Mutual Solubility for Systems Composed of Vegetable Oil + Ethanol + Water at Different Temperatures

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This study presents liquid−liquid equilibrium data for systems of interest in biodiesel production and the refining of edible oils by liquid−liquid extraction. These systems are composed of vegetable oils + anhydrous ethanol + water, at temperatures ranging from (298.15 to 333.15) K. The following vegetable oils were investigated: refined canola oil, refined corn oil, semiprocessed *Jatropha curcas* oil, and semiprocessed macauba (*Acrocomia aculeata*) pulp oil. According to the results, the enhancement of temperature within the study ranges increased oil−solvent miscibility in both phases. The liquid−liquid equilibrium experimental data were correlated using the non-random two liquid (NRTL) model. For all of these systems, the global deviations between calculated and experimental data were lower than 0.7 %, showing the good descriptive quality and applicability of the NRTL model in liquid−liquid analysis and computational simulation processes.

Introduction

Biodiesel, an alternative fuel for diesel engines, is produced from renewable biological sources such as vegetable oils and fats.[1] The most common process for producing biodiesel is known as transesterification. This process involves combining any lipid (vegetable or animal) with short-chain alcohol in the presence of a catalyst. Among the applicable lipid sources, vegetable oils are usually used in biodiesel production. Alcohols that are generally used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. Concerning environment aspects, ethanol has greater advantages when compared to the other short-chain alcohols. Ethanol shows low toxicity and can be produced from agricultural renewable resources, thus attaining total independence from petroleum-based alcohols.[2,3]

The transesterification process (also known as alcoholysis) is generally carried out at (313.15 to 343.15) K, once the reaction temperature is limited by the boiling point of the alcohol.[4] Because of the low mutual solubility of vegetable oil and ethanol at atmospheric pressure, the reaction mixture is usually mechanically stirred to enhance mass transfer.[3] Generally, to successful accomplish the transesterification process, it is required that oil has a water content in mass fraction lower than 0.1 %.[5] The presence of water in the investigated systems requires subsequent purification steps for biodiesel production and ethanol recovery. Solvent reuse would also lead to water accumulation in ethanol, affecting the initial stage of the reaction.

One factor of particular importance in the alcoholysis process is the degree of mixing between the alcohol and the triacylglycerol phases.[6,7] The stoichiometric ratio for the reaction requires 3 mol of alcohol and 1 mol of triacylglycerol to yield 3 mol of fatty acid ester and 1 mol of glycerol. However, because of the reversibility of the reaction, an excess of alcohol is usually needed to force the equilibrium to the product side.[3] In practice, 6 mol of alcohol and 1 mol of triacylglycerol are used to raise the product yield. Hence, the reaction rate depends on ethanol solubility in the oil phase.

Triacylglycerol solubility in aqueous ethanol solutions is widely reported in literature,[8−12] and it was observed in these works that the critical solution temperature increases linearly with the enhancement of water content in the alcohol solvent. Simulations for developing new processes for such reactional systems require a thermodynamic model that can adequately describe these multiphase systems. Therefore, knowledge on the mutual solubility between vegetable oils and ethanol is of utmost importance for better understanding of the process and improvement of reaction rates, as well as the subsequent purification steps for biodiesel production. It should also be emphasized that phase equilibrium data for systems composed of vegetable oils + aqueous ethanol or anhydrous ethanol is necessary for the design of liquid−liquid extraction processes in the refining of edible oils. Thus, the aim of the present work was to investigate the phase equilibrium of vegetable oils + ethanol + water at temperatures ranging from (298.15 to 333.15) K. The vegetable oils chosen for this study were refined canola oil, refined corn oil, semiprocessed *Jatropha curcas* oil, and semiprocessed macauba (*Acrocomia aculeata*) pulp oil. The experimental data were correlated with the non-random two liquid (NRTL) model, with an estimation of binary interaction parameters.

Experimental Section

Materials. Refined corn oil and refined canola oil were purchased from Cargill (Mairinque/SP, Brazil). Crude macauba (*A. aculeata*) pulp oil and crude *J. curcas* oil were kindly supplied by Paradigma Óleos Vegetais Ltda (Jaboticatubas/MG, Brazil) and Bionasa Combustível Natural S. A. (Porangatu/GO, Brazil), respectively. The crude oils were submitted to a prior deacidification treatment in the laboratory, and both were qualified as semiprocessed oils.

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10.1021/je900409p CCC: $40.75

Fatty acid composition of vegetable oils was determined by gas chromatography for the quantification of fatty acid methyl esters, according to the official method (1-62) of the American Oil Chemists' Society (AOCS).[13] Prior to chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters, according to the method of Hartman and Lago.[14] The samples were submitted to a CGC Agilent 6850 Series GC capillary gas chromatograph system under the following experimental conditions: DB-23 Agilent capillary column (50 % cyanopropyl-methylpolysiloxane), 0.25 μm, 60 m × 0.25 mm i.d.; helium as the carrier gas at a rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$; linear velocity of 24 $\text{cm}\cdot\text{s}^{-1}$; injection temperature of 523.2 K; column temperature of 383.2 K for 5 min, (383.2 to 488.2) K at a rate of 5 $\text{K}\cdot\text{min}^{-1}$, followed by 488.2 K for 24 min; detection temperature of 553.2 K; and injection volume of 1.0 μL. The fatty acid methyl esters were identified by comparison with the retention times of the Nu Check Prep (Elysian/MN, U.S.A.) standards, and the quantification was performed by internal normalization.

The free fatty acid contents of the vegetable oils were determined by titration according to the official method 2201 of IUPAC[15] using an automatic titrator (Metrohm, model Titrando 808, Herisan, Switzerland). Refined canola oil, refined corn oil, semiprocessed *J. curcas* oil, and semiprocessed macauba (*A. aculeata*) pulp oil presented free fatty acid contents of 0.016 %, 0.029 %, 0.017 %, and 0.038 %, respectively, expressed as mass fractions of oleic acid.

The solvents used were the following: anhydrous ethanol from Merck (Germany), with purity greater than 99.9 %; an alcoholic solution (w_{6s}) with a mass fraction of 6.00 ± 0.02 (mass of water in anhydrous ethanol), prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol; and hexane, also from Merck, with purity greater than 96 %.

In the present work, the following notations were given to the components utilized in the experiments: refined canola oil (1), refined corn oil (2), semiprocessed *J. curcas* oil (3), semiprocessed macauba (*A. aculeata*) pulp oil (4), anhydrous ethanol (5), and water (6).

Apparatus and Procedures. Determination of Liquid–Liquid Equilibrium Data. Glass equilibrium cells, such those described by Silva et al.,[16] were used for the experiments. Vegetable oils were mixed with ethanolic solvents, in oil/solvent mass ratios of 1:1. Each component was weighted on an analytical balance (Precisa, model XT220A, Sweden), accurate to ± 0.0001 g. The mixtures were prepared inside the cell and then vigorously agitated for 15 min with a magnetic stirrer (Ika Werke, model RH-KT/C, Staufen, Germany), and the temperature was controlled with a thermostatic bath (Cole Parmer, model 12101-55, Chicago, U.S.A.), accurate to ± 0.01 K. After a clear and well-defined interface was formed (approximately 12 h later), samples of both phases were collected separately using syringes. To determine the quantity of each component in the coexisting phases, the samples were diluted before measuring in a 1:1 (hexane:sample) mass ratio, to avoid phase separation in the syringe. Water content was determined by Karl Fisher titration, according to the AOCS method Ca 23-55.[17] The solvent was evaporated in an oven (Marconi, model MA 035/3, Piracicaba/SP, Brazil) at atmospheric pressure and 383.15 K for 3 h, sufficient conditions for the remaining mixture to achieve a constant mass. Having determined the amount of solvent, the quantity of oil was then found by calculating the difference.

In this work, all measurements were performed with at least three repetitions. Type A standard uncertainties[18] of the equilibrium data ranged from (0.02 to 0.17) % for the vegetable oils, (0.01 to 0.09) % for ethanol, and (0.03 to 0.17) % for water, where the lowest percentages were attained for the lowest compositions. Results indicated good precision and repeatability of the equilibrium data.

To test the quality of the obtained results, the procedure developed by Marcilla et al.[19] and previously applied for fatty systems by Rodrigues et al.[20] was utilized. This procedure consisted of calculating the masses for both liquid phases and comparing their sum with the actual value for the total mass used in the experiment, thus obtaining a relative error for each experimental result for an overall mixture. According to this approach, K independent component balances can be written, where K is the total number of pseudocomponents in the data group and i represents each component of the system, expressed as,

$$m^{\text{OC}} w_i^{\text{OC}} = m^{\text{AP}} w_i^{\text{AP}} + m^{\text{OP}} w_i^{\text{OP}} \qquad (1)$$

where m^{OC} is the mass of the overall composition, m^{AP} and m^{OP} are the masses of the alcoholic and oil phases, respectively, w_i^{OC} is the mass fraction of component i in the overall composition, and w_i^{AP} and w_i^{OP} are the mass fractions of component i in the alcoholic and oil phases, respectively. With these i equations, it was possible to calculate the values for m^{AP} and m^{OP} from the experimental values of w_i^{AP} and w_i^{OP} using least-squares fitting. If $\mathbf{M}$ is the matrix formed by the values of w_i^{OC}, $\mathbf{B}$ is the transformation matrix (formed by the values for w_i^{AP} and w_i^{OP}), and $\mathbf{P}$ is the matrix formed by the mass of each phase (m^{AP} and m^{OP}), the previous system can be written as,

$$\mathbf{M} = \mathbf{B} \cdot \mathbf{P} \qquad (2)$$

Mathematic calculations led to the expression:

$$\mathbf{P} = (\mathbf{B}^{\text{T}}\mathbf{B})^{-1}\mathbf{B}^{\text{T}}\mathbf{M} \qquad (3)$$

where $\mathbf{B}^{\text{T}}$ is the transpose matrix of $\mathbf{B}$ and $(\mathbf{B}^{\text{T}}\mathbf{B})^{-1}$ is the inverse matrix of $(\mathbf{B}^{\text{T}}\mathbf{B})$. Therefore, the values for m^{AP} and m^{OP} (matrix $\mathbf{P}$), which minimize the errors of the previous system, are calculated. When the absolute value of the difference between the sum of $(m^{\text{OP}} + m^{\text{AP}})$ and m^{OC} was higher than 0.5 %, the corresponding data was rejected, and the experimetal point was repeated.

Thermodynamic Modeling. The experimental data were used to adjust the NRTL binary interaction parameters. Mole fractions have traditionally been used in this model, but mass fractions provide a more convenient composition unit due to the large difference in the molar masses of the components such as vegetable oils, ethanol and water. Recently, several studies have been reported using this approach with the NRTL model.[2,20–26] Thus, when using mass fractions, the NRTL model for multicomponent mixtures is expressed as:

$$\ln \gamma_i^w = \left(\frac{\displaystyle\sum_{j=1}^{K} \frac{\tau_{ji} G_{ji} w_j}{\bar{M}_j}}{\displaystyle\sum_{j=1}^{K} \frac{G_{ji} w_j}{\bar{M}_j}} + \sum_{j=1}^{K} \left[\frac{w_j G_{ij}}{\bar{M}_j \displaystyle\sum_{k=1}^{K} \frac{G_{kj} w_k}{\bar{M}_k}} \times \left(\tau_{ij} - \frac{\displaystyle\sum_{k=1}^{K} \frac{\tau_{kj} G_{kj} w_k}{\bar{M}_k}}{\displaystyle\sum_{k=1}^{K} \frac{G_{kj} w_k}{\bar{M}_k}} \right) \right] \right) \Big/ \bar{M}_i \sum_{j=1}^{K} \left(\frac{w_j}{\bar{M}_j} \right) \qquad (4)$$

where

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \tag{5}$$

$$\frac{\Delta g_{ij}}{R} = A_{0,ij} + A_{1,ij}T \tag{6}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{7}$$

$$\alpha_{ij} = \alpha_{ji} \tag{8}$$

where γ_i^w is the corresponding activity coefficient of component i expressed on the mass fraction; $\bar{M}$ and w are the average molar mass and mass fraction, respectively, of the pseudocomponents; Δg_{ij} and τ_{ij} represent the molecular energy interactions between the components i and j; α_{ij} is the nonrandomness parameter of the mixture; T is the absolute temperature; and $A_{0,ij}$, $A_{0,ji}$, $A_{1,ij}$, and $A_{1,ji}$ are characteristic energy parameters of the i and j interactions. Thus, in the present study there are five adjustable parameters for each pair of components. These parameters can be estimated with experimental data by using the procedure below. When the data are at the same temperature or the number of points is small and there is not enough information, the extended NRTL model reduces to the original NRTL model, and hence the $A_{1,ij}$ and $A_{1,ji}$ terms from eq 6 vanish.

In this work, adjustments were made by treating the systems composed by vegetable oil + anhydrous ethanol as pseudobinary and the systems composed by vegetable oil + ethanol + water as pseudoternary. Each system was considered as composed of a single triacylglycerol having the corresponding average molar mass of vegetable oil. Estimation of interaction parameters was

Table 1. Fatty Acid Compositions of the Vegetable Oils

			M^a	canola oil		corn oil		*J. curcas* oil		macauba oil	
fatty acid	symbol	C*x*:*y*[b]	g·mol^{-1}	100 *x*	100 *w*	100 *x*	100 *w*	100 *x*	100 *w*	100 *x*	100 *w*
dodecanoic	L	C12:0	200.32							0.04	0.03
tetradecanoic	M	C14:0	228.38	0.09	0.07			0.07	0.06	0.07	0.06
hexadecanoic	P	C16:0	256.43	5.17	4.72	13.8	12.71	14.45	13.34	22.22	20.69
cis-hexadec-9-enoic	Po	C16:1	254.42	0.28	0.25	0.19	0.17	0.97	0.89	4.33	4.00
heptadecanoic	Ma	C17:0	270.45					0.13	0.13	0.09	0.09
cis-heptadec-9-enoic	Mg	C17:1	268.43					0.05	0.05	0.12	0.12
octadecanoic	S	C18:0	284.49	2.52	2.55	2.20	2.25	6.15	6.30	2.65	2.74
cis-octadec-9-enoic	O	C18:1	282.47	62.25	62.56	34.45	34.96	41.00	41.68	54.85	56.27
cis,*cis*-octadeca-9,12-dienoic	Li	C18:2	280.45	20.18	20.13	47.25	47.61	36.66	37.00	14.31	14.58
trans,*trans*-octadeca-9,12-dienoic		C18:2T[c]	278.44			0.14	0.14				
all-*cis*-octadeca-9,12,15-trienoic	Le	C18:3	278.44	7.15	7.08	0.83	0.83	0.21	0.21	1.03	1.04
all-*trans*-octadeca-9,12,15-trienoic		C18:3T[c]	278.44	0.41	0.41						
icosanoic	A	C20:0	312.54	0.56	0.62	0.48	0.54	0.18	0.20	0.16	0.18
cis-icos-9-enoic	Ga	C20:1	310.52	0.94	1.04	0.34	0.38	0.06	0.07	0.07	0.08
docosanoic	Be	C22:0	340.59	0.23	0.28	0.16	0.19	0.02	0.03	0.05	0.06
tetracosanoic	Lg	C24:0	368.65	0.13	0.17	0.17	0.22	0.03	0.04	0.04	0.06
cis-tetracos-15-enoic	Ne	C24:1	366.63	0.09	0.12						
IV[d]				109.27		114.45		100.46		78.96	

[a] M = molar mass. [b] Cx:y, where x = number of carbons and y = number of double bonds. [c] Trans isomers. [d] Iodine value (IV) calculated from the fatty acid composition according to the method Cd 1c-85.[28]

Table 2. Probable Triacylglycerol Compositions of the Vegetable Oils

		M^a	canola oil		corn oil		*J. curcas* oil		macauba oil	
main TAG[b]	group	g·mol^{-1}	100 *x*	100 *w*	100 *x*	100 *w*	100 *x*	100 *w*	100 *x*	100 *w*
PPP	48:0[c]	807.33							0.98	0.91
PPoP	48:1	805.32							0.62	0.57
PPS	50:0	835.39								
POP	50:1	833.37	0.53	0.50	1.92	1.83	2.46	2.35	7.85	7.56
PPoO	50:2	831.35							5.06	4.86
PLiP	50:2	831.35			2.69	2.56	2.51	2.39		
PPoLi	50:3	829.34							1.24	1.19
POS	52:1	861.42	0.51	0.50	0.63	0.62	2.21	2.19	2.00	1.99
POO	52:2	859.41	6.42	6.27	6.04	5.95	9.39	9.25	21.20	21.09
POLi	52:3	857.39	4.45	4.33	14.38	14.13	13.60	13.36	14.62	14.49
PoOLi	52:4	855.38							4.17	4.13
PLeO	52:4	855.38	2.39	2.32						
PLiLi	52:4	855.38			10.26	10.06	6.71	6.58		
PLeLi	52:5	853.36	0.61	0.59	0.48	0.47				
PoLiLi	52:5	853.36							0.61	0.60
SOS	54:1	889.48					0.57	0.59		
SOO	54:2	887.46	3.30	3.33	1.18	1.20	3.87	3.93	2.75	2.82
OOO	54:3	885.45	27.02	27.17	6.55	6.65	13.32	13.52	19.25	19.73
OOLi	54:4	883.43	25.33	25.43	18.63	18.88	22.34	22.60	14.19	14.50
OLiLi	54:5	881.41			23.77	24.03	17.63	17.81	4.63	4.72
OOLe	54:5	881.41	17.19	17.21						
OLiLe	54:6	879.40	6.79	6.78					0.83	0.84
LiLiLi	54:6	879.40			11.57	11.66	5.39	5.43		
LiLiLe	54:7	877.38			0.57	0.57				
OLeLe	54:7	877.38	2.06	2.05						
OOA	56:2	915.51	0.81	0.84						
OOGa	56:3	913.50	1.61	1.67						
OLiA	56:3	913.50			0.64	0.67				
OLiGa	56:4	911.48	0.98	1.01	0.69	0.72				

[a] M = molar mass. [b] Groups with a total triacylglycerol (TAG) composition lower than 0.5 % were ignored. [c] x:y, where x = number of carbons (except carbons of glycerol) and y = number of double bonds.

Table 3. Liquid−Liquid Equilibrium Data for the Pseudobinary Systems Containing Vegetable Oil (*x*) + Anhydrous Ethanol (5) at Different Temperatures

T		overall composition		ethanol-rich phase		oil-rich phase	
K	oil $(x)^a$	100 w_x	100 w_5	100 w_x	100 w_5	100 w_x	100 w_5
298.15	canola (1)	49.91	50.09	5.59	94.41	87.48	12.52
303.15		49.91	50.09	5.72	94.28	85.18	14.82
308.15		49.91	50.09	6.85	93.15	83.05	16.95
313.15		49.91	50.09	7.85	92.15	81.20	18.80
318.15		49.91	50.09	8.95	91.05	78.47	21.53
323.15		49.91	50.09	10.00	90.00	74.56	25.44
328.15		49.91	50.09	12.53	87.47	71.36	28.64
333.15		49.91	50.09	15.94	84.06	67.66	32.34
298.15	corn (2)	49.83	50.17	5.98	94.02	85.28	14.72
303.15		49.83	50.17	7.86	92.14	82.32	17.68
308.15		49.83	50.17	9.06	90.94	80.29	19.71
313.15		49.83	50.17	11.12	88.88	78.13	21.87
318.15		49.83	50.17	12.49	87.51	75.04	24.96
323.15		49.83	50.17	14.93	85.07	71.95	28.05
328.15		49.83	50.17	16.37	83.63	66.97	33.03
333.15		49.83	50.17	17.99	82.01	63.31	36.69
298.15	*J. curcas* (3)	50.00	50.00	6.88	93.12	84.92	15.08
303.15		50.00	50.00	7.76	92.24	83.72	16.28
308.15		50.00	50.00	8.56	91.44	81.69	18.31
313.15		50.00	50.00	9.82	90.18	79.20	20.80
318.15		50.00	50.00	10.85	89.15	77.49	22.51
323.15		50.00	50.00	11.69	88.31	75.75	24.25
328.15		50.00	50.00	13.18	86.82	72.84	27.16
333.15		50.00	50.00	14.13	85.87	69.13	30.87
298.15	macauba (4)	50.00	50.00	6.10	93.90	85.60	14.40
303.15		50.00	50.00	6.99	93.01	83.89	16.11
308.15		50.00	50.00	7.95	92.05	82.19	17.81
313.15		50.00	50.00	9.18	90.82	80.11	19.89
318.15		50.00	50.00	9.83	90.17	78.62	21.38
323.15		50.00	50.00	11.56	88.44	75.62	24.38
328.15		50.00	50.00	13.20	86.80	71.82	28.18
333.15		50.00	50.00	16.97	83.03	68.00	32.00

[a] x = reference number of the oil used.

based on the minimization of the objective function of composition, eq 9, according to the procedure developed by Stragevitch and d'Ávila:[27]

$$\mathrm{OF}(w) = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{K-1}\left[\left(\frac{w_{i,n,m}^{\mathrm{AP,exptl}} - w_{i,n,m}^{\mathrm{AP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{AP}}}}\right)^2 + \left(\frac{w_{i,n,m}^{\mathrm{OP,exptl}} - w_{i,n,m}^{\mathrm{OP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{OP}}}}\right)^2\right] \tag{9}$$

where D is the total number of data groups, N is the total number of tie lines in the data group, K is the total number of pseudocomponents in the data group, w is the mass fraction, the subscripts i, n, and m are component, tie line, and group numbers, respectively, the superscripts AP and OP stand for the alcoholic and oil phases, respectively, and exptl and calcd refer to experimental and calculated compositions. The symbols $\sigma_{w_{i,n,m}^{\mathrm{AP}}}$ and $\sigma_{w_{i,n,m}^{\mathrm{OP}}}$ represent the standard deviations observed in the compositions of the two liquid phases. The average deviations between experimental and calculated compositions were quoted according to:

$$\Delta w = \sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{K}\left[(w_{i,n}^{\mathrm{AP,exptl}} - w_{i,n}^{\mathrm{AP,calcd}})^2 + (w_{i,n}^{\mathrm{OP,exptl}} - w_{i,n}^{\mathrm{OP,calcd}})^2\right]}{2NK}} \tag{10}$$

Results and Discussion

Fatty acid compositions of the vegetable oils are presented in Table 1. From the fatty acid composition, it was possible to determine the probable triacylglycerol compositions of the

Table 4. Liquid−Liquid Equilibrium Data for the Pseudoternary Systems Containing Vegetable Oil (*x*) + Anhydrous Ethanol (5) + Water (6) at Different Temperatures

T		overall composition			ethanol-rich phase			oil-rich phase		
K	oil $(x)^a$	100 w_x	100 w_5	100 w_6	100 w_x	100 w_5	100 w_6	100 w_x	100 w_5	100 w_6
298.15	canola (1)	49.95	47.07	2.98	1.56	91.50	6.94	92.52	7.23	0.25
303.15		49.97	47.06	2.98	1.60	91.91	6.49	91.48	8.27	0.25
308.15		49.96	47.06	2.98	1.90	91.62	6.48	90.30	9.41	0.30
313.15		49.97	47.05	2.98	2.09	91.17	6.74	89.36	10.30	0.33
318.15		49.97	47.06	2.98	2.55	90.72	6.72	88.41	11.18	0.41
323.15		49.97	47.06	2.97	2.78	90.97	6.25	87.17	12.39	0.43
328.15		49.96	47.05	2.99	3.35	90.27	6.37	86.31	13.22	0.47
333.15		49.97	47.08	2.95	3.65	89.82	6.52	85.15	14.28	0.57
298.15	corn (2)	49.96	47.08	2.96	2.10	91.52	6.38	91.42	8.30	0.28
303.15		49.96	47.06	2.98	2.49	91.48	6.03	90.08	9.61	0.31
308.15		49.97	47.06	2.97	2.76	91.13	6.11	88.92	10.71	0.37
313.15		49.88	47.16	2.96	3.20	90.12	6.68	87.80	11.82	0.39
318.15		49.86	47.18	2.97	3.46	90.22	6.31	87.21	12.56	0.23
323.15		49.98	47.09	2.94	4.01	89.75	6.24	85.43	14.02	0.54
328.15		49.96	47.07	2.97	4.43	89.42	6.15	84.42	14.98	0.60
333.15		49.97	47.07	2.96	4.74	88.87	6.39	83.45	15.90	0.66
298.15	*J. curcas* (3)	49.96	47.06	2.97	2.01	91.12	6.16	91.66	8.06	0.27
303.15		49.97	47.07	2.96	2.08	91.87	6.04	90.67	9.04	0.29
308.15		49.97	47.07	2.96	2.47	91.41	6.12	89.16	10.51	0.33
313.15		49.97	47.08	2.96	2.77	90.41	6.81	88.66	10.86	0.49
318.15		49.97	47.06	2.97	3.23	89.94	6.83	88.15	11.40	0.44
323.15		49.97	47.09	2.94	3.37	90.40	6.23	86.64	12.88	0.48
328.15		49.98	47.07	2.95	3.88	90.03	6.10	85.38	14.09	0.53
333.15		49.97	47.09	2.94	4.46	89.44	6.11	83.89	15.49	0.62
298.15	macauba (4)	49.95	47.09	2.96	1.47	92.36	6.16	91.87	7.90	0.24
303.15		49.96	47.06	2.98	1.88	91.78	6.34	90.93	8.80	0.26
308.15		49.97	47.09	2.94	2.03	91.52	6.45	90.14	9.57	0.30
313.15		49.96	47.10	2.94	2.30	90.54	7.15	89.30	10.28	0.42
318.15		49.96	47.05	2.98	2.69	90.56	6.75	88.14	11.43	0.43
323.15		49.97	47.07	2.97	2.97	90.61	6.42	87.06	12.50	0.45
328.15		49.96	47.06	2.97	3.38	90.22	6.40	86.29	13.22	0.49
333.15		49.96	47.07	2.96	4.03	89.89	6.09	84.84	14.52	0.65

[a] x = reference number of the oil used.

Table 5. Temperature-Dependent NRTL Parameters

pair *ij*[a]	$A_{0,ij}$/K	$A_{0,ji}$/K	$A_{1,ij}$	$A_{1,ji}$	α_{ij}
15	3346.5	−1168.5	−12.577	10.402	0.3008
16	6357.4	−1208.2	−10.758	11.228	0.3105
25	2995.7	−1639.7	−12.277	12.914	0.2424
26	4279.2	−1560.4	−15.154	13.812	0.2003
35	2666.1	−1735.2	−11.350	13.553	0.2260
36	4749.2	−1843.6	−15.320	12.105	0.3309
45	2776.7	−1049.4	−11.288	10.744	0.2531
46	9652.1	−1499.2	−26.687	10.921	0.4529
56	−53.737	−1153.4	0.205	1.006	0.2001

[a] Refined canola oil (1), refined corn oil (2), semiprocessed *J. curcas* oil (3), semiprocessed macauba (*A. aculeata*) pulp oil (4), anhydrous ethanol (5), and water (6).

Table 6. Mean Deviations in Phase Compositions for Systems Composed of Vegetable Oils, Ethanol, and Water, from (298.15 to 333.15) K

system	100 Δ*w*
refined canola oil (1) + anhydrous ethanol (5)	0.37
refined canola oil (1) + anhydrous ethanol (5) + water (6) (6.00 % in mass of water in anhydrous ethanol)	0.39
refined corn oil (2) + anhydrous ethanol (5)	0.64
refined corn oil (2) + anhydrous ethanol (5) + water (6) (6.00 % in mass of water in anhydrous ethanol)	0.36
semiprocessed *J. curcas* oil (3) + anhydrous ethanol (5)	0.33
semiprocessed *J. curcas* oil (3) + anhydrous ethanol (5) + water (6) (6.00 % in mass of water in anhydrous ethanol)	0.27
semiprocessed macauba oil (4) + anhydrous ethanol (5)	0.42
semiprocessed macauba oil (4) + anhydrous ethanol (5) + water (6) (6.00 % in mass of water in anhydrous ethanol)	0.31
average overall deviation	0.39

vegetable oils (Table 2) by using the algorithm suggested by Antoniosi Filho et al.[29] In Table 2, the main triacylglycerol represents the component with the largest mass fraction in the isomer set with *x* carbon and *y* double bonds. The results shown in Tables 1 and 2 allow for calculation of the average molar masses of the canola oil, corn oil, *J. curcas* oil, and macauba oil. The values obtained were (880.4, 872.3, 872.6, and 864.7) $\text{g}\cdot\text{mol}^{-1}$, respectively.

The vegetable oils were treated in this work as pseudocompounds with the previously presented average molar masses. Tables 3 and 4 present the overall experimental composition and the phase compositions in the alcoholic and oil phases for the pseudobinary and pseudoternary systems, respectively. All compositions are presented as mass fractions.

The adjusted parameters of the NRTL model as functions of absolute temperature for each system are presented in Table 5. Deviations between experimental and calculated compositions in both phases were quoted according to eq 10 and are shown in Table 6. According to the results, the NRTL model accurately described the phase compositions of the investigated systems, with deviations between calculated and experimental results no higher than 0.64 %. Figures 1, 2, 3, and 4 show the experimental and calculated compositions using the NRTL model for pseudobinary and pseudoternary systems. The liquid−liquid equilibrium diagrams were plotted in rectangular coordinates where solvent was considered as a single component.

Comparing the systems with temperatures ranging from (298.15 to 333.15) K in Figures 1 to 4, it can be observed that in all oils the solubility of anhydrous ethanol with vegetable oil and vegetable oil with anhydrous ethanol increases with increasing temperature; that is, the miscibility of the two compounds is enhanced as temperature rises. As indicated by these results, despite the dissimilarity in polarity and size of the components, an increase in the mutual solubility of vegetable oil and aqueous ethanol was also observed with temperature escalation. According to Swern,[30] triacylglycerol has a low mutual solubility with water which decreases with the increase in chain length and decrease in temperature. This behavior is relevant for the refining of edible oils since the addition of water in the solvent increases the solvent selectivity and consequently reduces the loss of neutral oil in solvent extraction.[25]

For the pseudobinary systems, flash calculations[27,31] using the parameters presented in the Table 5 were carried out at higher temperatures to determine the critical solution temperature. The results indicate that, for these systems, the mutual solubility of vegetables oils, and anhydrous ethanol increases steadily until the critical temperature is reached. As can be seen in Figures 1 to 4, complete miscibility was attained at (347.0, 345.4, 359.4, and 350.0) K, for systems composed of canola oil + anhydrous ethanol, corn oil + anhydrous ethanol, *J. curcas* oil + anhydrous ethanol, and macauba oil + anhydrous ethanol, respectively.

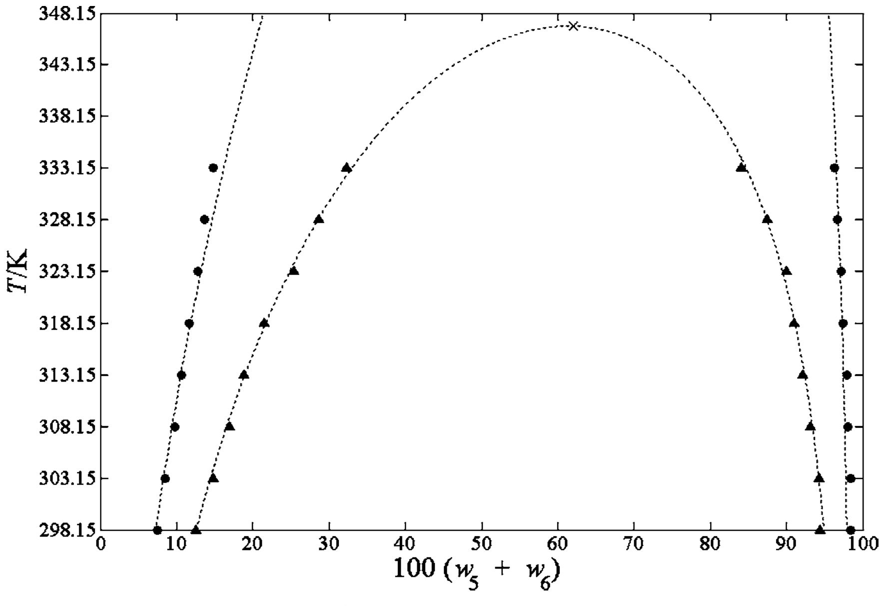

Figure 1. Liquid−liquid equilibrium for systems composed of refined canola oil (1) + ethanol (5) + water (6): ▲, experimental phase compositions ($100\,w_{6s} = 0.00$); ●, experimental phase compositions ($100\,w_{6s} = 6.00 \pm 0.02$); ----, NRTL; ×, calculated critical solution temperature.

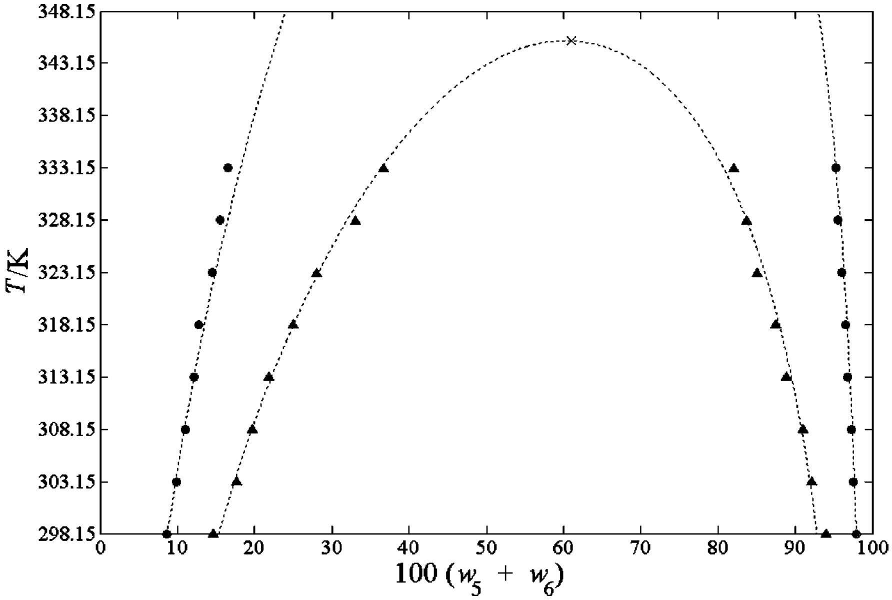

Figure 2. Liquid−liquid equilibrium for systems composed of refined corn oil (2) + ethanol (5) + water (6): ▲, experimental phase compositions (100 w_{6s} = 0.00); ●, experimental phase compositions (100 w_{6s} = 6.00 ± 0.02); ----, NRTL; ×, calculated critical solution temperature.

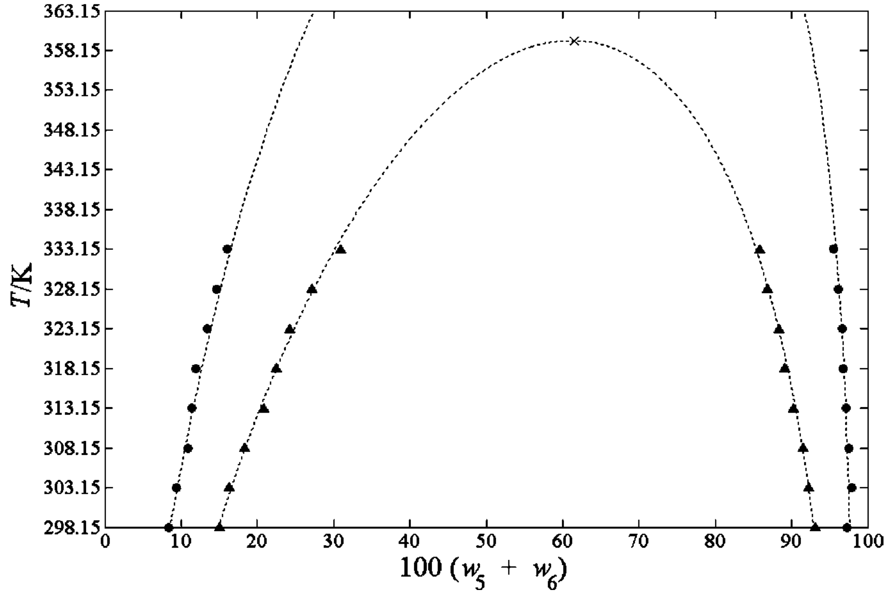

Figure 3. Liquid−liquid equilibrium for systems composed of semiprocessed *J. curcas* oil (3) + ethanol (5) + water (6): ▲, experimental phase compositions (100 w_{6s} = 0.00); ●, experimental phase compositions (100 w_{6s} = 6.00 ± 0.02); ----, NRTL; ×, calculated critical solution temperature.

Considering that the goal of this work was to apply the NRTL model and compare it to the experimental data shown in Tables 3 and 4, for the pseudoternary system, the flash calculations were also used to quote the critical solution temperature. However, the results show overestimated values at least 50 K greater than the temperature range studied. Therefore, the results of mutual solubility for each pseudoternary system were expanded until nearing the critical solution temperature reached by the pseudobinary systems, as can be verified in Figures 1 to 4.

In the transesterification process a molar ratio of 6:1 (ethanol to vegetable oil) is frequently used. Because of higher average molar mass differences between the ethanol and the vegetable oil, this molar ratio represents an ethanol molar fraction composition equal to 85.71 % and is close to that of the oil phase. Thus, the reaction rate greatly depends on the solubility of ethanol in the vegetable oil phase. In Figure 5, it is possible to verify the effect of temperature (T) on the ethanol molar fraction in the oil phase (x_5^{OP}). As it can be observed for a molar ratio of 6:1 (ethanol to vegetable oil), the temperature for the complete solubility of ethanol in the vegetable oil was attained at (321.7, 316.6, 321.6, and 322.1) K for canola oil, corn oil, *J. curcas* oil, and macauba oil, respectively. These temperatures were checked by liquid−liquid flash calculations. Moreover, it was verified that the solubility of ethanol in the oil phase increased with the enhancement of the temperature, and the solubility of corn oil in anhydrous ethanol was higher than other oils at equal conditions. This difference may be due to different fatty acid chains found in the analyzed vegetable oils. In general, solubility of fatty derivatives in organic solvents increases with the reduction in carbon chain length and enhancement in the number of double bonds.[30] In Table 1, it was verified that the fatty acids contained in corn oil, *J.*

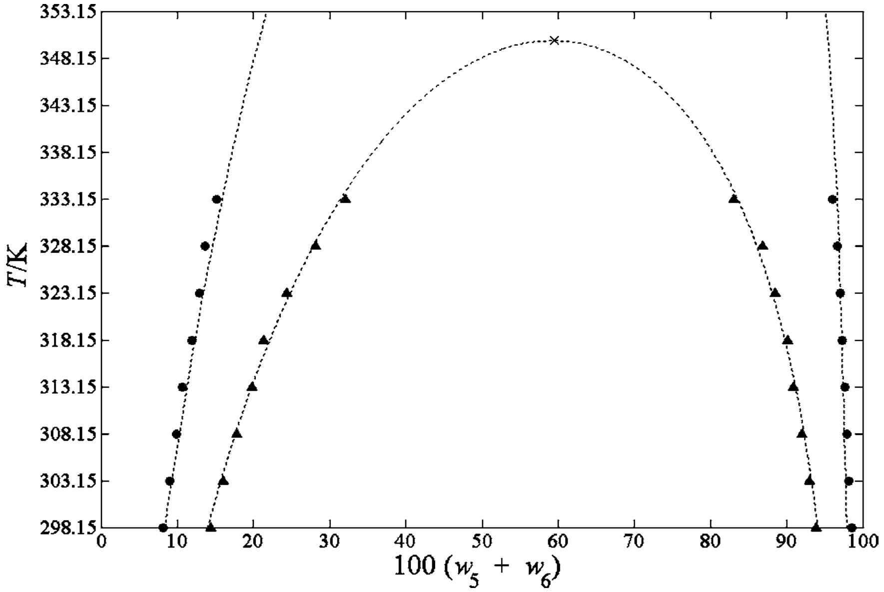

Figure 4. Liquid−liquid equilibrium for systems composed of semiprocessed macauba oil (4) + ethanol (5) + water (6): ▲, experimental phase compositions (100 w_{6s} = 0.00); ●, experimental phase compositions (100 w_{6s} = 6.00 ± 0.02); ----, NRTL; ×, calculated critical solution temperature.

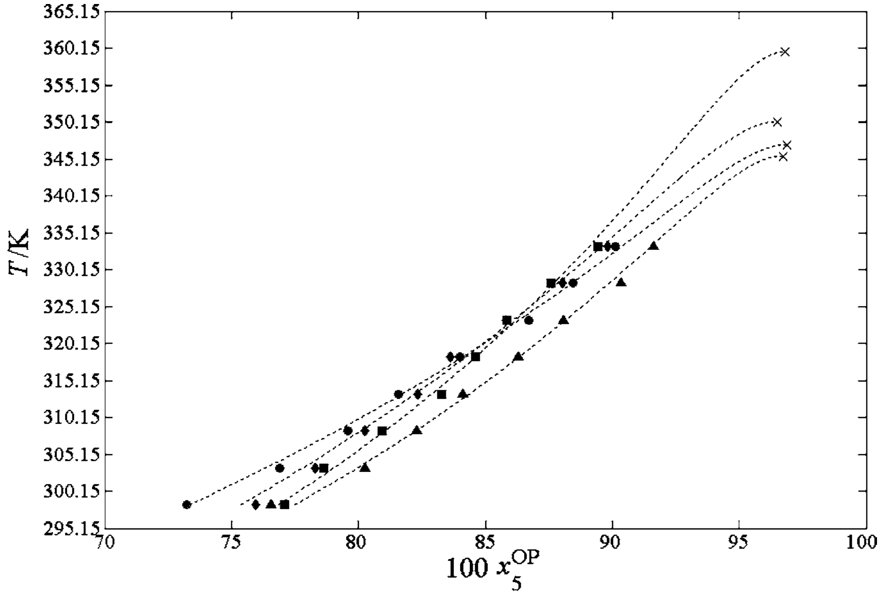

Figure 5. Effect of temperature (T) on the ethanol molar fraction in the oil phase (x_5^{OP}): ●, refined canola oil (100 w_{6s} = 0.00); ▲, refined corn oil (100 w_{6s} = 0.00); ■, semiprocessed *J. curcas* oil (100 w_{6s} = 0.00); ♦, semiprocessed macauba oil (100 w_{6s} = 0.00); ----, NRTL; ×, calculated critical solution temperatures.

curcas oil, and macauba oil have shorter chains; however, corn oil shows higher iodine value (IV), that is, the oil contains a greater number of double bonds, which corresponds to higher polarity, increasing the mutual solubility of the system.

Conclusions

Because of the limited mutual solubility of oil and ethanol in upstream steps during biodiesel production, knowledge on phase behavior for systems containing solvents is essential to optimize the reaction process, as well as the thermodynamic modeling to simulate the behavior. Mutual solubility of the reaction system depended on the oil type and was sensitive to temperature changes.

The estimated parameters of the NRTL model are representative and accurately described the phase behavior in comparison with the experimental data. Moreover, with the help of these parameters it is possible to model and simulate, with good accuracy, reactional systems of interest in the production of ethanol-based biodiesel and liquid−liquid extractors for vegetable oil deacidification.

Acknowledgment

The authors thank Paradigma Óleos Vegetais Ltd. (Jaboticatubas/MG, Brazil) and Ms. Camila Martins Garcia (IQM/UNICAMP) for kindly supplying the crude macauba (*A. aculeata*) and *J. curcas* oils, respectively.

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Received for review May 8, 2009. Accepted August 4, 2009. The authors wish to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, Processes 08/56258-8, 05/53095-2, and 04/09591-2), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, scholarship and process 306250/2007-1), and CAPES/PNPD (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior/Programa Nacional de Pós-Doutorado) for their financial support.

JE900409P