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

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The present work reports liquid−liquid equilibrium data for the systems containing refined rice bran oil + anhydrous ethanol + water + hexane at (298.15 ± 0.2) K with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol and at (313.15 ± 0.2) K with a mass fraction of 4.40 % of water in anhydrous ethanol. The instrumental technique of near-infrared spectroscopy allied to multivariate calibration (in this work, termed "NIR method") was used for determination of the phase compositions. To avoid phase separation in sampling for the system at 313.15 K, the phase samples were diluted with tetrahydrofuran. The results were evaluated by calculation of the global mass balance, resulting in relative deviations lower than 0.5 % to all systems studied in this work. The experimental data were correlated using the NRTL model, and for all systems, the global deviation was less than 1.0 %. These results indicate the good quality of the experimental data and that the NIR method gives good results even when the components have a low mass fraction in the mixture.

Introduction

The vegetable oil sector has been one of the most dynamic of the world agriculture in the last few decades. The importance of Brazil as a producer and exporter country of oilseeds is evidenced by the numbers of the international market. Among several species of oilseeds, the 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 rice bran. The extraction of oil from the rice bran aggregates value to the rice production. This oil has nutritional and nutraceutical properties and, therefore, the interest of industries in its use. Medical studies indicate the hypocholesterolemic effect of rice bran oil in humans and animals. The majority of such studies suggests that rice bran oil is more effective in decreasing serum and liver cholesterol concentrations than oils with similar fatty acid composition, such as groundnut oil.[1−3]

Crude vegetable oils are obtained by extraction from a solid matrix by pressing or using an organic solvent.[4,5] In the extraction process, the total/partial substitution of hexane petroleum fractions becomes necessary because this usual solvent is highly flammable and suspected to be dangerous to human health. The full treatment to make the rice bran oil suitable for human consumption consists of preparation, extraction from bran using solvent, solvent stripping, degumming, bleaching, deacidification, and deodorization.[6]

The vegetable oils can be deacidified by the traditional processes, such as chemical or physical refining; however, these present several disadvantages, such as the high losses of neutral oil, large production of soapstock, and high energy consumption.[7,8] Furthermore, a significant portion of the nutraceutical rice bran oil[3] and other desirable compounds is lost during the refining process. Some new techniques that may be tried out are biological deacidification, reesterification, solvent extraction, supercritical fluid extraction, and membrane technology.[9]

An alternative refining process carried out at room temperature and atmospheric pressure that avoids the formation of waste products is liquid−liquid extraction, which consists of using a solvent that has greater affinity with the free fatty acids (FFA) than the triacylglycerols (TAG), reducing the energy consumption and minimizing the losses of neutral oil. For the difference of the boiling point of each component, the posterior recovery of the solvent becomes possible. Several studies showed excellent results in the employment of short chain alcohols as solvent, such as anhydrous or hydrated ethanol, which present low toxicity, easy recovery, good values of selectivity, and distribution coefficients of free fatty acid.[10−14] Moreover, environmental and energy issues have focused attention on the use of vegetable oils in biodiesel production by transesterification reactions.

The knowledge of the liquid−liquid equilibrium of such fatty systems is an important stage in the optimization of the production of edible oil by liquid−liquid extraction or the production of biodiesel by transesterification reactions. Furthermore, knowledge of the behavior of these systems involving crude vegetable oil/solvents configures the principal topic in mass transfer operations and reactive mixtures. Thus, the aim of this work was to investigate the phase equilibrium of refined rice bran oil + anhydrous ethanol + water + hexane at 298.15 K, with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol and at 313.15 K with a mass fraction of 4.40 % of water in anhydrous ethanol, using NIR spectroscopy coupled with chemometric methods (multivariate calibration) based on statistical and mathematical procedures for the quantification of the components in each phase. The experimental data were correlated by the NRTL model.

Experimental Section

Materials. The refined rice bran oil was obtained commercially from Irgovel S.A. (RS/Brazil) and stored in a place

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Table 1. Fatty Acid Composition of the Refined Rice Bran Oil

fatty acids				M	composition	
usual name	proper name	symbol	Cx:y[a]	g·mol^{-1}	100 w	100 x
lauric	dodecanoic	L	C12:0	200.32	0.01	0.01
myristic	tetradecanoic	M	C14:0	228.37	0.24	0.29
palmitic	hexadecanoic	P	C16:0	256.42	17.92	19.07
palmitoleic	*cis*-9-hexadecenoic	Po	C16:1	254.41	0.15	0.16
stearic	octadecanoic	S	C18:0	284.48	2.08	2.01
oleic	*cis*-9-octadecenoic	O	C18:1	282.46	38.99	38.44
elaidic[b]	*trans*-9-octadecenoic		C18:1T[b]		0.04	0.03
linoleic	*cis*-9,*cis*-12-octadecadienoic	Li	C18:2	280.45	36.39	36.13
linolenic	all-*cis*-9,12,15-octadecatrienoic	Le	C18:3	278.43	1.87	1.87
translinolenic[b]	all-*trans*-9,12,15-octadecatrienoic		C18:3T[b]		0.42	0.38
arachidic	eicosanoic	A	C20:0	312.53	0.71	0.63
gadoleic	*cis*-9-eicosanoic	Ga	C20:1	310.51	0.51	0.46
behenic	docosanoic	Be	C22:0	340.58	0.28	0.23
lignoceric	tetracosanoic	Lg	C24:0	368.64	0.39	0.29

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

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

		M	composition	
main TAG[a]	group	g·mol^{-1}	100 w	100 x
POP[b]	50:1[c]	833.36	5.12	5.32
PLiP	50:2	831.34	5.11	5.32
POS	52:1	861.41	1.04	1.05
POO	52:2	859.40	11.18	11.27
POLi	52:3	857.38	19.53	19.73
PLiLi	52:4	855.36	10.54	10.67
PLiLe	52:5	853.35	1.23	1.25
SOO	54:2	887.45	1.50	1.46
OOO	54:3	885.43	7.24	7.08
OOLi	54:4	883.42	15.63	15.32
OLiLi	54:5	881.40	14.87	14.62
LiLiLi	54:6	879.38	6.13	6.04
LiLiLe	54:7	877.37	0.88	0.87

[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 fatty acid esterified to glycerol. [c] x:y, x = number of carbons (except carbons of glycerol), y = number of double bonds.

with controlled temperature. The solvents used in this work were anhydrous ethanol with purity of 99.9 % and hexane and tetrahydrofuran, both with purity of 99.0 %, all from Merck (Germany). Aqueous solvents with mass fractions of (4.14, 4.40, 9.84, and 14.79) % of water were prepared by the addition of deionized water to anhydrous ethanol. The reagent Karl Fischer (CombiTitrant 5, Merck, Germany) was also used. In this work, tetrahydrofuran was chosen as solvent to dilute the analytical samples because it is an aprotic and moderately polar solvent and can dissolve a wide range of nonpolar and polar chemical compounds. There are many other solvents that could be used to dilute the analytical samples, but tetrahydrofuran has high solvency power and could dissolve efficiently all samples of studied systems in this work, which contain nonpolar (rice bran oil and hexane) and polar (ethanol and water) compounds. Solvent mixtures would not be appropriate in our case because they would increase the component quantity and would make the quantification of the samples using the NIR method difficult. Quantifying systems containing more than five components leads to an increase of analytical error using the NIR method because of complexity in the selection of calibration and validation standards and sensitivity in reading and interpretation of the near-infrared spectra.[15−17]

The refined rice bran oil used in this work was analyzed by gas chromatography for the fatty acid methyl esters to determine the fatty acid composition, according to the official method (1−62) of the AOCS.[18] Prior to the chromatographic analysis, the fatty sample was prepared in the form of fatty acid methyl esters according to the method of Hartman and Lago.[19] The chromatographic analyses were carried out using a capillary gas chromatography system under the same experimental conditions shown in Priamo et al.[17]

The fatty acid composition of the vegetable oil is presented in Table 1, and from this composition, it was possible to determine the probable triacylglycerol composition of the refined rice bran oil (Table 2) using the algorithm suggested by Antoniosi Filho et al.[20]

To calculate the probable triacylglycerol composition, the quantities of trans isomers (see Table 1) were added 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. The results shown in Tables 1 and 2 allow us to calculate the average molar mass of the refined rice bran oil as 865.1 g·mol^{-1}.

Apparatus and Procedures. Measure of Density. The densities were determined experimentally at 298.15 K, using a digital densimeter (Anton Paar model DMA-58, Austria) of oscillatory tube, with precision of ± 0.00001 g·cm^{-3}, previously calibrated with air and water (distilled and deionized) at the temperature of the analysis. A thermostat inside the instrument allows the control of the temperature at ± 0.01 K.

Determination of Solubility Curves. The solubility curves were carried out by the cloud-point method[17] and are necessary to obtain preliminary information about the system of interest and auxiliary in the selection of the validation and calibration standards used by the NIR method for the quantification of the components in equilibrium. To determine the solubility curves, the same procedure of cloud-point method described by Priamo et al.[17] was used in this work. The complete details can be seen in that work.

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.[21] Known quantities of each component (rice bran oil, anhydrous ethanol, water, and hexane) were put in contact inside the glass cells to reach equilibrium following the same procedure described by Priamo et al.[17] The complete details can be seen in that work. In the end of the experiment, the samples of the phases were carefully collected for subsequent quantification of the components through the NIR method. For the systems at 313.15 K, a dilution technique was investigated. The phase samples of these systems were collected in duplicate. One of them was analyzed at the temperature of the experiment, and the other one was diluted with tetrahydrofuran to avoid the phase separation with the decrease of temperature to ambient temperature. This last sample was analyzed at 298.15 K.

NIR Method. The instrumental technique of near-infrared spectroscopy was used in combination with the method of multivariate regression for partial least-squares (PLS) and the chemometric method (multivariate calibration) based on statistical and mathematical procedures for the analytical determination of the mass fractions of the components in each phase of the system in equilibrium. In fact, for the utilization of the NIR spectroscopy, it is necessary to make an equipment calibration, through multivariate calibration relating the components of the studied system for then explorer to the quantitative determinations conjunctly with the infrared spectroscopy. To develop calibration models appropriate for each system, sets of mixtures with known compositions close to the solubility curve, previously determined, were selected.

The solubility curve was divided into two parts, the oil phase and the solvent phase, and for each part, 30 mixtures were prepared by gravimetry and used as calibration standards. A further set of about 10 mixtures for each part of the solubility curve was also prepared by gravimetry and used as an external validation set to check the accuracy of the calibration models.[15−17]

It is important to point out that in systems with water its composition was checked through Karl Fischer titration, according to the official method Ca 23−55 of the AOCS.[22]

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, Winchester, United Kingdom) assisted by temperature controller (Ventacon, model D-2). Thereby, the NIR spectra were able to be measured at temperatures of (298.15 ± 0.5 and 313.15 ± 0.5) K. Complete details about the procedures to measure the NIR spectra and the description of the PLS regression method can be seen in the work of Priamo et al.[17]

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) for the external validation standards. In the internal validation, the performance of the calibration models was 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

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

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

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".[23,24] The cross-validation and the corresponding rmsecv values together with the values of the relative errors were used for selecting the number of PLS factors considered in the construction of the calibration models for the systems. The uncertainties of the compositions for the NIR method varied within the following ranges: (0.02 to 0.70) % for refined rice bran oil, (0.03 to 0.58) % for anhydrous ethanol, (0.01 to 0.02) % for water, and (0.06 to 0.29) % for hexane, being the lowest figures obtained for the lowest compositions.

Theoretical Calculations

Calculation of the Deviations in the Mass Balance of the Phases. The quality and accuracy of the results of the liquid−liquid equilibrium experiments were tested according to the procedure developed by Marcilla et al.[25] and already applied to fatty systems by several works.[12,15−17,26] The balance equations and calculations for relative deviation for the global mass balance and for mass balance of each component used in this work are presented by Priamo et al.[17]

The procedure to determine the relative deviation for global mass balance 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. The relative deviation for mass balance of each compound in each tie line could be calculated comparing the actual mass of the component put in the overall composition by the sum of the calculated masses of the component in each phase (solvent and oil phases). These calculated masses for each component are obtained by the multiplication of the experimental mass fractions, determined by the NIR method, and the calculated masses for both liquid phases (solvent and oil phases).

Thermodynamic Modeling. The NRTL parameters were adjusted to the experimental data determined for the systems. Although the RBO is a mixture of many components, the several triacylglycerols present in the vegetable oil behave in a very similar way in the liquid−liquid system under analysis, and in this case, as an approach, 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] which proved the reliability of this hypothesis.

The mass fraction was used as a composition unit due to the large difference in molar mass of the components in the systems.[13−17,26−29] Lanza et al.[15] showed the activity coefficient equations and the isoactivity criterion, expressed in terms of mass fraction and for multicomponent mixtures.

Estimation of the NRTL parameters was based on minimization of the objective composition function following the procedure developed by Stragevitch and d'Avila.[30] The objective function of composition can be seen in the works of Lanza et al.[15,16] and Priamo et al.[17]

The parameter estimation procedure involves flash calculations[31] for the middle point compositions of the experimental tie lines and minimization of the objective function of composition.

The average deviations between the experimental and calculated compositions in both phases were calculated according to Lanza et al.[15,16] and Priamo et al.[17]

Results and Discussion

The components studied in this work received the following notation: refined rice bran oil (1), anhydrous ethanol (2), water (3), hexane (4) and tetrahydrofuran (5).

The content of water in refined rice bran oil was determined by Karl Fischer titration. The value obtained was 0.05 %, and this was always considered in the overall experimental composition of the mixtures and the calculation of calibration and validation standards.

Table 3 shows the results of the calibration models generated through the NIR method for the systems containing refined rice

Table 3. Relative Errors (E_R) and Root-Mean-Square Error of Cross-Validation (rmsecv) in the Quantification of the Validation Standards (External, E_R, and Internal, rmsecv) Using the NIR Method for the Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (298.15 ± 0.2) K with Mass Fractions of (4.14, 9.84, and 14.79) % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

		solvent phase				oil phase				
100 w_3'		oil	ethanol	water	hexane	oil	ethanol	water	hexane	E_R/%
4.14	E_R/%	12.50	0.45	0.20	1.13	0.25	0.40	3.48	1.14	2.44
	rmsecv/%	0.64	0.58	0.01	0.09	0.70	0.45	0.01	0.29	
9.84	E_R/%	66.43	0.13	0.56	3.37	0.07	0.36	0.83	2.10	9.23
	rmsecv/%	0.04	0.04	0.02	0.07	0.06	0.04	0.01	0.06	
14.79	E_R/%	9.15	0.06	0.02	1.19	0.13	0.59	1.89	1.68	1.84
	rmsecv/%	0.02	0.09	0.01	0.09	0.08	0.03	0.01	0.08	

bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (298.15 ± 0.2) K with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol using the NIR method: the errors between the compositions calculated by the calibration models and those calculated by gravimetry for the external validation standards (E_R) and for the cross-validation standards (rmsecv).

In Table 3, we can observe that the errors for the oil in the solvent phase and for water in the oil phase are higher than the other ones due to the small mass fraction of these components in those phases. The oil mass fraction in validation standards varied in the range of 0.0009 to 0.0011, and any small variations in the results lead to greater errors. However, the deviations of the calibration models present low values for the root-mean-square errors of cross-validation (rmsecv), for both phases, evident for points lined up in the tie line, shown in Figure 1.

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) + water (3) + hexane (4) at (298.15 ± 0.2) K with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol.

Figure 1 shows a comparative diagram of the experimental points of the liquid−liquid equilibrium for the three pseudoquaternary systems at (298.15 ± 0.2) K with different mass fractions of water in anhydrous ethanol. Through Figure 1, the effect of water content in the hexane distribution coefficient can be seen. Whereas the amount of water (highly polar) in the system increases, the hexane (apolar) tends to dislocate to the oil phase (apolar). The increase of the water in the system promotes an increase of the biphasic region, due to the decrease of the mutual solubility between refined rice bran oil and solvent, ethanol + water, inconvenient for obtaining a monophasic system desired in the production of biodiesel.

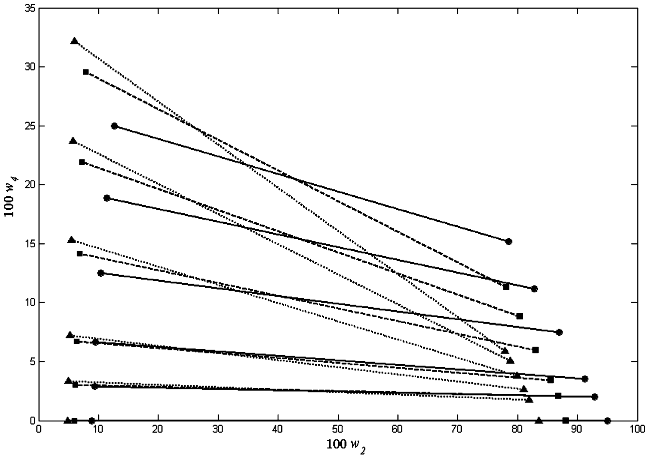

Figure 1. Liquid−liquid equilibrium for the pseudoquaternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (298.15 ± 0.2) K: ●, mass fraction of 4.14 % of water in anhydrous ethanol; —, tie lines; ■, mass fraction of 9.84 % of water in anhydrous ethanol; ----, tie lines; ▲, mass fraction of 14.79 % of water in anhydrous ethanol; ····, tie lines.

Table 5 shows the relative deviation for the global mass balance of the pseudoquaternary systems and for mass balance of each compound. The deviations for global mass balance for the systems evaluated according to the procedure suggested by Marcilla et al.[25] were (0.14, 0.41, and 0.40) % for the systems with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol, respectively. This indicates the good quality of the experimental data. Minor relative deviations were found for the refined rice bran oil and anhydrous ethanol. Water is the minor component, and due to that, it presented higher deviations of (5.37, 6.97, and 9.52) %. The system with 14.79 % in mass of water in anhydrous ethanol presented undesirable effects in two tie lines with higher mass fraction in hexane, as formations of small coalesced drops of the oil phase distributed in the solvent phase, and these remained until the end of the rest time (24 h). It can be explained due to the similarity in phase density (Table 6). Also in the last one, which corresponds to the tie line with 19.99 % of hexane in the global composition, phase inversion occurred.

Tables 7 and 8 present the comparison between content of water determined by Karl Fischer titration and by the NIR method for the pseudoquaternary systems determined at (298.15 and 313.15) K, respectively, with different contents in mass of water in anhydrous ethanol. It is possible to observe a good agreement between the analyses for both phases, but as water is presented in a very small mass fraction in the systems and any fluctuations on the measurement give high deviations.

To avoid phase separation in the samples of liquid−liquid equilibrium experiments at higher temperatures due to the decrease of temperature, a dilution technique was tested. This technique consists of diluting the samples with an inert solvent to keep them homogeneous.

First, to test this dilution technique, a well-known pseudoternary system, rice bran oil + anhydrous ethanol + hexane at 298.15 K,[17] was selected, and two samples of each phase were collected. One of these samples followed the usual NIR method. The other one was diluted with tetrahydrofuran in approximately 50 % in mass, before measurement by the NIR method. The composition of the diluted samples was calculated in free basis of tetrahydrofuran. The results showed a good agreement between both samples.

A second test was done with a well-known system at higher temperature, rice bran oil + anhydrous ethanol + hexane at 313.15 K,[17] to evaluate the effect of temperature in the dilution technique. Here again, two samples of each phase were collected. The nondiluted sample was kept at the temperature of the experiment to avoid phase separation in the quartz cell of the NIR spectrometer. The diluted sample was analyzed at room temperature. The results again showed a good agreement between both samples, and then the dilution technique could

Table 4. Liquid−Liquid Equilibrium Data for the Pseudoquaternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (298.15 ± 0.2) K with Mass Fractions of (4.14, 9.84, and 14.79) % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

	overall composition				solvent phase				oil phase			
100 w_3'	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
4.14	49.97	47.93	2.10	0.00	0.68	95.07	4.25	0.00	90.90	8.94	0.16	0.00
	47.46	47.93	2.10	2.51	0.82	92.91	4.23	2.04	87.54	9.39	0.19	2.88
	44.99	47.92	2.09	5.00	1.00	91.22	4.22	3.56	83.65	9.51	0.19	6.65
	40.00	47.93	2.09	9.98	1.40	86.91	4.19	7.50	76.83	10.40	0.25	12.52
	35.00	47.92	2.09	14.99	1.81	82.85	4.15	11.19	69.43	11.38	0.29	18.90
	30.09	47.93	2.08	19.90	2.22	78.52	4.10	15.16	62.07	12.61	0.35	24.97
9.84	49.97	45.08	4.95	0.00	0.84	88.55	10.61	0.00	93.77	5.99	0.24	0.00
	47.47	45.09	4.94	2.50	0.63	86.79	10.48	2.10	90.60	6.10	0.25	3.05
	44.97	45.09	4.94	5.00	0.62	85.53	10.42	3.43	86.74	6.32	0.25	6.69
	40.01	45.08	4.94	9.97	0.64	83.06	10.32	5.98	78.78	6.80	0.26	14.16
	35.00	45.08	4.94	14.98	0.56	80.39	10.22	8.83	70.51	7.29	0.26	21.94
	30.09	45.08	4.93	19.90	0.46	78.12	10.11	11.31	62.32	7.84	0.27	29.57
14.79	49.98	42.60	7.42	0.00	0.05	83.57	16.38	0.00	94.87	4.89	0.24	0.00
	47.47	42.61	7.42	2.50	0.05	81.96	16.24	1.75	91.44	4.97	0.24	3.35
	44.97	42.60	7.42	5.01	0.05	81.07	16.22	2.66	87.36	5.17	0.25	7.22
	39.99	42.60	7.42	9.99	0.05	79.97	16.18	3.80	79.02	5.46	0.24	15.28
	34.99	42.60	7.41	15.00	0.06	78.75	16.15	5.04	70.35	5.73	0.24	23.68
	30.05	42.56	7.40	19.99	0.06	78.18	16.09	5.67	61.79	5.84	0.24	32.13

Table 5. Relative Deviations for the Global Mass Balance and for Mass Balance of Each Compound in Equilibrium of the Pseudoquaternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (298.15 ± 0.2) K with Mass Fractions of (4.14, 9.84, and 14.79) % of Water in Anhydrous Ethanol (100 w_3') and at (313.15 ± 0.2) K with Mass Fraction of 4.40 % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

		average relative deviation/%				
T/K	100 w_3'	oil (1)	ethanol (2)	water (3)	hexane (4)	global deviation/%
298.15 ± 0.2	4.14	0.04	0.02	5.37	1.13	0.14
	9.84	0.10	0.12	6.97	1.88	0.41
	14.79	0.49	0.28	9.52	2.89	0.40
313.15 ± 0.2[a]	4.40	0.25	0.08	12.33	3.62	0.12

[a] System determined with dilution of analytical samples with tetrahydrofuran (5).

Table 6. Density of the Phases in Equilibrium for the Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (298.15 ± 0.2) K with Mass Fraction of 14.79 % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

	ρ/g·cm^{-3}	
overall composition in hexane (100 w_4)	solvent phase	oil phase
15.00	0.81716	0.83285
19.99	0.81344	0.80862

Table 7. Comparison between Mass Fractions of Water Determined by Karl Fischer Titration and by the NIR Method for the Pseudoquaternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (298.15 ± 0.2) K with Mass Fractions of (4.14, 9.84, and 14.79) % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

		100 w_3' = 4.14 %		100 w_3' = 9.84 %		100 w_3' = 14.79 %	
tie lines and phases		Karl Fischer	E_R/%	Karl Fischer	E_R/%	Karl Fischer	E_R/%
TL 1[a]	SP[b]	4.27	0.47	10.25	3.51	17.02	3.76
	OP[b]	0.19	15.79	0.26	7.69	0.32	25.0
TL 2	SP	4.23	0.01	10.11	3.66	16.94	4.13
	OP	0.2	5.00	0.27	7.41	0.33	27.27
TL 3	SP	4.16	1.44	10.0	4.20	15.81	2.59
	OP	0.21	9.52	0.27	7.41	0.30	16.67
TL 4	SP	4.86	13.79	9.81	5.20	16.86	4.03
	OP	0.28	10.71	0.29	10.34	0.34	29.41
TL 5	SP	4.63	10.37	9.53	7.24	15.02	7.52
	OP	0.32	9.38	0.32	18.75	0.33	27.27
TL 6	SP	4.24	3.30	9.43	7.21	14.91	7.91
	OP	0.37	5.41	0.34	20.59	0.30	20.0

[a] TL is tie line. [b] SP is solvent phase and OP is oil phase.

Table 8. Comparison between Mass Fractions of Water Determined by Karl Fischer Titration and by the NIR Method for the Pseudoquaternary Systems Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (313.15 ± 0.2) K with Mass Fraction of 4.40 % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

tie line and phases		Karl Fischer	E_R/%
TL 1[a]	SP[b]	4.61	4.56
	OP[b]	0.34	32.35
TL 2	SP	4.49	6.68
	OP	0.36	22.22
TL 3	SP	4.39	8.43
	OP	0.39	15.38
TL 4	SP	4.56	4.61
	OP	0.40	12.5
TL 5	SP	3.99	13.78
	OP	0.46	2.17
TL 6	SP	3.95	13.67
	OP	0.51	11.76

[a] TL is tie line. [b] SP is solvent phase and OP is oil phase.

be used in a new liquid−liquid equilibrium experiment at high temperature. The relative deviations for mass balance of components for the system using the dilution technique were lower than those found by Priamo et al.[17]

Table 9 presents the results of the calibration models generated by the NIR method for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (313.15 ± 0.2) K, with a mass fraction of 4.40 % of water in anhydrous ethanol, using the dilution technique of analytical samples with tetrahydrofuran (5): the low errors in the quantification for the external validation standards (E_R) and for the cross-validation standards (rmsecv).

The calibration and external validation standards generated for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) with mass fraction of 4.14 % of water in anhydrous ethanol at (298.15 ± 0.2) K were diluted with tetrahydrofuran (5) at dilution factor well-known of approximately 50 % (in mass fraction). Only the refined rice bran oil (1) in solvent phase presented high value error, due to small fraction when this is submitted to the dilution.

In Table 10 are shown the overall experimental composition of the mixture and the corresponding tie lines for the system containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (315.15 ± 0.2) K, with a mass fraction

Table 9. Relative Errors (E_R) and Root-Mean-Square Error of Cross-Validation (rmsecv) in the Quantification of the Validation Standards (External, E_R, and Internal, rmsecv) Using the NIR Method for the System Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (313.15 ± 0.2) K with a Mass Fraction of 4.40 % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

		solvent phase				oil phase				
100 w_3'		oil	ethanol	water	hexane	oil	ethanol	water	hexane	E_R/%
4.40	E_R/%	7.25	0.04	0.33	1.27	0.28	0.39	2.11	0.64	1.54
	rmsecv/%	0.10	0.06	0.01	0.13	0.13	0.03	0.01	0.10	

Table 10. Liquid−Liquid Equilibrium Data for the Pseudoquaternary System Containing Refined Rice Bran Oil (1) + Anhydrous Ethanol (2) + Water (3) + Hexane (4) at (313.15 ± 0.2) K with Mass Fraction of 4.40 % of Water in Anhydrous Ethanol (100 w_3') in Overall Composition

overall composition				solvent phase				oil phase			
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
49.97	47.81	2.22	0.00	4.54	90.64	4.82	0.00	87.20	12.35	0.45	0.00
47.46	47.80	2.22	2.52	4.15	89.59	4.79	1.47	83.33	13.15	0.44	3.08
44.97	47.80	2.22	5.01	4.67	87.14	4.76	3.43	79.80	13.77	0.45	5.98
39.93	47.88	2.22	9.97	4.74	83.08	4.77	7.41	72.61	14.97	0.45	11.97
34.99	47.80	2.22	14.99	6.39	77.98	4.54	11.09	64.89	17.33	0.45	17.33
30.08	47.80	2.21	19.91	7.05	72.84	4.49	15.62	57.34	18.85	0.45	23.36

of 4.40 % of water in anhydrous ethanol and using the dilution technique of the analytical samples with tetrahydrofuran (5).

In this work, equilibrium data were not determined for systems at 313.15 K containing mass fractions higher than 4.40 % of water in anhydrous ethanol because of the complexity in the selection of calibration and validation standards and sensitivity in reading and interpretation of the near-infrared spectra in samples containing high water content at a temperature higher than ambient temperature. Lanza et al.[15] determined liquid−liquid equilibrium data in 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 quantifying systems containing more than four components using NIR spectroscopy for systems at higher temperatures than ambient temperature leads to an increase in analytical error, and therefore the determination of good results would be affected.

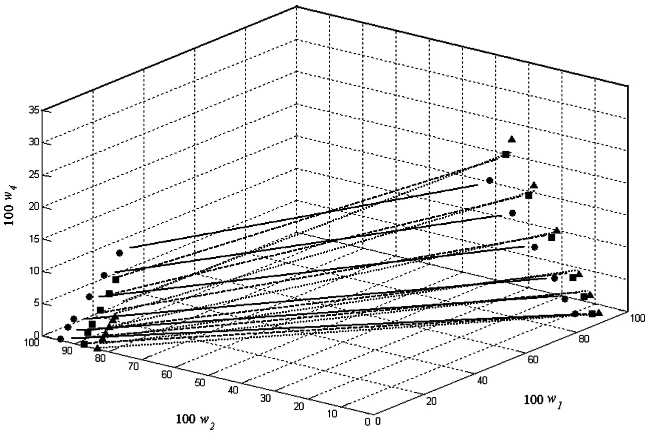

Figure 2. Liquid−liquid equilibrium for the pseudoquaternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (298.15 ± 0.2) K. ●, mass fraction of 4.14 % of water in anhydrous ethanol: —, NRTL model; ■, mass fraction of 9.84 % of water in anhydrous ethanol; ----, NRTL model; ▲ mass fraction of 14.79 % of water in anhydrous ethanol; ····, NRTL model.

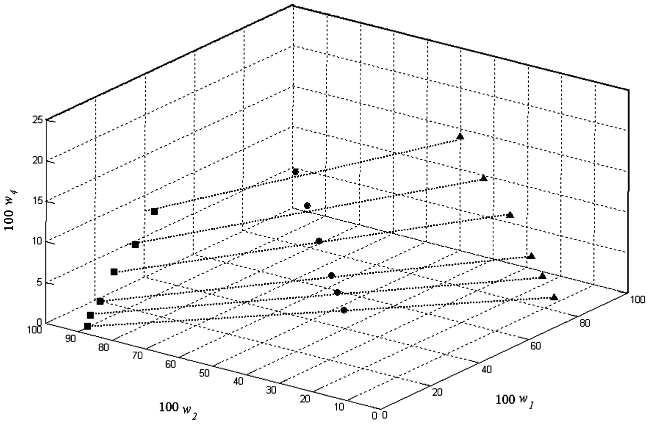

Figure 3. Liquid−liquid equilibrium for the pseudoquaternary systems containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at (313.15 ± 0.2) K, with mass fraction of 4.40 % of water in anhydrous ethanol: ▲, oil phase; ■, solvent phase; ●, initial mixture/overall; ····, NRTL model.

The relative deviations for the global mass balance and for the mass balance of each compound in the equilibrium of the pseudoquaternary system at (313.15 ± 0.2) K, with a dilution technique with tetrahydrofuran (5), are shown in the Table 5. It is possible to observe high relative deviations for the components water (3) and hexane (4), but these are in small mass fraction in the systems and diluted to measurement. However, the other components presented low relative deviations, substantiated the viability of the use of the dilution technique, and also measurement on NIR spectroscopy allied to chemometric in complex systems and temperature higher than 298.15 K.

The experimental data sets for all pseudoquaternary systems were correlated by the NRTL model (Figures 2 and 3), and the NRTL parameters are presented in Table 11.

Figure 2 shows a comparative diagram of the experimental points of the liquid−liquid equilibrium for three pseudoquaternary systems at (298.15 ± 0.2) K with mass fractions of (4.14, 9.84, and 14.79) % of water in anhydrous ethanol described by the NRTL model. Figure 3 presents the calculated and experimental data of the pseudoquaternary system containing refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) at 313.15 K, with mass fraction of 4.40 % of water in anhydrous ethanol.

The average deviations between the experimental and calculated compositions in both phases were calculated according to Lanza et al.[15,16] and Priamo et al.[17] and are shown in Table 12.

As can be seen in Figure 2, the NRTL model correctly describes the experimental data for the pseudoquaternary systems at 298.15 K, with an average overall deviation of 0.95 % (Table 12). For the system at 313.15 K, the NRTL model was also representative according to the low average overall deviation of 0.55 %. Thus, the very low values of relative deviations for the mass balance and low deviations found in the thermodynamic modeling using the NRTL model confirm the excellent quality of the experimental data.

Table 11. NRTL Parameters for the Binary Interaction between Refined Rice Bran Oil (1), Anhydrous Ethanol (2), Water (3), and Hexane (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[a]	−26.977	4624.6	0.16580
	14	−689.80	160.89	0.50542
	23[a]	−10.984	−173.64	0.15018
	24[b]	313.48	37.076	0.27200
	34	1701.2	1565.0	0.20000
313.15	12	−738.33	2295.1	0.26732
	13	−134.28	1301.8	0.69985
	14	−695.22	762.81	0.28831
	23	2429.1	−546.04	0.70000
	24[b]	38.0	1148.1	0.27200
	34	3000.0	1019.5	0.20347

[a] Parameters taken from Rodrigues et al.[28] [b] Parameters taken from Lanza et al.[15]

Table 12. Average Deviations between the Experimental and Calculated by NRTL Phase Compositions

system	100 Δw
refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) (mass fraction of 4.14 % of water in anhydrous ethanol) at (298.15 ± 0.2) K	1.22
refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) (mass fraction of 9.84 % of water in anhydrous ethanol) at (298.15 ± 0.2) K	0.70
refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) (mass fraction of 14.79 % of water in anhydrous ethanol) at (298.15 ± 0.2) K	0.83
average overall deviation for the systems at 298.15 K	0.95
refined rice bran oil (1) + anhydrous ethanol (2) + water (3) + hexane (4) (mass fraction of 4.40 % of water in anhydrous ethanol) at (313.15 ± 0.2) K	0.55

Conclusions

Phase equilibrium data with good accuracy for the system refined rice bran oil + anhydrous ethanol + water + hexane were experimentally obtained at (298.15 and 313.15) K using NIR spectroscopy for quantification of the phase compositions. The use of dilution of the analytical samples with an inert solvent, mainly in experiments at higher temperature than environment, demonstrates a viable alternative to get good results. Low deviations are obtained in the global mass balance, and the effect of temperature in the use of NIR spectroscopy is minimized.

Despite of complexity of the studied systems, the estimated parameters for the NRTL model are representative since the description of the liquid−liquid equilibrium for all the systems presented deviations lower than 1.22 % in relation to the experimental data. These parameters are useful in the design and simulation of liquid−liquid extractors, in the refining process of the rice bran oil, and in the production of biodiesel.

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