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Deacidification of Brazil Nut and Macadamia Nut Oils by Solvent Extraction: Liquid−Liquid Equilibrium Data at 298.2 K

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The present paper reports phase equilibrium experimental data for two systems composed by Brazil nut oil or macadamia nut oil + commercial oleic acid + ethanol + water, at 298.2 K and different water contents in the solvent. The addition of water to the solvent reduces the loss of neutral oil in the alcoholic phase and improves the solvent selectivity. The experimental data were subsequently correlated by the NRTL and UNIQUAC models. Global deviations between calculated and experimental results not higher than 1.5% were obtained for all systems, indicating that both models were able to reproduce correctly the experimental data, although the NRTL model presented a better performance.

Introduction

Brazil nut (*Bertholletia excelsa*) is a native plant from the Amazonian region and has a well-known nutritional value due to its high content of lipids (70% by mass) and proteins (20% by mass).[1]

The macadamia (*Macadamia integrifolia*) is a large evergreen tree indigenous to the coastal rainforests of Australia. The initial development of the macadamia nut industry occurred in Hawaii where the nut was taken from its native habitat in the 1890s.[2] The macadamia nut is nowadays commercially produced in Australia, Hawaii, New Zealand, Guatemala, Costa Rica, and Brazil.[2] This nut is rapidly gaining popularity, and the crops have never been sufficient to satisfy the demand, opening a promising market for countries with the appropriate climate such as Brazil.

Recently, macadamia nut oil has obtained considerable interest due to its blood cholesterol-lowering properties. This is a result especially from its high monounsaturated fatty acid content, such as oleic (around 60 mass %) and palmitoleic (around 20 mass %) acids.[3]

The stability of the oils extracted from some kinds of nuts is directly dependent on the handling that occurs during their harvesting, processing, and storage periods. The producing region is another important factor whose influence cannot be underestimated. The nut storage conditions, such as high temperature and high humidity, can affect the oil quality and increase its free acidity. This is especially important in the case of the Brazil nut, since the Amazonian region has a climate characterized by high temperature and high humidity.

Brazil nut oil, extracted from nuts, can be very unstable due to its high content of polyunsaturated fatty acids, mainly oleic and linoleic acids.[1,4] It is reported that the Brazil nut oil loses its natural antioxidants, phenolic compounds, that improve the oil oxidative stability, during the refining by the traditional chemical or physical methods.[5] As is the case for Brazil nut oil, macadamia nut oil refined by traditional technologies tends rapidly to develop rancidity by hydrolytic or oxidative mechanisms that compromise its suitable flavor and texture.[2]

In a general way, the refining processes of crude vegetable oils involve solvent stripping, in the case of oil extraction from nuts using solvent,[6,7] degumming, bleaching, deacidification, and deodorization.[8,9] The removal of free fatty acids (deacidification) is the most difficult step of the oil purification process, mainly because the yield of neutral oil in this operation has a significant effect in the cost of refining. Deacidification of oils is usually performed by chemical or physical methods. However, for oils with high acidity, chemical refining causes high losses of neutral oil due to saponification and emulsification. The physical method is also a feasible process for the deacidification of highly acidic oils, since it results in less loss of neutral oil than the chemical method, but more energy is consumed. Moreover, in some cases, the refined oil is subject to undesirable alterations in color and a reduction of stability to oxidation, as commented above.[10]

An alternative vegetable oil refining process, performed under more mild conditions (room temperature and atmospheric pressure), when compared with traditional methods, is the deacidification by liquid−liquid extraction, which also avoids the formation of waste products. This new approach has shown promising results concerning the refined oil acidic value with low losses of neutral oil and nutraceutical compounds.[11,12]

Liquid−liquid extraction for oil refining is based on the difference of solubility of free fatty acids and neutral triacylglycerols (main components of vegetable oils) in an appropriate solvent.[13] Bhattacharya et al.[14] and Shah and Venkatesan[15] studied the deacidification of rice bran and groundnut oils using aqueous isopropyl alcohol as solvent. Kim et al.[16] and Kale et al.[17] tested methanol in the refining of rice bran oil. All the studies showed a decrease of the oil acidic value. Pina and Meirelles[18] studied the performance of a perforated rotating disk column in the continuous deacidification of corn oil, obtaining good results in relation to the extraction of free fatty acids and the loss of neutral oil.

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Information on phase equilibrium and physical properties is necessary for designing separation processes involving fatty systems. Liquid−liquid equilibrium data for several vegetable oils (canola, corn, palm, and rice bran oils) have been reported by our research group, using always short-chain alcohols as solvent.[11−12,19−21]

In this paper, equilibrium data for the systems containing exotic oils (Brazil nut or macadamia nut oils) + commercial oleic acid + ethanol + water at 298.2 K are reported. The experimental data were correlated by the NRTL and UNIQUAC equations, and the adjusted interaction parameters enable the simulation of liquid−liquid extractors.

Materials

Brazil and macadamia nuts were kindly supplied by Exportadora Mutran (Pará, Brazil) and Queen Nut Macadâmia (São Paulo, Brazil), respectively. The oils from Brazil and macadamia nuts were extracted from broken nuts by cold pressing at 60 t in a manual control hydraulic press (Charlott Hydraulic Press, U.S.A.). The Brazil nut and macadamia nut oils obtained by cold pressing presented acidity values of 0.24 and 0.20, respectively, expressed as the mass % of oleic acid. Such acidity values are low, since the nuts were stored under appropriate conditions and the oil obtained was from the first cold pressing. Oil obtained either from nuts stored under bad conditions or from the residual pressing cake by solvent extraction can have high acidic values.

All fatty reagents, the oils and commercial oleic acid (Merck), 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.[22] The fatty samples were prepared in the form of fatty acid methyl esters according to the official method (2-66) of the AOCS.[23] An HP5890 gas chromatograph with a flame ionization detector was used under the following experimental conditions: fuse 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 solvents used in this work were anhydrous ethanol, from Merck, with a purity >99.5%, and aqueous solvents with different water contents (6 and 12 mass %), prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol.

Experimental Procedure

Model fatty systems containing fatty acids and triacylglycerols were prepared by the addition of known quantities of commercial oleic acid to the vegetable oils. 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 determination of the liquid−liquid equilibrium data used to adjust the NRTL and UNIQUAC parameters. In both systems, ethanolic solvents containing 0, 6, and 12% water were used.

The equilibrium data were determined using polypropylene centrifuge tubes (50 mL) (Corning Inc.). The components were weighed on an Adam model AAA200 analytical balance, accurate to 0.0001 g. The tubes were vigorously stirred for at least 15 min at room temperature (quite close to 298 K), centrifuged for 10 min at 4500*g* at (298.2 ± 1.5) K (Centrifuge Jouan, model BR4i, equipped with a temperature controller), 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.[11]

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[24]) with an automatic buret (Metrohm, model Dosimat 715). The total solvent concentration was determined by evaporation at 313.2 K in a vacuum oven (Napco, model 5831). The water concentration was determined by Karl Fischer titration, according to AOCS method Ca 23-55,[22] with a KF Titrino instrument (Metrohm, model 701). The triacylglycerol concentration was determined by difference.

In this work, all measurements were performed at least in triplicate. The uncertainties of the concentrations varied within the following ranges: (0.03 to 0.25) mass % for oils, (0.02 to 0.24) mass % for oleic acid, (0.02 to 0.15) mass % for ethanol, and (0.01 to 0.24) mass % for water, being the lowest figures obtained for the lowest concentrations.

To test the validity of the results obtained, the procedure developed by Marcilla et al.[25] was followed. According to this approach, i independent component balances can be written, with i being each component of the system:

$$M_{\mathrm{OC}}(w_i)_{\mathrm{OC}} = M_{\mathrm{OP}}(w_i)_{\mathrm{OP}} + M_{\mathrm{AP}}(w_i)_{\mathrm{AP}} \qquad (1)$$

where M_{OC} is the amount of the initial mixture, M_{OP} and M_{AP} are the amounts of the oil phase and alcoholic phase, respectively, $w_{i\mathrm{OC}}$ is the mass fraction of component i in the initial mixture, and $w_{i\mathrm{OP}}$ and $w_{i\mathrm{AP}}$ are the mass fraction of component i in the oil and alcoholic phases. With these i equations, it is possible to calculate the values of M_{OP} and M_{AP}, from the experimental values $w_{i\mathrm{OP}}$ and $w_{i\mathrm{AP}}$ by a least-squares fitting: if $\mathbf{M}$ is the matrix formed by the values of $w_{i\mathrm{OC}}$, $\mathbf{B}$ is the transformation matrix (formed by the values of $w_{i\mathrm{OP}}$ and $w_{i\mathrm{AP}}$), and $\mathbf{P}$ is the matrix formed by the amounts of each phase (M_{OP} and M_{AP}), the previous system can be written as

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

Mathematic calculations lead to the following expression

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

where $\mathbf{B}^T$ is the transpose matrix of $\mathbf{B}$ and $(\mathbf{B}^T\mathbf{B})^{-1}$ is the inverse matrix of $\mathbf{B}^T\mathbf{B}$. Thus, the values of M_{OP} and M_{AP} (matrix $\mathbf{P}$), which minimize the errors of the previous system, have been calculated. The deviation between the sum ($M_{\mathrm{OP}} + M_{\mathrm{AP}}$) and M_{OC} calculated according to $(|(M_{\mathrm{OP}} + M_{\mathrm{AP}}) - M_{\mathrm{OC}}|/M_{\mathrm{OC}}) \times 100$ was always lower than 0.5%, indicating the good quality of the experimental data.

Modeling Approach

In the present work, the experimental data measured for the model systems were used to adjust the NRTL and UNIQUAC interaction parameters between each vegetable oil and the other components of the system (commercial oleic acid, ethanol, and water). The parameters concerning the interaction between these other components with each other were taken from our prior work.[11]

The mass fraction was used as a concentration unit due to the large difference in molecular mass of the components in the system.[11,12,19−21] Rodrigues et al.[12] 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 vegetable oil + commercial oleic acid + anhydrous ethanol as a pseudoternary one and the system vegetable oil + commercial oleic acid + ethanol + water as a pseudoquaternary one. The systems were considered as being composed of a single triacylglycerol having the vegetable oil average molar masses, a representative fatty acid with the molar mass of the commercial oleic acid, ethanol, and water.

The values of r_i' and q_i', the volume and area parameters necessary for the UNIQUAC model, were calculated via eq 4, where x_j is the molar fraction of the triacylglycerols of the vegetable oils or the fatty acids of the commercial oleic acid, $v_k^{(j)}$ is the number of groups k in molecule j, $\bar{M}_i$ is the average molar mass of the vegetable oils or the fatty acids, C is the number of different components in the pseudocompounds, G is the total number of groups and R_i and Q_i are van der Waals parameters taken from Magnussen et al.[26]

$$r_i' = \frac{1}{\bar{M}_i}\sum_j^{C} x_j \sum_k^{G} v_k^{(j)} R_k; \quad q_i' = \frac{1}{\bar{M}_i}\sum_j^{C} x_j \sum_k^{G} v_k^{(j)} Q_k \tag{4}$$

The interaction parameter estimation was based on the minimization of the objective function of composition (eq 5), following the procedure developed by Stragevitch and d'Avila[27]

$$S = \sum_m^{D}\sum_n^{N}\sum_i^{K-1}\left[\left(\frac{w_{inm}^{\mathrm{OP,exptl}} - w_{inm}^{\mathrm{OP,calcd}}}{\sigma_{w_{inm}^{\mathrm{OP}}}}\right)^2 + \left(\frac{w_{inm}^{\mathrm{AP,exptl}} - w_{inm}^{\mathrm{AP,calcd}}}{\sigma_{w_{inm}^{\mathrm{AP}}}}\right)^2\right] \tag{5}$$

where D is the total number of groups of data, N is the total number of tie lines, and K 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 OP and AP stand for the oil and alcoholic phases, respectively; exptl and calcd refer to experimental and calculated concentrations. $\sigma_{w_{inm}^{\mathrm{OP}}}$ and $\sigma_{w_{inm}^{\mathrm{AP}}}$ are the standard deviations observed in the compositions of the two liquid phases.

The deviations between experimental and calculated compositions in both phases were calculated according to eq 6.

$$\Delta w = 100\sqrt{\frac{\sum_n^{N}\sum_i^{C}\left[(w_{i,n}^{\mathrm{OP,exptl}} - w_{i,n}^{\mathrm{OP,calcd}})^2 + (w_{i,n}^{\mathrm{AP,exptl}} - w_{i,n}^{\mathrm{AP,calcd}})^2\right]}{2NC}} \tag{6}$$

Results

The fatty acid compositions of Brazil nut and macadamia nut oils are presented in Table 1. The corresponding data for commercial oleic acid from Merck are published in the work of Rodrigues and co-workers.[11]

As Table 1 shows, oleic and linoleic acids are the most important fatty acids present in Brazil nut oil. In the case of macadamia nut oil, the main fatty acids are oleic and palmitoleic acids. These results are in accordance with works that present the fatty acid compositions of such oils reported in the literature.[3,4,27] The commercial oleic acid from Merck contains 78.02 mass % oleic acid, 11.97 mass % linoleic acid, 5.36 mass % palmitic acid, 1.42 mass % stearic acid, 1.13 mass % lauric acid, and myristic, palmitoleic, linolenic, and arachidic acids as minor compounds.[11]

From this fatty acid composition, it was possible to determine the probable triacylglycerol composition of the vegetable oils (Table 2) by using the procedure suggested by Antoniosi Filho et al.[29] In Table 2, the main triacylglycerol represents the component of greatest concentration in the isomer set with x carbons and y double bonds.

On the basis of the results shown in Table 2, it was possible to calculate the average molar masses of the

Table 1. Fatty Acid Composition of Vegetable Oils

			M^a	Brazil nut oil		macadamia nut oil	
symbol	fatty acid		g·mol^{-1}	mol %	mass %	mol %	mass %
M	miristic	C14:0[b]	228.38			0.81	0.98
P	palmitic	C16:0	256.43	14.65	15.86	8.73	9.38
Po	palmitoleic	C16:1	254.42			17.80	19.28
S	stearic	C18:0	284.49	11.61	11.34	3.51	3.40
O	oleic	C18:1	282.47	31.21	30.68	61.25	59.76
Li	linoleic	C18:2	280.45	42.53	42.12	2.06	2.03
Le	linolenic	C18:3	278.44			0.14	0.14
A	arachidic	C20:0	312.54			2.90	2.56
Ga	gadoleic	C20:1	310.52			2.80	2.48

[a] M = molar mass. [b] In Cx:y, x is the number of carbons and y is the number of double bonds.

Table 2. Probable Triacylglycerol Composition of Vegetable Oils

		M^a	Brazil nut oil		macadamia nut oil	
main group	triacylglycerol	g·mol^{-1}	mol %	mass %	mol %	mass %
48:1	PPoP	805.33			0.81	0.75
48:2	PPoPo	803.31			1.92	1.78
50:1[b]	POP	833.37	2.39	2.28	1.94	1.87
50:2	PLiP/PPoO[c]	831.35	3.27	3.12	8.85	8.51
50:3	PoPoO	829.35			6.99	6.70
52:1	POS	861.45	3.41	3.37	1.52	1.51
52:2	POO	859.40	9.69	9.55	14.48	14.39
52:3	POLi/PoOO	857.39	13.73	13.52	21.77	21.58
52:4	PLiLi/PoOLi	855.37	9.43	9.27	1.47	1.46
54:1	SOS/POA	889.51	1.22	1.24	1.12	1.16
54:2	SOO	887.46	5.25	5.35	7.06	7.25
54:3	SOLi/OOO	885.44	12.44	12.65	23.42	23.97
54:4	OOLi	883.43	17.55	17.79	2.26	2.31
54:5	OLiLi	881.41	14.83	15.01		
54:6	LiLiLi	879.43	6.79	6.85		
56:2	OOA	915.53			3.48	3.69
56:3	OOGa	913.52			2.91	3.07

[a] M = molar mass. [b] In x:y, x is the number of carbons (except glycerol carbons) and y is the number of double bonds. [c] In the case of Brazil nut oil, PLiP is the main triacylglycerol in the isomer set 50:2. In the case of macadamia nut oil, the main triacylglycerol is PPoO.

Table 3. Average Molar Masses, *M*, and the Structural Parameters r_i' and q_i'

compound	M g·mol^{-1}	r_i'	q_i'
macadamia nut oil (1)	864.83	0.044 224	0.035 888
Brazil nut oil (2)	871.20	0.044 117	0.035 771
commercial oleic acid (3)[a]	278.96	0.045 127	0.037 140
ethanol (4)	46.07	0.055 905	0.056 177
water (5)	18.02	0.051 069	0.077 713

[a] Data taken from Rodrigues et al.[11]

Table 4. Liquid−Liquid Equilibrium Data for the Systems Macadamia Nut Oil (1) + Commercial Oleic Acid (3) + Ethanol (4) and Brazil Nut Oil (2) + Commercial Oleic Acid (3) + Ethanol (4), at (298.2 ± 0.1) K

	OC[a]			OP[b]			AP[c]		
system	$100w_1$	$100w_3$	$100w_4$	$100w_1$	$100w_3$	$100w_4$	$100w_1$	$100w_3$	$100w_4$
macadamia nut	50.01	0.00	49.99	86.96	0.00	13.04	4.97	0.00	95.03
	48.90	0.70	50.40	85.64	0.63	13.73	5.19	0.76	94.05
	48.62	1.18	50.20	84.95	1.02	14.03	5.27	1.37	93.36
	47.93	2.11	49.96	83.23	1.80	14.97	5.78	2.45	91.77
	46.46	3.22	50.32	80.70	2.92	16.38	6.90	3.55	89.55
	44.77	5.16	50.07	76.06	4.67	19.27	11.61	5.65	82.74
	39.63	10.25	39.63	58.32	9.80	31.88	23.44	10.70	65.86
system	$100w_2$	$100w_3$	$100w_4$	$100w_2$	$100w_3$	$100w_4$	$100w_2$	$100w_3$	$100w_4$
Brazil nut	49.99	0.00	50.01	86.45	0.00	13.55	5.55	0.00	94.45
	49.34	0.67	50.00	85.72	0.57	13.71	5.78	0.73	93.49
	48.70	1.17	50.13	84.80	1.03	14.17	5.68	1.36	92.96
	47.73	2.11	50.16	83.26	1.87	14.87	6.09	2.49	91.42
	46.50	3.33	50.17	79.94	2.85	17.21	8.45	3.95	87.60
	44.88	5.19	49.93	74.42	4.60	20.98	11.75	5.87	82.38
	40.14	10.21	49.65	56.72	9.39	33.89	26.90	10.92	62.18

[a] OC = overall composition. [b] OP = oil phase composition. [c] AP = alcoholic phase composition.

Table 5. Liquid−Liquid Equilibrium Data for the Systems Macadamia Nut Oil (1) + Commercial Oleic Acid (3) + Solvent [Ethanol (4) + Water (5)] and Brazil Nut Oil (2) + Commercial Oleic Acid (3) + Solvent [Ethanol (4) + Water (5)], at (298.2 ± 0.1) K

		OC				OP				AP			
system	$100w_{5S}$[a]	$100w_1$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_3$	$100w_4$	$100w_5$
macadamia nut	6.22	50.01	0.00	46.88	3.11	95.10	0.00	4.41	0.49	1.03	0.00	91.98	6.99
		49.33	0.69	46.88	3.11	93.78	0.65	5.09	0.48	0.39	0.75	92.01	6.85
		48.85	1.13	46.90	3.11	93.97	1.09	4.54	0.4	0.62	1.28	91.17	6.93
		47.86	2.14	46.88	3.11	92.12	2.10	5.25	0.53	0.96	2.28	89.91	6.85
		46.90	3.11	46.89	3.11	90.66	3.09	5.66	0.59	1.08	3.31	89.69	5.92
		44.48	5.27	47.16	3.09	87.08	4.82	7.59	0.51	1.20	5.84	86.63	6.33
		39.79	10.01	47.08	3.12	78.15	9.54	11.59	0.72	3.36	10.57	79.36	6.71
		34.87	15.16	46.90	3.07	66.41	14.95	17.77	0.87	5.23	15.37	74.28	5.12
		29.94	20.03	46.88	3.15	54.77	19.69	24.14	1.40	9.47	20.44	65.56	4.53
	12.27	49.91	0.00	43.95	6.15	94.90	0.00	4.62	0.48	0.24	0.00	86.13	13.63
		49.34	0.71	43.81	6.13	93.87	0.90	4.73	0.50	0.07	0.70	85.47	13.76
		48.74	1.26	43.87	6.14	93.06	1.60	4.69	0.65	0.06	1.24	85.22	13.48
		47.78	2.25	43.84	6.13	91.89	2.63	4.97	0.51	0.50	2.13	84.17	13.20
		46.93	3.07	43.87	6.14	89.87	3.62	5.99	0.52	0.27	2.74	83.74	13.25
		45.51	5.15	43.21	6.13	86.95	5.82	6.35	0.88	0.05	4.66	81.99	13.30
		39.70	10.21	44.00	6.09	76.89	11.99	9.82	1.30	1.10	8.49	78.40	12.01
		29.31	20.22	44.39	6.08	58.52	22.40	17.33	1.75	3.86	18.29	66.32	11.53
system	$100w_{5S}$[a]	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_2$	$100w_3$	$100w_4$	$100w_5$
Brazil nut	6.22	49.98	0.00	46.91	3.11	92.28	0.00	7.05	0.67	1.49	0.00	91.93	6.58
		49.29	0.71	46.89	3.11	91.23	0.72	7.47	0.58	1.42	0.70	91.85	6.03
		48.84	1.15	46.90	3.11	90.98	1.13	7.35	0.54	1.53	1.17	90.72	6.58
		47.62	2.34	46.92	3.11	88.65	2.30	8.50	0.55	1.69	2.37	89.80	6.14
		46.96	3.05	46.89	3.11	87.92	2.90	8.63	0.55	1.56	3.25	88.61	6.58
		39.79	10.01	47.12	3.08	75.38	9.86	13.99	0.77	4.23	10.18	78.99	6.60
		34.78	15.23	46.87	3.12	65.60	14.87	18.68	0.89	7.07	15.53	71.90	5.58
		29.85	20.16	46.93	3.06	53.63	19.63	25.54	1.20	12.88	20.58	61.53	5.01
	12.27	50.01	0.00	43.85	6.13	94.67	0.00	4.81	0.52	0.70	0.00	87.43	11.87
		49.41	0.59	43.86	6.13	93.77	0.74	5.05	0.44	0.35	0.57	86.26	12.82
		48.87	1.13	43.87	6.14	92.89	1.39	5.29	0.43	0.39	1.04	85.63	12.94
		47.34	2.09	44.36	6.20	91.05	2.53	5.90	0.52	0.02	1.85	85.55	12.58
		46.90	3.12	43.85	6.13	89.25	3.81	6.48	0.46	0.04	2.79	84.36	12.81
		44.39	5.19	44.31	6.11	88.32	5.56	5.42	0.70	0.35	4.86	82.31	12.50
		39.58	10.28	44.06	6.08	76.84	12.03	9.92	1.20	1.12	8.47	78.84	12.01
		30.18	20.29	43.46	6.07	58.63	22.29	17.28	1.80	3.85	18.30	67.88	11.09

[a] $100w_{5S}$ = water mass percentage in the ethanolic solvent.

vegetable oils. The molar mass values obtained as well as the volume and area parameter values, calculated by eq 4, are presented in Table 3. The corresponding values for the commercial oleic acid as well as its composition were taken from Rodrigues et al.[11] Brazil nut oil, macadamia nut oil, and commercial oleic acid were treated in this work as pseudocompounds with the average molar masses indicated in Table 3.

Tables 4 and 5 present, respectively, the overall experimental composition of the mixtures and the corresponding tie lines for the pseudoternary (anhydrous ethanol as solvent) and pseudoquaternary (aqueous ethanol as solvent) model systems composed of macadamia nut oil + commercial oleic acid + solvent and Brazil nut oil + commercial oleic acid + solvent. All concentrations are given as mass percentages.

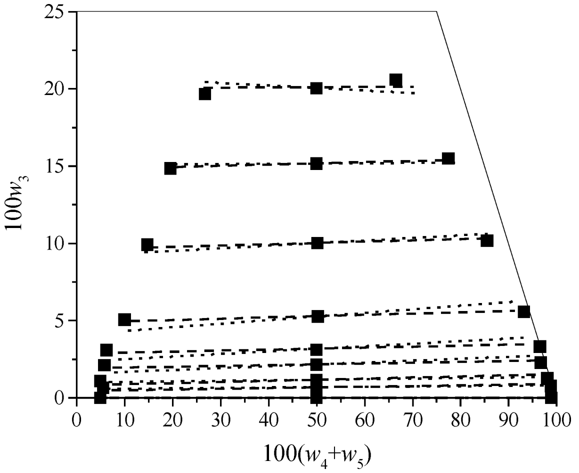

Figure 1. System of macadamia nut oil (1) + commercial oleic acid (3) + 6.22% aqueous solvent [ethanol (4) + water (5)] at (298.2 ± 0.1) K: ■, experimental; – – –, NRTL; · · · · ·, UNIQUAC.

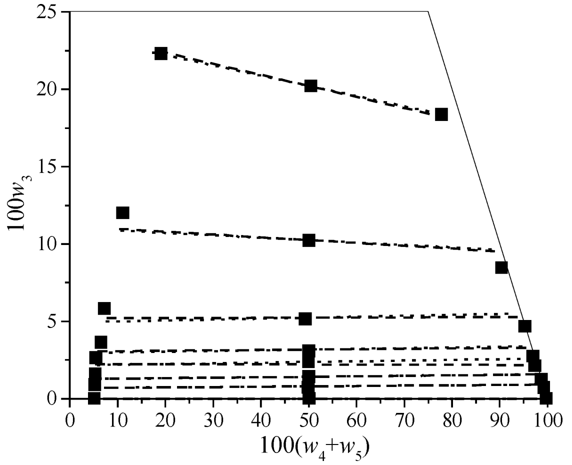

Figure 2. System of macadamia nut oil (1) + commercial oleic acid (3) + 12.27% aqueous solvent [ethanol (4) + water (5)] at (298.2 ± 0.1) K: ■, experimental; – – –, NRTL; · · · · ·, UNIQUAC.

Table 6. UNIQUAC and NRTL Parameters for the Systems with Macadamia Nut Oil and Brazil Nut Oil, at (298.2 ± 0.1) K

		UNIQUAC model		NRTL model		
system	pair ij[a]	A_{ij}/K	A_{ji}/K	A_{ij}/K	A_{ji}/K	α_{ij}
macadamia nut	13	309.51	−224.33	514.22	−336.72	0.233 14
	14	268.96	−62.445	503.38	1414.0	0.489 08
	15	1403.8	−96.396	−312.02	3753.5	0.154 04
	34[b]	67.641	−88.948	4800.0	−170.55	0.229 57
	35[b]	191.68	157.03	1006.7	4210.6	0.100 00
	45[b]	337.46	−279.92	−10.984	−173.64	0.150 18
Brazil nut	23	291.17	−215.98	−219.22	−142.57	0.700 00
	24	258.36	−58.900	346.82	1415.7	0.509 65
	25	1135.0	−105.77	−364.07	3779.9	0.162 14
	34[b]	67.641	−88.948	4800.0	−170.55	0.229 57
	35[b]	191.68	157.03	1006.7	4210.6	0.100 00
	45[b]	337.46	−279.92	−10.984	−173.64	0.150 18

[a] Macadamia nut oil (1), Brazil nut oil (2), commercial oleic acid (3), ethanol (4), and water (5). [b] Parameters taken from Rodrigues et al.[11]

The 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 around 99% were obtained for all tie lines, indicating a good alignment between the experimental data, relative to both overall and phase concentrations.

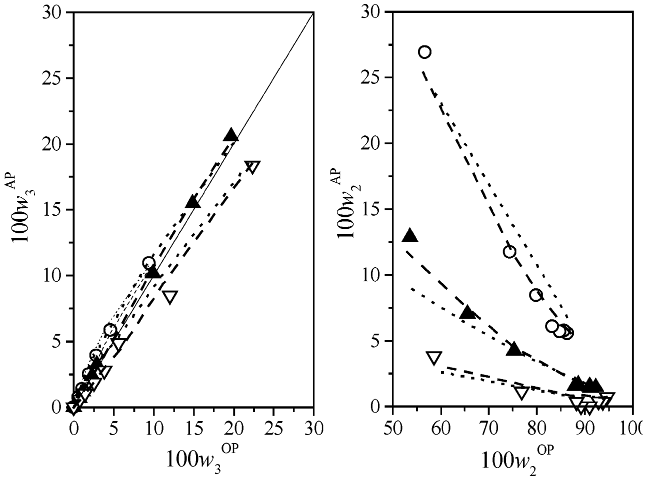

Figure 3. Distribution diagram at (298.2 ± 0.1) K for systems of Brazil nut oil (2) + commercial oleic acid (3) + ethanol (4) + water (5): ○, $100w_{5S}$ = 0 mass %; ▲, $100w_{5S}$ = 6.22%; ▽, $100w_{5S}$ = 12.27%; – – –, NRTL; · · · · ·, UNIQUAC.

Table 7. Mean Deviations in Phase Compositions for the Systems with Macadamia Nut Oil and Brazil Nut Oil, at (298.2 ± 0.1) K

		Δw/%	
system	$100w_{5S}$	UNIQUAC	NRTL
macadamia nut	0	1.55	1.40
	6.22	1.42	1.12
	12.27	0.77	0.72
	global deviation of the correlation	1.28	1.02
Brazil nut	0	1.45	0.64
	6.22	0.89	0.44
	12.27	0.78	0.64
	global deviation of the correlation	0.91	0.53

Figures 1 and 2 show the experimental points and calculated tie lines for the systems macadamia nut oil + commercial oleic acid + 6.22 mass % aqueous ethanol and macadamia nut oil + commercial oleic acid + 12.27 mass % aqueous ethanol, respectively. The equilibrium diagrams are plotted in triangular coordinates. To represent the pseudoquaternary systems in triangular coordinates, ethanol + water was admitted as a mixed solvent. Figures 1 and 2 indicate that both thermodynamic models studied are able to describe with accuracy the phase compositions for the systems investigated.

Figure 3 presents the distribution of oleic acid and oil between the phases for the system composed of Brazil nut oil + commercial oleic acid + solvent.

It can be observed that the addition of water reduces the solvent capacity of extracting free fatty acids. On the other hand, the loss of neutral oil is highly suppressed by the water content in the solvent. The results shown in Figure 3 indicate that both models provided a good representation of the fatty compound distribution between the two liquid phases, but the NRTL model allowed a better estimation of the fatty acid and oil concentrations.

Table 6 presents the adjusted parameters of the UNIQUAC and NRTL models for the systems composed of macadamia nut oil and Brazil nut oil. The deviations between experimental and calculated compositions in both phases were calculated according to eq 3 and are shown in Table 7. It should be emphasized that only the parameters between each vegetable oil and the other compounds of the system were adjusted, that is, only the pairs such as *13*,

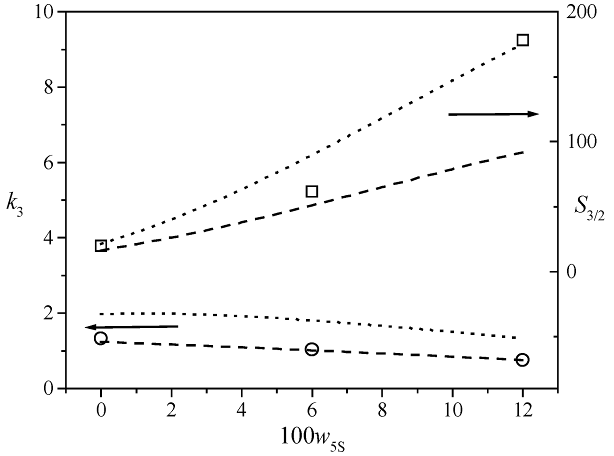

Figure 4. Experimental fatty acid distribution coefficient (○) and selectivities (□) for systems of Brazil nut oil (2) + commercial oleic acid (3) + ethanol (4) + water (5): − − −, NRTL; · · · · ·, UNIQUAC.

14, and *15* and *23*, *24*, and *25* (see the definitions in Table 3).

To have better insight on the influence of the water content on the performance of the solvent, flash calculations were performed using the NRTL and UNIQUAC models for a model system containing 2 mass % oleic acid and different water concentrations in the solvent, fixing the mass ratio between Brazil nut oil and solvent at the value 1:1.

Figure 4 shows experimental and estimated oleic acid distribution coefficients and acid/oil selectivities for the systems composed of Brazil nut oil + 2 mass % commercial oleic acid + solvent. The corresponding values were calculated according to eqs 7 and 8 below.

$$k_i = \frac{w_i^{\mathrm{AP}}}{w_i^{\mathrm{OP}}} \tag{7}$$

$$S_{i/j} = \frac{k_i}{k_j} \tag{8}$$

As can be seen, the addition of water causes a significant increase in the solvent selectivity. The thermodynamic model estimations of the fatty acid distribution coefficient are significantly different (Figure 4), and this result is in accordance with global deviations obtained for the two models (see Table 7). Such a result confirms that the NRTL model provided a better description of the fatty acid concentrations, especially in the case of Brazil nut oil.

Moreover, these results show that the NRTL model provides a good description of selectivity, except for the experimental points with 12 mass % water content in the solvent. For this system, 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 the case of the UNIQUAC model, the good result of selectivity estimation for high water content in the solvent is due to the bad estimation of the fatty acid and oil distribution coefficients (see eq 8).

The results shown in this paper corroborate the efforts to improve the vegetable oils deacidification technique by liquid−liquid extraction. The high values of selectivity coefficients obtained in the case of solvents with water show the feasibility of the use of ethanol as a free fatty acid extractant.

Apelblat and co-workers[30] published a paper that reports phase diagrams for soybean oil or jojoba oil plus oleic acid and several solvents (1,2-butanediol, dimethyl sulfoxide, *cis*-2-butene-1,4-diol, formamide, and *n*-methylformamide), at 298.15 K. Especially in the case of 1,2-butanediol, the fatty acid distribution coefficients and selectivity values are appropriate for an efficient deacidification process ($0.79 \le k \le 1.12$ and $3.3 \le S \le 77.4$).

As shown by the results of the present work, anhydrous ethanol guarantees distribution coefficients up to 1.39 but low selectivity values ($2.5 \le S \le 21.6$). However, the addition of small amounts of water to the solvent allows a significant increase of the selectivity without a major decrease of the distribution coefficients. In the case of ethanol with 6 mass % water, the following values were obtained: $0.97 \le k \le 1.21$ and $4.37 \le S \le 277.46$.

Conclusions

The results shown in this paper corroborate the efforts to improve the vegetable oil deacidification technique by liquid−liquid extraction. It can be observed that by adding water to the solvent there is a large increase in the heterogeneous region and in the selectivity, with a slight decrease of the oleic acid distribution coefficient.

Despite the complexity of the studied systems, the estimated parameters of the NRTL and UNIQUAC models are representative, since the description of the liquid−liquid equilibrium for all the systems had presented mean deviations lower than 1.5% in relation to the experimental data. With these parameters, the modeling and the simulation of liquid−liquid extractors for vegetable oil deacidification are possible.

Literature Cited

(1) Elias, L. G.; Bressani, R. The Nutritive Value of the Brazil Nut Oil. *J. Am. Oil Chem. Soc.* **1961**, *38*, 450−452.
(2) Mason, R. L. Macadamia nut Quality Research. The Processing Challenge. *Food Aust.* **2000**, *52*, 416−419.
(3) Kaijser, A.; Dutta, P.; Savage, G. Oxidative Stability and Lipid Composition of Macadamia Nuts grown in New Zealand. *Food Chem.* **2000**, *71*, 67−70.
(4) Assunção, F. P.; Bentes, M. H. S.; Serruya, H. A Comparison of Stability of Oils from Brazil Nut, Para Rubber and Passion Fruit Seeds. *J. Am. Oil Chem. Soc.* **1984**, *61*, 1031−1036.
(5) Vieira, T. M. F. S.; Regitano-d'Arce, M. A. B. Antioxidant Concentration effect on Stability of Brazil Nut (*Bertholletia excelsa*) crude oil. *Arch. Latinoam. Nutr.* **1999**, *3*, 271−274.
(6) Fornari, T.; Bottini, S.; Brignole, E. An Application of UNIFAC to Vegetable Oil-Alkane Mixtures. *J. Am. Oil Chem. Soc.* **1994**, *71* (4), 391−395.
(7) González, C.; Resa, J. M.; Ruiz, A.; Gutiérrez, J. I. Densities of Mixtures Containing *n*-Alkanes with Sunflower Seed Oil at Different Temperatures. *J. Chem. Eng. Data* **1996**, *41* (4), 796−798.
(8) Leibovitz, Z.; Ruckenstein, C. Our Experiences in Processing Maize (Corn) Germ Oil. *J. Am. Oil Chem. Soc.* **1983**, *60* (2), 347A−351A.
(9) Cvengros, J. Physical Refining of Edible Oils. *J. Am. Oil Chem. Soc.* **1995**, *72* (10), 1193−1196.
(10) Antoniassi, R.; Esteves, W.; Meirelles, A. J. A. Pretreatment of Corn Oil for Physical Refining. *J. Am. Oil Chem. Soc.* **1998**, *75* (10), 1411−1415.
(11) Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol + Water at 298.2 K. *J. Chem. Eng. Data* **2003**, *48* (2), 367−373.
(12) Rodrigues, C. E. C.; Pessôa Filho, P. A.; Meirelles, A. J. A. Phase Equilibrium for the System Rice Bran Oil + Fatty Acids + Ethanol + Water + γ-Oryzanol + Tocols. *Fluid Phase Equilib.* **2004**, *216* (2), 271−283.
(13) Thomopoulos, C. Méthode de Desacidification des Huiles par Solvant Sélectif. *Rev. Fr. Corps Gras* **1971**, *18*, 143−150.
(14) Bhattacharyya, A. C.; Majumdar, S.; Bhattacharyya, D. K. Refining of FFA Rice Bran Oil by Isopropanol Extraction and Alkali Neutralization. *Oleagineux* **1987**, *42*, 431−433.
(15) Shah, K. J.; Venkatesan, T. K. Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils. *J. Am. Oil Chem. Soc.* **1989**, *66*, 783−787.

(16) Kim, S.; Kim, C.; Cheigh, H.; Yoon, S. Effect of Caustic Refining, Solvent Refining and Steam Refining on the Deacidification and Color of Rice Bran Oil. *J. Am. Oil Chem. Soc*. **1985**, *62*, 1492−1495.

(17) Kale, V.; Katikaneni, S. P. R.; Cheryan, M. Deacidifying Rice Brain Oil by Solvent Extraction and Membrane Technology. *J. Am. Oil Chem. Soc*. **1999**, *76*, 723−727.

(18) Pina, C. G.; Meirelles, A. J. A. Deacidification of Corn Oil by Solvent Extraction in a Perforated Rotating Disc Column. *J. Am. Oil Chem. Soc*. **2000**, *77*, 553−559.

(19) Batista, E.; Monnerat, S.; Kato, K.; Stragevitch, L.; Meirelles, A. J. A. Liquid−Liquid Equilibrium for Systems of Canola Oil, Oleic Acid, and Short-Chain Alcohols. *J. Chem. Eng. Data* **1999**, *44*, 1360−1364.

(20) Gonçalves, B. G.; Batista, E.; Meirelles, A. J. A. Liquid−Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 416−420.

(21) Gonçalves, B. G.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2K. *Fluid Phase Equilib.* **2004**, *221*, 139−150.

(22) AOCS. *Official methods and recommended practices of the American Oil Chemists' Society*, 3rd ed.; AOCS Press: Champaign, IL, 1988; Vols. 1−2.

(23) AOCS. *Official methods and recommended practices of the American Oil Chemists' Society*, 5th ed.; AOCS Press: Champaign, IL, 1998.

(24) *IUPAC Standard methods for the analysis of oils*, *fats and derivatives*, 6th ed.; Paquot, C., Ed.; Pergamon Press: New York, 1979; Part 1 (sections I and II).

(25) Marcilla, A.; Ruiz, F.; García, A. N. Liquid-Liquid-Solid Equilibria of the Quaternary System Water−Ethanol−Acetone−Sodium Chloride at 25 °C. *Fluid Phase Equilib.* **1995**, *112*, 273−289.

(26) Magnussen, T.; Rasmussen, P.; Fredenslund, A. Unifac Parameter Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev*. **1981**, *20*, 331−339.

(27) Stragevitch, L.; d'Avila, S. G. Application of a Generalized Maximum Likelihood Method in the Reduction of Multicomponent Liquid-Liquid Equilibrium Data. *Braz. J. Chem. Eng.* **1997**, *14*, 41−52.

(28) Firestone, D., Ed. *Physical and Chemical Characteristics of Oils, Fats, and Waxes*; AOCS Press: Washington DC, 1999.

(29) Antoniosi Filho, N. R.; Mendes, O. L.; Lanças, F. M. Computer Prediction of Triacylglycerol Composition of Vegetable Oils by HRGC. *Chromatographia* **1995**, *40*, 557−562.

(30) Apelblat, A.; Zaharoskin, T.; Wisniak, J.; Korngold, E. Extraction of Oleic Acid from Soybean Oil and Jojoba Oil−Phase Diagrams. *J. Am. Oil Chem. Soc*. **1996**, *73*, 239−244.

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