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Phase Equilibrium for Systems Composed by High Unsaturated Vegetable Oils + Linoleic Acid + Ethanol + Water at 298.2 K

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This work reports experimental liquid−liquid equilibrium data for model systems composed by refined vegetable oils + linoleic acid + ethanol + water at 298.2 K. The experimental data were used for adjusting parameters of the NRTL and UNIQUAC models. Global deviations between calculated and experimental data not higher than 1 % were obtained for all systems, showing the good descriptive quality of the models.

Introduction

The application of liquid−liquid extraction technique for the deacidification of vegetable oils has shown good results in relation to decreasing the oil acidic value with low losses of neutral oil and nutraceutical compounds.[1,2] Liquid−liquid extraction for oil deacidification is based on the difference of solubility of free fatty acids and neutral triacylglycerols in an appropriate solvent.[3] Several studies show that deacidification can be conducted using short-chain alcohols as solvent,[4−10] although ethanol has been suggested to be the best solvent for the process. Ethanol shows low toxicity, ease of recovery in the process, and good values of selectivity and distribution coefficient for free fatty acids.[10]

Experimental data relating to the equilibrium of systems composed by vegetable oils + fatty acids + solvents are necessary for the design of the equipment that make industrial-scale liquid−liquid extraction feasible for refining oils. Previous papers reported equilibrium data for systems composed of vegetable oils and saturated or monounsaturated free fatty acids such as stearic, palmitic, and oleic acids.[1,2,10−13]

The aim of the present work was to investigate and to correlate with thermodynamic equations (UNIQUAC and NRTL models) the phase equilibrium of vegetable oils with a high level of unsaturated fatty acids + linoleic acid + ethanol + water at 298.2 K. The oils chosen for this study were garlic oil, grape seed oil, and sesame seed oil. All these oils exhibit, besides their high content of linoleic acid, antioxidant properties, characterizing them as healthy food solutions.[14−16]

Experimental Section

Materials. The solvents used in this work were anhydrous ethanol from Merck with purity greater than 99.5 % and aqueous solvents with different water contents (6, 12, and 18 mass %) prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol.

All fatty reagents used in this study [linoleic acid (99.9 mass %, Sigma), commercial linoleic acid (Fluka), and refined oils (kindly supplied by Campestre, Brazil) from grape seed, garlic, and sesame seed] were analyzed by gas chromatography of fatty acid methyl esters in order to determine the fatty acid composition, according to the official method (1-62) of the AOCS.[17] The fatty samples were prepared in the form of fatty acid methyl esters according to the official method (2-66) of the AOCS.[18] A 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 acids methyl esters were identified by comparison with external standards purchased from Nu Check Inc. (Elysian, IL). The quantification was accomplished by internal normalization. The residual acidity values, expressed as linoleic acid, for the grape seed oil, garlic oil, and sesame oil were 0.32 mass %, 0.11 mass %, and 0.42 mass %, respectively.

Experimental Procedure. Model fatty systems containing fatty acids and triacylglycerols were prepared by the addition of known quantities of linoleic acid to refined 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 liquid−liquid equilibrium data used to adjust NRTL and UNIQUAC parameters. In the systems containing garlic oil, pure linoleic acid was used as the fatty acid source. In the case of grape seed and sesame seed oils, a commercial linoleic acid was used.

Liquid−liquid equilibrium data were determined using polypropylene centrifuge tubes (50 mL) (Corning Inc.). The components were weighed on an analytical balance Adam model AAA200, 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 based on a previous study that showed phase equilibrium was attained after 1 h of rest.[1]

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[19]) with an

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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 [17] with a KF Titrino (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: (0.01 to 0.45) mass % for refined oils, (0.01 to 0.28) mass % for fatty acids, (0.01 to 0.40) mass % for ethanol, and (0.01 to 0.04) mass % for water, being the lowest figures obtained for the lowest concentrations.

To test the validity of results obtained, the procedure developed by Marcilla et al.[20] was followed. The composition of all the components was analyzed in the two liquid phases, and the corresponding triacylglycerol concentration was obtained by balance in each phase. Consequently, i independent component balances can be written where i is the component of system given by

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

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}), then the previous system can be written as

$$\mathbf{M} = \mathbf{B}\cdot\mathbf{P} \tag{2}$$

Mathematic calculations lead to the expression

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

where $\mathbf{B}^{\mathrm{T}}$ is the transpose matrix of $\mathbf{B}$ and $(\mathbf{B}^{\mathrm{T}}\mathbf{B})^{-1}$ is the inverse matrix of $(\mathbf{B}^{\mathrm{T}}B)$. So, the values of M_{OP} and M_{AP} (matrix $\mathbf{P}$), which minimize the errors of the previous system, have been calculated. When the absolute value of the difference of the sum ($M_{\mathrm{OP}} + M_{\mathrm{AP}}$) to M_{OC} was higher than 0.5 %, the corresponding data were rejected and the tie line was repeated.

Modeling Approach

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.[1,2,10,12,13,21] Rodrigues et al.[2] show the activity coefficient equations, expressed in mass fractions, according to the NRTL and UNIQUAC models.

The adjustments were made by treating the model systems refined vegetable oils + fatty acids + anhydrous ethanol as a pseudoternary one and the model systems refined vegetable oils + fatty acids + ethanol + water as pseudoquaternary ones. The systems were considered as composed by a single triacylglycerol having the refined vegetable oils average molar masses, a representative fatty acid with the molar mass of the commercial linoleic acid in the case of systems composed by grape and sesame oils, ethanol, and water.

The values of r_i' and q_i', 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 refined oils or the fatty acids of the commercial linoleic acid, $\upsilon_k^{(j)}$ 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 compounds in the oil or in the fatty acid, G is the total number of groups, and R_i and Q_i are van der Waals parameters taken from Magnussen et al.:[22]

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

The estimation of interaction parameters was based on the minimization of the objective function of composition (eq 5), following the procedure developed by Stragevitch and d'Avila:[23]

$$\mathrm{OF}(w) = \sum_m^D \sum_n^N \sum_i^{C-1} \left[\left(\frac{w_{inm}^{\mathrm{OP,ex}} - w_{inm}^{\mathrm{OP,calc}}}{\sigma_{w_{inm}^{\mathrm{OP}}}} \right)^2 + \left(\frac{w_{inm}^{\mathrm{AP,ex}} - w_{inm}^{\mathrm{AP,calc}}}{\sigma_{w_{inm}^{\mathrm{AP}}}} \right)^2 \right] \tag{5}$$

where D is the total number of groups of data, N is the total number of tie lines, and 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; the superscripts OP and AP stand for oil and alcoholic phases, respectively; and ex and calc 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.

In this work, the following parameters were adjusted: interaction parameters between refined garlic oil (1) + pure linoleic acid (4) + ethanol (6) + water (7) and between refined grape seed oil (2) + commercial linoleic acid (5) + ethanol (6) + water (7). In the case of systems composed by refined sesame oil (3) + commercial linoleic acid (5) + ethanol (6) + water (7), the interaction parameters between compounds (5), (6), and (7) were taken from the parameters adjusted for the grape seed oil system, being only the interaction parameters with sesame oil (3) submitted to a new adjustment. For all three adjusting cases, the parameters between ethanol (6) and water (7) were taken from the previous studies on phase equilibrium of the systems composed by vegetable oils + commercial oleic acid + ethanol + water at 298.2 ± 0.1 K.[1,12] The deviations between experimental and calculated compositions in both phases were calculated according to

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

Results

The fatty acid compositions of the refined oils are presented in Table 1. From this fatty acid composition, it was possible to determine the probable triacylglycerol composition of the refined oils (Table 2) by using the procedure suggested by Antoniosi Filho et al.[24] In Table 2, the main triacylglycerol represents the

Table 1. Fatty Acid Composition of Refined Oils

symbol	fatty acid		M^a g·mol^{-1}	garlic oil mol %	garlic oil mass %	grape seed oil mol %	grape seed oil mass %	sesame oil mol %	sesame oil mass %
M	miristic	C14:0^b	228.38	0.00	0.00	0.00	0.00	0.17	0.14
P	palmitic	C16:0	256.43	14.24	13.14	7.83	7.19	12.38	11.40
Po	palmitoleic	C16:1	254.42	0.00	0.00	0.00	0.00	0.12	0.11
S	stearic	C18:0	284.49	2.21	2.26	3.88	3.95	4.19	4.28
O	oleic	C18:1	282.47	34.05	34.59	20.58	20.80	25.07	25.44
Li	linoleic	C18:2	280.45	47.86	48.27	66.51	66.72	51.15	51.53
Le	linolenic	C18:3	278.44	0.87	0.87	0.38	0.38	5.87	5.87
A	arachidic	C20:0	312.54	0.51	0.58	0.26	0.29	0.39	0.44
Ga	gadoleic	C20:1	310.52	0.26	0.29	0.07	0.08	0.29	0.33
Be	behenic	C22:0	340.59	0.00	0.00	0.49	0.59	0.37	0.46

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

Table 2. Probable Triacylglycerol Composition of Refined Oils

main group	triacylglycerol	M^a g·mol^{-1}	garlic oil mol %	garlic oil mass %	grape seed oil mol %	grape seed oil mass %	sesame oil mol %	sesame oil mass %
50:1^b	POP	833.37	1.89	1.81			1.08	1.04
50:2	PLiP	831.35	2.66	2.53	1.08	1.03	2.27	2.16
52:1	POS	861.45	0.60	0.59			0.74	0.73
52:2	POO	859.40	6.24	6.15	2.16	2.12	4.09	4.03
52:3	POLi	857.39	15.24	14.98	7.04	6.89	10.84	10.65
52:4	PLiLi	855.37	10.97	10.77	11.41	11.14	12.15	11.91
52:5	PLeLi	853.37					2.59	2.54
54:2	SOO	887.46	1.18	1.20	0.88	0.90	1.33	1.35
54:3	OOO	885.44	6.36	6.46				
54:3	SLiO	885.44			4.40	4.59	5.35	5.43
54:4	OLiO	883.43	18.05	18.28	14.24	14.36	13.78	13.96
54:5	OLiLi	881.41	23.33	23.58	27.86	28.03	21.72	21.94
54:6	LiLiLi	879.43	11.60	11.70	30.21	30.33	18.03	18.17
54:7	LiLeLi	877.38	0.59	0.60			4.89	4.92
54:8	LiLeLe	875.38					0.53	0.53
56:3	OLiA	913.52	0.65	0.68				
56:4	LiLiA	911.50	0.64	0.69			0.61	0.64
58:4	LiLiBe	939.55			0.71	0.79		

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

Table 3. Fatty Acid Composition of Commercial Linoleic Acid

symbol	mol %	mass %	symbol	mol %	mass %
M	0.22	0.18	Li	72.08	72.41
P	6.95	6.38	Le	0.41	0.41
S	3.22	3.28	A	0.16	0.18
O	16.95	17.15			

Table 4. Average Molar Masses (*M*), Boiling Points (T_b), and Structural Parameters (r_i' and q_i')

compound	M^a g·mol^{-1}	$T_b{}^b$ K	r_i'	q_i'
refined garlic oil (1)	872.00	641.99	0.044035	0.035689
refined grape seed oil (2)	876.07	639.81	0.043947	0.035595
refined sesame oil (3)	872.39	640.09	0.043976	0.035628
pure linoleic acid (4)	280.45		0.044672	0.036676
commercial linoleic acid (5)	279.18		0.044839	0.036850
ethanol (6)	46.07		0.055905	0.056177
water (7)	18.02		0.051069	0.077713

[a] Oils average molar masses calculated using the procedure suggested by Antoniosi Filho et al.[24] [b] Boiling points at low pressure (P = 1 kPa) calculated according to Ceriani and Meirelles.[26]

component of greatest concentration in the isomer set with x carbons and y double bonds.

Table 3 presents the fatty acid composition of commercial linoleic acid. This fatty acid was also analyzed by gas chromatograph using the methodology described above. The results shown in Tables 2 and 3 allow us to calculate the average molar masses of the refined oils and commercial linoleic acid. The molar masses values obtained as well as volume and area parameters values, calculated by eq 4, are presented in Table 4. Refined grape seed oil, refined garlic oil, refined sesame oil, and commercial linoleic acid were treated in this work as pseudocompounds with the average molar masses indicated in Table 4.

As can be seen in Table 4, the two free fatty acid sources used in this work, pure linoleic acid and commercial linoleic acid, are similar in terms of average molar masses and structural parameters. According to the paper published by Gonçalves and Meirelles,[13] the distribution coefficients of palmitic (C16:0) and oleic (C18:1) acids in the systems composed by palm oil + oleic or palmitic acid + ethanol + water are similar, despite the difference of two carbons and one double bond in the carbonic chain of those fatty acids.

In Table 4, the predicted boiling points at low pressure of vegetable oils used in this work are shown. Vapor−liquid processes in the edible oil industry usually occur at low pressures (0.1−1 kPa).[25] This additional information was calculated using the procedure suggested by Ceriani and Meirelles.[26] The calculated results indicate and show that the edible oils are very similar, differing only 1.2 K in their estimated boiling points.

Tables 5 to 7 present 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 by refined garlic oil + pure linoleic acid + solvent (Table 5), refined grape seed oil + commercial linoleic acid + solvent (Table 6), and refined sesame oil + commercial linoleic acid + solvent (Table 7). All concentrations are given as mass percentages.

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

Table 5. Liquid−Liquid Equilibrium Data for the System Refined Garlic Oil (1) + Linoleic Acid (4) + Solvent [Ethanol (6) + Water (7)] at (298.2 ± 0.1) K

	OC[a]				OP[b]				AP[c]			
$100w_{7S}$[d]	$100w_1$	$100w_4$	$100w_6$	$100w_7$	$100w_1$	$100w_4$	$100w_6$	$100w_7$	$100w_1$	$100w_4$	$100w_6$	$100w_7$
0	50.0	0.0	50.0	0.0	85.8	0.0	14.3	0.0	6.9	0	93.1	0.0
	49.0	1.0	50.0	0.0	83.6	0.9	15.5	0.0	7.2	1.3	91.5	0.0
	47.8	2.1	50.2	0.0	82.2	1.9	15.9	0.0	7.9	2.6	89.4	0.0
	46.9	3.1	50.0	0.0	79.9	2.8	17.3	0.0	8.5	3.9	87.6	0.0
	44.9	5.1	50.0	0.0	74.4	4.6	21.0	0.0	11.8	5.9	82.4	0.0
	40.9	10.2	48.9	0.0	56.7	9.4	33.9	0.0	26.9	10.9	62.2	0.0
6.22	50.0	0.0	46.9	3.1	91.9	0.0	7.5	0.6	1.5	0.0	92.1	6.4
	49.3	0.7	46.9	3.1	91.3	0.7	7.4	0.6	1.5	0.8	91.1	6.7
	48.8	1.2	46.9	3.1	90.2	1.1	8.2	0.5	1.6	1.3	90.6	6.5
	47.8	2.2	47.0	3.1	88.8	2.1	8.3	0.8	1.6	2.4	89.3	6.7
	46.9	3.1	46.9	3.1	87.1	3.0	9.1	0.8	1.7	3.4	88.1	6.8
	44.9	5.1	46.9	3.1	84.0	4.9	10.2	0.9	2.1	5.6	85.4	6.9
	40.1	10.1	46.8	3.1	75.3	9.9	14.0	0.7	4.3	10.2	79.9	5.7
	34.7	15.2	47.0	3.1	65.6	14.9	18.7	0.9	7.0	15.5	72.4	5.1
	29.9	20.3	46.8	3.1	53.6	19.7	25.3	1.5	12.9	20.6	62.0	4.5
12.27	50.0	0.0	43.9	6.1	94.0	0.0	5.4	0.6	0.6	0.0	86.6	12.8
	49.3	0.7	43.9	6.1	93.1	0.9	5.4	0.7	0.4	0.7	85.3	13.6
	48.9	1.1	43.9	6.1	92.7	1.2	5.5	0.6	0.3	1.1	85.4	13.2
	47.9	2.1	43.9	6.1	91.2	2.3	6.0	0.6	0.2	2.0	84.6	13.2
	46.9	3.2	43.9	6.1	89.5	3.5	6.2	0.8	0.2	3.0	83.5	13.3
	44.9	5.1	43.9	6.1	88.3	5.6	5.9	0.9	0.3	4.9	81.3	13.5
	39.7	10.2	44.0	6.1	76.9	12.0	9.7	1.4	1.1	8.5	78.6	11.8
	31.0	20.4	42.5	6.1	58.6	22.3	16.9	2.2	3.8	18.4	67.3	10.5
18.07	49.8	0.0	40.7	9.4	95.0	0.0	4.6	0.4	0.2	0.0	81.9	17.8
	49.4	0.6	40.6	9.4	94.2	0.8	4.5	0.5	0.1	0.5	80.6	18.8
	48.9	1.1	40.6	9.4	93.2	1.5	4.8	0.6	0.1	0.9	80.4	18.6
	48.0	2.1	40.6	9.4	91.5	2.8	5.2	0.5	0.2	1.6	79.5	18.8
	46.9	3.1	40.6	9.4	89.8	4.1	5.7	0.4	0.1	2.4	78.6	18.9
	44.9	5.1	40.6	9.4	86.5	6.6	6.0	0.9	0.3	3.8	77.4	18.5
	40.4	9.7	40.4	9.6	77.1	13.3	8.7	0.9	0.1	6.1	73.6	20.2
	29.5	20.5	40.5	9.4	57.4	25.8	14.9	1.9	0.6	14.9	65.6	18.9

[a] OC = overall composition. [b] OP = oil phase. [c] AP = alcoholic phase. [d] $100w_{7S}$ = water mass percentage in the ethanolic solvent.

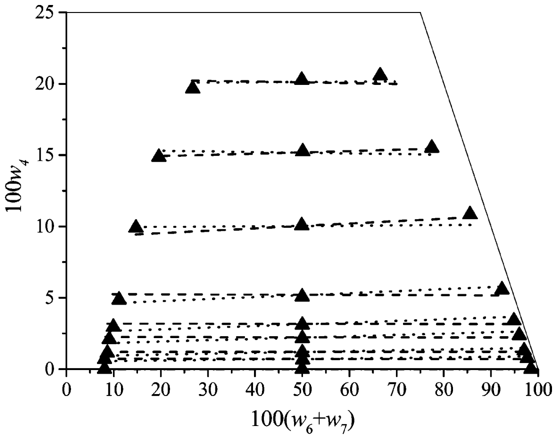

Figure 1. System of refined garlic oil (1) + pure linoleic acid (4) + 6.22 % aqueous solvent [ethanol (6) + water (7)] at (298.2 ± 0.1) K: ▲, experimental; - — -, NRTL model; ···, UNIQUAC model.

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

Figures 1 and 2 show the experimental points and the tie lines calculated using the NRTL and UNIQUAC models for the systems refined garlic oil + linoleic acid + 6.22 mass % aqueous ethanol and refined garlic oil + linoleic 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.

Furthermore, it can be seen that the addition of water to solvent expands the region of phase splitting, allowing the refining of highly acidic oils by solvent extraction. In addition to this, it can be observed that the addition of water to solvent minimizes the losses of neutral oil to alcoholic phase and of the solvent to oil phase (see the baseline in the Figures 1 and 2). This fact occurs due to the decrease of mutual solubility between oil and solvent by the presence of the water in the system.

Table 8 presents the adjusted parameters of the UNIQUAC and NRTL models for the systems composed by garlic oil (system A), grape seed oil (B), and sesame oil (C). The deviations between experimental and calculated compositions in both phases were calculated according to eq 6 and are shown in Table 9.

Figure 3 presents the distribution of linoleic acid and refined oil between the phases for the system composed by refined garlic oil + linoleic 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. In this figure, the good performance of NRTL model to describe the distribution of fatty compounds between the liquid phases can be noted.

Experimental and estimated distribution coefficients and selectivities for the systems composed by refined grape seed oil + commercial linoleic acid + solvent are shown in Figure 4. These entities were calculated according to eqs 7 and 8 below, where the subscript i is fatty acid and j is oil. In this case flash calculations were performed for a model system containing 2 mass % of linoleic acid and different water concentrations in the solvent, fixing the mass

Table 6. Liquid−Liquid Equilibrium Data for the System Refined Grape Seed Oil (2) + Commercial Linoleic Acid (5) + Solvent [Ethanol (6) + Water (7)] at (298.2 ± 0.1) K

	OC[a]				OP[b]				AP[c]			
$100w_{7S}$[d]	$100w_2$	$100w_5$	$100w_6$	$100w_7$	$100w_2$	$100w_5$	$100w_6$	$100w_7$	$100w_2$	$100w_5$	$100w_6$	$100w_7$
0	50.0	0.0	50.0	0.0	86.1	0.0	13.9	0.0	6.2	0.0	93.8	0.0
	48.9	1.1	50.0	0.0	84.7	1.0	14.4	0.0	6.4	1.3	92.3	0.0
	47.8	2.2	50.0	0.0	82.7	1.9	15.5	0.0	7.1	2.6	90.3	0.0
	46.8	3.2	50.0	0.0	80.1	2.8	17.1	0.0	6.1	3.7	90.1	0.0
	45.0	5.1	49.9	0.0	74.4	4.6	21.0	0.0	11.8	5.7	82.4	0.0
	39.8	10.3	49.9	0.0	56.7	9.4	33.9	0.0	26.9	10.9	62.2	0.0
6.22	50.0	0.0	46.9	3.1	93.6	0.0	5.9	0.5	1.4	0.0	91.9	6.7
	49.2	0.8	46.9	3.1	91.9	0.8	6.9	0.5	0.8	0.8	92.1	6.2
	48.8	1.2	46.9	3.1	92.4	1.2	5.8	0.6	0.7	1.4	91.0	6.7
	47.7	2.2	47.0	3.1	90.9	2.1	6.4	0.6	1.3	2.4	90.1	6.3
	46.8	3.2	46.9	3.1	87.9	3.2	8.3	0.6	0.1	3.5	90.3	6.1
	44.7	5.3	46.9	3.1	85.0	5.1	9.5	0.5	1.2	5.6	87.9	5.3
	40.1	10.0	46.8	3.1	75.3	9.9	14.0	0.7	4.3	10.2	79.9	5.7
	34.8	15.3	46.8	3.1	65.6	14.9	18.7	0.9	7.0	15.5	72.4	5.1
	30.8	20.1	45.9	3.1	53.6	19.7	25.3	1.5	12.9	20.6	62.0	4.5
12.27	50.0	0.0	43.9	6.1	94.9	0.0	4.7	0.3	0.5	0.0	87.5	12.0
	49.2	0.8	43.9	6.1	94.0	1.0	4.7	0.4	0.1	0.8	87.1	12.0
	48.8	1.2	43.9	6.1	93.4	1.3	4.9	0.5	0.2	1.0	86.7	12.1
	47.8	2.2	43.8	6.1	91.9	2.4	5.1	0.5	0.6	2.0	85.5	11.9
	46.8	3.2	43.9	6.1	90.2	3.6	5.9	0.3	0.5	2.9	84.6	12.1
	44.8	5.2	43.9	6.1	87.0	5.8	6.6	0.6	0.1	4.7	83.7	11.6
	39.6	10.3	44.1	6.1	76.9	12.0	9.7	1.4	1.1	8.5	78.6	11.8
	30.0	20.3	43.6	6.1	58.6	22.3	16.9	2.2	3.8	18.4	67.3	10.5
18.07	50.0	0.0	40.6	9.4	97.6	0.0	2.1	0.3	0.1	0.0	81.9	18.1
	49.0	0.8	40.8	9.4	94.9	0.9	3.9	0.3	0.5	0.5	80.1	18.9
	48.7	1.3	40.6	9.4	95.0	1.6	3.0	0.4	0.4	1.0	80.6	18.1
	47.9	2.1	40.6	9.4	94.4	2.8	2.5	0.3	0.4	1.6	80.0	18.0
	46.8	3.1	40.7	9.4	90.8	4.1	4.8	0.4	0.3	2.3	79.7	17.8
	44.7	5.3	40.6	9.4	86.8	6.8	6.1	0.4	0.3	3.8	77.5	18.5
	40.2	9.9	40.8	9.1	77.1	13.3	8.7	0.9	0.1	6.1	73.6	20.2
	29.2	20.6	40.6	9.6	57.4	25.8	14.9	1.9	0.6	14.9	65.6	18.9

[a] OC = overall composition. [b] OP = oil phase. [c] AP = alcoholic phase. [d] $100w_{7S}$ = water mass percentage in the ethanolic solvent.

Table 7. Liquid-liquid Equilibrium Data for the System Refined Sesame Oil (3) + Commercial Linoleic Acid (5) + Solvent [Ethanol (6) + Water (7)], at (298.2±0.1) K

	OC[a]				OP[b]				AP[c]			
$100w_{7S}$[d]	$100w_3$	$100w_5$	$100w_6$	$100w_7$	$100w_3$	$100w_5$	$100w_6$	$100w_7$	$100w_3$	$100w_5$	$100w_6$	$100w_7$
0	50.0	0.0	50.0	0.0	85.3	0.0	14.7	0.0	6.6	0.0	93.5	0.0
	48.5	1.5	50.0	0.0	82.7	1.5	15.8	0.0	7.0	1.9	91.1	0.0
	47.5	2.4	50.1	0.0	81.0	2.3	16.7	0.0	7.5	3.1	89.4	0.0
	46.8	3.3	50.0	0.0	79.0	3.1	18.0	0.0	8.2	4.1	87.7	0.0
	44.7	5.1	50.2	0.0	74.4	4.6	21.0	0.0	11.8	5.9	82.4	0.0
	40.6	10.2	49.2	0.0	56.7	9.4	33.9	0.0	26.9	10.9	62.2	0.0
6.22	49.9	0.0	47.0	3.1	92.7	0.0	6.7	0.6	1.5	0.0	91.7	6.8
	49.1	0.9	46.9	3.1	91.2	0.9	7.4	0.5	1.2	1.0	91.2	6.5
	48.8	1.2	46.9	3.1	91.5	1.1	6.7	0.7	1.3	1.2	90.6	6.9
	47.7	2.3	46.9	3.1	89.3	2.1	8.0	0.5	1.0	2.3	90.1	6.6
	46.7	3.3	46.9	3.1	87.2	3.1	9.0	0.6	0.3	3.5	89.4	6.8
	44.7	5.3	46.9	3.1	84.6	4.9	9.9	0.7	2.0	5.5	86.3	6.2
	40.4	10.0	46.6	3.1	75.3	9.9	14.0	0.7	4.3	10.2	79.9	5.7
	34.7	15.2	47.0	3.1	65.6	14.9	18.7	0.9	7.0	15.5	72.4	5.1
	29.9	20.2	46.9	3.1	53.6	19.7	25.3	1.5	12.9	20.6	62.0	4.5
12.27	50.0	0.0	43.9	6.1	94.8	0.0	4.8	0.4	0.4	0.0	86.6	13.0
	49.2	0.8	43.9	6.1	94.5	0.9	4.2	0.5	0.0	0.7	86.4	12.9
	48.6	1.4	43.9	6.1	92.2	1.6	5.7	0.5	0.4	1.5	85.5	12.7
	47.5	2.5	43.9	6.1	90.9	2.7	5.9	0.5	0.3	2.2	84.9	12.5
	46.7	3.3	43.9	6.1	89.6	3.5	6.3	0.6	0.3	2.8	85.4	11.6
	44.7	5.3	43.9	6.1	86.3	5.6	7.5	0.6	0.3	4.5	82.9	12.3
	40.0	10.1	43.9	6.1	76.9	12.0	9.7	1.4	1.1	8.5	78.6	11.8
	29.9	20.3	43.8	6.0	58.6	22.3	16.9	2.2	3.8	18.4	67.3	10.5

[a] OC = overall composition. [b] OP = oil phase. [c] AP = alcoholic phase. [d] $100w_{7S}$ = water mass percentage in the ethanolic solvent.

ratio between oil and solvent at the value 1:1:

$$k_i = \frac{w_i^{\mathrm{AP}}}{w_i^{\mathrm{OP}}} \qquad (7)$$

$$S_{i/j} = \frac{k_i}{k_j} \qquad (8)$$

Figure 4 shows that the addition of water to ethanol increases the solvent selectivity, reducing the loss of neutral oil. On the other hand, the fatty acid distribution coefficient is reduced with the increase of water content in the solvent. Based on this fact, it should be considered that a higher number of theorical stages would be necessary in order to totally deacidify the oil in an industrial operation.

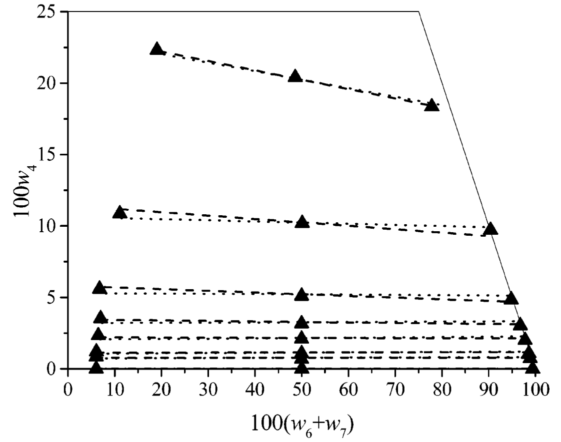

Figure 2. System of refined garlic oil (1) + pure linoleic acid (4) + 12.27 % aqueous solvent [ethanol (6) + water (7)] at (298.2 ± 0.1) K: ▲, experimental; - — -, NRTL model; ···, UNIQUAC model.

Table 8. UNIQUAC and NRTL Parameters for the Systems with Refined Garlic Oil, Refined Grape Seed Oil, and Refined Sesame Oil at (298.2 ± 0.1) K

	UNIQUAC model		NRTL model		
	A_{ij}	A_{ji}	A_{ij}	A_{ji}	
pair *ij* [a]	K	K	K	K	α_{ij}
14	279.09	−212.48	−2001.4	−119.70	0.69996
16	256.09	−59.397	214.87	1402.6	0.52262
17	5001.9	−114.35	−1022.4	3359.5	0.12628
25	299.99	−221.19	−1980.6	−127.03	0.69996
26	266.86	−62.682	329.87	1408.3	0.52262
27	4992.3	−110.32	−1043.3	3870.1	0.12628
35	278.30	−212.87	−1985.5	−111.24	0.69735
36	257.71	−59.762	229.62	1406.3	0.52746
37	4810.9	−119.35	−735.40	3807.7	0.14089
46	18.5923	−39.008	5077.3	−2003.4	0.21917
47	100.32	238.70	2497.5	1410.8	0.10121
56	17.954	−38.548	5000.0	−2020.2	0.21917
57	99.383	239.65	2546.1	1400.4	0.10121
67[b]	337.46	−279.92	−10.984	−173.64	0.15018

[a] Refined garlic oil (1), refined grape seed oil (2), refined sesame oil (3), linoleic acid (4), commercial linoleic acid (5), ethanol (6), and Water (7). [b] Parameters taken from Rodrigues et al.[1] and Gonçalves et al.[12]

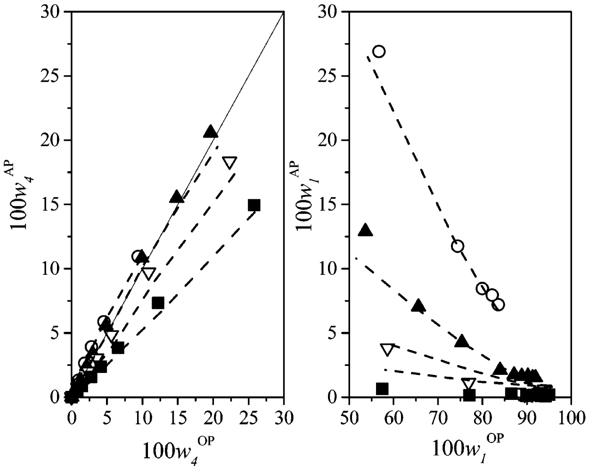

Figure 3. Distribution diagram at (298.2 ± 0.1) K for systems of refined garlic oil (1) + pure linoleic acid (4) + ethanol (6) + water (7): ○, 100 w_{7S} = 0 mass %; ▲, 100 w_{7S} = 6.22 %; ▽, 100 w_{7S} = 12.27 %; ■, 100 w_{7S} = 18.07 %; - — -, NRTL model.

Moreover, these results show that both thermodynamic models provide a good prediction of linoleic acid distribution coefficient. In relation to selectivity, the deviation obtained for UNIQUAC equation was very high in the case of high contents of water in the solvent.

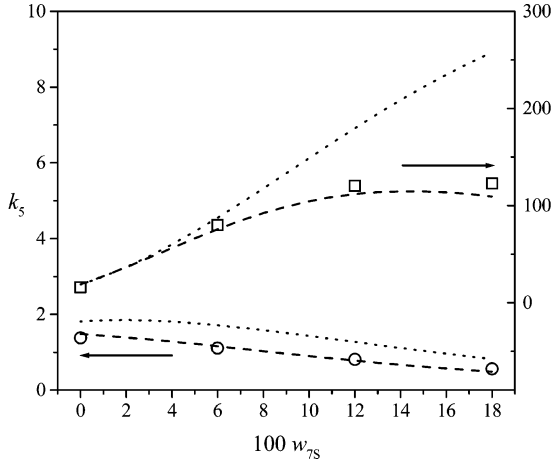

Figure 4. Experimental fatty acid distribution coefficient (○) and selectivities (□) for systems of refined grape seed oil (2) + commercial linoleic acid (5) + ethanol (6) + water (7): prediction by - — -, NRTL model; ···, UNIQUAC model.

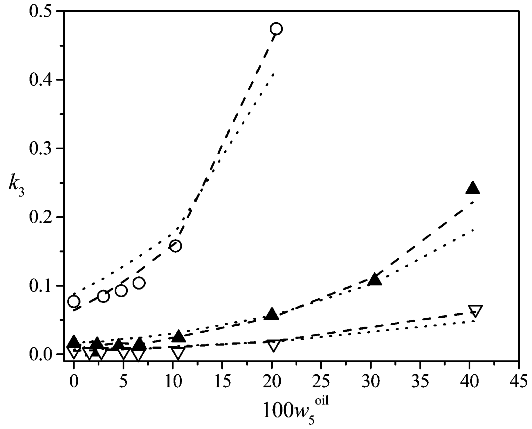

Figure 5. Distribution coefficient of refined sesame oil (3) at (298.2 ± 0.1) K: ○, 100 w_{7S} = 0 mass %; ▲, 100 w_{7S} = 6.22 %; ▽, 100 w_{7S} = 12.27 %; - — -, NRTL model; ···, UNIQUAC model.

Table 9. Mean Deviations in Phase Compositions

		Δ*w* (%)	
system	$100w_{7S}$	UNIQUAC	NRTL
refined garlic oil	0	1.33	0.58
	6.22	0.84	0.69
	12.27	0.67	0.58
	18.07	0.45	0.85
	global deviation of correlation	0.71	0.71
refined grape seed oil	0	1.40	0.99
	6.22	1.18	0.68
	12.27	0.70	0.49
	18.07	0.59	0.97
	global deviation of correlation	0.98	0.74
refined sesame oil	0	1.62	0.72
	6.22	0.92	0.59
	12.27	0.67	0.68
	global deviation of correlation	0.90	0.63

Figure 5 shows the partition coefficient of refined sesame oil (k_3) as a function of acidity level in the oil ($100w_5^{\text{oil}}$). It can be observed that higher free fatty acid content in the system increases the partition coefficient of oil. This can be attributed to the increase of the oil and solvent mutual solubility at higher free fatty acid concentration. In this figure, the effect of water in the neutral oil loss minimization is confirmed.

Conclusions

It can be concluded that by adding water to the solvent there is a large increase in the heterogeneous region and on the selectivity, with a slight decrease of the linoleic acid distribution coefficient. The estimated parameters of the NRTL and UNIQUAC models seem to be representative. With these parameters, the modeling and the simulation of liquid−liquid extractors for vegetable oils deacidification are possible. The results presented in this paper, phase equilibrium for systems involving vegetable oils with high level of diunsaturated fatty acids, will support an ample study about the deacidification of vegetable oils that is being developed by the authors.

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