Liquid−Liquid Equilibrium Data for Fatty Systems Containing Refined Rice Bran Oil, Oleic Acid, Anhydrous Ethanol, and Hexane

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The objective of this work was to determine liquid−liquid equilibrium data for fatty systems of interest in the extraction/refining process of vegetable oils and in the biodiesel production. The following systems were investigated: refined rice bran oil + anhydrous ethanol + hexane at (298.15 ± 0.2) K and (313.15 ± 0.2) K and refined rice bran oil + commercial oleic acid + anhydrous ethanol + hexane at (298.15 ± 0.2) K with mass fractions of (5.08, 7.98, 10.65, and 15.09) % of fatty acid in oil. The instrumental technique of near-infrared spectroscopy allied to multivariate calibration (in this work, termed "NIR method") was used for quantification of the phase compositions. For the pseudoternary system, the relative deviations for global mass balance were (0.10 and 0.11) % for the temperature of (298.15 and 313.15) K, respectively. For the pseudoquaternary systems, the relative deviations for global mass balance varied in the range from (0.15 to 0.31) %. The experimental data were correlated using the NRTL model with overall deviations lower than 1.15 %. We can conclude that the NIR method is highly accurate, and the low deviations obtained indicate the good quality of the equilibrium data.

Introduction

Brazil is a departure from the worldwide agricultural picture because it is a country that produces a considerable amount of commodities from biomass sources and possesses a high index of exportations. Among several species of oil seeds, rice bran oil (RBO) has been used only to a small extent of its potential as edible oil because of problems with the stability and storage of the rice bran. Also, the RBO is extensively consumed as edible oil in Asian countries such as Japan, China, Korea, and Pakistan, but its low production in western countries may be attributed to difficulties in its processing.[1] In comparison with other vegetables oils, RBO tends to contain higher levels of free fatty acids (FFA) induced by intensive enzymatic activity that hinders its deacidification by conventional processes, such as chemical or physical refining. Crude vegetable oils are obtained by extraction from solid matrix by pressing or using organic solvent.[2,3] In the extraction process, the total/partial substitution of hexane becomes necessary because this usual solvent is highly flammable and suspected to be dangerous to human health. The refining of crude vegetable oils involves solvent stripping, degumming,[4] bleaching, deacidification, and deodorization.[5,6] The vegetable oils can be deacidified by conventional processes; however, these present several disadvantages, such as the high losses of triacylglycerols, large production of soapstock, and high energy consumption.[5,6] Orthoefer[1] reported that a significant portion of the nutraceutical RBO compounds is lost during these processes. Rodrigues et al.[7] studied the optimization of the rice bran oil deacidification by liquid−liquid extraction to reduce the losses of neutral oil and nutraceutical compounds as γ-oryzanol.

An alternative for the deacidification of edible oils is the liquid−liquid extraction; this process is carried out at room temperature, at atmospheric pressure, and avoids the formation of waste products. Deacidification by solvent extraction is based on the difference of solubility of free fatty acids and triacylglycerols in an appropriate solvent.[8] The solvent selection is important for the good performance of such processes, minimizing the losses of neutral oil and other desirable components. Works of Gonçalves et al.,[9] Pina and Meirelles,[10] and Kale et al.[11] indicate the decrease of the free fatty acid content in oil using this technique.

On the other hand, the conventional production of biodiesel by the alcoholic transesterification of vegetable oils with methanol or ethanol can be catalyzed by enzymes,[12,13] and the use of organics solvents that increase the solubility between oil/ethanol or methanol is fundamental for promoting high diffusion coefficients.[14,15] Furthermore, the knowledge of the phase behavior of these systems involving crude vegetable oil/solvents configures the principal topic in mass transfer operations and reactional mixtures. Thus, the scope of the present work was to determine liquid−liquid equilibrium data for the fatty systems containing refined rice bran oil + commercial oleic acid + anhydrous ethanol + hexane at 298.15 K, with mass fractions of (5.08, 7.98, 10.65, and 15.09) % of acid in oil, using NIR spectroscopy coupled with chemometric methods based on statistical and mathematical procedures for quantification of the components in each phase. In the literature, only the works reported by Lanza et al.[16,17] used NIR spectroscopy to get information about liquid−liquid equilibrium data for the reactional systems of ethanolysis, while other works[18−20] cite the use of this technique for analysis of vegetables oils and biodiesel. The first part of this work presents the apparatus and experimental procedures and also the general information about the analytical technique based on near-infrared spectroscopy applied to quantify the phase compositions of liquid−liquid equilibrium data. The second section reports the equilibrium data for all

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10.1021/je9002338 CCC: $40.75

Table 1. Fatty Acid Compositions of the Refined Rice Bran Oil and Commercial Oleic Acid

fatty acids				M	refined rice bran oil		commercial oleic acid	
usual name	proper name	symbol	C*x*:*y*[a]	$\text{g}\cdot\text{mol}^{-1}$	100 w	100 x	100 w	100 x
capric	decanoic	C	C10:0	172.26			0.05	0.08
lauric	dodecanoic	L	C12:0	200.32			0.23	0.32
myristic	tetradecanoic	M	C14:0	228.37	0.24	0.29	0.38	0.47
palmitic	hexadecanoic	P	C16:0	256.42	19.42	20.92	6.16	6.72
palmitoleic	*cis*-9-hexadecenoic	Po	C16:1	254.41	0.21	0.23	0.21	0.23
stearic	octadecanoic	S	C18:0	284.48	1.51	1.47	0.90	0.89
oleic	*cis*-9-octadecenoic	O	C18:1	282.46	39.59	38.72	74.90	74.20
elaidic[b]	*trans*-9-octadecenoic		C18:1T[b]				0.22	0.22
linoleic	*cis*-9,*cis*-12-octadecadienoic	Li	C18:2	280.45	36.37	35.83	16.08	16.04
linoelaidic[b]	*trans*-9,*trans*-12-octadecadienoic		C18:2T[b]		0.15	0.15	0.30	0.30
linolenic	all-*cis*-9,12,15-octadecatrienoic	Le	C18:3	278.43	1.48	1.47	0.20	0.20
translinolenic[b]	all-*trans*-9,12,15-octadecatrienoic		C18:3T[b]		0.16	0.16		
arachidic	eicosanoic	A	C20:0	312.53	0.42	0.37	0.09	0.08
gadoleic	*cis*-9-eicosanoic	Ga	C20:1	310.51	0.35	0.31	0.28	0.25
behenic	docosanoic	Be	C22:0	340.58	0.10	0.08		

[a] C*x*:*y*, x = number of carbons and y = number of double bonds. [b] Trans isomers.

the pseudoternary and pseudoquaternary systems of interest and the thermodynamic modeling.

Experimental Section

Materials. The refined rice bran oil used was obtained commercially from Irgovel S.A. (RS/Brazil), and it was stored in a place with controlled temperature. The solvents used in this work were anhydrous ethanol and hexane, both from Merck (Germany), with a purity of (99.9 and 99.0) %, respectively. Commercial oleic acid was used, also from Merck, with a purity of about 75.0 %.

All fatty reagents used in this work were analyzed by gas chromatography of the fatty acid methyl esters to determine the fatty acid composition, according to the official method (1−62) of the AOCS.[21] Prior to the chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters according to Hartman and Lago.[22] The chromatographic analyses were carried out using 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 523.15 K; column temperature of 383.15 K for 5 min, (383.15 to 488.15) K (rate of 5 $\text{K}\cdot\text{min}^{-1}$), 488.15 K for 24 min; detection temperature of 553.15 K; and injection volume of 1.0 μL. The fatty acid methyl esters were identified by comparison with external standards purchased from Nu Check Prep (Elysian/MN, USA). Quantification was accomplished by internal normalization.

The fatty acid compositions of the vegetable oil and commercial oleic acid are presented in Table 1, from which the probable triacylglycerol composition of the rice bran oil could be determined (Table 2) using the algorithm suggested by Antoniosi Filho et al.[23]

To calculate the probable triacylglycerol composition, the quantities of trans isomers (see Table 1) were added up 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. Through the results shown in Tables 1 and 2, the average molar mass of the refined rice bran oil was calculated, and the value obtained was 866.9 $\text{g}\cdot\text{mol}^{-1}$. The average molar mass of the commercial oleic acid was estimated from the fatty acid composition shown also in Table 1. The obtained value for the average molar mass of the commercial oleic acid was 279.8 $\text{g}\cdot\text{mol}^{-1}$.

Table 2. Probable Triacylglycerol Composition of the Refined Rice Bran Oil

		M	composition	
main TAG[a]	group	$\text{g}\cdot\text{mol}^{-1}$	100 w	100 x
POP[b]	50:1[c]	833.36	5.07	5.28
PLiP	50:2	831.34	4.94	5.15
PLeP	50:3	829.35	0.56	0.58
POS	52:1	861.41	0.79	0.79
POO	52:2	859.40	10.35	10.44
POLi	52:3	857.38	18.04	18.27
PLiLi	52:4	855.36	9.31	9.43
PLiLe	52:5	853.35	0.85	0.86
SOO	54:2	887.45	1.06	1.04
OOO	54:3	885.43	7.60	7.44
OOLi	54:4	883.42	17.74	17.41
OLiLi	54:5	881.40	16.66	16.38
LiLiLi	54:6	879.38	6.33	6.24
LiLiLe	54:7	877.37	0.70	0.69

[a] Groups with a total triacylglycerol (TAG) composition lower than 0.5 % were ignored. [b] Each letter, whose name is given in Table 1, represents a fatty acid esterified to glycerol. [c] *x*:*y*, x = number of carbons (except carbons of glycerol), y = number of double bonds.

Apparatus and Procedures. Determination of Solubility Curves. The solubility curves, determined by the cloud-point method, are necessary to obtain preliminary information about the system of interest and auxiliary in the selection of the calibration standards used by the NIR method for the quantification of the components in equilibrium. Mixtures were prepared with refined rice bran oil and anhydrous ethanol in mass fractions ranging from (15 to 90) % using an analytical balance (Precisa, model XT220A, Sweden) with a precision of 0.0001 g. This mixture was weighed directly in the equilibrium glass cell (50 mL) similar to those used by Silva et al.,[24] generating the obligatory two liquid phases. After this preparation, hexane was added vigorously in the glass cell using an automatic buret (Metrohm, model Dosimat 715, Herisan, Switzerland) until the system becomes transparent, indicating the formation of a homogeneous liquid phase or monophasic region. Thus, the corresponding solubility curve was calculated by the amount of each component added.

All measurements were carried out in cells where the temperature was controlled using a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA). A magnetic stirrer was used (Ika Werke, model RH-KT/C, Staufen, Germany) to promote the agitation in the mixture, and a digital thermometer (Alla, model (223.15 to 473.15) K, France) with 0.1 K of variation was used to monitor the temperature inside the cell.

The digital thermometer was previously calibrated with a standard thermometer in a range of temperature between (293.15 and 333.15) K.

Determination of Liquid−Liquid Equilibrium Data. The equilibrium data were determined using equilibrium glass cells (50 mL) similar to those used by Silva et al.[24] Known quantities of each component, weighed on an analytical balance with a precision of 0.0001 g (Adam, model AAA 250 L, Milton Keynes, United Kingdom), were added directly inside the equilibrium glass cells. The cell temperature was controlled using a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA). Digital thermometers (Alla, model (223.15 to 473.15) K, France) with 0.1 K of variation were used to monitor the cell temperature. The mixture was stirred vigorously with a magnetic stirrer (Ika Werke, model RH-KT/C, Staufen, Germany) for 20 min and left to rest for (20 to 24) h. This led to the formation of two clear, transparent phases, with a well-defined interface, and finally, the samples of the phases were carefully collected for subsequent quantification of the components through the NIR method.

NIR Method. Validation of the Analytical Method Based on NIR. In this work, near-infrared spectroscopy was applied for quantification of the phase compositions of the systems in equilibrium. The validation of this technique is reported by Lanza et al.,[16] where the authors studied the use of the NIR method to quantify the compounds involved in the liquid−liquid equilibrium for the deacidification system at 298.3 K and compared it to a conventional analytical method. The relative errors between the phase compositions determined by both analytical methods were 2.12 % for the solvent phase and 2.01 % for the oil phase. The average deviations for global mass balance of the phases in equilibrium were 0.06 % in the case of the NIR method and 0.10 % for the conventional method.

Near Infrared Spectroscopy Technique. The near-infrared spectra were measured using a Thermo Nicolet infrared spectrometer (Nexus, model 670 FT-IR Esp, Madison, USA) connected to an air purging system, with a heated cuvette holder (Ventacon, model HNIR-1−1, Winchester, United Kingdom) and controlled temperature at (298.15 or 313.15) (± 0.5) K for a universal power supply (Ventacon, model D-2). Near infrared absorbance spectra were registered in the range from (4400 to 11000) cm^{-1}, making 64 scans with 4 cm^{-1} resolution using a quartz cell (Hellma, model 110-QX, Müllheim/Baden, Germany) with a 1 mm optical path and 1 cm^{-1} spectra resolution. Spectra of air (empty cell without liquid), obtained before each measured experiment, were used as background. The background spectra (64 scans at 4 cm^{-1} resolution) were recorded to each measured experiment, whereas for the samples, the 64 scans were taken with two repetitions to reduce instrument noise. The calibration and prediction methods were developed by PLS regression, available in PLS_Toolbox version 4.0, from Eigenvector Research (Wenatchee, WA, USA) for use with MATLAB 7.0 (The MathWorks, Natick/MA, USA).

Multivariate Calibration. The near-infrared spectroscopy is a technique that supplies qualitative data about the samples that can be transformed into quantitative information using chemometric methods based on statistical and mathematical procedures. To develop multivariate calibration models appropriate for each type of system, sets of mixtures with known compositions were selected of different forms. The calibration and external validation standards for the pseudoternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) were selected using the solubility curve by the cloud-point method explained earlier. This curve was divided into two parts, the oil phase and the solvent phase, and for each part 30 mixtures were obtained by gravimetry and used as calibration standards. On the basis of these sets and the near-infrared spectra, the PLS regression generated the calibration models. A further set of about 10 pseudoternary mixtures for each part of the solubility curve was also obtained by gravimetry and used as external validation standards (prediction set) to check the accuracy of the calibration models.[16,17]

The compositions of the calibration and external validation standards for the pseudoquaternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) were selected using the liquid−liquid equilibrium data previously determined for the pseudoternary systems at 298.15 K. The commercial oleic acid was added in several compositions in both phases, solvent and oil, of the calibration set to obtain a distribution coefficient varying in the approximate range from (0.90 to 1.90), comprehending all ranges in overall composition (initial mixture). To verify this range, two equilibrium cells for two different tie lines containing a mass fraction of 5.08 % of oleic acid were prepared, and an average distribution coefficient of 1.25 was obtained, using the conventional analytical method. Rodrigues et al.[25] found a similar result equal to 1.28 when they studied the phase behavior of analogous systems containing refined bran oil + commercial oleic acid + anhydrous ethanol at 298.15 K.

In the external validation, the accuracy of the models was evaluated by the relative error (E_R), obtained from the difference between the predicted value and the actual value (gravimetry), and by the coefficient of determination (R^2), the linear plot between the predicted values and the actual ones for the external validation standards. In the internal validation, the performances of the calibration models were evaluated by the root-mean-square error of cross-validation (rmsecv). These values express the accuracy of the models and the proximity between the values predicted by the model ($w_{i,\text{pred}}$) and the actual values ($w_{i,\text{actual}}$) obtained using the reference method. The errors were defined as

$$E_R = \frac{1}{n}\sum_{i=1}^{n}\frac{|w_{i,\text{pred}} - w_{i,\text{actual}}|}{w_{i,\text{actual}}} \tag{1}$$

$$\text{rmsecv} = \sqrt{\frac{\sum_{i=1}^{n}(w_{i,\text{pred}} - w_{i,\text{actual}})^2}{n}} \tag{2}$$

where n is the total number of validation (external or internal) standards and the subscript i is the number of the standard.

The rmsecv (root-mean-square error of cross-validation) is calculated using the cross-validation standards (internal validation), according to the cross-validation procedure known as "leave one out".[26,27] The cross-validation procedure and the corresponding rmsecv values were used for selecting the number of PLS factors considered in the construction of the calibration models for the pseudoternary systems.[16,17] The selection of the calibration models for the pseudoquaternary systems will be explained in the section Results and Discussion. After determining and checking the calibration models for each phase, solvent or oil, of each system, these models could be used to calculate the compositions of the samples obtained in the equilibrium experiments. The uncertainties of the compositions for the NIR method varied within the following ranges: (0.07 to 2.80) % for refined rice bran oil, (0.02 to 0.70) % for anhydrous ethanol, (0.04 to 0.20) % for hexane, and (0.08 to 0.16) % for commercial oleic acid, being the lowest figures obtained for the lowest compositions.

Theoretical Calculations

Calculation of the Deviations in the Mass Balance of the Phases. The results of the liquid−liquid equilibrium experiments were tested according to the procedure developed by Marcilla et al.[28] and already applied to fatty systems by Rodrigues et al.[29,30] This procedure consists of calculating the masses for both liquid phases and comparing their sum with the actual value for total mass used in the experiment, thus obtaining a relative deviation for each point of the overall mixture. According to this approach, i independent component balances can be written, with i being each component of the system, given by

$$m^{OC}w_i^{OC} = m^{SP}w_i^{SP} + m^{OP}w_i^{OP} \tag{3}$$

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

$$\mathbf{M} = \mathbf{B}\cdot\mathbf{P} \tag{4}$$

Mathematical calculations transform eq 4 into the following expression

$$\mathbf{P} = (\mathbf{B}^{\mathbf{T}}\mathbf{B})^{-1}\mathbf{B}^{\mathbf{T}}\mathbf{M} \tag{5}$$

where $\mathbf{B}^{\mathbf{T}}$ is the transpose matrix of $\mathbf{B}$ and $(\mathbf{B}^{\mathbf{T}}\mathbf{B})^{-1}$ is the inverse matrix of $(\mathbf{B}^{\mathbf{T}}\mathbf{B})$. In this way, the values for m^{SP} and m^{OP} (matrix $\mathbf{P}$), which minimize the errors of the previous system, have been calculated. The sum between m^{SP} and m^{OP} can be compared to m^{OC} to estimate a relative deviation for the global mass balance (δ), expressed as

$$\delta = \frac{|m^{OC} - (m^{SP} + m^{OP})|}{m^{OC}} \tag{6}$$

The relative deviation for mass balance of each compound i (δ_i) in each tie line n could be calculated according to eq 7

$$\delta_{i,n} = \frac{|m_n^{OC}w_{i,n}^{OC} - (m_n^{SP}w_{i,n}^{SP} + m_n^{OP}w_{i,n}^{OP})|}{m_n^{OC}w_{i,n}^{OC}} \tag{7}$$

Thermodynamic Modeling. The experimental data determined for these systems were used to adjust the binary interaction parameters of the NRTL model. The mass fraction was used as a composition unit due to the large difference in molar mass of the components in the systems.[16,17,29−35] Rodrigues et al.[32] showed the activity coefficient equations and the isoactivity criterion, expressed in terms of mass fraction, according to the NRTL model. The isoactivity criterion of the phase equilibrium developed on a molar fraction basis can be expressed in a mass fraction unity as follows

$$(\gamma_i x_i)^{SP} = (\gamma_i x_i)^{OP} \tag{8}$$

$$(\gamma_i^w w_i)^{SP} = (\gamma_i^w w_i)^{OP} \tag{9}$$

where

$$\gamma_i^w = \frac{\gamma_i}{M_i \sum_j^K \left(\frac{w_j}{M_j}\right)} \tag{10}$$

γ_i is the activity coefficient of component i estimated according to the NRTL model; γ_i^w is the corresponding activity coefficient expressed on the mass fraction scale; M_i is molar mass of component i; the subscript j is a component; and K is the total number of components in the mixture. For the fitting process, the vegetable oil was treated as a single triacylglycerol with the average molar mass of the triacylglycerols presented in the vegetable oil. The same approach was extended to the commercial oleic acid. This approach assumes that the different triacylglycerols and fatty acids present in the rice bran oil and the commercial oleic acid, respectively, behave 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.,[16] who proved the reliability of this hypothesis.

Estimation of the binary interaction parameters was based on minimization of the objective composition function, eq 11, following the procedure developed by Stragevitch and d'Avila.[36]

$$\mathrm{OF}(w) = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{K-1}\left[\left(\frac{w_{i,n,m}^{SP,exptl} - w_{i,n,m}^{SP,calcd}}{\sigma_{w_{i,n,m}^{SP}}}\right)^2 + \left(\frac{w_{i,n,m}^{OP,exptl} - w_{i,n,m}^{OP,calcd}}{\sigma_{w_{i,n,m}^{OP}}}\right)^2\right] \tag{11}$$

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 components in the data group; w is the mass fraction; the subscripts i, n, and m are component, tie line, and group number, respectively; the superscripts SP and OP stand for the solvent and oil phases, respectively; and exptl and calcd refer to experimental and calculated compositions. $\sigma_{w_{i,n,m}^{SP}}$ and $\sigma_{w_{i,n,m}^{OP}}$ are the standard deviations observed in the compositions of the two liquid phases. The parameter estimation procedure involves flash calculations[37] for the middle point compositions of the experimental tie lines and minimization of the objective function given by eq 11.

The average deviations between the experimental and calculated compositions in both phases were calculated according to eq 12

$$\Delta w = \sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{K}[(w_{i,n}^{SP,exptl} - w_{i,n}^{SP,calcd})^2 + (w_{i,n}^{OP,exptl} - w_{i,n}^{OP,calcd})^2]}{2NK}} \tag{12}$$

Results and Discussion

The notation for each compound used in this work was the following: refined rice bran oil (1), anhydrous ethanol (2), hexane (3), and commercial oleic acid (4). In Table 3, the results of the calibration models generated through the NIR method for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) at (298.15 ± 0.2) K and (313.15 ± 0.2) K are shown.

Through the errors of the calibration models found in Table 3, we can note the low values for the root-mean-square errors of cross-validation (rmsecv), and high coefficients of determi-

Table 3. Relative Errors (E_R), Coefficients of Determination (R^2), and Root-Mean-Square Error of Cross-Validation (rmsecv) in the Quantification of the Validation Standards (External, E_R and R^2, and Internal, rmsecv) Using the NIR Method for the Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) at (298.15 ± 0.2) K and (313.15 ± 0.2) K

		solvent phase			oil phase			E_R
T/K		oil (1)	ethanol (2)	hexane (3)	oil (1)	ethanol (2)	hexane (3)	%
298.15 ± 0.2	E_R/%	1.18	0.08	0.60	0.29	0.83	1.25	0.71
	rmsecv/%	0.07	0.06	0.09	0.34	0.19	0.20	
	R^2	0.99971	0.99898	0.99878	0.99998	0.99991	0.99967	
313.15 ± 0.2	E_R/%	0.78	0.11	1.53	0.30	0.73	1.39	0.81
	rmsecv/%	0.10	0.07	0.14	0.11	0.09	0.07	
	R^2	0.99998	0.99984	0.99946	0.99988	0.99996	0.99898	

Table 4. Liquid−Liquid Equilibrium Data for the Pseudoternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) at (298.15 ± 0.2) K and (313.15 ± 0.2) K

	overall composition			solvent phase			oil phase		
T/K	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
298.15 ± 0.2	49.99	50.01	0.00	6.84	93.16	0.00	85.26	14.74	0.00
	48.01	49.96	2.03	7.47	90.97	1.56	82.66	15.29	2.05
	45.99	50.00	4.01	8.26	88.20	3.54	79.28	16.31	4.41
	44.03	49.96	6.01	8.89	85.86	5.25	76.32	17.28	6.40
	41.98	50.03	7.99	10.07	82.63	7.30	73.29	18.50	8.21
	40.00	49.99	10.01	11.48	79.11	9.41	69.37	20.10	10.53
	38.00	50.00	12.00	12.95	75.73	11.32	66.43	21.38	12.19
	35.99	50.01	14.00	15.11	71.47	13.42	61.71	23.76	14.53
	34.03	49.97	16.00	18.18	66.31	15.51	56.65	27.10	16.25
313.15 ± 0.2	50.01	49.99	0.00	9.26	90.74	0.00	79.47	20.53	0.00
	48.00	49.97	2.03	10.36	87.81	1.83	76.19	21.81	2.00
	45.98	50.00	4.02	11.35	85.10	3.55	72.82	23.20	3.98
	44.07	49.93	6.00	12.71	81.50	5.79	69.16	24.75	6.09
	41.97	50.04	7.99	15.51	76.97	7.52	64.54	27.53	7.93

nation (R^2) obtained a global error lower than 1.0 %. Table 4 presents the overall experimental composition of the mixtures and the corresponding tie lines for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) at (298.15 ± 0.2) K and (313.15 ± 0.2) K.

Figure 1 shows a comparative diagram of the experimental points of the liquid−liquid equilibrium for the pseudoternary systems in the temperature of (298.15 ± 0.2) K and (313.15 ± 0.2) K. Table 5 shows the relative deviations for the global mass balance of the pseudoternary systems and for mass balance of each compound.

As can be seen, the increase of the temperature promotes a decay of the biphasic region, given the increase of the mutual solubility between refined rice bran oil (1) and ethanol (2). The relative deviations of global mass balance for both systems, evaluated according to the procedure suggested by Marcilla et al.,[28] were 0.10 % and 0.11 %, respectively, and they indicate the good quality of the experimental data. Low values were also observed for the relative deviations for mass balance of all components, where minor deviations were found for the refined rice bran oil (1) and anhydrous ethanol (2). Hexane (3), the minor component in the systems, presented the highest deviations varying by 2.37 % and 3.02 %.

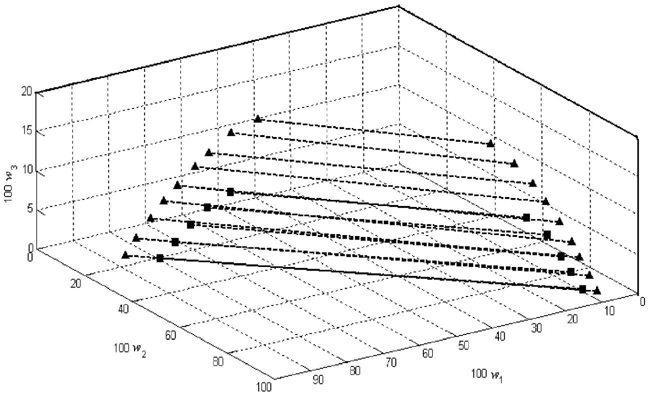

Figure 1. Liquid−liquid equilibrium for the pseudoternary system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) at two temperatures. ▲, (298.15 ± 0.2) K; ■, (313.15 ± 0.2) K; ---, experimental tie lines.

Table 5. Relative Deviations for the Global Mass Balance and for Mass Balance of Each Compound in Equilibrium of the Pseudoternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) at (298.15 ± 0.2) K and (313.15 ± 0.2) K

	average relative deviation/%			global
T/K	oil (1)	ethanol (2)	hexane (3)	%
298.15 ± 0.2	0.62	0.03	2.37	0.10
313.15 ± 0.2	0.01	0.01	3.02	0.11

Table 6 presents the results of the calibration models generated through the NIR method for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) with compositions of (5.08, 7.98, 10.65, and 15.09) % of acid in oil at (298.15 ± 0.2) K.

Table 7 presents the overall experimental composition of the mixtures and the corresponding tie lines for the pseudoquaternary system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) at (298.15 ± 0.2) K, with mass fractions of (5.08, 7.98, 10.65, and 15.09) % of acid in oil. Figure 2 shows a comparative diagram of the experimental points of the liquid−liquid equilibrium obtained for these systems in the temperature range of (298.15 ± 0.2) K.

Through the diagrams present in Figure 2, it can be noted that by increasing the oleic acid composition in the rice bran oil the solubility of the systems increases, furnishing a decrease of the separation region viewed mainly in the basis line of the systems.

Table 8 presents the relative deviation for the global mass balance and for mass balance of each compound of the pseudoquaternary systems. It can be seen that all systems

Table 6. Relative Errors (E_R), Coefficients of Determination (R^2), and Root-Mean-Square Error of Cross-Validation (rmsecv) in the Quantification of the Validation Standards (External, E_R and R^2, and Internal, rmsecv) Using the NIR Method for the Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) + Commercial Oleic Acid (4) with Mass Fractions of (5.08, 7.98, 10.65, and 15.09) % of Acid in Oil at (298.15 ± 0.2) K

		solvent phase				oil phase				E_R
oil[a]		oil (1)	ethanol (2)	hexane (3)	acid (4)	oil (1)	ethanol (2)	hexane (3)	acid (4)	%
5.08	E_R/%	1.36	0.14	0.81	6.18	0.41	0.56	3.10	4.34	2.11
	rmsecv/%	0.21	0.12	0.07	0.12	0.13	0.06	0.04	0.16	
	R^2	0.99787	0.99972	0.99917	0.94695	0.99974	0.99958	0.99986	0.99982	
7.98	E_R/%	3.61	0.32	3.13	4.98	0.29	0.40	1.03	5.29	2.38
	rmsecv/%	2.80	0.44	0.20	0.10	0.09	0.06	0.05	0.08	
	R^2	0.99315	0.99901	0.99948	0.99985	0.99924	0.99956	0.99964	0.99979	
10.65	E_R/%	9.02	0.62	6.95	3.32	0.56	0.78	0.82	4.08	3.27
	rmsecv/%	0.10	0.02	0.19	0.08	0.12	0.05	0.05	0.08	
	R^2	0.95881	0.9902	0.99774	0.99989	0.99995	0.99999	0.99997	0.99978	
15.09	E_R/%	2.17	0.19	5.02	2.14	0.36	0.53	0.99	3.02	1.80
	rmsecv/%	0.78	0.70	0.13	0.11	0.14	0.11	0.07	0.09	
	R^2	0.99646	0.99975	0.99956	0.99989	0.99895	0.99898	0.99978	0.99999	

[a] Each value of the column represents a type of rice bran oil with different quantities of commercial oleic acid. For each oil was added a quantity of commercial oleic acid manually to obtain the amount of desired acid.

Table 7. Liquid−Liquid Equilibrium Data for the Pseudoquaternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) + Commercial Oleic Acid (4) with Mass Fractions of (5.08, 7.98, 10.65, and 15.09) % of Acid in Oil at (298.15 ± 0.2) K

	overall composition				solvent phase				oil phase			
oil[a]	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
5.08	47.42	50.04	0.00	2.54	7.40	88.90	0.00	3.70	80.53	17.81	0.00	1.66
	45.60	49.95	2.00	2.45	8.43	85.88	1.83	3.86	77.75	18.75	2.18	1.32
	42.66	50.02	5.04	2.28	10.04	81.69	4.55	3.72	73.40	20.08	5.12	1.40
	41.71	50.01	6.05	2.23	10.58	80.12	5.58	3.72	71.42	20.97	6.28	1.33
	39.85	50.05	7.97	2.13	11.87	77.64	7.47	3.02	68.93	21.84	8.17	1.06
	37.85	50.08	10.05	2.02	13.23	74.57	9.29	2.91	65.82	23.07	9.99	1.12
	36.00	50.11	11.96	1.93	14.28	71.71	11.33	2.68	61.60	25.05	12.01	1.34
	34.03	50.20	13.95	1.82	18.57	65.26	13.54	2.63	55.07	29.32	14.29	1.32
7.98	46.01	50.02	0.00	3.97	9.38	86.25	0.00	4.37	74.90	21.45	0.00	3.65
	46.01	48.55	1.46	3.98	10.67	83.42	1.40	4.51	72.18	22.31	1.89	3.62
	46.00	46.60	3.40	4.00	12.06	80.41	3.00	4.53	68.91	23.62	3.77	3.70
	46.00	42.91	7.06	4.03	16.73	71.95	6.75	4.57	60.10	28.51	7.66	3.73
10.65	44.98	49.66	0.00	5.36	8.48	85.30	0.00	6.22	73.48	22.10	0.00	4.42
	43.48	49.89	1.45	5.18	9.16	83.22	1.51	6.11	70.94	23.01	1.77	4.28
	41.65	49.98	3.41	4.96	11.92	78.96	2.91	6.21	67.66	24.48	3.60	4.26
	39.80	50.10	5.36	4.74	12.06	77.03	5.49	5.42	64.42	25.65	5.87	4.06
	38.18	50.17	7.10	4.55	15.19	73.04	6.74	5.03	61.69	26.95	7.66	3.70
	36.51	50.07	9.07	4.35	14.94	71.23	8.95	4.88	56.81	29.60	9.81	3.78
15.09	42.46	49.99	0.00	7.55	15.93	75.28	0.00	8.79	69.64	23.88	0.00	6.48
	41.22	50.00	1.45	7.33	17.44	72.41	1.61	8.54	64.27	27.74	1.67	6.32
	39.60	49.96	3.40	7.04	19.82	68.38	3.40	8.40	60.75	29.42	3.71	6.12
	37.91	49.99	5.36	6.74	22.97	63.76	5.08	8.19	54.99	33.23	5.74	6.04

[a] Each value of the column represents a type of rice bran oil with different quantities of commercial oleic acid. For each oil was added a quantity of commercial oleic acid manually to obtain the amount of desired acid.

presented low relative deviations in their global mass balance. For mass balance of components, for refined rice bran oil (1) and anhydrous ethanol (2), values lower than 1 % in both compounds were found. High deviations were obtained for the hexane (3) and commercial oleic acid (4), being in mean (4.2 and 3.4) %, respectively. These results can be considered acceptable because the compositions of the hexane and the oleic acid in both phases are very low, and consequently small fluctuations close to these values promote higher relative deviation. In all cases, the prediction deviations in both phases, solvent and oil, were in the order of 10^{-3} and 10^{-4}, expressed in mass fraction, respectively.

The refined rice bran oil and anhydrous ethanol compositions were determined from the calibration models with minor errors in the predictions of the external validation standards (E_R). The choice of the calibration models based only on minor errors in the prediction of external validation standard was not quite successful for the hexane and the commercial oleic acid. Then, other calibration models with low errors allied to the calculation of the mass balance of the components were tested to evaluate

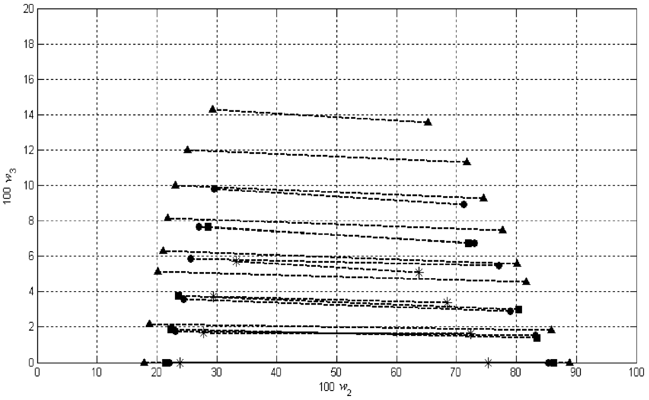

Figure 2. Liquid−liquid equilibrium for the pseudoquaternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) at (298.15 ± 0.2) K. ▲, mass fraction of 5.08 % of acid in oil; ■, mass fraction of 7.98 % of acid in oil; ●, mass fraction of 10.65 % of acid in oil; *, mass fraction of 15.09 % of acid in oil; ---, tie lines.

Table 8. Relative Deviations for the Global Mass Balance and for Mass Balance of Each Compound in Equilibrium of the Pseudoquaternary System Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Hexane (3) + Commercial Oleic Acid (4) at (298.15 ± 0.2) K

	average relative deviation/%				
100 w_4	oil (1)	ethanol (2)	hexane (3)	acid (4)	global/%
5.08	0.84	0.82	1.53	7.10	0.15
7.98	0.02	0.02	5.48	0.55	0.15
10.65	0.03	0.03	4.86	2.33	0.16
15.09	0.04	0.06	4.89	3.62	0.31

Table 9. NRTL Parameters for the Binary Interaction between Refined Rice Bran Oil (1), Anhydrous Ethanol (2), Hexane (3), and Commercial Oleic Acid (4) at Temperatures of (298.15 and 313.15) K

T/K	pair ij	A_{ij}/K	A_{ji}/K	α_{ij}
298.15	12[a]	873.64	1416.8	0.49874
	13	−689.80	160.89	0.50542
	14[a]	−290.55	−165.70	0.49968
	23[b]	313.48	37.076	0.27200
	24[a]	−170.55	4800.0	0.22957
	34	256.33	−676.06	0.67900
313.15	12	−738.33	2295.1	0.26732
	13	−695.22	762.81	0.28831
	23[b]	38.0	1148.1	0.27200

[a] Parameters taken from Rodrigues et al.[25] [b] Parameters taken from Lanza et al.[17]

the best results for each compound and for each system in general. This procedure was done because previous results indicated that the calibration models with minor errors (for the hexane and the oleic acid) in prediction of the external validation standards do not necessarily provide the best quantifications in equilibrium and consequently minor relative deviations for mass balance.

In this work, equilibrium data were not determined for the pseudoquaternary systems at 313.15 K, just at 298.15 K, because of the complexity in selection of calibration and validation standards and sensitivity in reading and interpretation of the near-infrared spectra. Lanza et al.[17] determined liquid−liquid equilibrium data at temperatures higher than 298.15 K for pseudoternary systems in temperatures of 313.15 K, 318.15 K, and 328.15 K and concluded that analytical errors using NIR spectroscopy for systems at high temperatures are higher than at ambient temperature. Quantifying systems containing more than four components also leads to increase analytical error, and therefore, the achievement of good results would be affected.

The NRTL parameters for the studied systems at (298.15 and 313.15) K are presented in Table 9. The average deviations between the experimental and calculated compositions in both phases were calculated according to eq 12 and are shown in Table 10. For the systems at 298.15 K, the NRTL model can describe quite well the liquid−liquid equilibrium data with an average overall deviation of 1.15 %. A low value for deviation was found for the pseudoternary systems at 313.15 K, 0.89 %. Thus, the very low values of deviations for mass balance and low deviations found in the thermodynamic modeling using the NRTL confirm the excellent quality of the experimental data.

Figure 3 shows the good agreement of the experimental and calculated compositions by the NRTL model for the pseudoquaternary system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) at 298.15 K, with a mass fraction of 5.08 % of acid in oil.

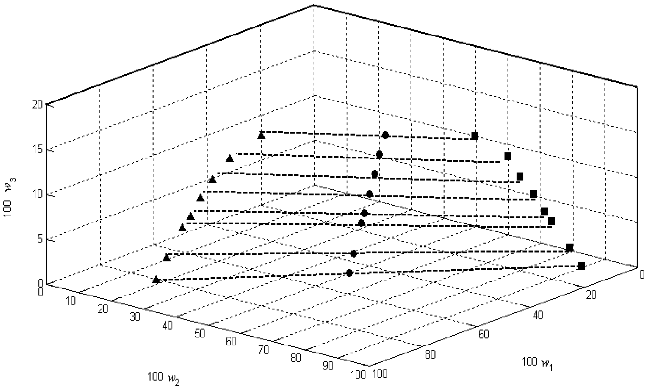

Figure 3. Liquid−liquid equilibrium for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (4) at (298.15 ± 0.2) K, with a mass fraction of 5.08 % of acid in oil. ■, solvent phase; ▲, oil phase; ●, initial mixture/overall composition; ---, NRTL model.

Table 10. Average Deviations between the Experimental and Calculated by NRTL Phase Compositions

system	100 Δw
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) at (298.15 ± 0.2) K	0.75
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (mass fraction of 5.08 % of acid in oil) (4) at (298.15 ± 0.2) K	0.83
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (mass fraction of 7.98 % of acid in oil) (4) at (298.15 ± 0.2) K	1.47
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (mass fraction of 10.65 % of acid in oil) (4) at (298.15 ± 0.2) K	1.56
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) + commercial oleic acid (mass fraction of 15.09 % of acid in oil) (4) at (298.15 ± 0.2) K	1.15
average overall deviation for the systems at 298.15 K	1.15
refined rice bran oil (1) + anhydrous ethanol (2) + hexane (3) at (313.15 ± 0.2) K	0.89

Conclusions

The results presented in this paper show that the NIR method is highly accurate, with the further advantage of being less time intensive than other analytical methods and can guarantee reliable results in the determination of equilibrium data for the fatty systems. The low uncertainties of the experimental data, low deviations obtained in the global mass balance, and good correlation of the experimental data by the NRTL model indicate the good quality of the equilibrium data of interest in the extraction/refining process of the rice bran oil and in the production of biodiesel.

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Received for review March 4, 2009. Accepted May 28, 2009. The authors wish to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, Processes 06/01864-5, 08/56258-8, 05/53095-2, and 04/09591-2), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Process 306250/2007-1), and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for their financial support.

JE9002338