Mutual Solubility of Pseudobinary Systems Containing Vegetable Oils and Anhydrous Ethanol from (298.15 to 333.15) K

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The two-phase base-catalyzed transesterification of vegetable oils with short chain alcohols is common in the production of biodiesel. The reactants (vegetable oil and ethanol) are partially soluble, and this phase behavior can significantly impact the reaction process. To better understand this phase behavior, the liquid−liquid equilibrium data for pseudobinary systems containing vegetable oils (soybean oil, sunflower oil, rice bran oil, cottonseed oil, palm olein, and palm oil) + anhydrous ethanol in the range from (298.15 to 333.15) K were determined experimentally. The mutual solubility increased as the temperature rose in all the systems examined. The equilibrium data were correlated with the NRTL model using temperature-dependent parameters which represented satisfactorily the experimental results.

Introduction

Biodiesel, as an alternative fuel, has many merits. It is biodegradable, is produced from renewable energy sources (vegetable oils and animal fats), is nontoxic, and may decrease the emission levels of some pollutant gases. Depending on the climate and soil conditions, different countries are looking for different types of vegetable oils for the production of biodiesel as a promising substitute for petroleum-based fuels. For example, soybean oil is of primary interest as a source of biodiesel in Brazil and in the United States, while many European countries are using rapeseed oil and Asian countries prefer to use palm oil. In fact, any vegetable oil, such as cottonseed, sunflower, or rice bran oils could be used to produce biodiesel.[1,2]

The interest in using ethanol as a reactant in transesterification of oils has significantly increased in recent years since it is derived from agricultural products, is renewable, and is biologically less objectionable to the environment. Although ethanolysis has technological limitations when compared to methanolysis, it is the better route chosen in the Brazilian case since Brazil is one of the biggest ethanol producers.[2]

The most widely used method to produce biodiesel is that of transesterification, where the chemical reaction between the vegetable oils and the alcohol occurs in the presence of an alkaline catalyst to generate a fatty acid ester and glycerol, the latter being considered as a byproduct.[3] Biodiesel reaction can be catalyzed by sodium or potassium hydroxides, acids, enzymes, ion exchange resins, and oxides. In most cases, the reaction is conducted at a temperature within the range from (303.15 to 343.15) K.[4–8] As normally practiced, transesterification shows a complex phase behavior, starting with two phases due to the fact that the reactants (alcohol and vegetable oil) are partially miscible. Thus, there is an upper alcohol phase in which the catalyst is dissolved and a lower vegetable oil phase, requiring vigorous stirring to promote mass transfer between the oil and the ethanol phases.[9]

Several studies have identified the important variables that influence the transesterification reaction, including: the reaction time and temperature, the molar alcohol to oil ratio, the type and amount of catalyst, and the purity of the reactants.[10,11] However, the mutual solubility of the reactants at these temperature has not been extensively studied. The solubility of ethanol in the oil can greatly influence the reaction rate during the production of biodiesel. For this reason, the liquid−liquid equilibrium for the pseudobinary systems containing alcohol and different vegetable oils must be known to design and develop the reactive process. Some research groups have recently published experimental results on the phase behavior of reactants and products present in the biodiesel reaction.[12–15]

In this work, the values for the mutual solubility of different vegetable oils (soybean, sunflower, rice bran, cottonseed, and palm) and palm olein (liquid fraction from palm oil) in anhydrous ethanol were measured. The following pseudobinary systems were investigated at temperatures between (298.15 and 333.15) (± 0.1) K: refined soybean oil + anhydrous ethanol, refined sunflower oil + anhydrous ethanol, refined rice bran oil + anhydrous ethanol, pretreated cottonseed oil (neutral) + anhydrous ethanol, and refined palm olein + anhydrous ethanol. The refined palm oil + anhydrous ethanol system was investigated in the temperature range from (318.15 to 333.15) (± 0.1) K because the melting point of this oil is about 309.15 K, and it is semi-solid at room temperature.[16] The experimental data were correlated with the NRTL[17] (*nonrandom, two-liquid*) model using temperature-dependent parameters.

Experimental Section

Materials. The solvents used in this work were anhydrous ethanol and hexane, both from Merck (Germany) and with a mass purity of 99.9 %. Refined soybean and sunflower oils were

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Table 1. Fatty Acid Compositions of the Vegetable Oils

			M[b]	refined soybean	refined sunflower	refined rice bran	pretreated cottonseed	refined palm olein	refined palm
fatty acids	symbol	C*x*:y[a]	$g \cdot mol^{-1}$	100 w	100 w	100 w	100 w	100 w	100 w
octanoic	Cp	C8:0	144.22						0.08
decanoic	C	C10:0	172.27						0.09
dodecanoic	L	C12:0	200.32					0.27	1.15
tetradecanoic	M	C14:0	228.38	0.09	0.09	0.24	0.75	0.80	1.24
hexadecanoic	P	C16:0	256.43	11.54	6.40	19.42	22.79	35.11	40.68
cis-hexadec-9-enoic	Po	C16:1	254.42	0.08	0.13	0.21	0.93	0.17	0.15
heptadecanoic	Ma	C17:0	270.45	0.05				0.09	0.10
cis-heptadec-9-enoic	Mg	C17:1	268.48		0.04			0.03	
octadecanoic	S	C18:0	284.49	2.98	3.23	1.51	2.35	4.42	4.72
cis-octadec-9-enoic	O	C18:1	282.47	22.91	31.89	39.59	16.04	46.55	41.78
cis,*cis*-octadeca-9,12-dienoic	Li	C18:2	280.45	55.76	56.27	36.37	56.41	11.4	8.84
trans,*trans*-octadeca-9,12-dienoic[c]		C18:2t[c]		0.24	0.17	0.15		0.13	0.31
all-*cis*-octadeca-9,12,15-trienoic	Le	C18:3	278.44	5.27	0.33	1.48	0.16	0.32	0.18
all-*trans*-octadeca-9,12,15-trienoic[c]		C18:3t[c]		0.55		0.16			
icosanoic	A	C20:0	312.54	0.25	0.27	0.42	0.26	0.38	0.39
cis-icos-9-enoic	Ga	C20:1	310.52	0.10	0.23	0.35	0.12	0.17	0.15
docosanoic	Be	C22:0	340.59	0.23	0.65	0.10	0.19	0.07	0.07
tetracosanoic	Lg	C24:0	368.65		0.25			0.09	0.07
IV[d]				130.90	126.01	100.18	110.47	59.20	49.61

[a] C*x*:*y*, x = number of carbons and y = number of double bonds. [b] M = molar mass [c] *trans* isomers. [d] Iodine value (IV) calculated from the fatty acid composition according to the method Cd 1c−85.[35]

purchased from Cargill (Mairinque/SP, Brazil) and refined rice bran oil from Irgovel S.A. (Pelotas/RS, Brazil). The pretreated cottonseed oil (neutral oil) was submitted to a prior treatment (deacidification) in the refinery (kindly supplied by Maeda, Itumbiara/GO, Brazil), being qualified as a semiprocessed oil. Refined palm oil and palm olein were kindly supplied by Agropalma (Belém/PA, Brazil). Due to its composition, the palm oil can be fractionated by crystallization into a liquid fraction (65 to 70) %, known as palm olein, and a solid fraction (30 to 35) %, known as palm stearin.[16]

The fatty acid compositions of the vegetable oils studied in this work are presented in Table 1. These compositions were determined by gas chromatography of the fatty acid methyl esters using the official AOCS method (1−62).[18] Prior to the chromatographic analysis, the fatty acids of the samples were transformed into the respective fatty acid methyl ester using the method of Hartman and Lago.[19] The chromatographic analyses were carried out using a capillary gas chromatographic system under the same experimental conditions shown in Lanza et al.[20] From the fatty acid compositions, the probable triacylglycerol compositions (Table 2) of the vegetable oils were calculated using the algorithm suggested by Antoniosi Filho et al.[21] To calculate the probable triacylglycerol compositions, the quantities of *trans* isomers (see Table 1) were computed with their respective *cis* isomers. In Table 2 the main triacylglycerol represents the component with the greatest composition in the isomer set with x carbons and y double bonds. For the fitting process of the thermodynamic model, the vegetable oil was treated as a single triacylglycerol with the average molar mass of the oil. For this reason, the average molar masses of the vegetable oils were calculated using the probable triacylglycerol compositions (Table 2). The values obtained for the refined soybean, sunflower, rice bran, and cottonseed oils, refined palm olein, and refined palm oil were (871.8, 877.0, 880.0, 861.0, 853.5, and 845.7) $g \cdot mol^{-1}$, respectively.

Apparatus and Procedures. The liquid−liquid equilibrium data for the model systems containing vegetable oils + anhydrous ethanol were measured from (298.15 to 333.15) (± 0.1) K. The mutual solubility data were determined using equilibrium glass cells (50 mL) similar to those used by Silva et al.[22] Known quantities of each component, weighed on an analytical balance with a precision of 0.0001 g (Precisa, model XT220A, Sweden), were added directly to the equilibrium glass cells and allowed to reach equilibrium following the same procedures described by Lanza et al.[20] At the end of the experiment, samples were taken separately from the upper and bottom phases using syringes containing previously weighed masses of hexane, to instantly dilute the samples and avoid their separation into two liquid phases at ambient temperature.

The composition of both phases was determined in triplicate by gravimetric analysis. The anhydrous ethanol and hexane were removed by evaporation using an air-circulating oven at 353.15 K for 12 h and subsequently in a vacuum oven (pressure = 4.67 kPa, temperature = 323.15 K) to complete the removal of both solvents. The samples were then weighed again to determine the mass of vegetable oil in the sample since this was nonvolatile. The compositions of the two phases were easily calculated from the masses of vegetable oils and ethanol.

Thermodynamic Modeling. The concept of local composition basically establishes that the composition of the system in the neighborhood of a given molecule is not the same as the "bulk" composition because of intermolecular forces.[23] The NRTL model is based on the local composition concept and is applicable to partially miscible systems.[24,25]

Due to the large difference in molar mass between vegetable oils and ethanol, some prior investigations have opted for expressing the NRTL model in terms of mass fraction.[12] In this case, the NRTL model for pseudobinary mixtures is expressed as follows

$$\gamma_i^w = \exp\left\{\left(\frac{w_7}{M_7}\right)^2\left[\tau_{7i}\left(\frac{G_{7i}}{\frac{w_i}{\bar{M}_i} + \frac{G_{7i}w_7}{M_7}}\right)^2 + \frac{\tau_{i7}G_{i7}}{\left(\frac{w_7}{M_7} + \frac{G_{i7}w_i}{\bar{M}_i}\right)^2}\right]\right\} \Big/ \bar{M}_i\left(\frac{w_i}{\bar{M}_i} + \frac{w_7}{M_7}\right) \tag{1}$$

Table 2. Probable Triacylglycerol Compositions of the Vegetable Oils

main TAG[a]	group	M g·mol^{-1}	refined soybean 100 w	refined sunflower 100 w	refined rice bran 100 w	pretreated cottonseed 100 w	refined palm olein 100 w	refined palm 100 w
LOP	46:1[b]	777.25					0.52	2.30
PPP	48:0	807.32					1.96	4.71
MOP	48:0	805.31					1.44	2.05
MLiP	48:2	803.30				0.73	0.59	
LOO	48:2	803.29						2.22
PPS	50:0	835.37					0.64	1.50
POP	50:2	833.36	1.01	0.50	5.10	2.90	23.45	26.68
PLiP	50:3	831.34	2.08	0.97	4.97	10.44	6.82	6.77
PPoLi	50:3	829.33				1.42		
PLeP	50:3	829.33			0.56			
MLiO	50:4	829.34					0.57	
MLiLi	52:1	827.31				0.92		
POS	52:2	861.41	0.71		0.79	0.58	5.24	5.81
POO	52:3	859.40	3.91	3.27	10.41	3.98	25.82	23.24
POLi	52:4	857.38	10.30	8.88	18.15	14.39	12.42	9.75
PLiLi	52:5	855.36	11.44	8.59	9.36	25.66	1.94	1.28
PoLiLi	52:5	853.35				0.98		
PLiLe	54:1	853.35	2.52		0.85			
POA	54:1	889.46					0.69	0.78
SOO	54:3	887.45	1.31	1.91	1.07		3.04	2.68
PLiA	54:3	887.45				0.53		
SOLi	54:4	885.43	5.27			1.84		
OOO	54:5	885.43		7.88	7.09		8.16	6.03
OOLi	54:6	883.42	13.79	20.65	17.84	6.23	5.28	3.41
OLiLi	54:7	881.40	21.86	29.53	16.75	13.47	1.42	0.79
LiLiLi	54:8	879.38	18.11	17.82	6.36	15.93		
LiLiLe	56:2	877.37	5.84		0.70			
OLiA	58:3	913.49	1.85					

[a] Groups with a total triacylglycerol (TAG) composition lower than 0.5 % were ignored. [b] $x{:}y$, x = number of carbons (except carbons of glycerol), y = number of double bonds.

$$\gamma_7^w = \exp\left\{\left(\frac{w_i}{\bar{M}_i}\right)^2\left[\tau_{i7}\left(\frac{G_{i7}}{\frac{w_7}{M_7}+\frac{G_{i7}w_i}{\bar{M}_i}}\right)^2 + \frac{\tau_{7i}G_{7i}}{\left(\frac{w_i}{\bar{M}_i}+\frac{G_{7i}w_7}{M_7}\right)^2}\right]\right\}\Big/M_7\left(\frac{w_i}{\bar{M}_i}+\frac{w_7}{M_7}\right) \qquad (2)$$

and

$$\tau_{i7} = \frac{(g_{i7} - g_{77})}{RT} \qquad (3)$$

$$\tau_{7i} = \frac{(g_{7i} - g_{ii})}{RT} \qquad (4)$$

$$\frac{(g_{i7} - g_{77})}{R} = A_{0,i7} + A_{1,i7}T \qquad (5)$$

$$\frac{(g_{7i} - g_{ii})}{R} = A_{0,7i} + A_{1,7i}T \qquad (6)$$

$$G_{i7} = \exp(-\alpha_{i7}\tau_{i7}) \qquad (7)$$

$$G_{7i} = \exp(-\alpha_{7i}\tau_{7i}) \qquad (8)$$

$$\alpha_{i7} = \alpha_{7i} \qquad (9)$$

where γ_i^w is the activity coefficient of the vegetable oil ($i = 1$ to 6), i.e., refined soybean oil (1), refined sunflower oil (2), refined rice bran oil (3), pretreated cottonseed oil (4), refined palm olein (5), refined palm oil (6); γ_7^w is the activity coefficient of ethanol, both expressed on the mass fraction scale; $\bar{M}_i$, M_7, and w are the average molar mass of vegetable oil, molar mass of ethanol, and mass fraction of the components in the mixture, respectively. $(g_{i7} - g_{77})$ and τ_{i7} ($\neq \tau_{7i}$) represent the molecular energy interactions between components $i - 7$; α_{i7} ($= \alpha_{7i}$) is the nonrandomness parameter of the mixture, meaning that the components are distributed in a pattern dictated by the local composition; T is the absolute temperature; and $A_{0,i7}$, $A_{0,7i}$, $A_{1,i7}$, and $A_{1,7i}$ are the characteristic energy parameters of the interactions between molecules i and 7.

The values for the nonrandomness parameter α were not adjusted in the present work but fixed according to the following criteria: the molecular weight of the edible oils are very similar, with a difference not larger than 4.0 %, but their iodine values show significant differences (see Table 1). Sunflower and soybean oils have a very similar unsaturation degree, so that the α-value for the system sunflower oil + ethanol was fixed at the value adjusted by Lanza et al.[20] for the soybean oil + ethanol system. The same occurs for palm oil and palm olein, and the α-value adjusted by Lanza et al.[20] for the first system was also selected for the olein + ethanol system. Cottonseed and rice bran oils form a third group with an iodine value close to the average of the values observed for soybean and palm oils. For this reason, the α-value for the systems cottonseed oil + ethanol and rice bran oil + ethanol was fixed at 0.3. Note that in all cases the α-values are within the range 0.2 to 0.47 suggested by Renon and Prausnitz.[26]

In the present work, the parameters published by Lanza et al.[20] were used to predict the LLE data for the refined palm oil + ethanol and refined soybean oil + ethanol systems (see Table 4). For the other pseudobinary systems, the experimental data were used to fit the temperature-dependent parameters of the NRTL model. This fitting was done by treating the vegetable oil + anhydrous ethanol system as a pseudobinary one, the vegetable oil being considered as a single triacylglycerol with the average molar mass of the oil. This approach assumes that the different triacylglycerols present in the vegetable oil behave

Table 3. Experimental Liquid−Liquid Equilibrium Data for the Pseudobinary Systems Containing Vegetable Oils (i) + Anhydrous Ethanol (7) at (298.15 to 333.15) (± 0.1) K

		overall composition		alcohol phase		oil phase	
T/K	oil (i)[a]	100 w_i	100 w_7	100 w_i	100 w_7	100 w_i	100 w_7
298.15	soybean (1)	49.95	50.05	6.88	93.12	83.70	16.30
303.15		49.95	50.05	7.72	92.28	82.06	17.94
308.15		49.94	50.06	8.79	91.21	80.96	19.04
313.15		50.00	50.00	9.97	90.03	78.71	21.29
318.15		49.96	50.04	11.57	88.43	74.90	25.10
323.15		49.95	50.05	14.61	85.39	72.45	27.55
328.15		49.95	50.05	16.99	83.01	68.61	31.39
333.15		49.95	50.05	22.98	77.02	63.81	36.19
298.15	sunflower (2)	49.92	50.08	6.21	93.79	83.95	16.05
303.15		49.95	50.05	7.47	92.53	82.21	17.79
308.15		49.96	50.04	8.72	91.28	80.94	19.06
313.15		49.95	50.05	9.25	90.75	79.07	20.93
318.15		49.95	50.05	10.95	89.05	77.56	22.44
323.15		49.95	50.05	12.32	87.68	74.25	25.75
328.15		49.95	50.05	15.81	84.19	69.19	30.81
333.15		49.95	50.05	19.60	80.40	64.02	35.98
298.15	rice bran (3)	50.00	50.00	7.04	92.96	85.39	14.61
303.15		49.95	50.05	9.01	90.99	83.54	16.46
308.15		49.95	50.05	10.32	89.68	81.49	18.51
313.15		49.95	50.05	12.21	87.79	78.04	21.96
318.15		49.95	50.05	13.42	86.58	75.99	24.01
323.15		49.94	50.06	15.49	84.51	71.81	28.19
328.15		49.95	50.05	18.91	81.09	66.56	33.44
333.15		50.05	49.95	23.99	76.01	60.66	39.34
298.15	cottonseed (4)	49.95	50.05	7.93	92.07	84.39	15.61
303.15		49.95	50.05	9.01	90.99	82.22	17.78
308.15		49.95	50.05	10.35	89.65	79.19	20.81
313.15		49.94	50.06	12.55	87.45	75.84	24.16
318.15		49.96	50.04	13.70	86.30	73.21	26.79
323.15		49.95	50.05	17.38	82.62	70.28	29.72
328.15		49.95	50.05	20.52	79.48	64.87	35.13
333.15		49.95	50.05	26.54	73.46	58.57	41.43
298.15	palm olein (5)	49.95	50.05	7.13	92.87	85.50	14.50
303.15		49.95	50.05	8.49	91.51	83.37	16.63
308.15		49.96	50.04	9.63	90.37	81.81	18.19
313.15		49.95	50.05	10.63	89.37	78.31	21.69
318.15		49.97	50.03	12.58	87.42	75.98	24.02
323.15		49.95	50.05	14.85	85.15	73.49	26.51
328.15		49.95	50.05	17.60	82.40	70.50	29.50
333.15		49.95	50.05	20.25	79.75	65.73	34.27
318.15	palm (6)	49.99	50.01	12.04	87.96	77.89	22.11
323.15		49.95	50.05	15.65	84.35	73.70	26.30
328.15		49.95	50.05	17.03	82.97	69.41	30.59
333.15		49.95	50.05	22.61	77.39	62.39	37.61

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

in a very similar way in the liquid−liquid system under analysis. In this case, such compounds can be adequately replaced by a pseudocomponent having the corresponding average physical-chemical properties. This approach was already evaluated by Lanza et al.,[12] who proved its veracity. Estimation of the parameters was based on minimization of the objective function of compositions, eq 10, following the algorithm developed in FORTRAN language by Stragevitch and d'Avila.[27]

$$\mathrm{OF}_{i,7}(w) = \sum_{n}^{N}\left[\left(\frac{w_{i,n}^{\mathrm{AP,exptl}} - w_{i,n}^{\mathrm{AP,calcd}}}{\sigma_{w_{i,n}^{\mathrm{AP}}}}\right)^2 + \left(\frac{w_{i,n}^{\mathrm{OP,exptl}} - w_{i,n}^{\mathrm{OP,calcd}}}{\sigma_{w_{i,n}^{\mathrm{OP}}}}\right)^2\right] \qquad (10)$$

where $\mathrm{OF}_{i7}(w)$ is the objective function for each system; N is the total number of tie lines of the corresponding system; w is the mass fraction; i is the vegetable oil (for instance, $i = 1$ for soybean oil); the subscript n is tie line number; the superscripts AP and OP stand for the alcohol and oil phases, respectively; exptl and calcd refer to experimental and calculated compositions; and $\sigma_{w_{i,n}^{\mathrm{AP}}}$ and $\sigma_{w_{i,n}^{\mathrm{OP}}}$ are the standard deviations observed in the compositions of the two liquid phases.

The parameter estimation procedure is based on liquid−liquid flash calculations using the compositions at the midpoint of the experimental tie lines as the feed stream concentration.[27,28] For both phases, the average deviation (Δw_{i7}) between the experimental and calculated compositions was calculated according to eq 11, where K is the total number of pseudocomponents in the fatty system ($K = 2$).

$$\Delta w_{i7} = \sqrt{\frac{[(w_{i,n}^{\mathrm{AP,exptl}} - w_{i,n}^{\mathrm{AP,calcd}})^2] + [(w_{i,n}^{\mathrm{OP,exptl}} - w_{i,n}^{\mathrm{OP,calcd}})^2] + [(w_{7,n}^{\mathrm{AP,exptl}} - w_{7,n}^{\mathrm{AP,calcd}})^2] + [(w_{7,n}^{\mathrm{OP,exptl}} - w_{7,n}^{\mathrm{OP,calcd}})^2]}{2NK}} \qquad (11)$$

Results and Discussion

Table 3 gives the experimental liquid−liquid equilibrium data for the studied pseudobinary systems. Figures 1 to 5 show the

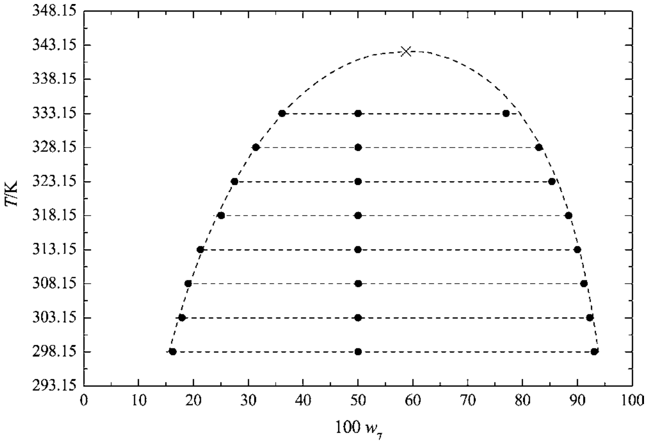

Figure 1. Liquid−liquid equilibrium for the system containing soybean oil (1) + ethanol (7) from (298.15 to 333.15) (± 0.1) K: ●, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

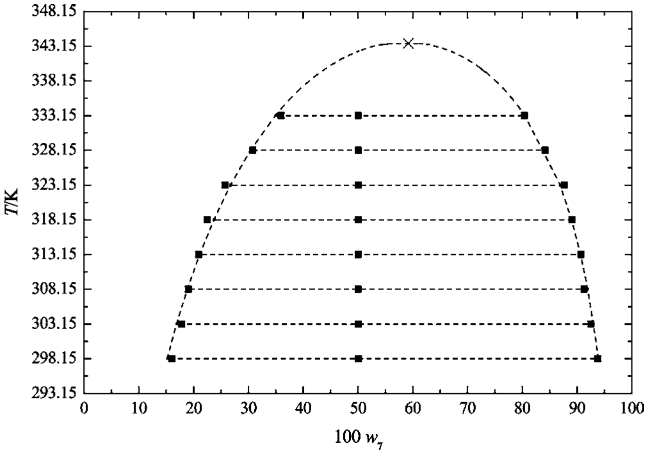

Figure 2. Liquid−liquid equilibrium for the system containing sunflower oil (2) + ethanol (7) from (298.15 to 333.15) (± 0.1) K: ■, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

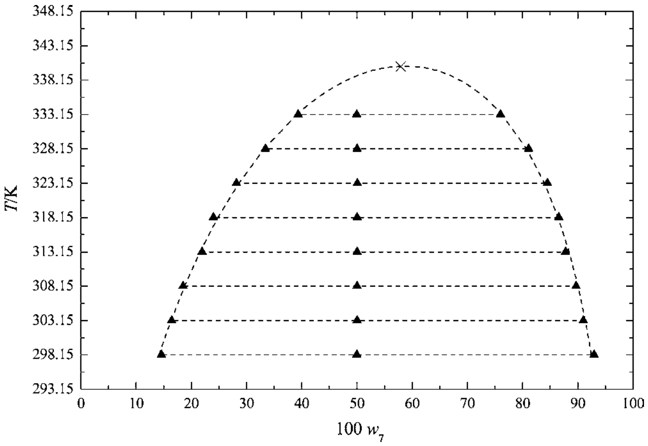

Figure 3. Liquid−liquid equilibrium for the system containing rice bran oil (3) + ethanol (7) from (298.15 to 333.15) (± 0.1) K: ▲, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

equilibrium diagrams for the systems containing vegetable oils (soybean, sunflower, rice bran, cottonseed oil, and palm olein) + anhydrous ethanol from (298.15 to 333.15) (± 0.1) K. The equilibrium diagram for the system containing refined palm oil + ethanol was studied from (318.15 to 333.15) (± 0.1) K, and it is shown in Figure 6. As can be observed in these figures, the mutual solubility of vegetable oils and ethanol was enhanced by the increase in temperature.

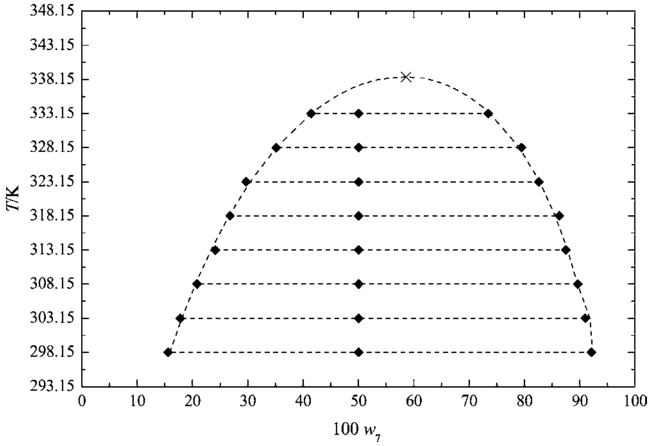

Figure 4. Liquid−liquid equilibrium for the system containing cottonseed oil (4) + ethanol (7) from (298.15 to 333.15) (± 0.1) K: ♦, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

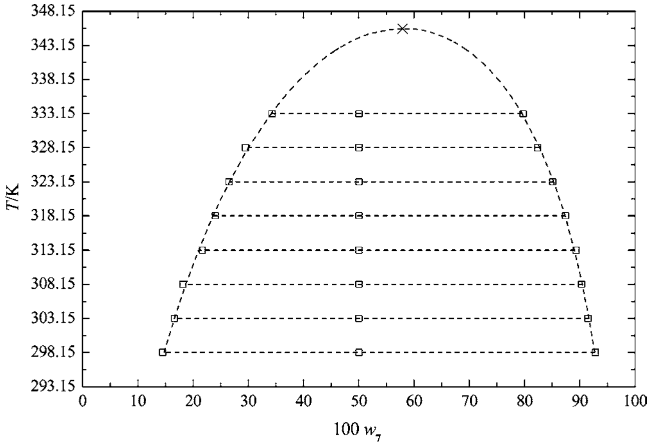

Figure 5. Liquid−liquid equilibrium for the system containing palm olein (5) + ethanol (7) from (298.15 to 333.15) (± 0.1) K: □, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

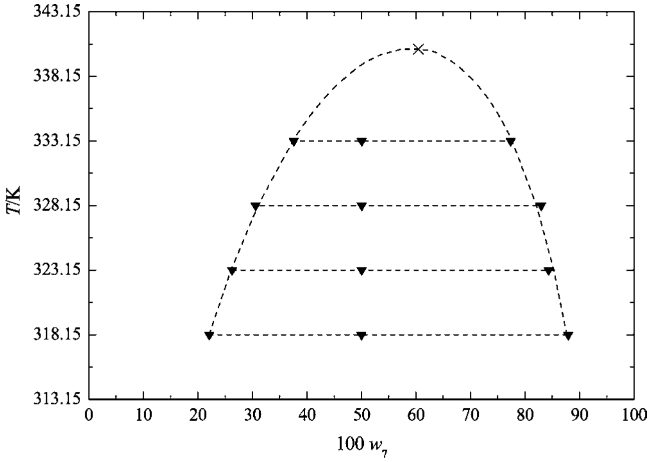

Figure 6. Liquid−liquid equilibrium for the system containing palm oil (6) + ethanol (7) from (318.15 to 333.15) (± 0.1) K: ▼, experimental; ---, NRTL model; ×, extrapolated critical solution temperature.

The NRTL model was used to correlate the experimental data, and the corresponding temperature-dependent parameters are shown in Table 4. The average deviations between the experimental and calculated compositions in both phases are given in Table 5. As can be seen, the thermodynamic model was able to accurately describe the phase compositions with deviations below 0.84 %.

Table 4. Temperature-Dependent NRTL Parameters

pair	$A_{0,i7}$/K	$A_{0,7i}$/K	$A_{1,i7}$	$A_{1,7i}$	α_{i7}
soybean oil + ethanol[20]	2592.5	−12.56	−9.698	5.731	0.3761
sunflower oil + ethanol	2609.8	−66.07	−9.735	5.905	0.3761
rice bran oil + ethanol	3103.6	−1193.9	−11.913	10.295	0.3
cottonseed oil + ethanol	2736.7	−756.09	−10.812	8.921	0.3
palm olein + ethanol	2810.8	−1295.1	−11.689	11.826	0.2325
palm oil + ethanol[20]	4240.5	−2651.5	−16.070	15.961	0.2325

Table 5. Average Deviations between Experimental and Calculated Phase Compositions of the Systems

systems	100 Δw
soybean oil + ethanol from (298.15 to 333.15) (± 0.1) K	0.84
sunflower oil + ethanol from (298.15 to 333.15) (± 0.1) K	0.51
rice bran oil + ethanol from (298.15 to 333.15) (± 0.1) K	0.39
cottonseed oil + ethanol from (298.15 to 333.15) (± 0.1) K	0.39
palm olein + ethanol from (298.15 to 333.15) (± 0.1) K	0.32
palm oil + ethanol from (318.15 to 333.15) (± 0.1) K	0.50

For each pseudobinary system (vegetable oil + ethanol), the critical solution temperature was determined using flash calculations with the same parameters presented in Table 4. The procedure consisted of a gradual increase of the temperature and overall composition to determine new tie lines, until the critical solution temperature of each system is reached. The extrapolated critical solution temperatures are (342.25, 343.55, 340.08, 338.50, 345.55, and 340.25) K for the systems composed of soybean oil + anhydrous ethanol, sunflower oil + anhydrous ethanol, rice bran oil + anhydrous ethanol, cottonseed oil + anhydrous ethanol, palm olein + anhydrous ethanol, and palm oil + anhydrous ethanol, respectively. The critical temperatures and corresponding compositions can be seen in Figures 1 to 6 and are represented by the symbol ×.

In the present work, all the measurements were performed in triplicate. The type A standard uncertainties[29] of the equilibrium data ranged from (0.03 to 0.57) % for the vegetable oils and from (0.03 to 0.57) % for ethanol, the lowest figures being attained for the lowest compositions. These results were similar to the values reported in the literature for the uncertainties of the measurements for some systems containing vegetable oils, for example, for soybean oil from (0.06 to 0.55) %,[30] for cottonseed oil from (0.04 to 0.67) %,[31] and for rice bran oil from (0.01 to 0.28) %.[32]

Table 6 shows the deviations between the phase compositions determined in the present work and those reported by other authors in the literature for some pseudobinary systems containing vegetable oils + anhydrous ethanol. These results are considered consistent, considering factors such as vegetable oils with different fatty acid compositions, the saturation degree of the vegetable oils (for example, the iodine values calculated were 49.46 for palm oil[33] and 127.46 for soybean oil,[30] and in the present work these values were 49.61 and 130.90, respectively), the methods of analysis, the ability of the analyst, etc.

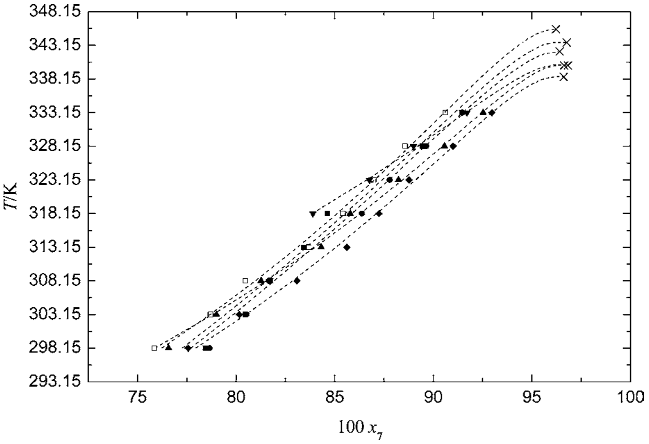

Figure 7. Effect of temperature (T) on the ethanol molar fraction in the oil phase (x_7): ●, soybean oil; ■, sunflower oil; ▲, rice bran oil; ♦, cottonseed oil; □, palm olein; ▼, palm oil; ---, NRTL; ×, extrapolated critical solution temperatures.

One important variable in the transesterification process is the molar ratio of alcohol to vegetable oil. From a stoichiometric point of view, a 3:1 molar ratio of alcohol to vegetable oil is needed. However, a large excess of alcohol is required to conduct the reversible reaction in the direction of product formation, and for maximum conversion to the ester, a molar ratio of 6:1 is normally used.[10] In this case, ethanol must have, in the initial reaction mixture, a molar fraction of 0.8571, a value that is obtained at (317.75, 318.64, 316.12, 314.91, 319.69, or 321.45) K for soybean, sunflower, rice bran, cottonseed, palm olein, or palm oils, respectively (Figure 7). These temperatures were checked by liquid−liquid flash calculations following the same procedure explained above. Moreover, it was observed that the solubility was influenced by the degree of unsaturation or iodine value (IV) of the studied vegetable oils (see Table 1). The results showed that the solubility of the unsaturated vegetable oils (soybean, sunflower, rice bran, and cottonseed oils) in anhydrous ethanol was higher than that of the saturated oils under the same conditions, due to the fact that the solubility of fatty derivates in organic solvents increases with the reduction in the carbon chain length and the increase in the number of double bonds, increasing the polarity and hence the mutual solubility of the systems.[34]

Conclusions

Liquid−liquid equilibrium data for pseudobinary systems containing vegetable oils + ethanol were obtained in the temperature range from (298.15 to 333.15) (± 0.1) K. The solubility of vegetable oils in ethanol could be enhanced effectively by increasing the temperature. The experimental data were correlated successfully with the NRTL model, and the

Table 6. Absolute Deviations between Liquid−Liquid Equilibrium Data of This Work and Those Reported in the Literature for the Systems Containing Vegetable Oils + Ethanol

	alcohol phase	oil phase
systems	$100\cdot\lvert w_i^{\text{this work}} - w_i^{\text{literature}}\rvert$	$100\cdot\lvert w_i^{\text{this work}} - w_i^{\text{literature}}\rvert$
soybean oil + ethanol at 298.15 K[12]	0.76	0.69
soybean oil + ethanol at 313.15 K[20]	0.55	0.11
soybean oil + ethanol at 328.15 K[20]	1.11	2.05
soybean oil + ethanol at 323.15 K[30]	1.08	0.95
rice bran oil + ethanol at 298.15 K[32]	0.44	0.17
cottonseed oil + ethanol at 298.15 K[31]	1.23	0.80
palm oil + ethanol at 318.15 K[20]	0.67	0.48
palm oil + ethanol at 328.15 K[33]	0.40	2.89
palm oil + ethanol at 328.15 K[20]	0.38	0.49

average deviations between the experimental data and the calculated compositions presented values between (0.32 and 0.84) %.

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Literature Cited

(1) Barnwal, B. K.; Sharma, M. P. Prospects of Biodiesel Production from Vegetable Oils in India. *Renewable Sustainable Energy Rev.* **2005**, *9*, 363–378.
(2) Pousa, G. P. A. G.; Santos, A. L. F.; Suarez, P. A. Z. History and Policy of Biodiesel in Brazil. *Energy Policy* **2007**, *35*, 5393–5398.
(3) Fukuda, H.; Kondo, A.; Noda, H. Review: Biodiesel Fuel Production by Transesterification of Oils. *J. Biosci. Bioeng.* **2001**, *92*, 405–416.
(4) Kucek, K. T.; César-Oliveira, M. A. F.; Wilhelm, H. M.; Ramos, L. P. Ethanolysis of Refined Soybean Oil Assisted by Sodium and Potassium Hydroxides. *J. Am. Oil Chem. Soc.* **2007**, *84*, 385–392.
(5) Abreu, F. R.; Lima, D. G.; Hamú, E. H.; Wolf, C.; Suarez, P. A. Z. Utilization of Metal Complexes as Catalysts in the Transesterification of Brazilian Vegetable Oils with Different Alcohols. *J. Mol. Catal. A-Chem.* **2004**, *209*, 29–33.
(6) Oliveira, D.; Filho, I. N.; Di Luccio, M.; Faccio, C.; Dalla Rosa, C.; Bender, J. P.; Lipke, N.; Amroginski, C.; Dariva, C.; Oliveira, J. V. Kinetics of Enzyme-Catalyzed Alcoholysis of Soybean Oil in n-Hexane. *Appl. Biochem. Biotechnol.* **2005**, *21*, 231–242.
(7) Shibasaki-Kitakawa, N.; Honda, H.; Kuribayashi, H.; Toda, T.; Fukumura, T.; Yonemoto, T. Biodiesel Production Using Anionic Ion-Exchange Resin as Heterogeneous Catalyst. *Bioresour. Technol.* **2007**, *98*, 416–421.
(8) Liu, X.; He, H.; Wang, Y.; Zhu, S.; Piao, X. Transesterification of Soybean Oil to Biodiesel Using CaO as a Solid Base Catalyst. *Fuel* **2008**, *87*, 216–221.
(9) Zhou, W.; Boocock, D. G. B. Phase Behavior of the Base-Catalyzed Transesterification of Soybean Oil. *J. Am. Oil Chem. Soc.* **2006**, *83*, 1041–1045.
(10) Meher, L. C.; Sagar, D. V.; Naik, S. N. Technical Aspects of Biodiesel Production by Transesterification - A review. *Renewable Sustainable Energy Rev.* **2006**, *10*, 248–268.
(11) Gerpen, J. V. Biodiesel Processing and Production. *Fuel Process. Technol.* **2005**, *86*, 1097–1107.
(12) Lanza, M.; Borges Neto, W.; Batista, E.; Poppi, R. J.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for Reactional Systems of Ethanolysis at 298.3K. *J. Chem. Eng. Data* **2008**, *53*, 5–15.
(13) Zhou, H.; Lu, H.; Liang, B. Solubility of Multicomponent Systems in the Biodiesel Production by Transesterification of *Jatropha curcas* L. Oil with Methanol. *J. Chem. Eng. Data* **2006**, *51*, 1130–1135.
(14) Tang, Z.; Du, Z.; Min, E.; Gao, L.; Jiang, T.; Han, B. Phase Equilibria of Methanol-Triolein System at Elevated Temperature and Pressure. *Fluid Phase Equilib.* **2006**, *239*, 8–11.
(15) Liu, X.; Piao, X.; Wang, Y.; Zhu, S. Liquid-Liquid Equilibrium for Systems of (Fatty Acid Ethyl Esters + Ethanol + Soybean Oil and Fatty Acid Ethyl Esters + Ethanol + Glycerol). *J. Chem. Eng. Data* **2008**, *53*, 359–362.
(16) Firestone, D. *Physical and Chemical Characteristics of Oils, Fats and Waxes*; AOCS Press, 1999.
(17) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
(18) AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 3rd ed.; AOCS Press: Champaign, 1988; Vols. 1−2.
(19) Hartman, L.; Lago, R. C. A. Rapid Preparation of Fatty Acid Methyl Esters from Lipids. *Lab. Pract.* **1973**, *22*, 475–476.
(20) Lanza, M.; Sanaiotti, G.; Batista, E.; Poppi, R. J.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for Systems Containing Vegetable Oils, Anhydrous Ethanol, and Hexane at (313.15, 318.15, and 328.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1850–1859.
(21) Antoniosi Filho, N. R.; Mendes, O. L.; Lanças, F. M. Computer Prediction of Triacylglycerol Composition of Vegetable Oils by HRGC. *Chromatographia* **1995**, *40*, 557–562.
(22) Silva, L. H. M.; Coimbra, J. S.; Meirelles, A. J. A. Equilibrium Phase Behavior of Poly(Ethylene Glycol) + Potassium Phosphate + Water Two Phase Systems at Various pH and Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 398–401.
(23) Wilson, G. M. Vapor-Liquid Equilibrium. XI: A New Expression for the Excess Gibbs Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.
(24) Aznar, M. Correlation of (Liquid + Liquid) Equilibrium of Systems Including Ionic Liquids. *Braz. J. Chem. Eng.* **2007**, *24*, 143–149.
(25) Sé, R. A. G.; Aznar, M. Thermodynamic Modelling of Phase Equilibrium for Water + Poly(Ethylene Glycol) + Salt Aqueous Two-Phase Systems. *Braz. J. Chem. Eng.* **2002**, *19*, 255–266.
(26) Renon, H.; Prausnitz, J. M. Estimation of Parameters for the NRTL Equation for Excess Gibbs Energies of Strongly Nonideal Liquid Mixtures. *Ind. Eng. Chem. Proc. Des. Dev.* **1969**, *8*, 413–419.
(27) Stragevitch, L.; d'Avila, S. G. Application of a Generalized Maximum Likelihood Method in the Reduction of Multicomponent Liquid-Liquid Equilibrium Data. *Braz. J. Chem. Eng.* **1997**, *14*, 41–52.
(28) Null, H. R. *Phase Equilibrium in Process Design*; Wiley-Interscience: New York, 1970.
(29) Taylor, B. N.; Kuyatt, C. E. *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results*; NIST Technical Note 1297, **1994**.
(30) Rodrigues, C. E. C.; Peixoto, E. C. E.; Meirelles, A. J. A. Phase equilibrium for Systems Composed by Refined Soybean Oil + Commercial Linoleic Acid + Ethanol + Water, at 323.2 K. *Fluid Phase Equilib.* **2007**, *261*, 122–128.
(31) Rodrigues, C. E. C.; Reipert, E. C. D.; Souza, A. F.; Pessôa Filho, P. A.; Meirelles, A. J. A. Equilibrium Data for Systems Composed by Cottonseed Oil + Commercial Linoleic Acid + Ethanol + Water + Tocopherols at 298.2 K. *Fluid Phase Equilib.* **2005**, *238*, 193–203.
(32) Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol +Water at 298.2 K. *J. Chem. Eng. Data* **2003**, *48*, 367–373.
(33) Gonçalves, C. B.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol +Water at 318.2 K. *Fluid Phase Equilib.* **2004**, *221*, 139–150.
(34) Swern, D. *Bailey's Industrial Oil and Fat Products*; Mattil, K. F., Norris, F. A., Stirton, A. J., Eds.; Wiley: New York, 1964.
(35) AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 5th ed.; AOCS Press: Champaign, IL, 1998.

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