Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol + Water at 298.2 K

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This work presents experimental data for the model system refined rice bran oil + commercial oleic acid + ethanol + water at 298.2 K. These data were correlated by the NRTL and UNIQUAC models, with a global deviation of approximately 0.7% for both models. The equilibrium of crude rice bran oil + aqueous ethanol was predicted with success using the adjusted interaction parameters, with deviation between calculated and experimental results not higher than 0.54%. The results showed that the addition of water to the solvent increases the solvent selectivity, reducing the losses of neutral oil and nutraceutical compounds, and expands the region of phase splitting, allowing the refining of highly acidic crude rice bran oils by solvent extraction.

Introduction

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]

The lowering of cholesterol levels by rice oil may be attributed to its high level of unsaponifiable matter.[1,2,4] Crude rice bran oil may contain up to 5% of unsaponifiable matter. This level is reduced to values up to 1.5% in the refined rice bran oil. In contrast, most refined vegetable oils contains only 0.3−0.9% of unsaponifiable matter.[5] The crude rice bran oil unsaponifiable matter contains a unique complex of antioxidant compounds, such as (100 to 1000) ppm of vitamin E (tocopherols and tocotrienols) and (0.9 to 2.9)% of γ-orizanol. This last compound is in fact a complex mixture of triterpene alcohols and phytosterols esterified with ferulic acid.[6,7]

In addition to the hypocholesterolemic activity of these rice oil minor compounds, the isolated ingestion of γ-orizanol may decrease early atherosclerosis,[3] to treat nerve imbalance disorders of menopause[8] and inflammatory processes.[9] In relation to vitamin E, with special attention to the tocotrienol fraction, some investigations suggest that these compounds are useful in the prevention of cardiovascular disease and some forms of cancer.[10−12]

Despite these advantages that make the rice bran oil a functional food, its world production in edible grade is very low (1% of all vegetable oil production) due to difficulties in its processing. The production and refining of vegetable oils consist in extraction from oilseeds, bran, or fruit pulps using hexane petroleum fractions as solvent,[13,14] solvent stripping, degumming, bleaching, deacidification, and deodorization.[15,16] In comparison with other vegetable oils, crude rice oil tends to contain higher levels of free fatty acids (FFA) induced by intensive enzymatic activity. The high FFA content makes the oil deacidification difficult by the traditional processes, chemical or physical refining.

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The chemical refining is based on a saponification reaction of FFA with an alkali solution and can result in oil losses of (18 to 22) mass % according to Orthoefer;[3] furthermore, the production of soapstock is very large. In relation to physical refining, which is performed at high temperatures and very low pressures, several authors mention disadvantages, such as alterations in oil color, reduction of stability to oxidation, and high energy consumption.[17−19]

It should be further emphasized that both processes induce a significant loss of nutraceutical compounds. Rice bran oil refined by the chemical method contains less than 0.2 mass % of oryzanol,[3,20] and, in the physical refining, a significant portion of vitamin E is stripped away with the distillate during the deodorization step.[4]

An alternative refining process, performed under more mild conditions (room temperature and atmospheric pressure), is the deacidification by liquid−liquid extraction, which also avoids the formation of waste products. Liquid−liquid extraction for oil refining is based on the difference of the solubilities of FFA and neutral triacylglycerols in an appropriate solvent.[21] Bhatacharyya et al.[22] and Shah and Venkatesan[23] studied the deacidification of rice bran and groundnut oils using aqueous 2-propanol as solvent. Kim et al.[24] and Kale et al.[18] tested methanol in the refining of rice bran oil. All studies showed a decreasing of the oil acidic value. Deacidification by liquid−liquid extraction may produce vegetable oils with low acidic levels and simultaneously minimize the loss of neutral oil and nutraceutical compounds.[24]

Phase equilibrium data are necessary for the design of extraction processes. Batista et al.[25,26] and Gonçalves et al.[27] reported liquid−liquid equilibrium data for systems composed by canola oil + oleic acid + short chain alcohols and corn oil + oleic acid + ethanol + water, respectively. However, equilibrium data for rice oil has not been reported up to date. The aim of this work was to investigate the phase equilibrium of rice bran oil + commercial oleic acid + ethanol + water at 298.2 K. The experimental data were correlated by the NRTL and UNIQUAC equations, and the adjusted interaction parameters were used to predict the equilibrium of crude rice bran oil + aqueous ethanol.

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Table 1. Fatty Acid Composition of Refined and Crude Rice Bran Oils

			M^b	refined		crude	
symbol	fatty acid		g·mol^{-1}	mole %	mass %	mole %	mass %
M	miristic	C14:0[a]	228.38	1.16	0.96		
P	palmitic	C16:0	256.43	19.57	18.17	21.44	19.91
Po	palmitoleic	C16:1	254.42	0.66	0.61		
S	stearic	C18:0	284.49	1.50	1.54	1.79	1.84
O	oleic	C18:1	282.47	37.66	38.50	39.11	40.01
Li	linoleic	C18:2	280.45	35.08	35.61	35.78	36.34
Le	linolenic	C18:3	278.44	2.65	2.67	1.88	1.90
A	arachidic	C20:0	312.54	1.57	1.78		
Ga	gadoleic	C20:1	310.52	0.15	0.16		

[a] In C*x*:*y*. *x* = number of carbons and *y* = number of double bonds. [b] *M* = molar mass.

Table 2. Probable Triacylglycerol Composition of Refined and Crude Rice Bran Oils

	main triacyl	M^b	refined		crude	
group	glycerol	g·mol^{-1}	mole %	mass %	mole %	mass %
50:1[a]	POP	833.37	4.66	4.48	5.29	5.09
50:2	PLiP	831.35	4.25	4.07	4.84	4.64
50:3	PLeP	829.35	0.63	0.60		
52:1	POS	861.45	0.87	0.86	0.88	0.88
52:2	POO	859.40	11.73	11.61	11.72	11.63
52:3	POLi	857.39	18.84	18.62	20.01	19.80
52:4	PLiLi	855.37	8.98	8.85	10.18	10.05
52:5	PLiLe	853.37	0.80	0.78	0.96	0.95
54:2	SOO	887.46	1.30	1.33	0.94	0.97
54:3	OOO	885.44	8.25	8.42	7.30	7.46
54:4	OOLi	883.43	17.51	17.83	16.31	16.63
54:5	OLiLi	881.41	15.18	15.42	15.04	15.29
54:6	LiLiLi	879.43	5.49	5.56	5.80	5.89
54:7	LiLiLe	877.38	0.64	0.65	0.72	0.73
56:3	OLiA	913.52	0.59	0.62		
56:4	LiLiA	911.50	0.28	0.30		

[a] In *x*:*y*. *x* = number of carbons (except glycerol carbons) and *y* = number of double bonds. [b] *M* = molar mass.

Material

The solvents used in this work were anhydrous ethanol, from Merck, with purity greater than 99.5%, and aqueous solvents with different water contents of (2.40 ± 0.02, 6.03 ± 0.01, 6.38 ± 0.02, 8.96 ± 0.05, 10.59 ± 0.04, and 12.41 ± 0.01) mass %, prepared by the addition of deionized water to anhydrous ethanol.

All fatty reagents used in this study, commercial oleic acid (Merck), refined rice bran oil (Tio João, Brazil), and crude rice bran oil (kindly supplied by Helmut Tessmann, Brazil), were analyzed by gas chromatography of fatty acid methyl esters to determine the fatty acid composition, according to the official method (1-62) of the AOCS.[28] Samples were prepared in the form of fatty acid methyl esters according to the methodology developed by Hartman and Lago.[29] A HP5890 gas chromatograph with a flame ionization detector was used under the following experimental conditions: fused silica column of cyanopropylsiloxane 0.25 μm, 60 m × 0.32 mm i.d.; hydrogen as the carrier gas at a rate of 2.5 mL/min; injection temperature of 548.2 K; column temperature of (448.2 to 498.2) K (rate of 1.3 K/min); detection temperature of 578.2 K.

The fatty acid methyl esters were identified by comparison with external standards purchased from Nu Check Inc. (Elysian, IL). The quantification was accomplished by internal normalization. The fatty acid compositions of the refined and crude rice bran oils are presented in Table 1. From this fatty acid composition it was possible to determine the probable triacylglycerol composition of the refined and crude rice bran oil (Table 2) by using the algorithm suggested by Antoniosi Filho et al.[30] In Table 2 the main triacylglycerol represents the component of greatest concentration in the isomer set with *x* carbons and *y* double bonds.

Table 3. Fatty Acid Composition of Commercial Oleic Acid

symbol	mole %	mass %
L	1.58	1.13
M	1.09	0.89
P	5.83	5.36
Po	0.13	0.12
S	1.39	1.42
O	77.05	78.02
Li	11.91	11.97
Le	0.49	0.50
A	0.53	0.59

Table 3 presents the fatty acid composition of commercial oleic acid. This fatty acid was also analyzed by gas chromatograph using the methodology described above. The results shown in Tables 1−3 allow us to calculate the average molar mass of free fatty acids in crude rice oil, refined rice oil, crude rice oil, and commercial oleic acid. The values obtained were 276.13, 867.78, 866.50, and 278.96 g·mol^{-1}, respectively. Crude and refined rice bran oils, free fatty acids in crude rice oil, and commercial oleic acid were treated in this work as pseudocompounds with the average molar masses indicated above.

Refined rice bran oil had a residual acidity of 0.07%, expressed as oleic acid. The crude rice oil used in this work presented an acidic value of (9.34 ± 0.01) mass %, expressed as oleic acid. Both oils were analyzed by spectrophotometry, using a UV−vis dual beam spectrophotometer (Perkin-Elmer, model Lambda 40), to determine the presence and concentration of nutraceutical compounds. The concentration of γ-oryzanol was determined at 314.5 nm, as suggested by Seetharamaiah and Prabakar,[31] using heptane (UV-Fluo, Carlo Erba) as solvent and γ-oryzanol, purity greater than 99 mass %, kindly supplied by Tsuno Rice Fine Chemicals Co., as standard. The quantification of total tocopherols was determined at 520 nm according to the methodology developed by Emmerie-Engel.[32] α-Tocopherol, purity greater than 99% (Sigma), was used as standard, and toluene (Em Science), as solvent.

Crude rice bran oil presented (1.72 ± 0.05) mass % of γ-oryzanol and (622.3 ± 4.0) ppm of total tocopherols. The γ-oryzanol concentration in refined rice oil was (0.12 ± 0.01) mass %, and tocopherols were not detected in this oil.

Experimental Procedure

Model fatty systems containing fatty acids and triacylglycerols were prepared by the addition of known quantities of commercial oleic acid to refined rice bran oil. The model fatty systems were mixed with the ethanolic solvents, in the mass ratio oil/solvent 1:1, at (298.2 ± 0.1) K, for

Table 4. Liquid−Liquid Equilibrium Data for the System Refined Rice Bran Oil (1) + Commercial Oleic Acid (2) + Anhydrous Ethanol (3) at (298.2 ± 0.1) K

overall composition			alcohol phase (II)			oil phase (I)		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
50.01	0.00	49.99	7.48	0.00	92.52	85.22	0.00	14.78
47.45	2.50	50.06	9.14	2.99	87.87	80.12	2.26	17.62
44.75	5.02	50.23	11.75	5.86	82.38	74.42	4.56	21.01
45.41	4.49	50.10	15.48	8.43	76.09	68.33	6.87	24.80
40.00	10.01	49.99	22.85	10.97	66.18	58.14	9.51	32.34

Table 5. Liquid−Liquid Equilibrium Data for the System Refined Rice Bran Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at (298.2 ± 0.1) K

	Overall Composition				Alcohol Phase (II)				Oil Phase (I)			
$100w_{4S}$[a]	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
2.40 ± 0.02	49.99	0.00	48.81	1.20	4.21	0.00	93.26	2.53	88.56	0.00	11.22	0.22
	47.97	2.01	48.82	1.20	4.92	2.42	90.35	2.31	84.93	2.07	12.70	0.30
	45.70	3.97	49.12	1.21	5.70	4.44	87.46	2.41	82.06	3.72	13.85	0.36
	43.77	6.00	49.02	1.21	6.97	6.82	83.91	2.30	77.91	5.54	16.20	0.36
	41.77	7.98	49.03	1.21	8.48	8.84	80.48	2.20	73.96	7.46	18.18	0.40
6.38 ± 0.02	49.90	0.00	46.90	3.20	2.14	0.00	90.85	7.01	91.95	0.00	7.54	0.51
	49.99	2.51	46.82	3.19	2.15	2.61	88.67	6.56	88.36	2.27	9.16	0.21
	49.96	5.00	46.85	3.19	2.88	5.01	86.24	5.88	83.86	5.05	10.45	0.64
	49.80	9.98	47.00	3.20	4.25	10.16	79.88	5.71	75.34	9.90	14.04	0.72
	49.93	14.99	46.88	3.19	7.03	15.49	72.36	5.11	65.58	14.85	18.70	0.88
	49.77	19.90	47.03	3.20	12.89	20.57	62.01	4.53	53.61	19.65	25.25	1.49
10.59 ± 0.04	49.88	0.00	44.81	5.31	0.63	0.00	88.42	10.96	93.08	0.00	6.34	0.58
	44.95	5.04	44.71	5.30	1.09	4.53	83.75	10.63	84.70	5.78	8.75	0.78
	39.98	10.01	44.72	5.30	1.94	9.16	79.05	9.85	76.41	11.06	11.60	0.94
	34.92	14.95	44.82	5.31	3.61	14.10	73.36	8.94	67.51	15.89	14.98	1.62
	29.76	20.01	44.73	5.30	6.67	19.42	65.95	7.97	57.39	21.03	19.51	2.07
12.41 ± 0.01	49.93	0.00	43.86	6.21	0.16	0.00	88.68	11.16	94.43	0.00	4.54	1.03
	47.31	2.57	43.90	6.22	0.37	2.14	85.49	12.00	89.71	3.24	5.77	1.28
	45.00	5.01	43.79	6.20	0.31	4.06	83.13	12.50	85.68	6.13	6.95	1.23
	39.94	10.04	43.82	6.21	1.13	8.46	78.62	11.78	76.87	12.01	9.74	1.38
	29.95	20.00	43.84	6.21	3.80	18.35	67.32	10.53	58.61	22.31	16.86	2.22

[a] $100w_{4S}$ = water mass percentage in the solvent

determination of liquid−liquid equilibrium data used to adjust NRTL and UNIQUAC parameters. Crude rice bran oil was mixed with aqueous ethanol containing (6.03 ± 0.01) mass % of water or (8.96 ± 0.05) mass % of water, in the mass ratios oil/solvent (1:1, 1:2, 1:3) and (1:1, 1:3), respectively. These data were used to test the prediction capability of the adjusted NRTL and UNIQUAC parameters.

Liquid−liquid equilibrium data were determined using polypropylene centrifuge tubes (50 mL) (Corning Inc.). The components were weighed on an analytical balance Sartorius model A200S, accurate to 0.0001 g. The tubes were vigorously stirred for at least 15 min, centrifuged for 10 min at 4500*g* (Centrifuge Jouan model BR4i), and left to rest for 2 h in a thermostatic bath at (298.2 ± 0.1) K (Cole Parmer, model 12101-05). This contact time was stated on the basis of a previous study that showed the phase equilibrium was attained after 1 h of rest.

After this treatment, the two phases became clear, with a well-defined interface, and the composition of both phases was measured. The concentration of free fatty acids was determined by titration (official method 2201 of the IUPAC[33]) with an automatic buret (Metrohm, model Dosimat 715). The total solvent concentration was determined by evaporation at 338.2 K in a vacuum oven (Napco model 5831). The water concentration was determined by Karl Fischer titration, according to AOCS method Ca 23-55[28] with a KF Titrino (Metrohm, model 701). For the refined oil the γ-oryzanol concentration was very low, so that the system was considered as a pseudoquaternary one composed only by triacylglycerols, fatty acids, ethanol, and water. In this case, having determined the concentration of fatty acids, solvent, and water, the triacylglycerol concentration can be obtained by difference.

For the crude oil the γ-oryzanol concentration in each phase was measured according to the procedure suggested by Seetharamaiah and Prabakar.[31] In this case the system was considered a pseudoquinary one and the triacylglycerol concentration can also be determined by difference.

To have a better insight on the quality of rice bran oil refined by solvent extraction, a further set of experiments were performed to measure only the partition coefficients of the nutraceutical compounds. Such experiments were performed by mixing crude rice bran oil with different aqueous solvents, in the mass ratio oil/solvent 1:1, at (298.2 ± 0.1) K. The concentrations of γ-oryzanol and tocopherol were measured according to the procedure described above.

In this work all measurements were performed at least in triplicate. The uncertainties of the concentrations varied within the following ranges: (0.01 to 0.45) mass % for rice oil, (0.01 to 0.28) mass % for fatty acids, (0.01 to 0.40) mass % for ethanol, (0.01 to 0.04) mass % for water, (0.01 to 0.13) mass % for γ-oryzanol, and (0.001 to 0.01) mass % for tocopherols.

Results

Tables 4 and 5 present the overall experimental composition of the mixtures, and the corresponding tie lines for the pseudoternary and pseudoquaternary model systems composed by refined rice bran oil + commercial oleic acid + ethanol and refined rice bran oil + commercial oleic acid + ethanol + water, respectively. Table 6 shows the overall experimental composition of the mixtures, and the corresponding tie lines for the systems composed by crude rice

Table 6. Liquid−Liquid Equilibrium Data for the System Crude Rice Bran Oil (1) + Fatty Acids (2) + Ethanol (3) + Water (4) at (298.2 ± 0.1) K

	overall composition					alcohol phase (II)					oil phase (I)				
$100w_{4S}$[a]	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$
6.03 ± 0.01	22.25	2.34	70.46	4.52	0.43	1.80	2.39	89.22	6.44	0.16	86.30	2.34	9.44	0.66	1.26
	29.61	3.11	62.69	4.02	0.57	2.08	3.12	88.27	6.33	0.19	84.96	3.08	9.78	0.85	1.34
	44.24	4.64	47.23	3.03	0.86	2.08	4.66	86.44	6.59	0.23	82.11	4.60	11.18	0.70	1.41
8.96 ± 0.05	22.28	2.34	68.24	6.71	0.43	0.57	2.31	87.97	8.97	0.18	87.70	2.42	7.66	0.58	1.65
	44.48	4.67	45.51	4.48	0.86	0.61	4.35	85.14	8.86	0.14	84.08	4.86	9.02	0.67	1.37

[a] $100w_{4S}$ = water mass percentage in the solvent

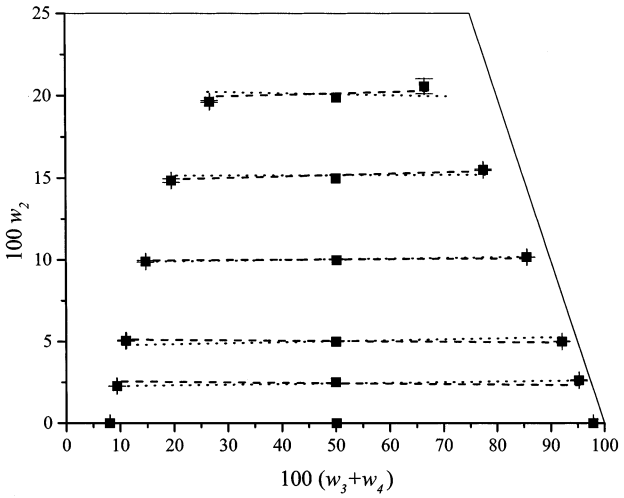

Figure 1. System of refined rice bran oil (1) + commercial oleic acid (2) + (6.38 ± 0.02) mass % aqueous solvent [ethanol (3) + water (4)] at (298.2 ± 0.1) K: experimental (■); (- - -) NRTL; (···) UNIQUAC.

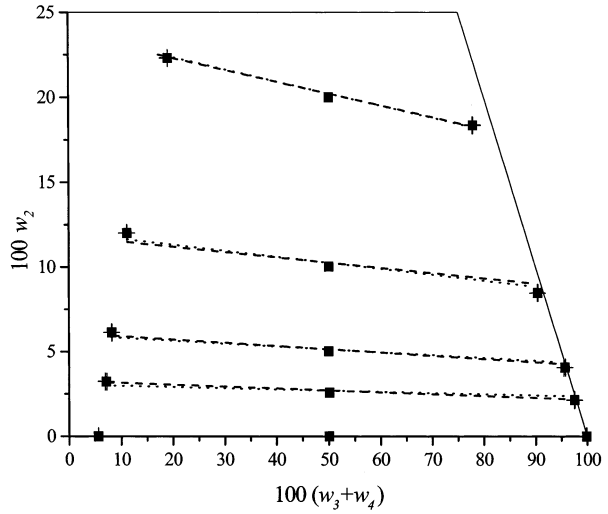

Figure 2. System of refined rice bran oil (1) + commercial oleic acid (2) + (12.41 ± 0.01) mass % aqueous solvent [ethanol (3) + water (4)] at (298.2 ± 0.1) K: experimental (■); (- - -) NRTL; (···) UNIQUAC.

oil + free fatty acids + ethanolic solution. All concentrations are given as mass percentages.

In Figures 1 and 2 the equilibrium data for the model systems refined rice bran oil + commercial oleic acid + (6.38 ± 0.02) mass % aqueous solvent and refined rice bran oil + commercial oleic acid + (12.41 ± 0.02) mass % aqueous solvent are shown. Figure 3 presents the equilibrium data for the system crude rice oil + free fatty acids + (6.03 ± 0.01) mass % aqueous solvent. In these figures ethanol + water were considered as a mixed solvent.

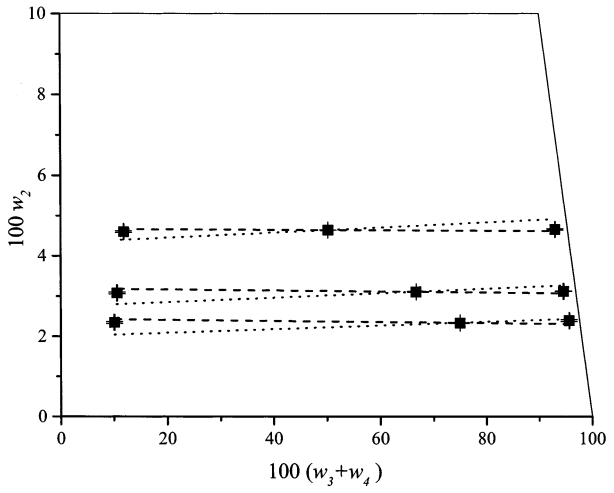

Figure 3. Prediction of the liquid−liquid equilibrium for the system of crude rice bran oil (1) + fatty acids (2) + (6.03 ± 0.01) mass % aqueous solvent [ethanol (3) + water (4)] at (298.2 ± 0.1) K: experimental (■); (- - -) NRTL; (···) UNIQUAC.

A good alignment can be observed between the experimental data, relative to both overall and phase concentrations. Tie lines based on the experimental data were determined by linear regression of each corresponding set of overall, oil, and alcoholic phase concentrations. Correlation coefficients higher than 99.5% were obtained for all tie lines, indicating a low error in the experimental determination of the tie line compositions. The low experimental deviations obtained in the measurement of the phase composition strengthen this comment.

Modeling

The experimental equilibrium data determined for the model systems were used to adjust the interaction parameters of the NRTL and UNIQUAC models. Mass fraction was used as concentration unit due to the large difference in molecular mass of the components in the system.[25,26] Gonçalves et al.[27] show the activity coefficient equations, expressed in mass fractions, according to the NRTL and UNIQUAC models.

The adjustments were made by treating the model system refined rice bran oil + commercial oleic acid + anhydrous ethanol as a pseudoternary one and the model systems rice bran oil + commercial oleic acid + ethanol + water as pseudoquaternary ones. The systems were considered as composed by a single triacylglycerol having the refined rice bran oil average molecular mass, a representative fatty acid with the molecular mass of the commercial oleic acid, ethanol, and water.

This approach assumes that the different triacylglycerols present in the rice bran oil behave in a very similar way in the liquid−liquid system under analysis. In this case such components can be adequately replaced by a pseudo-

Table 7. Parameters r_i' and q_i' for Refined Rice Bran Oil, Commercial Oleic Acid, Ethanol, Water, Free Fatty Acids in Crude Rice Bran Oil, and Crude Rice Bran Oil

compound	r_i'	q_i'
refined rice bran oil	0.044 094	0.035 753
commercial oleic acid	0.045 127	0.037 140
ethanol	0.055 905	0.056 177
water	0.051 069	0.077 713
crude rice bran oil	0.044 084	0.035 746
free fatty acids in crude rice bran oil	0.045 028	0.037 058

Table 8. UNIQUAC Parameters for the System Refined Rice Bran Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at (298.2 ± 0.1) K

pair ij	A_{ij}/K	A_{ji}/K
12	252.66	−207.24
13	250.71	−56.595
14	7643.9	−134.68
23	67.641	−88.948
24	191.68	157.03
34	337.46	−279.92

compound having the corresponding average physical−chemical properties. The same hypothesis is assumed in relation to the fatty acid mixture. Such a hypothesis will be tested by the adjustment of parameters to the model systems and the subsequent use of these parameters in the equilibrium prediction for systems containing crude rice bran oil.

The values of r_i' and q_i', volume and area parameters necessary for the UNIQUAC model, are given in Table 7. These parameters were calculated according to the traditional way via eq 1, where x_j is the molar fraction of the component present in the pseudocompound i, $\bar{M}_i$ is the average molecular mass of the pseudocompounds rice oils or fatty acids, C is the number of different components in the pseudocompounds (oils or fatty acids), G is the total number of groups, and R_i and Q_i are van der Waals parameters taken from Magnussen et al.[34]

$$r_i' = \frac{1}{\bar{M}_i}\sum_j^C x_j \sum_k^G \nu_k^{(i)} R_k$$

$$q_i' = \frac{1}{\bar{M}_i}\sum_j^C x_j \sum_k^G \nu_k^{(i)} Q_k \qquad (1)$$

The interaction parameters estimation was based on the minimization of the objective function of composition (eq 2), following the procedure developed by Stragevitch and d'Avila.[35]

$$S = \sum_m^D \sum_n^N \sum_i^{C-1} \left[\left(\frac{w_{inm}^{\mathrm{I,ex}} - w_{inm}^{\mathrm{I,calc}}}{\sigma_{w_{inm}{}^{\mathrm{I}}}} \right)^2 + \left(\frac{w_{inm}^{\mathrm{II,ex}} - w_{inm}^{\mathrm{II,calc}}}{\sigma_{w_{inm}{}^{\mathrm{II}}}} \right)^2 \right] \qquad (2)$$

where D is the total number of groups of data, N is the total number of tie lines, and C is the total number of components or pseudocompounds in the group of data m. w is the mass fraction, the subscripts i, n, and m are component, tie line, and group number, respectively, and the superscripts I and II stand for oil and alcoholic phases, respectively; ex and calc refer to experimental and calculated concentrations. $\sigma_{w_{inm}{}^{\mathrm{I}}}$ and $\sigma_{w_{inm}{}^{\mathrm{II}}}$ are the standard deviations observed in the compositions of the two liquid phases.

The adjusted parameters of the UNIQUAC and NRTL models are shown in Tables 8 and 9, respectively. The interaction parameters between ethanol (3) and water (4) were taken from the previous study on the phase equilibrium of the system corn oil + oleic acid + ethanol + water at (298.2 ± 0.1) K.[27]

Table 9. NRTL Parameters for the System Refined Rice Bran Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at (298.2 ± 0.1) K

pair ij	A_{ij}/K	A_{ji}/K	α_{ij}
12	−290.55	−165.70	0.499 68
13	873.64	1416.8	0.498 74
14	−26.977	4624.6	0.165 80
23	4800.0	−170.55	0.229 57
24	1006.7	4210.6	0.100 00
34	−10.984	−173.64	0.150 18

The deviations between experimental and calculated compositions in both phases were calculated according to eq 3 and are shown in Table 10.

$$\Delta w = 100\sqrt{\frac{\sum_n^N \sum_i^C [(w_{i,n}^{\mathrm{I,ex}} - w_{i,n}^{\mathrm{I,calc}})^2 + (w_{i,n}^{\mathrm{II,ex}} - w_{i,n}^{\mathrm{II,calc}})^2]}{2NC}} \qquad (3)$$

Figures 1 and 2 show that both thermodynamic models are able to describe with accuracy the phase compositions for the model systems investigated (Table 10). Furthermore, it can be seen that the addition of water expands the region of phase splitting, allowing the refining of highly acidic crude rice bran oils by solvent extraction.

Figure 4 shows the fatty acid distribution between the phases, indicating that the addition of water reduces the solvent capacity of extracting free fatty acids. Experimental and estimated selectivities, calculated according to eqs 4 and 5,

$$k_i = \frac{w_i^{\mathrm{II}}}{w_i^{\mathrm{I}}} \qquad (4)$$

$$S = \frac{k_2}{k_1} \qquad (5)$$

are shown in Figure 5. This figure shows that the addition of water to ethanol increases the solvent selectivity, reducing the loss of neutral oil. Moreover, these results show that the NRTL model provides a good description of selectivity, except for the experimental points with 5 and 10 mass % of free fatty acids measured at 12 mass % water content in the solvent. For these systems, the oil concentration in the alcoholic phase is very low and exhibits a relatively high experimental uncertainty, which influences the uncertainties of the oil distribution coefficient and the experimental solvent selectivity. In addition, it should be observed that in this case the model does not describe the oil distribution coefficient and, in consequence, the solvent selectivity with accuracy.

Prediction of Liquid−Liquid Equilibrium

The adjusted parameters for the NRTL and UNIQUAC models were tested in the prediction of liquid−liquid equilibrium for the system crude rice bran oil + ethanol + water at (298.2 ± 0.1) K. Liquid−liquid flash calculations for the estimation of phase compositions were performed on the basis of the overall experimental composition of the mixtures. The r_i' and q_i' values for crude rice bran oil and free fatty acids are given in Table 7. Since no interaction parameters involving γ-oryzanol were available, this com-

Table 10. Mean Deviations in Phase Compositions for the Model Systems and Predictions

system	Δw (%) NRTL	Δw (%) UNIQUAC
refined rice oil + oleic acid + anhydrous ethanol	0.43	0.46
refined rice oil + oleic acid + aqueous ethanol 2.40 ± 0.02%	0.44	0.23
refined rice oil + oleic acid + aqueous ethanol 6.38 ± 0.02%	0.87	0.90
refined rice oil + oleic acid + aqueous ethanol 10.59 ± 0.04%	0.53	0.68
refined rice oil + oleic acid + aqueous ethanol 12.41 ± 0.01%	0.71	0.76
global deviation of the correlation	0.68	0.71
crude rice oil + free fatty acids + aqueous ethanol 6.03 ± 0.01%	0.35	0.45
crude rice oil + free fatty acids + aqueous ethanol 8.96 ± 0.05%	0.38	0.54
global deviation of the prediction	0.37	0.49

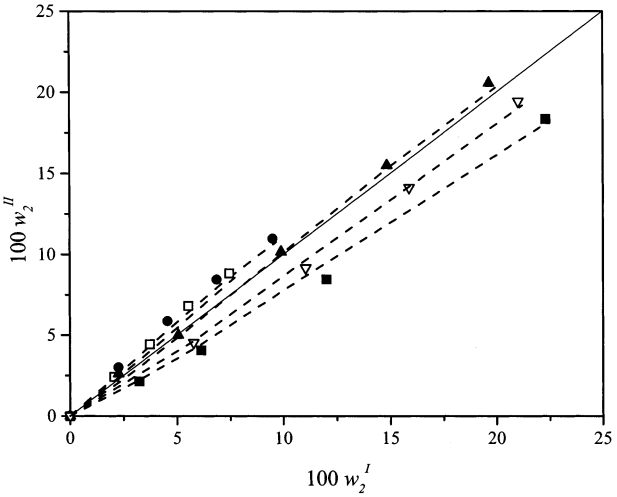

Figure 4. Distribution diagram at (298.2 ± 0.1) K for systems of refined rice bran oil (1) + commercial oleic acid (2) + ethanol (3) + water (4): (●) anhydrous ethanol; (□) (2.40 ± 0.02) mass % aqueous solvent; (▲) (6.38 ± 0.02) mass % aqueous solvent; (▽) (10.59 ± 0.04) mass % aqueous solvent; (■) (12.41 ± 0.01) mass % aqueous solvent; (- - -) NRTL.

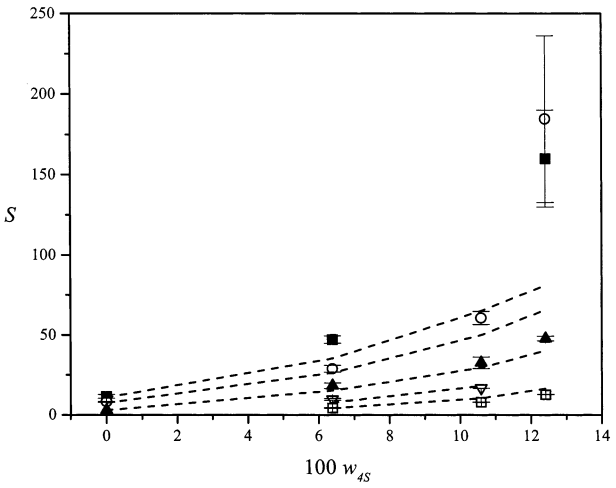

Figure 5. Selectivity diagram at (298.2 ± 0.1) K for systems of refined rice bran oil (1) + commercial oleic acid (2) + ethanol (3) + water (4): (- - -) NRTL model; (■) 5 mass % FFA; (○) 10 mass % FFA; (▲) 20 mass % FFA; (▽) 30 mass % FFA; (□) 40 mass % FFA.

pound was considered as part of the triacylglycerol fraction in the flash calculations.

The deviations between experimental and estimated compositions in both phases are calculated according to eq 3 and are shown in Table 10. Figure 3 shows the experimental points and the predicted tie lines for the system crude rice oil + free fatty acids + (6.03 ± 0.01) mass % aqueous solvent.

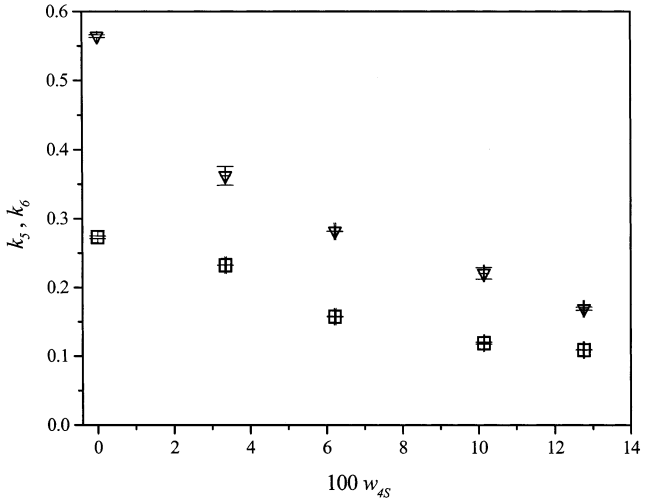

Figure 6. Partition of γ-oryzanol (□) and total tocopherols (▽) in several aqueous solvents at (298.2 ± 0.1) K.

Despite the differences in composition of the refined and crude rice bran oils and the approach incorporating the γ-oryzanol concentration in the triacylglycerol fraction, the parameters adjusted to the model systems allow a good prediction of phase equilibrium for the systems containing crude rice bran oil. This occurs for both activity coefficient models; nevertheless, the UNIQUAC equation overestimated the extraction of free fatty acids for both systems studied, resulting in somewhat higher values for the average percentual deviation (Table 10).

It is interesting to note that the prediction global deviations were lower than the corresponding values for the correlations. This occurs because, for the crude oil system, the highest fatty acid concentration in the overall composition was 4.67%. For the model systems this concentration was varied up to 20.0%, measuring tie lines near the plait point. In the case of the crude oil the highest possible fatty acid concentration in the overall mixture was limited by the original acid content in the oil. Correlation global deviations, calculated for tie lines with up to 5.0% of fatty acids in the overall composition, were 0.33% and 0.40% for the NRTL and UNIQUAC models, respectively.

Partition of Nutraceutical Compounds

The partition of nutraceutical compounds, γ-oryzanol (5) and total tocopherols (6), naturally present in crude rice bran oil was studied to evaluate the impact of solvent extraction upon the loss of such compounds. Figure 6 presents the distribution coefficients for γ-oryzanol (5) and total tocopherols (6), k_5 and k_6, respectively, calculated according to eq 4, for different water contents in the solvent (w_{4S}). The equilibrium data for γ-oryzanol (5) and total tocopherols (6) are shown in Table 11. It can be observed that the distribution coefficient values were less than unity

Table 11. γ-Oryzanol (5) and Total Tocopherols (6) Partition Data for Different Water Contents in the Solvent (w_{4S}) at (298.2 ± 0.1) K

	alcohol phase (II)	oil phase (I)	alcohol phase (II)	oil phase (I)
$100w_{4S}$[a]	$100w_5$	$100w_5$	$100w_6$	$100w_6$
0	0.3510	1.2851	0.0225	0.0398
3.35 ± 0.02	0.2343	1.4881	0.0187	0.0401
6.22 ± 0.02	0.3081	1.3246	0.0132	0.0469
10.14 ± 0.01	0.1772	1.4902	0.0114	0.0516
12.76 ± 0.02	0.1615	1.4807	0.0084	0.0496

[a] $100w_{4S}$ = water mass percentage in the solvent

for both compounds. As the water content increases, the distribution coefficients of both compounds decrease, minimizing the loss of nutraceutical components during the refining by liquid−liquid extraction.

Conclusion

Phase equilibrium data for the system refined rice bran oil + commercial oleic acid + ethanol + water were experimentally determined at 298.2 K. The data sets were correlated by the NRTL and UNIQUAC models, and the adjusted parameters were used in the prediction of liquid−liquid equilibrium for systems composed by crude rice bran oil + aqueous ethanol. Despite the difference in composition of the crude and refined rice bran oils, both molecular thermodynamic models allow a good prediction of phase equilibrium. The presence of water in the solvent minimizes the loss of neutral oil, making the extraction process more economic. Furthermore, the preliminary studies presented in this work on the minor component partition show that it is possible to refine rice bran oil by liquid−liquid extraction with a minimum loss of nutraceutical compounds.

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