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Densities, Viscosities, Interfacial Tensions, and Liquid−Liquid Equilibrium Data for Systems Composed of Soybean Oil + Commercial Linoleic Acid + Ethanol + Water at 298.2 K

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This work presents densities, viscosities, interfacial tensions, and liquid−liquid equilibrium data for systems of interest in vegetable oil refining and biodiesel production, composed of soybean oil + commercial *cis*,*cis*-octadeca-9,12-dienoic acid (linoleic acid) + ethanol + water at 298.2 K with water mass fractions in the alcohol solvent (ethanol + water) of 0.05, 0.08, 0.11, and 0.14. Experimental phase compositions at equilibrium were correlated using the nonrandom two-liquid (NRTL) model. For all systems, the global deviations between calculated and experimental phase compositions were no greater than 0.0005. All physical properties were evaluated by empirical correlations as functions of phase compositions. The absolute relative deviations between calculated and experimental data were no greater than 6.36 %. Water content in the solvent presented a considerable effect on the physical properties of the systems and phase compositions at equilibrium, even more so on its interfacial tensions.

Introduction

The removal of free fatty acids (long chain carboxylic acids derived from triacylglycerol hydrolysis), also known as deacidification, may be considered the most important operation in vegetable oil refining because triacylglycerol losses in this procedure have a significant effect on the process costs.[1] The presence of free fatty acids in the final product can also adversely affect oxidation stability, especially when encountered in high compositions of unsaturated free fatty acids typically found in soybean oil.[2] In biodiesel production using alkaline catalysts, the presence of free fatty acids can lead to the formation of alkaline carboxylates with high surfactant capacities, encumbering further purification steps. Therefore, it is advisible to reduce the free fatty acid content to levels similar to those found in refined oils.[3]

Deacidification is usually performed by chemical or physical refining in almost all vegetable oil industries. Physical refining requires high temperatures (493 to 543) K and low pressures (0.666 to 1.333) kPa, demanding high capital and operating costs.[1] Once these high temperatures are reached, the decomposition of compounds such as vitamins and antioxidants is favored which is undesirable in the current market of edible vegetable oils.

During chemical refining, losses are largely due to the formation of long chain carboxylates which act as anionic surfactants,[4] decreasing the interfacial tension at the oil−water interface and consequently causing greater mass transfer of triacylglycerols to the water bulk. This effect is even more amplified when the degumming operation is skipped.

Deacidification by countercurrent liquid−liquid extraction seems to be an attractive alternative to physical or chemical refining to achieve Codex Alimentarius quality specifications,[5] since it can be performed at mild temperatures and atmospheric pressure. Several studies suggest that hydrous ethanol is more appropriate for the deacidification of vegetable oils when compared to other short-chain alcohols and various selective solvents such as acetone, furfural, ethyl acetate, and ethyl methyl ketone.[6−16] Results showed high solvent selectivity and satisfactory free fatty acid distribution coefficients.[6−13]

Crude soybean oil can be considered a low acidity vegetable oil when compared to oils extracted from other oleaginous raw materials (e.g., corn, palm, and rice bran), usually presenting free fatty acid mass fractions of 0.0030 to 0.0070, expressed as oleic acid.[3,17] However, oils extracted from damaged soybean grains can have free fatty acid mass fractions of roughly 0.0800.[17]

Although Codex Alimentarius quality specifications allow that refined vegetable oils can be commercialized with free fatty acids mass fractions up to 0.0030,[5] expressed as oleic acid, considerably lower values are verified in common industrial practice (e.g., 0.0006). This fact is probably due to characteristics and requirements of the consumption market, generating a greater acceptance and shelf life of the final product. Thus, soybean oil deacidification by liquid−liquid extraction to such free fatty acid contents could be accomplished at lower operational costs if this method were applied to oils extracted from oleaginous raw materials with high acidity, demanding lower solvent-to-oil ratios.

The development of physical and transport property correlations as functions of phase composition are essential for the improvement in design and scale-up methods of liquid−liquid extractors, especially for partially miscible systems.[1] Hence, this work presents densities, viscosities, interfacial tensions, and liquid−liquid equilibrium data for systems composed of soybean oil + commercial *cis*,*cis*-octadeca-9,12-dienoic acid + ethanol

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+ water at 298.2 K, which were correlated to empirical equations and models encountered in literature.

Experimental Section

Materials. Gas chromatography was used to determine the fatty acid composition of commercial *cis*,*cis*-octadeca-9,12-dienoic acid (linoleic acid, CAS No. 60-33-3), purchased from MP Biomedicals (U.S.A.), with a mass fraction purity of 0.82, and refined soybean oil (Cargill, Brazil), according to the official method (1-62) of the American Oil Chemists' Society (AOCS).[18] Prior to quantification, the samples were converted to methyl esters according to the method of Hartman and Lago.[19] An Agilent 6850 Series chromatograph equipped with a 0.25 μm, 60 m × 0.25 mm inner diameter (i.d.) (0,50 cyanopropyl-methylpolysiloxane) capillary column (Agilent, model DB-23) and a flame ionization detector were used for determination of the fatty acid compositions. The equipment was utilized under the following experimental conditions: helium as the carrier gas at a rate of 16.67 $\text{mm}^3 \cdot \text{s}^{-1}$; a linear velocity of 24 $\text{cm} \cdot \text{s}^{-1}$; an injection temperature of 523.2 K; a column temperature of 383.2 K for 5 min, with the temperature increased from (383.2 to 488.2) K at a rate of $8.33 \cdot 10^{-2}$ $\text{K} \cdot \text{s}^{-1}$, followed by 488.2 K for 24 min; a detection temperature of 553.2 K; and an injection volume of 1.0 mm^3. The methyl esters were identified by comparison with the retention times of external standards purchased from Nu-Check (U.S.A.), and quantification was done by area normalization.

Anhydrous ethanol (CAS No. 64-17-5) was purchased from Merck (Germany), with a mass fraction purity greater than 0.999. The hydrous ethanol solvents with water mass fractions of 0.05, 0.08, 0.11, and 0.14 were then prepared by the addition of deionized water (Milli-Q, Millipore), CAS No. 7732-18-5, to the anhydrous ethanol.

Karl Fischer reagent was purchased from Merck (Germany), which was regularly standardized with the Riedel de Haën Hydranal volumetric standard (Germany).

In the present work, the following notations were given to the components utilized in the experiments: refined soybean oil (1), commercial linoleic acid (2), ethanol (3), and water (4).

Apparatus and Procedures. Sampling of the Phases in Equilibrium. Equilibrium cells, such those described by Silva et al.,[20] were used for determination of phase compositions, densities, viscosities, and interfacial tensions of multicomponent mixtures in equilibrium, composed of soybean oil + commercial linoleic acid + ethanol + water at 298.2 K.

Initially, the components were weighed on an analytical balance (Precisa, model XT220A), accurate to ± 0.0001 g. The mixture was then vigorously agitated for 15 min with a magnetic stirrer (Ika Werke, model RH-KT/C), and the temperature was controlled by a thermostatic bath (Cole Parmer, model 12101-55), accurate to ± 0.1 K. After a clear and well-defined interface was formed (approximately 8 h later), samples were collected from each phase.

Determination of Liquid−Liquid Equilibrium Phase Compositions. The commercial linoleic acid mass fraction in each phase was determined according to the official method 2201 of the International Union of Pure and Applied Chemistry (IUPAC)[21] using an automatic titrator (Metrohm, model Titrando 808), accurate to ± 0.001 cm^3. Water content was determined by Karl Fischer titration according to AOCS method Ca23-55,[22] using an automatic titrator (Metrohm, model 701 KF Titrino), accurate to ± 0.001 cm^3. The water and free fatty acid mass fractions of soybean oil were used in the calculation of the overall composition of all tie lines.

The solvent (ethanol + water) was evaporated in an oven (Marconi, model MA-035/3) at atmospheric pressure and 383.2 K for 3 h, sufficient conditions for the remaining mixture to achieve a constant mass.[12,13] Triacylglycerols were then quantified by calculating the mass difference.

All measurements were performed with at least three repetitions. The type A expanded uncertainties[23] of the equilibrium data ranged from 0.0001 to 0.0013 for triacylglycerols, 0.0001 to 0.0006 for commercial linoleic acid, 0.0001 to 0.0017 for ethanol, and 0.0001 to 0.0013 for water, being that the lowest figures were attained for the lowest mass fractions. Results indicated good precision and repeatability of the equilibrium data.

To test the quality and accuracy of the results obtained, the mass balance of each component was evaluated according to a modified procedure developed by Marcilla et al.[24] The relative deviation (Er_{in}) of component i in each tie line n was calculated according to:

$$\text{Er}_{in} = \frac{|m_n^{\text{OC}}(w_{in}^{\text{OC}}) - m_n^{\text{OP}}(w_{in}^{\text{OP}}) - m_n^{\text{AP}}(w_{in}^{\text{AP}})|}{m_n^{\text{OC}}(w_{in}^{\text{OC}})} \qquad (1)$$

where w_{in}^{OC} is the mass fraction of component i associated to the overall mass composition m_n^{OC}, both being gravimetrically attained. m_n^{AP} and m_n^{OP} are, respectively, the masses of the alcohol and oil phases, calculated using the procedure developed by Marcilla et al.[24] w_{in}^{AP} and w_{in}^{OP} are the mass fractions of component i in the alcohol and oil phases, experimentally determined.

The relative deviations (Er_{in}) varied within the following ranges: (0.00 to 0.01) % for triacylglycerols, (0.02 to 2.20) % for commercial linoleic acid, (0.00 to 0.07) % for ethanol, and (0.34 to 4.45) % for water, being that the lowest values were obtained for the greatest compositions. The relative deviations attained between the sum of ($m_n^{\text{OP}} + m_n^{\text{AP}}$) and m_n^{OC} were lower than 0.21 %, with an average of 0.07 %, confirming the high quality of the experimental data.[24]

Determination of Densities. Densities of soybean oil, commercial linoleic acid, and multicomponent mixtures were measured using an oscillating U-tube densimeter (Anton-Paar, model DMA 4500), accurate to ± 0.01 $\text{kg} \cdot \text{m}^{-3}$. The temperature of the experiments was controlled by a thermostat inherent to the equipment, accurate to ± 0.01 K. The device was regularly calibrated by measuring the densities of air and water, according to procedures suggested by the manufacturer. All measurements were performed with at least three repetitions. The type A expanded uncertainties[23] of the density data ranged from (0.01 to 0.04) $\text{kg} \cdot \text{m}^{-3}$.

Determination of Viscosities. Viscosities were measured using a falling ball viscosimeter (Anton-Paar, model AMVn), accurate to ± 0.001 $\text{mPa} \cdot \text{s}$. Capillary tubes with (1.6 and 1.8) mm i.d. were used to determine viscosities of the mixtures with greater mass fractions of ethanol and fatty components, respectively. The temperature of the experiments was controlled by a thermostat inherent to the equipment, accurate to ± 0.01 K. Viscosities were indirectly quantified by the falling times of steel spheres with 7650 $\text{kg} \cdot \text{m}^{-3}$, considering empirical equations suggested by the manufacturer. All measurements were performed with at least three repetitions. The type A expanded uncertainties[23] of the viscosity data ranged from (0.001 to 0.067) $\text{mPa} \cdot \text{s}$.

Determination of Interfacial Tensions. Interfacial tensions between phases in equilibrium were determined using a spinning drop tensiometer (Krüss, model Site 100), coupled to a device required for rotational frequencies greater than 125.00 s^{-1} (Krüss, SQ-set). Initially, the capillary tube of the equipment, with 3.5 mm i.d., was filled with the oil phase and the temperature controlled by a thermostatic bath (Julabo, model ED-5) accurate to ± 0.1 K. In all measurements, 8.0 mm^3 of the alcohol phase was injected in the equipment and the rotational frequency set at 183.33 s^{-1}. Images were taken after 1 min of operation, sufficient time for the gyrostatic equilibrium to be achieved, verified by the absence of movements at the interface in relation to the capillary tube walls.

The images taken by a charge-coupled device camera (Toshiba, model CS-8310BCi), connected to a magnification lens, were then analyzed using the software DSA II (Krüss), in which the equatorial diameters of the drops were measured. Before adding the alcohol phase to the equipment, the reference scale of the software (in pixels·mm^{-1}) was calibrated using a needle provided by the manufacturer with 0.696 mm in diameter. The experimental interfacial tensions were indirectly quantified according to the correlation suggested by Vonnegut,[25] cited by Giraldo-Zuniga et al.,[26] presented in eq 2, and also recommended by the manufacturer of the equipment.

$$\sigma/\mathrm{N\cdot m^{-1}} = \frac{\Delta\rho\omega^2 d^3}{32} \tag{2}$$

where ω represents the angular velocity of the capillary tube in rad·s^{-1}, d the equatorial diameter of the drop in m, and $\Delta\rho$ the density difference between phases in kg·m^{-3}.

In all measurements the ratio between the drop length and its equatorial diameter was greater than 10 due to the high rotational frequency adopted. The conditions suggested by Manning and Scriven,[27] for which the gyrostatic equilibrium is highly favored ($1/\mathrm{Fr} < 1$ and $\mathrm{Bo} < \mathrm{Ta}$), were satisfied. The Froude number (Fr), Bond number (Bo), and Taylor number (Ta) dimensionless groups are defined in eqs 3 to 5.

$$\mathrm{Fr} = \frac{\omega^2 d}{2g} \tag{3}$$

$$\mathrm{Bo} = \frac{\omega^2 d^3 \Delta\rho}{8\sigma} \tag{4}$$

$$\mathrm{Ta} = \frac{\rho^{\mathrm{AP}}\omega d^2}{4\eta^{\mathrm{AP}}} \tag{5}$$

All measurements were performed with at least three repetitions. The type A expanded uncertainties[23] of the interfacial tension data ranged from (0.01 to 0.03) mN·m^{-1}.

Modeling and Experimental Data Correlation. Thermodynamic Modeling of Phase Compositions in Equilibrium. The experimental phase compositions were used to adjust the nonrandom two-liquid (NRTL) binary interaction parameters. Mole fractions have traditionally been used in this model, but mass fractions provide a more convenient composition unit due to the large differences in molar masses of components such as vegetable oils, ethanol, and water. Recently, several studies have been reported using this approach with the NRTL model.[6−12] According to the presuppositions of the NRTL model, the activity coefficient of component i, related to a given phase in equilibrium, can be calculated by eq 6.

$$\ln\gamma_i = \frac{\sum_{j=1}^{C}\frac{\tau_{ji}G_{ji}w_j}{\bar{M}_j}}{\sum_{j=1}^{C}\frac{G_{ji}w_j}{\bar{M}_j}} + \sum_{j=1}^{C}\left[\frac{w_jG_{ij}}{\bar{M}_j\sum_{k=1}^{C}\frac{G_{kj}w_k}{\bar{M}_k}}\left(\tau_{ij} - \frac{\sum_{k=1}^{C}\frac{\tau_{kj}G_{kj}w_k}{\bar{M}_k}}{\sum_{k=1}^{C}\frac{G_{kj}w_k}{\bar{M}_k}}\right)\right] \tag{6}$$

where

$$G_{ij}/\mathrm{J} = \exp(-\alpha_{ij}\tau_{ij}) \tag{7}$$

$$\tau_{ij} = \frac{A_{ij}}{T} \tag{8}$$

$$\alpha_{ij} = \alpha_{ji} \tag{9}$$

In the NRTL model, A_{ij}, A_{ji}, and α_{ij} are the adjustable interaction parameters between the pair of components i and j, C is the number of components, and T is the absolute equilibrium temperature. $\bar{M}$ represents the average molar mass of the pseudocomponents.

Following the procedure developed by Stragevitch and d'Ávila,[28] the NRTL interaction parameters were calculated on the basis of minimization of the composition objective function expressed as:

$$\mathrm{OF}(w) = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{C-1}\left[\left(\frac{w_{inm}^{\mathrm{AP,expt}} - w_{inm}^{\mathrm{AP,calc}}}{s_{w_{inm}^{\mathrm{AP}}}}\right)^2 + \left(\frac{w_{inm}^{\mathrm{OP,expt}} - w_{inm}^{\mathrm{OP,calc}}}{s_{w_{inm}^{\mathrm{OP}}}}\right)^2\right] \tag{10}$$

where D is the total number of data groups, N the total number of tie lines, and C the total number of components in the data group m. The subscripts i, n, and m define the component, tie line, and group number, respectively. The superscripts expt and calc refer to experimental and calculated data. $s_{w_{inm}^{\mathrm{AP}}}$ and $s_{w_{inm}^{\mathrm{OP}}}$ 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:

$$\Delta w = \sqrt{\left(\frac{\sum_{n=1}^{N}\sum_{i=1}^{C}[(w_{in}^{\mathrm{AP,expt}} - w_{in}^{\mathrm{AP,calc}})^2 + (w_{in}^{\mathrm{OP,expt}} - w_{in}^{\mathrm{OP,calc}})^2]}{2NC}\right)} \tag{11}$$

Densities, Viscosities, and Interfacial Tensions Correlation. Because of the well-known deviations from ideality of ethanol + water binary mixtures, densities and viscosities of multicomponent mixtures were calculated considering systems of soybean oil (1) + commercial linoleic acid (2) + ethanol (3) + water (4) as pseudoternary, composed of soybean oil (1) + commercial linoleic acid (2) + solvent (5). Hence, ethanol and water were considered a single component (i.e., $w_5 = w_3 + w_4$ and $x_5 = x_3 + x_4$).

Densities and viscosities of ethanol + water binary mixtures were calculated from the polynomial equations presented in eqs

Table 1. Fatty Acid Composition of Soybean Oil and Commercial Linoleic Acid

			M^b	soybean oil		linoleic acid	
fatty acid	symbol	$C_{x:y}$[a]	$g \cdot mol^{-1}$	100 x	100 w	100 x	100 w
octanoic	C	$C_{8:0}$	114.21			0.14	0.07
decanoic	Ca	$C_{10:0}$	172.26			0.06	0.04
dodecanoic	La	$C_{12:0}$	200.32	0.03	0.02		
tetradecanoic	M	$C_{14:0}$	228.37	0.11	0.09	0.09	0.07
pentadecanoic	Pt	$C_{15:0}$	242.40	0.03	0.03		
hexadecanoic	P	$C_{16:0}$	256.42	11.75	10.82	5.33	4.89
cis-hexadec-9-enoic	Po	$C_{16:1}$	254.41	0.10	0.09	0.12	0.11
heptadecanoic	Ma	$C_{17:0}$	270.45	0.10	0.10		
cis-heptadec-9-enoic	Mo	$C_{17:1}$	268.43	0.05	0.05		
octadecanoic	S	$C_{18:0}$	284.48	3.56	3.64	1.52	1.55
cis-octadec-9-enoic	O	$C_{18:1}$	282.46	24.11	24.45	10.31	10.43
cis,*cis*-octadeca-9,12-dienoic	L	$C_{18:2}$	280.45	52.12	52.48	81.68	82.04
trans,*trans*-octadeca-9,12-dienoic		$C_{18:2}$	280.45	0.35	0.35	0.25	0.25
all-*cis*-octadeca-9,12,15-trienoic	Ln	$C_{18:3}$	278.43	5.53	5.53	0.10	0.10
all-*trans*-octadeca-9,12,15-trienoic		$C_{18:3}$	278.43	1.11	1.11		
icosanoic	A	$C_{20:0}$	312.53	0.33	0.37	0.16	0.18
cis-icos-9-enoic	Ga	$C_{20:1}$	310.51	0.20	0.22	0.13	0.14
docosanoic	Be	$C_{22:0}$	340.58	0.39	0.48		
cis-docos-9-enoic	E	$C_{22:1}$	338.57			0.11	0.13
tetracosanoic	Lg	$C_{24:0}$	368.64	0.13	0.17		

[a] $C_{x:y}$; x: number of carbons; y: number of double bonds. [b] Molar mass.

12 and 13, which were interpolated to the experimental data described by Perry and Green[29] and Arce et al.,[30] respectively. Both equations presented determination coefficients (R^2) equal to 1.000.

$$\rho_5/\mathrm{kg \cdot m^{-3}} = -177.90w_4'^2 + 302.80w_4' + 785.16 \tag{12}$$

$$\eta_5/\mathrm{Pa \cdot s} = -2.703 \cdot 10^{-3}w_4'^2 + 3.626 \cdot 10^{-3}w_4' + 1.089 \cdot 10^{-3} \tag{13}$$

where w_4' represents the water mass fraction of a multicomponent mixture on a triacylglycerol and commercial linoleic acid free basis.

The experimental densities of each phase were correlated to eq 14.

$$\rho/\mathrm{kg \cdot m^{-3}} = \left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} + \frac{w_5}{\rho_5}\right)^{-1} + C_1 \tag{14}$$

where C_1 represents the average deviation between the experimental data of each phase and the values calculated by the first term of the second member of eq 14.

Experimental viscosities of the alcohol phase were correlated to the Kay rule,[31] presented in eq 15. A modified form of the equation proposed by Kendall and Monroe,[32] presented in eq 16, was used to correlate the experimental viscosities of the oil phase.

$$\eta^{\mathrm{AP}}/\mathrm{Pa \cdot s} = x_1^{\mathrm{AP}}\eta_1 + x_2^{\mathrm{AP}}\eta_2 + x_5^{\mathrm{AP}}\eta_5 \tag{15}$$

$$\eta^{\mathrm{OP}}/\mathrm{Pa \cdot s} = (x_1^{\mathrm{OP}}\eta_1^n + x_2^{\mathrm{OP}}\eta_2^n + x_5^{\mathrm{OP}}\eta_5^n)^{1/n} \tag{16}$$

The exponent n of eq 16 was adjusted by minimizing the sum of the square of the residuals.

Experimental interfacial tensions were correlated to a modified form of the empirical equation suggested by Treybal,[33] presented in eq 17.

$$\sigma/\mathrm{N \cdot m^{-1}} = a - b \ln\left(x_1^{\mathrm{AP}} + \frac{x_2^{\mathrm{AP}} + x_2^{\mathrm{OP}}}{2} + x_3^{\mathrm{OP}} + x_4^{\mathrm{OP}}\right) \tag{17}$$

The empirical constants a and b in eq 17 were adjusted to the experimental data according to the least-squares fitting method.

Results and Discussion

Characterizations of the fatty acid compositions in refined soybean oil and commercial linoleic acid are presented in Table 1. From the fatty acid molar fractions of soybean oil, it was possible to determine its probable triacylglycerol composition (Table 2) by using the procedure suggested by Antoniosi Filho et al.,[34] being that the mass fractions of trans configurational isomers were added to their respective cis configurational isomers.

The average molar masses of the soybean oil and commercial linoleic acid were 874.29 g·mol^{-1} and 279.25 g·mol^{-1}, respectively. The refined soybean oil presented a free fatty acid mass fraction of 0.0006 and a water mass fraction of 0.0002, both of which were used in the calculation of the overall composition of all tie lines.

The overall compositions and the corresponding tie lines for the studied systems are presented in Table 3, and the adjusted NRTL binary interaction parameters are shown in Table 4. Mean deviations in the phase compositions (Δw), calculated according to eq 11, for systems composed of soybean oil + commercial linoleic acid + ethanol + water at 298.2 K with water mass fractions in the solvent (w_{4s}) of 0.05, 0.08, 0.11, and 0.14 were equal to 0.0003, 0.0005, 0.0004, and 0.0004, respectively.

Figure 1 presents experimental phase compositions and calculated tie lines for systems composed of soybean oil + commercial linoleic acid + ethanol + water at 298.2 K with water mass fractions in the alcohol solvent equal to 0.05 and 0.14. The NRTL model was able to satisfactorily describe the

Table 2. Probable Triacylglycerol Composition of Soybean Oil

group[a]	main TAG[b]	M^c / $g \cdot mol^{-1}$	100 x	100 w
48:0	PPP	807.32	0.14	0.13
50:0	PPS	835.37	0.14	0.13
50:1	POP	833.36	0.92	0.88
50:2	PLP	831.34	2.02	1.92
50:3	PLnP	829.33	0.36	0.34
52:1	POS	861.41	0.60	0.59
52:2	POO	859.39	3.29	3.23
52:3	PLO	857.38	8.85	8.68
52:4	PLL	855.36	10.54	10.31
52:5	PLnL	853.35	2.45	2.39
52:6	PLnLn	851.33	0.17	0.16
54:1	SOS	889.46	0.16	0.16
54:2	SOO	887.45	1.02	1.04
54:3	SLO	885.43	4.40	4.46
54:4	OLO	883.42	12.91	13.05
54:5	OLL	881.40	22.52	22.71
54:6	LLL	879.38	20.07	20.20
54:7	LLnL	877.37	5.94	5.96
54:8	LLnLn	875.35	0.71	0.71
56:2	PLBe	915.50	0.28	0.29
56:3	OLA	913.49	0.37	0.38
56:4	LLA	911.47	0.50	0.53
56:5	LLGa	909.45	0.28	0.29
58:2	OOBe	943.55	0.19	0.21
58:3	OLBe	941.54	0.37	0.39
58:4	LLBe	939.52	0.42	0.46
58:5	LLnBe	937.51	0.10	0.10
60:3	OLLg	969.59	0.13	0.14
60:4	LLLg	967.58	0.15	0.16

[a] x:y; x: number of carbons (except glycerol carbons); y: number of double bonds. [b] Groups with a total triacylglycerol (TAG) composition lower than 0.10 % were ignored. [c] Molar mass.

Table 4. Adjusted NRTL Interaction Parameters for Systems Composed of Soybean Oil (1) + Commercial Linoleic Acid (2) + Ethanol (3) + Water (4) at 298.2 K

pair ij	A_{ij}/K	A_{ji}/K	α_{ij}
12	−5267.9	−218.92	0.19089
13	190.42	1218.3	0.56790
14	−574.73	4058.7	0.11490
23	205.19	−5526.7	0.12909
24	62.904	−3742.1	0.20289
34	1.0345	453.23	0.10001

liquid−liquid equilibrium, presenting excellent alignment between the phases and the overall compositions. The increase of the water content in the solvent within the studied range decreased the triacylglycerol mass fractions in the alcohol phase, which, however, led to undesirable lower commercial linoleic acid distribution coefficients, results commonly found for such systems.[6−9,11−13]

The densities of soybean oil and commercial linoleic acid were, respectively, found to be (916.59 ± 0.02) $kg \cdot m^{-3}$ and (904.77 ± 0.01) $kg \cdot m^{-3}$. The viscosities of such pseudocompounds were equal to (49.937 ± 0.047) mPa·s and (28.787 ± 0.018) mPa·s, respectively.

Table 5 presents experimental densities, viscosities, and interfacial tensions for the corresponding tie lines presented in Table 3. From the experimental data shown in Tables 3 and 5, it was possible to adjust the parameters presented in eqs 14, 16, and 17. The calculated values of the constant C_1, presented in eq 14, were found to be 0.18 and −0.91 for the alcohol and oil phases, respectively. Exponent n, presented in eq 16, which minimizes the sum of the squares of the residuals between calculated and experimental oil phase viscosities, was found to be 1.92. The adjusted values of constants a and b, determined by the least-squares fitting method and presented in eq 17, were equal to $-1.578 \cdot 10^{-3}$ and $-7.828 \cdot 10^{-3}$, respectively.

The absolute relative deviations between experimental and calculated data, using the proposed correlations and phase compositions presented in Table 3, varied within the following ranges: (0.00 to 0.09) % for densities, (0.04 to 1.20) % for viscosities, and (0.40 to 6.36) % for interfacial tensions.

As can be verified in Figures 2 and 3, the densities and viscosities of the alcohol phase increased with the enhancement of the commercial linoleic acid and water mass fractions of the systems.

In Figures 2 and 3, as well in the following discussions, the experimental data are presented with the values calculated using the correlations proposed in this work, where the phase compositions were estimated by liquid−liquid equilibrium flash calculations using the parameters presented in Table 4.[28,35] This procedure was performed to verify the capability of the proposed equations in describing the experimental data when calculated phase compositions are used, an important insight for the possible applicability of such empirical correlations for solvent compositions different from those experimentally used in this work.

The densities and viscosities of the oil phase decreased with enhancement of the commercial linoleic acid mass fractions of the systems, as shown in Figures 4 and 5. The antagonistic results in respect to those verified for the alcohol phase are probably due to the increased ethanol contents in the systems. However, greater water mass fractions in the solvent led to greater densities and viscosities of the oil phase.

The enhancement of commercial linoleic acid and water contents in the systems caused, respectively, the reduction and

Table 3. Liquid−Liquid Equilibrium Data for Systems Composed of Soybean Oil (1) + Commercial Linoleic Acid (2) + Ethanol (3) + Water (4) at 298.2 K

		overall composition				alcohol phase				oil phase			
100 w_{4s}[a]	TLN[b]	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
5.00	1	48.05	2.00	47.44	2.51	2.25 ± 0.12	2.24 ± 0.03	90.43 ± 0.16	5.08 ± 0.09	88.15 ± 0.02	1.71 ± 0.05	9.85 ± 0.06	0.29 ± 0.01
	2	49.16	1.01	47.33	2.50	1.99 ± 0.10	1.15 ± 0.06	91.58 ± 0.14	5.28 ± 0.04	89.68 ± 0.13	0.86 ± 0.03	9.20 ± 0.15	0.26 ± 0.01
	3	49.96	0.03	47.50	2.51	1.81 ± 0.05	0.03 ± 0.01	92.85 ± 0.05	5.31 ± 0.05	91.02 ± 0.07	0.03 ± 0.01	8.71 ± 0.07	0.24 ± 0.01
8.00	4	48.03	2.00	45.96	4.01	1.15 ± 0.02	2.15 ± 0.03	88.65 ± 0.05	8.05 ± 0.10	89.89 ± 0.05	1.91 ± 0.05	7.87 ± 0.02	0.33 ± 0.01
	5	49.12	1.04	45.84	4.00	1.10 ± 0.05	1.10 ± 0.02	89.65 ± 0.05	8.15 ± 0.10	91.21 ± 0.01	0.98 ± 0.02	7.51 ± 0.02	0.30 ± 0.01
	6	49.47	0.03	46.45	4.05	1.01 ± 0.02	0.03 ± 0.01	90.79 ± 0.04	8.17 ± 0.05	92.72 ± 0.01	0.03 ± 0.01	6.98 ± 0.01	0.27 ± 0.01
11.00	7	51.83	1.99	41.09	5.09	0.70 ± 0.06	1.96 ± 0.01	86.00 ± 0.07	11.34 ± 0.08	90.88 ± 0.08	1.97 ± 0.03	6.77 ± 0.01	0.38 ± 0.04
	8	48.98	1.02	44.49	5.51	0.60 ± 0.08	1.01 ± 0.01	86.74 ± 0.16	11.65 ± 0.10	92.36 ± 0.07	1.04 ± 0.01	6.27 ± 0.07	0.33 ± 0.01
	9	49.96	0.03	44.50	5.51	0.53 ± 0.05	0.03 ± 0.01	87.59 ± 0.09	11.85 ± 0.05	93.86 ± 0.10	0.03 ± 0.01	5.82 ± 0.09	0.29 ± 0.01
14.00	10	47.95	1.99	43.04	7.02	0.42 ± 0.04	1.80 ± 0.04	83.65 ± 0.13	14.13 ± 0.13	91.55 ± 0.04	2.12 ± 0.02	5.95 ± 0.03	0.38 ± 0.03
	11	49.00	0.99	43.00	7.01	0.36 ± 0.06	0.91 ± 0.01	84.30 ± 0.05	14.43 ± 0.03	93.15 ± 0.07	1.08 ± 0.02	5.43 ± 0.04	0.34 ± 0.01
	12	49.96	0.03	43.00	7.01	0.33 ± 0.04	0.03 ± 0.01	85.13 ± 0.17	14.51 ± 0.13	94.58 ± 0.05	0.03 ± 0.01	5.08 ± 0.08	0.31 ± 0.03

[a] w_{4s}: water mass fraction in the solvent. [b] TLN: tie line number.

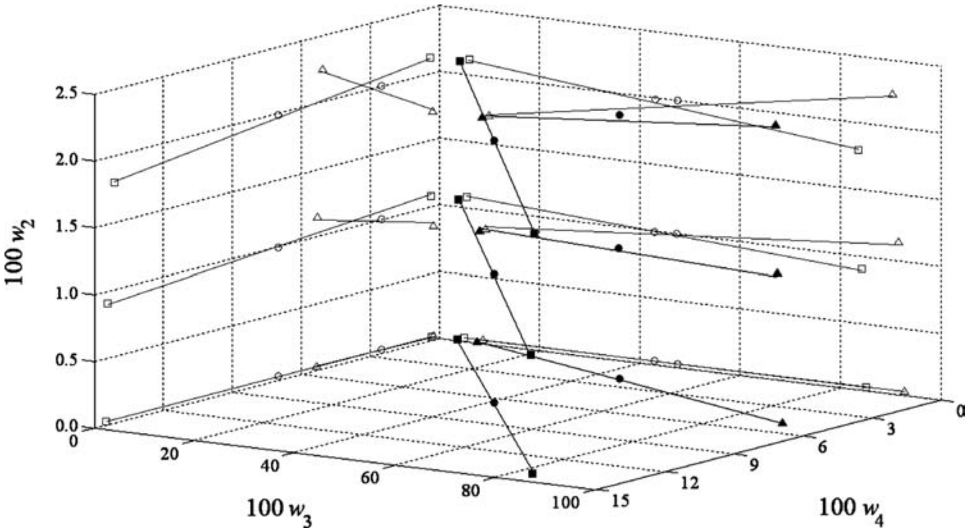

Figure 1. System of soybean oil (1) + commercial linoleic acid (2) + ethanol (3) + water (4) at 298.2 K: ●, experimental overall compositions; ▲, experimental phase compositions (100 w_{4s} = 5.00); ■, experimental phase compositions (100 w_{4s} = 14.00); continuous line, NRTL.

Table 5. Densities, Viscosities, and Interfacial Tensions of Multicomponent Mixtures in Equilibrium, Composed of Soybean Oil (1) + Commercial Linoleic Acid (2) + Ethanol (3) + Water (4) at 298.2 K

	ρ^{AP}	η^{AP}	ρ^{OP}	η^{OP}	σ
TLN[a]	$kg \cdot m^{-3}$	mPa·s	$kg \cdot m^{-3}$	mPa·s	$mN \cdot m^{-1}$
1	805.77 ± 0.01	1.415 ± 0.004	901.36 ± 0.02	26.776 ± 0.026	1.29 ± 0.03
2	804.31 ± 0.04	1.376 ± 0.001	902.29 ± 0.01	27.529 ± 0.030	1.52 ± 0.01
3	802.99 ± 0.03	1.333 ± 0.001	903.23 ± 0.01	28.401 ± 0.045	1.72 ± 0.02
4	812.88 ± 0.02	1.486 ± 0.006	903.99 ± 0.00	29.088 ± 0.047	1.73 ± 0.01
5	811.90 ± 0.02	1.446 ± 0.010	905.07 ± 0.01	29.823 ± 0.008	2.05 ± 0.03
6	810.54 ± 0.01	1.404 ± 0.005	905.83 ± 0.03	30.782 ± 0.021	2.29 ± 0.03
7	820.22 ± 0.01	1.574 ± 0.004	906.03 ± 0.01	30.189 ± 0.067	2.17 ± 0.02
8	819.32 ± 0.03	1.539 ± 0.003	906.77 ± 0.02	31.237 ± 0.019	2.49 ± 0.02
9	818.63 ± 0.01	1.501 ± 0.005	907.59 ± 0.01	32.118 ± 0.042	2.83 ± 0.01
10	827.26 ± 0.01	1.630 ± 0.002	907.12 ± 0.03	31.398 ± 0.048	2.54 ± 0.02
11	826.81 ± 0.04	1.612 ± 0.009	908.05 ± 0.02	32.442 ± 0.039	2.90 ± 0.01
12	825.54 ± 0.02	1.588 ± 0.001	908.82 ± 0.01	33.562 ± 0.029	3.30 ± 0.01

[a] TLN: corresponding tie line number presented in Table 3.

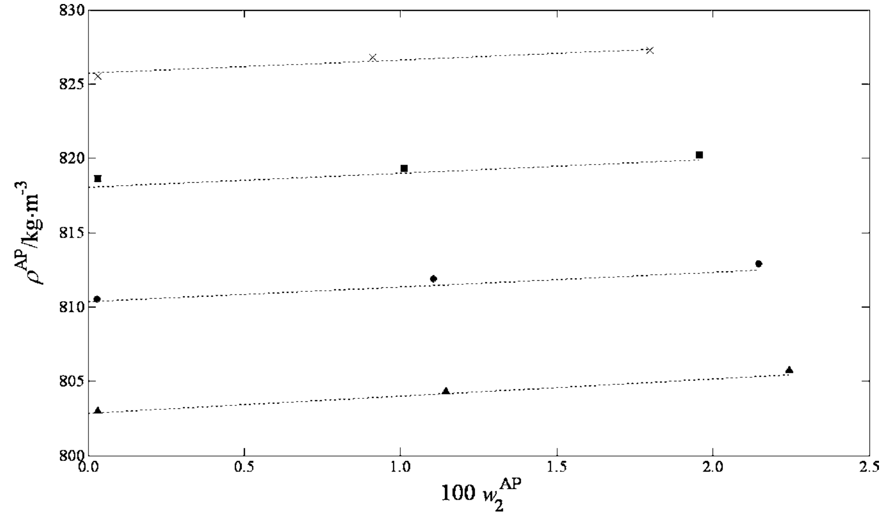

Figure 2. Effect of the commercial linoleic acid mass fraction (w_2^{AP}) on the alcohol phase densities (ρ^{AP}): ▲, $\rho^{AP,expt}$ (100 w_{4s} = 5.00); ●, $\rho^{AP,expt}$ (100 w_{4s} = 8.00); ■, $\rho^{AP,expt}$ (100 w_{4s} = 11.00); ×, $\rho^{AP,expt}$ (100 w_{4s} = 14.00); dashed line, $\rho^{AP,calc}$ (eq 14 using calculated phase compositions).

increase of the interfacial tension between phases, as can be confirmed in Figure 6. These behaviors can be explained by the adsorption of free fatty acids at the interface and formation of oriented monomolecular films, consequently providing a more energetically stable state to overcome hydrophobic repulsions between oil and water molecules that contribute to the increase of interfacial tension in the systems.[4]

According to Godfrey and Slater,[36] the density difference between phases is one of the most relevant parameters in the selection of equipment for liquid−liquid extraction processes. Density differences between phases greater than 80 $kg \cdot m^{-3}$ are desirable for the utilization of mechanically stirred columns, making its operation safer, providing greater capacities, and avoiding flooding phenomena.[36] For density differences between

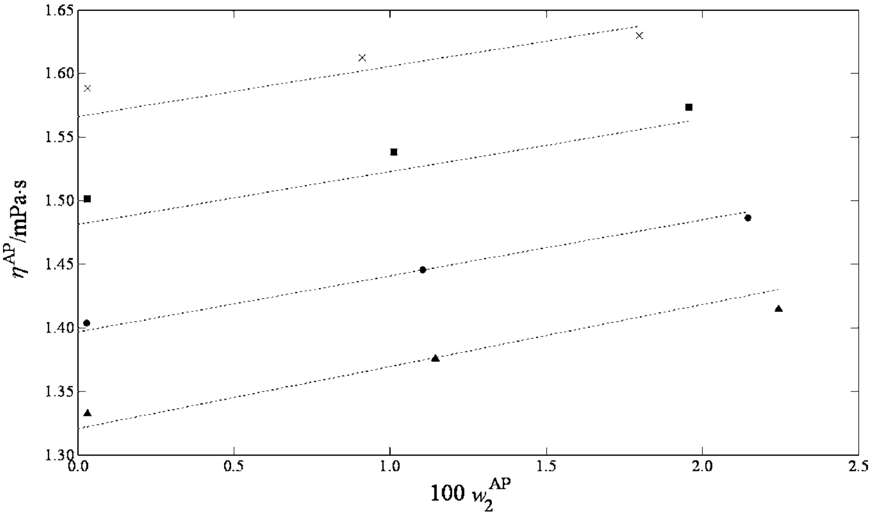

Figure 3. Effect of the commercial linoleic acid mass fraction (w_2^{AP}) on the alcohol phase viscosities (η^{AP}): ▲, $\eta^{AP,expt}$ (100 w_{4s} = 5.00); ●, $\eta^{AP,expt}$ (100 w_{4s} = 8.00); ■, $\eta^{AP,expt}$ (100 w_{4s} = 11.00); ×, $\eta^{AP,expt}$ (100 w_{4s} = 14.00); dashed line, $\eta^{AP,calc}$ (eq 15 using calculated phase compositions).

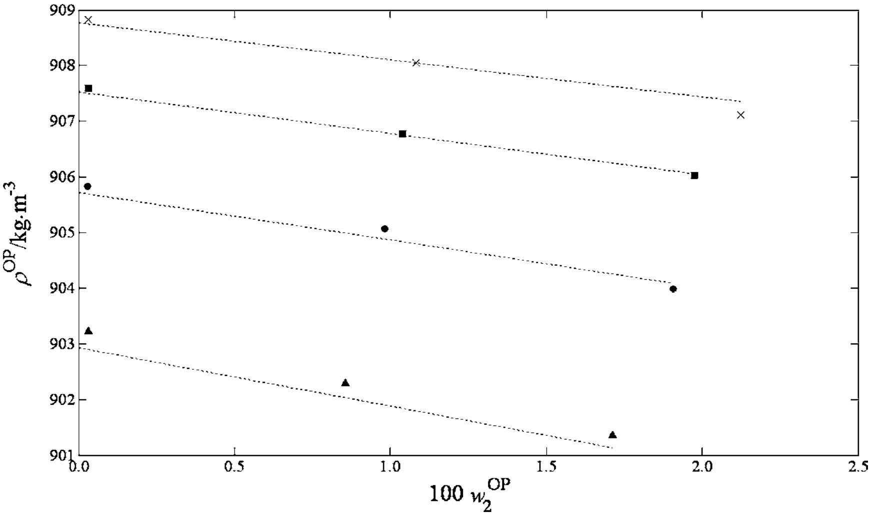

Figure 4. Effect of the commercial linoleic acid mass fraction (w_2^{OP}) on the oil phase densities (ρ^{OP}): ▲, $\rho^{OP,expt}$ (100 w_{4s} = 5.00); ●, $\rho^{OP,expt}$ (100 w_{4s} = 8.00); ■, $\rho^{OP,expt}$ (100 w_{4s} = 11.00); ×, $\rho^{OP,expt}$ (100 w_{4s} = 14.00); dashed line, $\rho^{OP,calc}$ (eq 14 using calculated phase compositions).

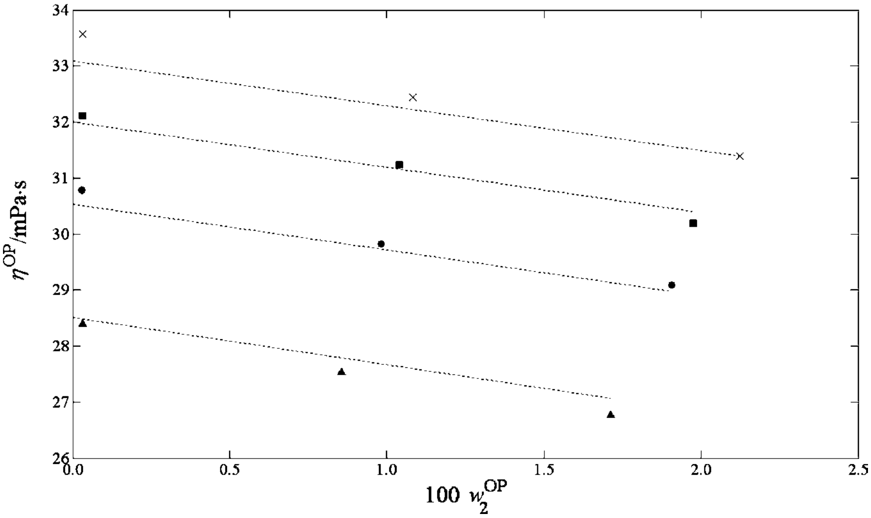

Figure 5. Effect of the commercial linoleic acid mass fraction (w_2^{OP}) on the oil phase viscosities (η^{OP}): ▲, $\eta^{OP,expt}$ (100 w_{4s} = 5.00); ●, $\eta^{OP,expt}$ (100 w_{4s} = 8.00); ■, $\eta^{OP,expt}$ (100 w_{4s} = 11.00); ×, $\eta^{OP,expt}$ (100 w_{4s} = 14.00); dashed line, $\eta^{OP,calc}$ (eq 16 using calculated phase compositions).

phases lower than 50 kg·m^{-3}, centrifugal extractors or sets of mixer-settlers are recommended.

Figure 7 presents the effect of water and commercial linoleic acid contents of the systems on the density difference between phases, which ranged from (79.86 to 100.24) kg·m^{-3}. As can be observed, the increase of commercial linoleic acid and water content in the systems promoted the reduction of the density difference between phases. Although liquid−liquid equilibrium

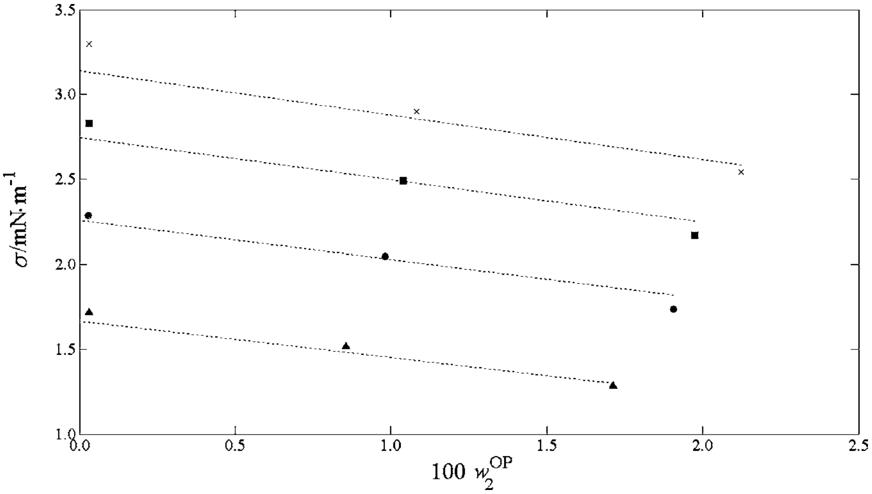

Figure 6. Effect of the commercial linoleic acid mass fraction in the oil phase (w_2^{OP}) on the interfacial tensions of the systems (σ): ▲, σ^{expt} (100 w_{4s} = 5.00); ●, σ^{expt} (100 w_{4s} = 8.00); ■, σ^{expt} (100 w_{4s} = 11.00); ×, σ^{expt} (100 w_{4s} = 14.00); dashed line, σ^{calc} (eq 17 using calculated phase compositions).

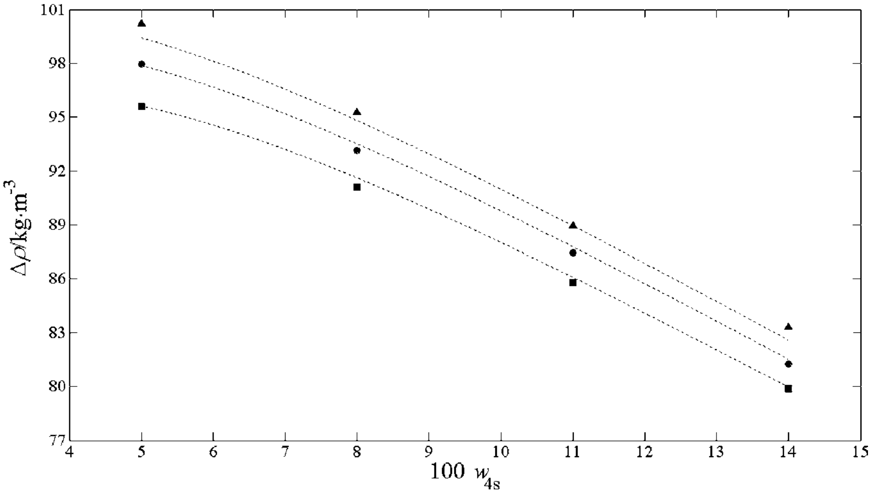

Figure 7. Effect of the water mass fraction in the solvent (w_{4s}) on the density differences between phases ($\Delta\rho$): ▲, $\Delta\rho^{expt}$ (100 w_2^{OC} = 0.03); ●, $\Delta\rho^{expt}$ (100 w_2^{OC} = 1.00); ■, $\Delta\rho^{expt}$ (100 w_2^{OC} = 2.00); dashed line, $\Delta\rho^{calc}$ (eq 14 using calculated phase compositions).

is never reached in a practical extraction process, it can be inferred that the utilization of solvents with water mass fractions greater than 0.14 are probably characterized by density differences lower than 80 $\text{kg}\cdot\text{m}^{-3}$.

Because of the high viscosity differences between phases, the utilization of the oil phase as the continuous phase is not recommended for mechanically stirred columns. Besides the greater resistance to mass transfer of free fatty acids, greater mechanical power dissipation per unit mass and consequently higher energy requirements would be necessary to achieve an equivalent interfacial area if this phase was considered the dispersed phase.

The studied systems presented low interfacial tensions, even for compositions with high water mass fractions. However, the variation determined in this work may present a relevant effect on the operational condition specifications of mechanically stirred columns, such as rotor speed, which is an essential argument for quantifying drop size distributions and phase composition profiles in design and scale-up methods.

Conclusions

The addition of water to the alcohol solvent presented significant effects on the physical properties and phase compositions at equilibrium. The estimated parameters of the NRTL model were very representative since the description of the liquid−liquid equilibrium behavior for all systems presented average deviations no greater than 0.0005. The suggested correlations of densities, viscosities, and interfacial tensions for systems composed of soybean oil + commercial linoleic acid + ethanol + water appeared to be excellent alternatives, even when phase compositions calculated by the NRTL were used, providing absolute relative deviations between experimental and calculated data no greater than 4.91 %.

The set of equations proposed in this work also appears to be an effective tool for use in scale-up and design methods of liquid−liquid extractors for soybean oil deacidification, as well as in the selection of solvents and determination of suitable operational conditions. All equations are presented in elementary forms, enabling easy and fast calculations, a highly relevant feature in process simulations with iterative steps.

In conclusion, the results presented in this paper show that soybean oil deacidification by liquid−liquid extraction using aqueous ethanol as a solvent allows for the extraction of free fatty acids with only slight triacylglycerol losses, making the extraction process more economic and capable of being used for edible oil refining or biodiesel production.

Literature Cited

(1) Lo, T. C.; Baird, M. H.; Hanson, C. *Handbook of Solvent Extraction*; John Wiley & Sons: New York, 1983.

(2) Araújo, J. M. A. *Química de Alimentos: Teoria e Prática* (in Portuguese) 2nd ed.; Editora UFV: Viçosa, Brazil, 1999.

(3) Liu, K. *Soybeans: Chemistry, Technology and Utilization*; Chapman & Hall: New York, 1997.

(4) Shaw, D. J. *Introduction to Colloid and Surface Chemistry*; Butterworth: London, 1970.

(5) Codex Alimentarius. *Codex Standard for Named Vegetable Oils, Codex Stan-210 (Amended 2003)*; Codex Alimentarius: Rome, 2003.

(6) Rodrigues, C. E. C.; Filipini, A.; Meirelles, A. J. A. Phase Equilibrium for Systems Composed by High Unsatured Vegetable Oils + Linoleic Acid + Ethanol + Water at 298.2 K. *J. Chem. Eng. Data* **2006**, *51*, 15–21.

(7) Rodrigues, C. E. C.; Meirelles, A. J. A. Extraction of Free Fatty Acids from Peanut Oil and Avocado Seed Oil: Liquid−Liquid Equilibrium Data at 298.2 K. *J. Chem. Eng. Data* **2008**, *53*, 1698–1704.

(8) 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*, 367–373.

(9) Gonçalves, C. B.; 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.

(10) Batista, E.; Monnerat, S.; Kato, K.; Stragevich, 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.

(11) Silva, C. A. S.; Sanaiotti, G.; Lanza, M.; Follegatti-Romero, L. A.; Meirelles, A. J. A.; Batista, E. A. C. Mutual Solubility for Systems Composed of Vegetable Oil + Ethanol + Water at Different Temperatures. *J. Chem. Eng. Data* **2010**, *55*, 440–447.

(12) Silva, C. A. S.; Sanaiotti, G.; Lanza, M.; Meirelles, A. J. A.; Batista, E. A. C. Liquid−Liquid Equilibrium Data for Systems Containing *Jatropha curcas* Oil + Oleic Acid + Anhydrous Ethanol + Water at (288.15 to 318.15) K. *J. Chem. Eng. Data* **2010**, *55*, 2416–2423.

(13) Sanaiotti, G.; Coimbra, J. S. R.; Gomes, J. C.; Minim, L. A. Liquid−Liquid Equilibrium for Systems Composed of Grape Seed Oil + Oleic Acid + Ethanol + Water at (283.2, 290.7, and 298.2) K. *J. Chem. Eng. Data* **2008**, *53*, 1492–1497.

(14) Shah, K. J.; Venkatesan, T. K. Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils. *J. Am. Chem. Soc.* **1989**, *66*, 783–787.

(15) 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. Chem. Soc.* **1985**, *62*, 1492–1495.

(16) Thomopoulos, C. Méthode de désacidification des huiles par solvent sélectif. *Rev. Fr. Corps Gras* **1971**, *18*, 143–150.

(17) Hui, Y. H. *Bailey's Industrial Oil and Fat Products*, 6th ed.; John Wiley & Sons: New York, 2005; Vol. 2.

(18) AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 3rd ed.; AOCS Press: Champaign, IL, 1988; Vols. 1−2.

(19) Hartman, L.; Lago, R. C. A. Rapid Preparation of Fatty Acid Methyl Esters from Lipids. *Lab. Pract.* **1973**, *22*, 475–476.

(20) Silva, L. H. M.; Coimbra, J. S. R.; Meirelles, A. J. A. Equilibrium Phase Behavior of Poly(ethylene glycol). Potassium Phosphate. Water Two Phase Systems at Various pH and Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 398–401.

(21) 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).

(22) AOCS. *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd ed.; AOCS Press: Champaign, IL, 1993; Vol. 1.

(23) Taylor, B. N.; Kuyatt, C. E. *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results*; NIST Technical Note 1297; NIST: Gaithersburg, MD, 1994.

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

(25) Vonnegut, B. Rotating Bubble Method for the Determination of Surface and Interfacial Tensions. *Rev. Sci. Instrum.* **1942**, *13*, 6–9.

(26) Giraldo-Zuniga, A. D.; Coimbra, J. S. R.; Arquete, D. A.; Minim, L. A.; Silva, L. H. M.; Maffia, M. C. Interfacial Tension and Viscosity for Poly(Ethylene)Glycol/Maltodextrin Aqueous Two-Phase Systems. *J. Chem. Eng. Data* **2006**, *51*, 1144–1147.

(27) Manning, C. D.; Scriven, L. E. On Interfacial Tension Measurement with a Spinning Drop in Gyrostatic Equilibrium. *Rev. Sci. Instrum.* **1977**, *48*, 1699–1705.

(28) Stragevitch, L.; d'Ávila, 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.

(29) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1997.

(30) Arce, A.; Soto, A.; Ortega, J.; Sabater, G. Viscosities and Volumetric Properties of Binary and Ternary Mixtures of Tris(2-hydroxyethyl) Methylammonium Methylsulfate + Water + Ethanol at 298.15 K. *J. Chem. Eng. Data* **2008**, *53*, 770–775.

(31) Azian, M. N.; Kamal, A. A. M.; Panau, F.; Ten, W. K. Viscosity Estimation of Triacylglycerols and of Some Vegetable Oils on Their Triacilglycerol Composition. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1001–1005.

(32) Kendall, J.; Monroe, K. P. The Viscosity of Liquids. II. The Viscosity-Composition Curve for Ideal Liquid Mixtures. *J. Am. Chem. Soc.* **1917**, *39*, 1787–1802.

(33) Treybal, R. E. *Liquid Extraction*, 2nd ed.; McGraw Hill: New York, 1963.

(34) 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.

(35) Null, H. R. *Phase Equilibrium in Process Design*; Wiley-Interscience: New York, 1970.

(36) Godfrey, J. C.; Slater, M. J. *Liquid−liquid extraction equipment*; John Wiley & Sons: Chichester, 1994.

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