 K. Experimental data were well correlated using NRTL, with a maximum deviation of 0.688%. As for UNIFAC, the deviations between predicted and experimental data ranged from 3.13 to 9.21%.

Keywords: partial acylglycerols; biodiesel; ethanol; modeling.

INTRODUCTION

Recent concerns over diminishing fossil fuel supplies and rising oil prices, as well as adverse environmental and human health impacts from the use of petroleum fuel, have prompted considerable interest in research and development of fuels from renewable resources (West *et al.*, 2008). Biofuels are renewable fuels derived from biomass that can replace, partially or completely, petroleum-derived fuels in engines.

Biodiesel is defined as a mixture of fatty acid alkyl esters commonly produced from triacylglycerols and a short-chain alcohol through a transesterification reaction in the presence of catalysts (Knothe *et al.*, 2005). Transesterification leads to high conversion of triacylglycerols (TAG) into ethyl esters (Marjanovic *et al.*, 2010) with diacylglycerols (DAG) and monoacylglycerols (MAG) as reaction intermediates and glycerol as product. Indeed, the overall process is a sequence of three consecutive steps, which are

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reversible reactions. In the first step, DAGs are obtained from TAGs; MAGs are then produced from DAGs and, in the last step, glycerol is obtained from MAGs. In all these reactions, ethyl esters are produced. Concentrations of DAG and MAG intermediates rise initially, passing through respective maxima, and decline. Stoichiometrically, the reaction requires a molar ratio alcohol:oil of 3:1, but excess alcohol is usually added to drive the reaction towards the products (West *et al.*, 2008; Mazutti *et al.*, 2013). Methanol is the most commonly used alcohol, which is mainly produced by oxidation processes of methane. Ethanol, however, is preferable due to its superior dissolving power for vegetable oils, low toxicity and its renewable origin (Richard *et al.*, 2013).

The transesterification system is complex due to changing phase equilibria: two immiscible phases are present at the beginning (vegetable oil and ethanol), then a single phase appears after a few minutes of reaction. Finally, two phases are obtained at the end of the reaction, composed principally of ethyl esters and glycerol (Richard *et al.*, 2013). Hence, to properly design a continuous process, numerous data must be acquired.

Liquid-liquid equilibrium (LLE) data on systems composed of mixtures of triacylglycerols, fatty acids, alcohol, alkyl esters and glycerol are largely available in the literature, but data on systems involving partial acylglycerols are still scarce. In the present work, the LLE database was extended by providing information related to systems involved in reactive and purification steps of the ethylic biodiesel production. Furthermore, the experimental data were used to adjust the NRTL binary interaction parameters and to evaluate two different sets of parameters for the original UNIFAC model.

MATERIALS AND METHODS

Suppliers and mass fraction purities of the solvents and fatty compounds used in this work are listed in Table 1; none of them was subjected to further purification.

Table 1: Reagents and fatty compounds – suppliers and purity.

Component	Supplier	Mass fraction purity[a]
Ethanol	Merck	> 0.995
Toluene HPLC grade	Sigma Aldrich	> 0.999
Acetic acid	Merck	> 0.998
Soybean oil	Cargill	> 0.999[b]
Mixture M/D[c]	SGS Agriculture and Industry Ltd.	> 0.52[d]
Commercial ethyl oleate	Tecnosyn	> 0.75

[a] As reported by the supplier

[b] of fatty compounds

[c] Commercial mixtures of mono- and diacylglycerols from soybean oil

[d] of monoacylglycerols

Experimental procedures

All fatty compounds used in this work were analyzed by gas chromatography of the fatty acid methyl esters, according to the official method Ce 1f−62 of the American Oil Chemists' Society (AOCS, 2009) to determine their fatty acid composition. Prior to the chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters according to Hartman and Lago (1973). The chromatographic analysis was carried out using a capillary gas chromatography system under the same experimental conditions shown in Hirata *et al.* (2013). The composition of the commercial ethyl oleate was also determined by gas chromatography. The analyses were carried out in triplicate.

From the fatty acid compositions, the probable triacylglycerol compositions of soybean oil could be determined, using the statistical algorithm suggested by Antoniosi Filho *et al.* (1995), ignoring triacylglycerols with a total concentration less than 0.5 wt.%. For the mixture M/D, the probable TAG composition was determined using the same procedure and, from this composition, the compositions in mono- and diacylglycerols were estimated considering the probability of the partial rupture of the triacylglycerols without preference for specific ester bonds.

LLE data for the systems (soybean oil + ethyl oleate + oleic acid + ethanol) and (soybean oil + mixture M/D + ethyl oleate + oleic acid + ethanol) were studied at 303.15 and 318.15 K, at atmospheric pressure. These data were measured using sealed headspace glass tubes (10 mL) (PerkinElmer), as described by Basso *et al.* (2012). Components were weighted on an analytical balance (Precisa, model XT220A, Sweden, ±0.0001 g). The tubes were vigorously stirred for 30 min using a vortex (IKA, model Genius3) and then all systems were left to rest for at least 36 hours at constant temperature in a thermostatic bath with temperature control (Cole Parmer, model 12101-55, USA, ±0.01 K). Two clear layers and a well-defined interface were formed when the systems reached the equilibrium state. Samples of both phases were carefully collected with syringes and diluted directly with toluene for quantification of the components. The compounds of each phase were identified and quantified by size exclusion chromatography conducted in a HPLC (High-Performance Liquid Chromatography) Shimadzu, model 20AT, under the same experimental conditions shown in Bessa *et al.* (2015). These analyses were also performed in triplicate.

The quantitative analysis was performed using calibration curves obtained using solutions made with the same components used in the equilibrium systems. The data obtained were fitted by linear regression and the corresponding equations were generated for quantification. In order to check the quality of the LLE results, the procedure developed by Marcilla *et al.* (1995) and applied to fatty systems by Rodrigues *et al.* (2005) was used. According to Marcilla *et al.* (1995) deviation values in the global mass balance lower than 0.5% guarantee the quality of the experimental data.

Thermodynamic modeling

The experimental data were used to adjust the NRTL binary interaction parameters. The adjustments were made by treating the systems as a pseudoquaternary (soybean oil + ethyl oleate + oleic acid + ethanol) or pseudosenary (soybean oil + mixture M/D + ethyl oleate + oleic acid + ethanol). For each system pseudocomponents with the average molar masses of the triacylglycerols, diacylglycerols, monoacylglycerols and ethyl esters were considered. Lanza *et al.* (2007) and Basso *et al.* (2012) validated this approach when studying the LLE of systems containing soybean oil and ethylic biodiesel from crambe oil, respectively.

Estimation of the NRTL parameters was performed by minimizing the objective function of compositions, shown in Equation (1), using the simplex method, according to the procedure suggested by Stragevitch and D'ávila (1997):

$$S = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{P-1}\left[\left(\frac{w_{inm}^{FI,exp} - w_{inm}^{FI,calc}}{\sigma_{w_{inm}^{FI}}}\right)^2 + \left(\frac{w_{inm}^{FII,exp} - w_{inm}^{FII,calc}}{\sigma_{w_{inm}^{FII}}}\right)^2\right] \quad (1)$$

where D is the total number of data sets, N is the total number of tie lines, P is the total number of pseudocomponents in each data set; i, n, and m stand for component, tie line and data group, respectively; FI and FII refer to phases I and II, respectively; *exp* and *calc* stand for experimental and calculated mass fractions (w), respectively, $\sigma_{w_{inm}^{FI}}$ and $\sigma_{w_{inm}^{FII}}$ are the standard deviations observed in the composition of the two liquid phases. The equilibrium compositions were calculated using the average value between the experimental equilibrium compositions.

The average deviations between experimental and calculated compositions in both phases were calculated according to Equation (2):

$$\Delta w = 100\sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{P}\left[\left(w_{in}^{FI,exp} - w_{in}^{FI,calc}\right)^2 + \left(w_{in}^{FII,exp} - w_{in}^{FII,calc}\right)^2\right]}{2NP}} \quad (2)$$

The UNIFAC thermodynamic model was also used to predict the LLE of the systems. Two sets of interaction parameters were used: *(i)* UNIFAC-LLE, proposed by Magnussen *et al.* (1981), and *(ii)* UNIFAC-HIR, presented by Hirata *et al.* (2013), who adjusted UNIFAC parameters for the systems present in the oil deacidification, i.e., systems composed of vegetable oil + fatty acid + ethanol + water. In both cases, the model used was that presented by Fredenslund *et al.* (1975). In this case, all individual components – tri-, di- and monoacylglycerols, and ethyl esters – were considered for modeling calculations. The average deviation between calculated and experimental compositions in both phases was also calculated according to Equation (2). Although the equilibrium calculations take into account the diversity of components present in every pseudocomponent, it should be noted that the objective function and the deviation calculation were based on the composition of the whole pseudocomponents, since the experimental information is available only in this form. This means that phase equilibrium is evaluated taking into account all the main components and then the sets of compositions of TAGs, DAGs, MAGs and esters are summed in each phase in order to obtain the compositions of the pseudocomponents.

RESULTS AND DISCUSSION

LLE experimental data

The fatty acid compositions of soybean oil and commercial mixture M/D are shown in Table 2, as well as the composition of ethyl esters of commercial ethyl oleate. Table 3 shows the probable TAG composition of soybean oil and Table 4 is the probable composition of TAG, DAG and MAG of the mixture M/D.

Fatty compounds used were also preliminarily analyzed by size exclusion chromatography (HPSEC). Through this analysis, it was possible to identify the classes of components present in each compound. Thus, it was observed that commercial mixtures M/D, in addition to these components, also contain a small amount of triacylglycerols. Among all the fatty compounds used, only ethyl oleate presented a significant content of fatty acids, which was determined by titration according to the official method 2201 of the

Table 2: Fatty acid composition of fatty reagents (% mass)[a].

Fatty acid / Ethyl ester	Symbol	Cx:y[b]	Soybean oil	Mixture M/D	Ethyl oleate
Lauric	L	C12:0	-	0.04	2.54
Myristic	M	C14:0	0.08	0.09	0.29
Palmitic	P	C16:0	10.83	11.38	4.62
Palmitoleic	Po	C16:1	0.08	0.08	-
Stearic	S	C18:0	3.89	5.52	1.84
Oleic	O	C18:1	24.49	23.38	78.08
Linoleic	Li	C18:2	52.86	52.21	11.93
trans-Linoleic	Li T[c]	C18:2 T[c]	0.44	2.57	-
Linolenic	Ln	C18:3	6.34	3.53	-
trans-Linolenic	Ln T[c]	C18:3 T[c]	-	0.20	-
Arachidic	A	C20:0	0.36	0.41	0.08
Gadoleic	Ga	C20:1	0.18	0.14	0.08
Behenic	B	C22:0	0.45	0.45	0.13
Erucic	E	C22:1	-	-	0.41

[a] Standard uncertainties u are $u(w/\%) = 0.02$.
[b] Cx:y: x is the number of carbons and y is the number of double bonds.
[c] Trans isomers

Table 3: Probable triacylglycerol composition of soybean oil[a].

Group x:y[b]	Main TAG	M (g.mol^{-1})	100x	100w
50:1	POP	833.37	0.91	0.95
50:2	PPLi	831.35	2.02	2.12
52:1	POS	861.42	0.61	0.62
52:2	OOP	859.41	3.55	3.61
52:3	POLi	857.39	9.91	10.09
52:4	LiLiP	855.38	11.86	12.10
52:5	PLnLi	853.36	2.62	2.68
54:2	OOS	887.46	1.11	1.09
54:3	SOLi	885.45	4.81	4.74
54:4	OOLi	883.43	13.43	13.26
54:5	LiLiO	881.41	22.71	22.46
54:6	LiLiLi	879.40	20.10	19.95
54:7	LiLiLn	877.38	5.71	5.68
54:8	LnLnLi	875.37	0.65	0.65

[a] Standard uncertainties u are $u(x/\%) = 0.5$.
[b] x:y, x = number of carbons (except carbons of glycerol) and y = number of double bonds.

IUPAC (1987) with an automatic buret (Metrohm, Model Dosimat 715). This analysis was replicated three times and the average value is 8.43% by weight, expressed as oleic acid.

The composition expressed in terms of mono-, di-, and triacylglycerols of the commercial mixture M/D was obtained using gas chromatography, with flame ionization detector according to the standard test method ASTM D6584 (2013) of the American Society for Testing and Materials, obtaining the result of 5.26%, 34.86% and 59.89% of TAG, DAG and MAG, respectively, expressed in mass percentage.

Despite being small, the composition of TAG in the mixture M/D was taken into account in both the experimental data and in the thermodynamic calculations. However, in the case of the NRTL model, the molar mass of the representative TAG was calculated considering only the molar composition of the vegetable oil. According to Table 3, the value was 872.71 g.mol^{-1}. It is important to mention that the error introduced

Table 4: Probable tri-, di- and monoacylglycerol compositions of the commercial mixture M/D[a].

Main TAG	M ($g.mol^{-1}$)	100x	DAG	M ($g.mol^{-1}$)	100x	MAG	M ($g.mol^{-1}$)	100x
PPO	833.37	1.03	PP	568.91	1.16	P	330.48	12.49
PPLi	831.35	2.46	PS	596.96	0.30	S	358.54	2.78
LiLiP	855.38	13.01	PO	594.95	7.36	O	356.52	26.87
PLnLi	853.36	1.76	PLi	592.93	14.41	Li	354.51	56.13
POS	861.42	0.90	PLn	590.91	0.59	Ln	352.49	1.72
OOP	859.41	4.30	SO	623.00	3.31			
POLi	857.39	10.54	SLi	620.98	1.95			
OOS	887.46	1.59	OO	620.98	6.74			
SOLi	885.45	5.86	OLi	618.97	29.59			
OOLi	883.43	14.35	LiLi	616.95	31.73			
LiLiO	881.41	21.84	LiLn	614.94	2.86			
LiLiLi	879.40	18.97						
LiLiLn	877.38	3.41						

[a] Standard uncertainties u are $u(x/\%) = 0.5$.

by considering only the composition of the vegetable oil in the calculation of the TAG molar mass is quite small, since the amount of TAG in the commercial mixture M/D is low, as mentioned before, and because the average molar masses of TAGs from the mixture M/D (872.25 $g.mol^{-1}$, determined according to the triacylglycerols composition shown in Table 4) did not differ significantly from that calculated for vegetable oil.

The average molar masses of di- and monoacylglycerols from the mixture M/D were calculated according to Table 4 and the values obtained were 612.19 and 352.12 $g.mol^{-1}$ for the DAG and MAG, respectively. The average molar mass of the commercial ethyl oleate was determined from its ethyl ester composition, shown in Table 2, and the obtained value was 306.33 $g.mol^{-1}$.

As for the UNIFAC model, all the various components were taken into account in the calculations, i.e., all the triacylglycerols from the vegetable oil, all tri-, di- and monoacylglycerols from the commercial mixture M/D and all the ethyl esters from commercial ethyl oleate, so that the input data used were as accurate as possible. This means that a total of 44 different components were considered.

Table 5 shows the overall compositions and the corresponding tie lines at 303.15 and 318.15 K for the systems composed of (soybean oil + ethyl oleate + oleic acid + ethanol) and (soybean oil + mixture M/D + ethyl oleate + oleic acid + ethanol). Regarding the overall mass balance deviations, the average results obtained, according to Marcilla *et al.* (1995), were 0.048 and 0.036% for the systems at 303.15 and 318.15 K, respectively, confirming the quality of the experimental data.

Figure 1 shows the experimental data for the system (soybean oil + ethyl oleate + oleic acid + ethanol) at 303.15 and 318.15 K. It can be seen that an increase in temperature leads to a decrease in the two-phase region, indicating an improvement in the mutual solubility of the soybean oil and ethanol. This behavior has been previously reported in the literature (Mazutti *et al.*, 2013; Bessa *et al.*, 2015; Ferreira *et al.*, 2015; Shiozawa *et al.*, 2015).

It is also interesting to observe the behavior of the minor components in the system, represented by the distribution coefficient, given by Equation (3):

$$k_i = \frac{w_i^{FI}}{w_i^{FII}} \tag{3}$$

where w_i^{FI} corresponds to the content of component i (each DAG, MAG, fatty acid or ethyl ester) in the alcoholic phase and w_i^{FII} corresponds to the content of component i in the oil phase.

Figure 2 shows the average values of k_i and their corresponding error bars. It can be observed that diacylglycerols and ethyl esters presented a preference for the oil phase, since their distribution coefficient values are smaller than one. On the other hand, oleic acid and monoacylglycerols have distribution coefficients greater than one, indicating the preference of these components for the alcoholic phase. This occurs because monoacylglycerols contain a higher number of polar groups (hydroxyl groups) than diacylglycerols,

Table 5: Liquid-liquid equilibrium data for the system soybean oil (1) + DAG (2) + MAG (3) + ethyl oleate (4) + oleic acid (5) + ethanol (6) at 303.15 K and 318.15 K, and 93.9 kPa[a].

T(K)	Overall Composition						Solvent Phase (*FI*)						Oil Phase (*FII*)						δ (%)[b]
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_6$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_6$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_6$	
303.15	50.01	0.00	0.00	0.00	0.00	49.99	6.53	0.00	0.00	0.00	0.00	93.47	83.99	0.00	0.00	0.00	0.00	16.01	0.00
	45.06	0.00	0.00	4.50	0.41	50.03	7.89	0.00	0.00	3.08	0.47	88.56	75.37	0.00	0.00	5.67	0.32	18.64	0.01
	40.79	0.00	0.00	7.56	0.70	50.95	9.63	0.00	0.00	5.47	0.78	84.12	68.52	0.00	0.00	9.45	0.57	21.46	0.01
	40.07	0.00	0.00	9.17	0.84	49.92	10.80	0.00	0.00	6.91	0.95	81.34	65.18	0.00	0.00	11.22	0.70	22.90	0.02
	36.90	0.00	0.00	12.09	1.11	49.90	13.59	0.00	0.00	9.79	1.24	75.38	58.10	0.00	0.00	14.46	0.97	26.47	0.09
	33.95	0.00	0.00	14.58	1.34	50.13	17.63	0.00	0.00	12.59	1.44	68.34	50.25	0.00	0.00	16.85	1.21	31.69	0.08
	48.64	0.88	1.52	0.00	0.00	48.96	7.74	0.73	2.33	0.00	0.00	89.20	80.21	1.03	0.83	0.00	0.00	17.93	0.03
	46.51	0.86	1.48	1.84	0.17	49.14	8.20	0.74	2.38	1.25	0.20	87.23	76.80	1.02	0.86	2.28	0.14	18.90	0.06
	44.52	0.92	1.58	3.71	0.34	48.93	9.20	0.76	2.45	2.61	0.38	84.60	72.76	1.00	1.07	4.59	0.28	20.30	0.07
	41.55	0.87	1.49	6.54	0.60	48.95	10.36	0.76	2.27	4.72	0.68	81.21	66.61	0.96	1.00	7.96	0.51	22.96	0.05
	39.33	0.85	1.47	8.25	0.76	49.34	13.19	0.77	2.03	6.38	0.84	76.79	61.89	0.89	0.97	9.89	0.65	25.71	0.05
	37.31	0.85	1.46	10.36	0.95	49.07	16.27	0.78	1.96	8.66	1.04	71.29	55.65	0.88	1.14	12.01	0.85	29.47	0.10
318.15	48.66	0.00	0.00	0.00	0.00	51.34	9.07	0.00	0.00	0.00	0.00	90.93	80.60	0.00	0.00	0.00	0.00	19.40	0.00
	45.66	0.00	0.00	2.55	0.23	51.55	9.12	0.00	0.00	1.84	0.26	88.78	75.73	0.00	0.00	3.16	0.17	20.94	0.02
	42.33	0.00	0.00	5.35	0.49	51.82	10.39	0.00	0.00	3.91	0.54	85.16	69.56	0.00	0.00	6.57	0.39	23.48	0.05
	40.20	0.00	0.00	8.05	0.74	51.00	11.28	0.00	0.00	6.07	0.82	81.83	63.43	0.00	0.00	9.61	0.62	26.34	0.06
	36.94	0.00	0.00	10.62	0.98	51.47	12.88	0.00	0.00	8.34	1.06	77.72	55.48	0.00	0.00	12.36	0.87	31.29	0.02
	34.76	0.00	0.00	13.28	1.22	50.73	17.03	0.00	0.00	11.25	1.29	70.43	47.72	0.00	0.00	14.85	1.11	36.32	0.01
	48.67	0.86	1.48	0.00	0.00	48.99	10.15	0.79	2.08	0.00	0.00	86.98	78.50	0.98	0.93	0.00	0.00	19.59	0.01
	47.70	0.87	1.50	0.79	0.07	49.07	11.54	0.83	2.34	0.59	0.09	84.61	76.30	1.00	0.85	0.93	0.06	20.86	0.05
	45.46	0.88	1.51	2.75	0.25	49.15	11.58	0.77	2.50	2.05	0.30	82.80	71.75	0.99	0.90	3.29	0.21	22.86	0.10
	43.33	0.87	1.50	4.70	0.43	49.17	13.08	0.81	2.22	3.59	0.50	79.80	67.02	0.96	0.86	5.59	0.36	25.21	0.02
	40.10	0.84	1.45	7.35	0.68	49.58	15.95	0.76	2.12	5.88	0.74	74.55	59.13	0.91	1.15	8.50	0.58	29.73	0.10
	38.42	0.89	1.53	9.36	0.86	48.94	16.92	0.81	2.05	7.63	0.91	71.68	54.27	0.94	1.33	10.51	0.77	32.18	0.01

[a] Standard uncertainties *u* are *u*(T/K) = 0.1. *u*(P/kPa) = 0.21. *u*(*w*) = 0.0019;

[b] Overall mass balance deviation (Marcilla *et al*., 1995).

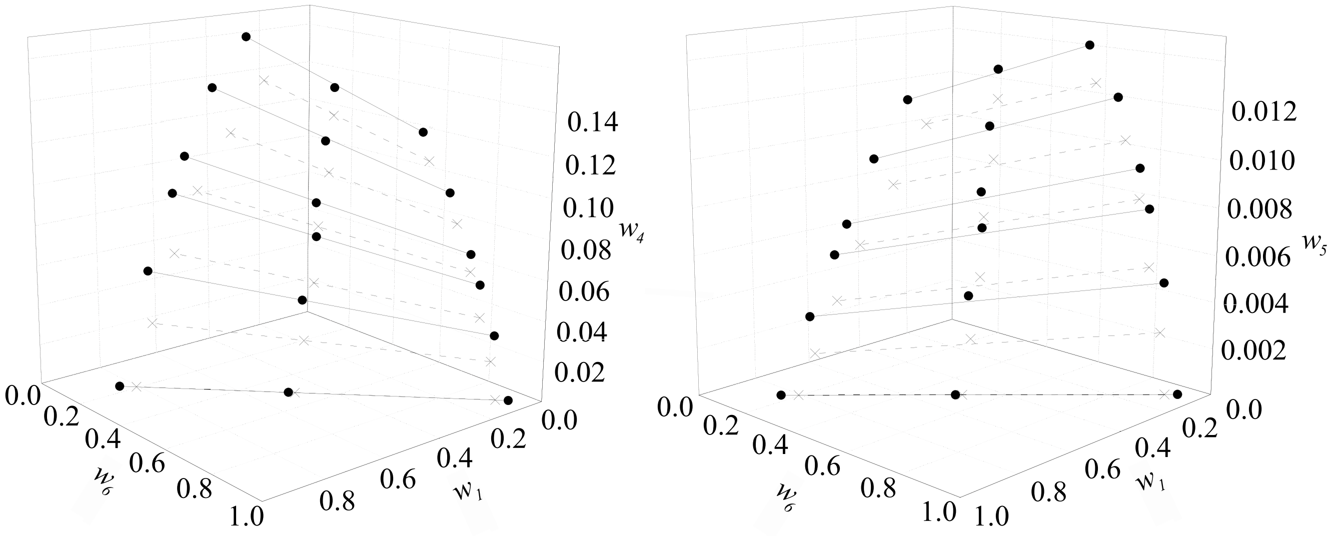

Figure 1: LLE for the system soybean oil (1) + DAG (2) + MAG (3) + ethyl oleate (4) + oleic acid (5) + ethanol (6) at –●–: 303,15 K e - - - -: 318,15 K.

increasing their preference for the alcoholic phase. This behavior is observed at both temperatures. In addition, as shown in Figure 2, an increase in the temperature little affects the distribution coefficients.

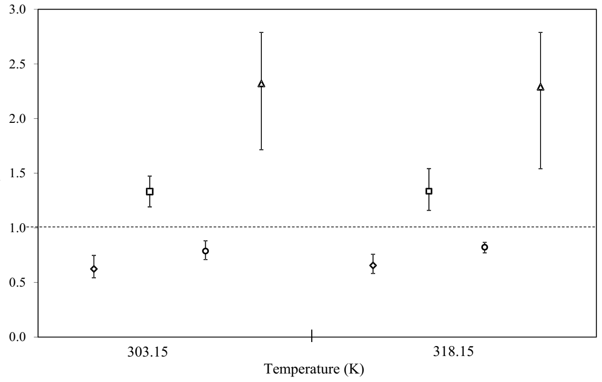

Figure 2: Average distribution coefficient (k_i) of ◊: ethyl oleate; □: oleic acid; ○: DAG; Δ: MAG.

NRTL modeling approach

Figure 3 shows the experimental and calculated tie lines for the system (soybean oil + commercial mixture M/D + ethyl oleate + oleic acid + ethanol) at 303.15 K, indicating the distribution of ethyl oleate and oleic acid. In order to facilitate the interpretation of the six-component phase equilibrium data, they were transposed into a quaternary diagram by grouping similar components (TAG-DAG-MAG) on one axis. The NRTL model accurately describes the LLE of this system. The experimental and calculated tie lines nearly overlap, confirming the good description and the low deviation values, which were 0.657% for the system at 303.15 K and 0.410% at 318.15 K. The NRTL interaction parameters fitted to the experimental data are shown in Table 6. The standard deviations for the fitted parameters were considered to be the same as the experimental uncertainty *u* shown in Table 5.

UNIFAC modeling approach

Regarding the UNIFAC, this model did not show the same accuracy, as shown in Figure 4. The slope of the calculated tie lines using UNIFAC-LLE parameters is much more accentuated than the experimental ones. In addition, the use of these parameters led to a different behavior of oleic acid, indicating a preference for the oil phase, contrary to what was experimentally observed. As regards the UNIFAC-HIR parameters, although the calculated biphasic region is greater than the experimental one, a significant improvement can be observed in the LLE prediction, and this is particularly significant considering the ethyl oleate behavior. The deviations observed using UNIFAC were 8.42 and 9.21% at 303.15 and 318.15 K, respectively, with the UNIFAC-LLE parameters and 3.46 and 3.13% using the UNIFAC-HIR parameters at 303.15 and 318.15 K, respectively. The improvement in average deviations between experimental data and predicted values using UNIFAC-HIR can be explained by the fact that the parameters presented by Hirata *et al.* (2013) were obtained from systems containing triacylglycerols, free fatty acids and ethanol, which are part of the components of the systems studied in this work.

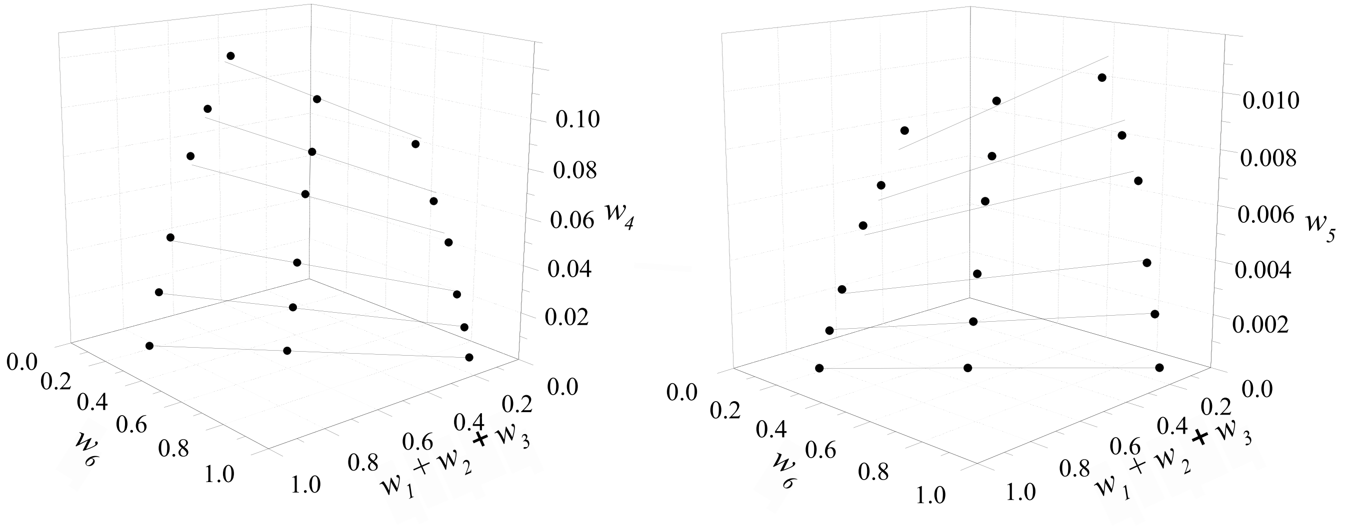

Figure 3: LLE for the system soybean oil (1) + DAG (2) + MAG (3) + ethyl oleate (4) + oleic acid (5) + ethanol (6) at 303.15 K (●: experimental data; —— : calculated values using NRTL).

Table 6: NRTL parameters for the system soybean oil (1) + DAG (2) + MAG (3) + ethyl oleate (4) + oleic acid (5) + ethanol (6) at 303.15 and 318.15 K.

		303.15 K			**318.15 K**	
pair *i-j*	**A_{ij}/K**	**A_{ji}/K**	**α_{ij}**	**A_{ij}/K**	**A_{ji}/K**	**α_{ij}**
01-02	608.930	-234.060	0.44593	546.890	-209.480	0.56443
01-03	-19.456	-24.650	0.44737	-79.146	-56.635	0.40548
01-04	-523.350	283.250	0.10000	-749.400	232.420	0.11944
01-05	13708.000	-414.000	0.12887	7205.100	-203.210	0.10023
01-06	-15.611	1455.400	0.49047	-277.450	1634.900	0.43250
02-03	641.470	-601.150	0.10105	728.920	-663.020	0.10013
02-04	-3.065	-2316.300	0.56992	-101.450	-1085.500	0.10000
02-05	14597.000	150.980	0.10004	2919.000	37.010	0.18892
02-06	4700.400	-70.263	0.25760	2469.700	-28.569	0.57000
03-04	-160.150	-13.354	0.13943	-132.180	-13.578	0.15407
03-05	1855.500	631.230	0.10585	2142.300	793.500	0.10002
03-06	-327.150	940.350	0.44749	-334.060	955.190	0.45553
04-05	-59.733	-803.630	0.44596	-92.819	-782.900	0.34846
04-06	-35.525	-83.099	0.13313	-44.798	-84.608	0.11002
05-06	-474.940	339.780	0.48174	-223.970	437.600	0.41941

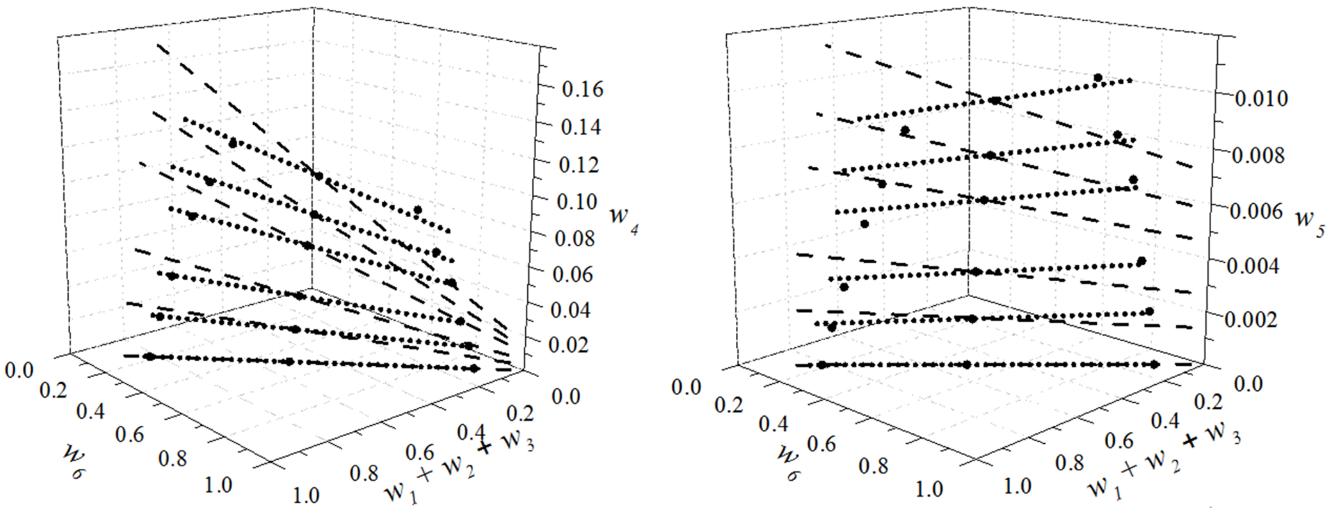

Figure 4: LLE for the system soybean oil (1) + DAG (2) + MAG (3) + ethyl oleate (4) + oleic acid (5) + ethanol (6) at 303.15 K (●: experimental data; - - - -: calculated values using UNIFAC-LLE; ········: calculated values using UNIFAC-HIR).

CONCLUSIONS

The information acquired in this study showed that monoacylglycerols, which have a greater number of polar groups (hydroxyl groups) have a greater affinity with the alcoholic phase when compared to diacylglycerols. The NRTL model was fitted to equilibrium data and binary interaction parameters were obtained. A good agreement between experimental and calculated values could be observed, indicating the applicability of this model to such systems. In contrast, the UNIFAC model using two sets of parameters from the literature resulted in higher values of deviations, which motivates future work to further improve the model by adjusting a specific set of parameters. The results of this study allow a more precise description of the actual behavior of systems involved in the transesterification of the ethyl biodiesel production process and, consequently, its optimization.

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