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Liquid−Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15 K

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Deacidification of vegetable oils can be performed by liquid−liquid extraction. The present paper reports experimental data for the system corn oil + oleic acid + ethanol + water at 298.15 K and different water contents. 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 correlated by the NRTL and UNIQUAC models, with a global deviation of 0.89% and 0.92%, respectively.

Introduction

Crude vegetable oils consist predominantly of triacylglycerols and free fatty acids, with mono- and diacylglycerols also present at a lower level. They are obtained mainly by solid−liquid extraction from oil seeds using hexane petroleum fractions as solvent.[1,2] The refining processes of crude vegetable oils involve solvent stripping, degummimg, bleaching, deacidification, and deodorization.[3,4] The removal of free fatty acids (FFAs) is the most important stage of the purification process of oils, mainly because the yield of neutral oil in this operation has a significant effect on the cost of refining.[5] Besides, the presence of these compounds can adversely affect oil quality and stability to oxidation.

Deacidification of oils is usually performed by chemical or physical refining. However, for oils with high acidity, chemical refining causes high losses of neutral oil due to saponification and emulsification. Physical refining is also a feasible process for deacidification of highly acidic oils, since it results in less loss of neutral oil than the traditional process, 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.[6] Thus, it is important to develop alternative processes for the deacidification of edible oils.

The deacidification of oils by liquid−liquid extraction using an appropriate solvent has been receiving attention because of its advantages in comparison to the physical and chemical refining. Kale et al.[7] studied the deacidification of crude rice bran oil by extraction with methanol. Turkay and Civelekoglu[8] investigated the liquid−liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions. As this process is carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments. Besides, the liquid−liquid extraction has the advantages of avoiding the formation of waste products and reducing the loss of neutral oil. Furthermore, solvent stripping from refined oil and solvent recovery from the extract stream can be easily carried out, because of the high difference between the boiling points of the solvent, fatty acids, and triacylglycerols. In fact, these operations can be accomplished by evaporation or distillation at relatively low temperatures, in most cases lower than 353.15 K.[9]

Liquid−liquid equilibrium data for systems containing vegetable oils and fatty acids are relatively scarce in the literature, yet such information is essential for studying the deacidification of edible oils by solvent extraction. The present paper reports liquid−liquid equilibrium data for the system corn oil + oleic acid + ethanol + water at 298.15 K and different water contents. The addition of water to the solvent reduces the loss of neutral oil and improves the solvent selectivity.[9] The experimental data set was used for adjusting the parameters of the NRTL and UNIQUAC models.

Material

Refined corn oil of the Mazzola brand (Brazil) was utilized as a source of triacylglycerols, and commercial oleic acid of Riedel-deHaen as the source of fatty acids. The chemical composition of these reagents was determined by gas chromatography of fatty acid methyl esters (these data are published in ref 10). Corn oil contains 12 different isomer sets with molecular weights varying in the range (831.35 to 887.46) g/mol. The commercial oleic acid contains 83.13 mass % oleic acid, 5.82 mass % palmitoleic acid, 5.05 mass % linoleic acid, 4.05 mass % palmitic acid, and linonenic, stearic, and myristic acids as minor components. The average molecular weight was 872.61 g/mol for the corn oil and 278.59 g/mol for the commercial oleic acid.

The solvent used was ethanol, from Merck, with purity greater than 99.5%. Distilled water was used to obtain the aqueous solvent at different water contents (5, 8, 12, 18 wt %).

Experimental Procedure

Equilibrium cells similar to those of Silva et al.[11] were used for the determination of liquid−liquid equilibrium data. The cell temperature was controlled with a thermostatic bath (Cole-Parmer, Model 12101-15, accurate to 0.1 K). Thermometers (Cole-Parmer Instrument Co.) with subdivisions of 0.1 K were used for monitoring the cell temperature. The component quantity was determined by weighing on a Sartorius analytical balance (Model A200 S, accurate to 0.0001 g). The mixture was stirred vigorously with a magnetic stirrer (FISATOM, Model 752A) for 20 min

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Table 1. Quaternary Liquid−Liquid Equilibrium Data for the System Corn Oil (1) + Commercial Oleic Acid (2) + Solvent [Ethanol (3) + Water (4)] at 298.15 K

water conc in solvent	overall composition				alcohol phase (II)				oil phase (I)			
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
5 wt %	47.98	0	49.40	2.63	1.61	0	92.39	5.99	91.63	0	8.07	0.30
	47.21	2.53	47.72	2.54	2.33	2.40	89.93	5.34	87.79	2.24	9.65	0.33
	43.46	4.91	49.02	2.61	1.61	5.11	87.91	5.37	84.23	4.64	10.74	0.39
	39.25	9.87	48.32	2.57	4.33	10.26	80.39	5.03	75.20	9.35	14.89	0.56
	35.65	14.52	47.32	2.51	7.35	15.11	73.06	4.48	65.77	13.87	19.70	0.67
	29.85	19.99	47.62	2.53	16.72	20.25	59.17	3.86	50.11	19.29	28.51	2.09
8 wt %	49.97	0	46.03	4.00	0.66	0	88.38	10.96	93.76	0	5.64	0.60
	44.97	5.39	45.67	3.97	1.34	4.54	83.36	10.76	85.34	5.64	8.36	0.66
	39.78	9.81	46.38	4.03	1.71	8.73	79.45	10.11	77.96	10.39	10.88	0.76
	35.49	14.59	45.93	3.99	2.57	13.82	73.76	9.86	69.63	15.34	13.91	1.11
	30.99	19.77	45.30	3.94	5.14	19.33	66.49	9.03	58.97	20.97	18.40	1.66
12 wt %	50.07	0	43.94	5.99	0.44	0	85.59	13.97	94.57	0	5.10	0.34
	47.94	2.40	43.70	5.96	0.67	1.81	83.73	13.80	90.56	2.71	6.08	0.65
	45.85	4.92	43.32	5.91	0.82	3.80	81.62	13.76	86.09	5.65	7.59	0.66
	41.49	9.65	43.26	5.90	1.21	7.86	77.73	13.21	78.14	10.97	10.13	0.77
	34.15	14.79	44.93	6.13	2.03	12.99	72.49	12.49	69.08	16.54	13.37	1.01
	30.04	19.99	43.97	5.99	3.98	18.34	66.19	11.48	59.72	21.67	17.08	1.53
	24.59	25.06	44.30	6.04	8.31	24.04	57.41	10.24	48.27	26.35	22.83	2.55
18 wt %	50.35	0	40.72	8.94	0.20	0	79.52	20.28	95.71	0	3.68	0.61
	48.27	2.42	40.44	8.88	0.19	1.43	77.88	20.49	91.12	3.20	5.05	0.63
	44.10	4.91	41.81	9.18	0.21	2.84	76.69	20.26	86.36	6.63	6.24	0.77
	39.94	9.80	41.22	9.05	0.12	6.08	73.56	20.24	77.07	13.27	8.72	0.94
	34.70	15.08	41.18	9.04	0.07	10.30	69.60	20.03	66.88	20.10	11.60	1.43
	29.66	20.15	41.16	9.03	0.64	14.94	65.56	18.86	57.37	25.80	14.89	1.94
	25.22	24.89	40.91	8.97	3.23	19.77	59.94	17.07	48.58	29.92	18.56	2.94

and left to rest for 12 h at least. This led to the formation of two clear and transparent phases, with a well-defined interface.

The oleic acid concentration was determined using potentiometric titration (Modified AOCS Method Ca 5a-40)[12] with an automatic buret (METROHM, Model Dosimat 715); the solvent was determined by evaporation in a vacuum oven (Model EIV-1). The water concentration was determined by Karl Fisher titration, according to AOCS method Ca 23-55.[13] Having determined the fatty acids concentration, solvent, and water, the triacylglycerols concentration was obtained by difference. The uncertainties of the concentrations varied within the following ranges: (0.02 to 0.24)% for oleic acid, (0.02 to 0.11)% for ethanol, (0.02 to 0.18)% for water, and (0.03 to 0.24)% for corn oil, being the lowest figures obtained for the lowest concentrations.

Results

The overall experimental compositions of the mixtures and the corresponding tie lines for the systems of interest are presented in Table 1. All concentrations are expressed as mass percentages.

Modeling. The experimental equilibrium data determined in this work and the data for corn oil + oleic acid + anhydrous ethanol reported by Batista et al.[10] were used together to adjust the parameters of the NRTL and UNIQUAC models. Because of the large difference in molecular weights of the components, mass fractions were used as unity of concentration.[14] In the NRTL model, the activity coefficient (γ_i) assumes the following form:

$$\ln \gamma_i = \frac{\displaystyle\sum_{j=1}^{K} \frac{\tau_{ji} G_{ji} w_j}{\overline{M}_j}}{\displaystyle\sum_{j=1}^{K} \frac{G_{ji} w_j}{\overline{M}_j}} + \sum_{j=1}^{K} \left[\frac{w_j G_{ji}}{\overline{M}_j \displaystyle\sum_{l=1}^{n} \frac{G_{lj} w_l}{\overline{M}_l}} \left(\tau_{ij} - \frac{\displaystyle\sum_{l=1}^{K} \frac{\tau_{lj} G_{lj} w_l}{\overline{M}_l}}{\displaystyle\sum_{l=1}^{K} \frac{G_{lj} w_l}{\overline{M}_l}} \right) \right] \quad (1)$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (2)$$

$$\tau_{ij} = A_{ji}/T \quad (3)$$

$$\alpha_{ij} = \alpha_{ji} \quad (4)$$

In the equations above, A_{ij} and α_{ij} are the interaction parameters of the NRTL model, w is the mass fraction, $\overline{M}$ is the molecular weight of the compounds or pseudocompounds, K is the number of compunds or pseudocompunds, and T is the equilibrium temperature (K).

The equations for the UNIQUAC model are given below:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \quad (5)$$

$$\ln \gamma_i^{\text{comb}} = \frac{\ln \Psi'_i}{\ln(w_i/\zeta\overline{M}_i)} + 1 - \frac{\zeta\overline{M}_i\Psi'_i}{w_i} + \frac{z}{2}\overline{M}_i q'_i \ln\frac{\theta'_i}{\Psi'_i} - \frac{z}{2}\overline{\mathrm{M}}_i q'_i\left(1 - \frac{\Psi'_i}{\theta'_i}\right) \quad (6)$$

where

$$\zeta = \sum_{j=1}^{K} \frac{w_j}{\overline{M}_j} \quad (7)$$

$$\theta'_i = \frac{q'_i w_i}{\displaystyle\sum_{j=1}^{K} q'_j w_j}; \quad \Psi'_i = \frac{r'_i \mathrm{w}_\mathrm{i}}{\displaystyle\sum_{j=1}^{K} r'_j w_j} \quad (8)$$

and

$$\ln \gamma_i^{\text{res}} = \overline{M}_i q'_i \left[1 - \ln\left(\sum_{j=1}^{K} \theta'_j \tau_{ji}\right) - \sum_{j=1}^{K}\left(\theta'_i \tau_{ij} / \sum_{k=1}^{K} \theta'_k \tau_{kj}\right)\right] \quad (9)$$

Table 2. Parameters r'_i and q'_i for Corn Oil, Riedel–deHaen Oleic Acid, Ethanol, and Water

compound	r'_i	q'_i
corn oil (1)	0.044 023	0.035 675
commercial oleic acid (2)	0.045 142	0.037 157
ethanol (3)	0.055 905	0.056 177
water (4)	0.051 069	0.077 713

Table 3. NRTL Parameters for the System Corn Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at 298.15 K

pair *ij*	A_{ij}/K	A_{ji}/K	α_{ij}
12	198.39	−289.66	0.370 20
13	−166.14	1620.9	0.401 15
14	17.625	2911.2	0.177 23
23	−652.55	778.64	0.335 41
24	3500.0	3483.4	0.254 28
34	−10.984	−173.64	0.150 18

where

$$\tau_{ij} = \exp\left(-\frac{A_{ij}}{T}\right) \tag{10}$$

In eqs 5−10, $\ln \gamma_i^{\mathrm{comb}}$ and $\ln \gamma_i^{\mathrm{res}}$ represent the combinatorial and residual contributions, respectively, and $\overline{M}_i$ is the average molecular weight of the corn oil or the commercial fatty acid. As usual in the UNIQUAC model, the lattice coordination number z was assumed to be equal to 10. A_{ij} and A_{ji} are the adjustable parameters. The adjustments were made by treating the system as a pseudoquaternary one, composed of a single triacylglycerol having the corn oil average molecular weight, a representative fatty acid with the molecular weight of the commercial oleic acid, ethanol, and water. The values of r'_i and q'_i for the UNIQUAC model were calculated via eq 11:

$$r'_i = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G \nu_k^{(i)} R_k; \quad q'_i = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G \nu_k^{(i)} Q_k \tag{11}$$

where x_j is the molar fraction of the triacylglycerols of the corn oil or the fatty acids of the commercial oleic acid and $\nu_k^{(i)}$ is the number of groups k in molecule i. C is the number of components in the oil or in the commercial fatty acid, and G is the number of groups. As already mentioned, the compositions of the corn oil and the commercial oleic acid used in the present paper are reported by Batista et al.[10] The parameters R_i and Q_i were obtained from Magnussen et al.[15] The calculated r'_i and q'_i values are furnished in Table 2.

The parameter estimation was based on the minimization of the objective function of composition, following the procedure developed by Stragevitch and d'Avila.[16]

$$S = \sum_m^D \sum_n^N \sum_i^{K-1}\left[\left(\frac{w_{inm}^{\mathrm{I,ex}} - w_{inm}^{\mathrm{I,calc}}}{\sigma_{w_{inm}^{\mathrm{I}}}}\right)^2 + \left(\frac{w_{inm}^{\mathrm{II,ex}} - w_{inm}^{\mathrm{II,calc}}}{\sigma_{w_{inm}^{\mathrm{II}}}}\right)^2\right] \tag{12}$$

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 compounds or pseudocompounds in the group of data m. The subscripts i, n, and m are compound, tie line, and group number, respectively, and the superscripts I and II are the phases; ex and calc refer to experimental and calculated concentrations. $\sigma_{w_{inm}^{\mathrm{I}}}$ and $\sigma_{w_{inm}^{\mathrm{II}}}$ are the standard deviations observed in the compositions of the two liquid phases. Adjusted parameters of the NRTL and UNIQUAC models are shown in Tables 3 and 4, respectively.

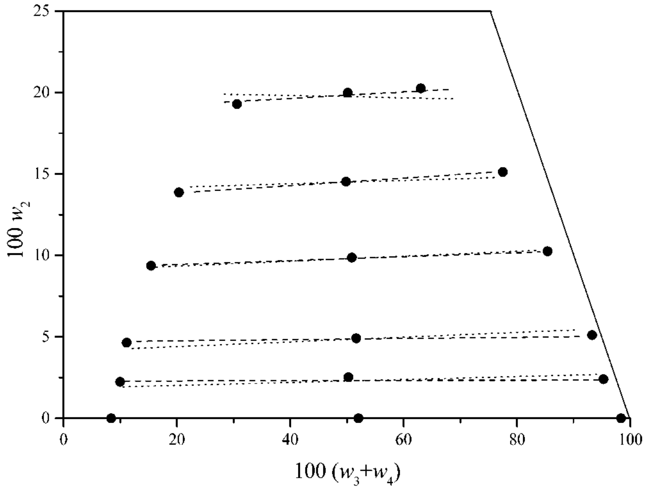

Figure 1. System of corn oil (1) + oleic acid (2) + 5% aqueous solvent [ethanol (3) + water (4)] at 298.15 K: (●) experimental; (− − −) NRTL; (- - -) UNIQUAC.

Table 4. UNIQUAC Parameters for the System Corn Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at 298.15 K

pair *ij*	A_{ij}/K	A_{ji}/K
12	273.64	−212.27
13	246.94	−54.214
14	3032.0	−148.81
23	56.468	−80.240
24	235.76	49.931
34	337.46	−279.92

Table 5. Mean Deviations in Phase Compositions

	Δ*w* (%)	
system	NRTL	UNIQUAC
corn oil + oleic acid + anhydrous ethanol	0.82	0.84
corn oil + oleic acid + 5% aqueous ethanol	1.27	1.39
corn oil + oleic acid + 8% aqueous ethanol	0.82	0.79
corn oil + oleic acid + 12% aqueous ethanol	0.71	0.79
corn oil + oleic acid + 18% aqueous ethanol	0.81	0.79
global deviation	0.89	0.92

The deviations between experimental and calculated compositions in both phases for each system can be found in Table 5. These deviations are calculated according to eq 13:

$$\Delta w = 100\sqrt{\frac{\sum_n^N \sum_i^K [(w_{i,n}^{\mathrm{I,ex}} - w_{i,n}^{\mathrm{I,calc}})^2 + (w_{i,n}^{\mathrm{II,ex}} - w_{i,n}^{\mathrm{II,calc}})^2]}{2NK}} \tag{13}$$

Figures 1 and 2 show the experimental points and calculated tie lines for the systems corn oil/oleic acid/5% aqueous ethanol and corn oil/oleic acid/8% aqueous ethanol. The equilibrium diagrams were plotted in triangular coordinates. For representing the pseudoquaternary systems in triangular coordinates, ethanol + water was admitted as a mixed solvent. Figures 1 and 2 indicate that both models provided a good representation of phase compositions, but the NRTL model allowed a better estimation of the fatty acid concentration in both phases.

Figure 3 presents the distribution coefficient at 298.15 K for the systems studied in the present work. As can be observed, the addition of water in the solvent decreases the fatty acid distribution coefficient, which is calculated according to eq 14 below. These results indicate that

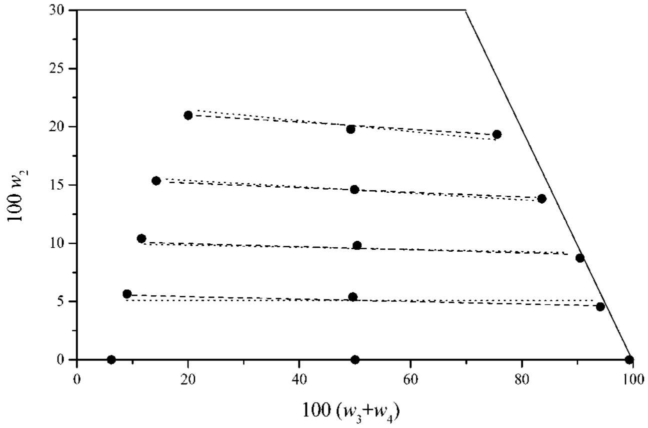

Figure 2. System of corn oil (1) + oleic acid (2) + 8% aqueous solvent [ethanol (3) + water (4)] at 298.15 K: (●) experimental; (— — —) NRTL; (- - -) UNIQUAC.

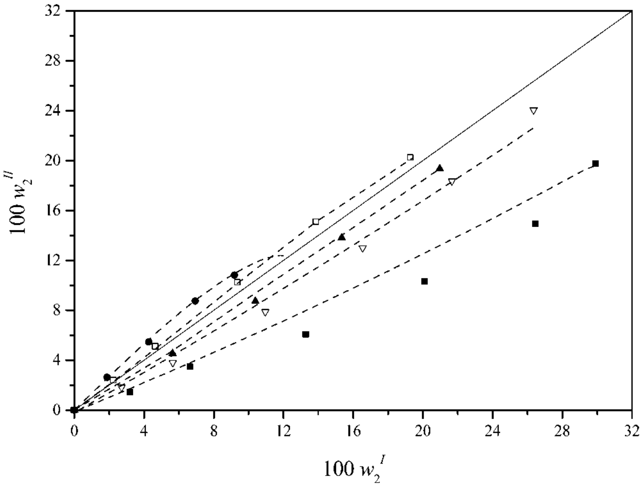

Figure 3. Distribution diagram at 298.15 K for systems of corn oil (1) + oleic acid (2) + ethanol (3) + water (4): (●) anhydrous ethanol; (□) 5 wt % aqueous ethanol; (▲) 8 wt % aqueous ethanol; (▽) 12 wt % aqueous ethanol; (■) 18 wt % aqueous ethanol; (— — —) NRTL.

aqueous ethanol has a lower capacity for extraction of fatty acids. Otherwise, the addition of water increases the solvent selectivity and consequently reduces the loss of neutral oil in solvent extraction. Solvent selectivity can be calculated by eq 15 below. Figure 3 also shows that the NRTL model reproduces very well the experimental distribution coefficients, except for the system with 18% aqueous ethanol.

$$k_i = \frac{w_i^{\mathrm{II}}}{w_i^{\mathrm{I}}} \tag{14}$$

$$S = \frac{k_2}{k_1} \tag{15}$$

To have a better insight about the influence of the water content on the performance of the solvent, flash calculations were performed for a crude oil containing 5 wt % FFA and different water concentrations in the solvent. The mass ratio between crude oil and aqueous solvent was fixed at the value 1:1, corresponding to a concentration of 2.5 wt % of FFA in the overall mixture. The results were presented in Figure 4.

As can be seen, the addition of water causes a significant increase in the solvent selectivity. Despite the small difference between the global deviations obtained for the two models (see Table 5), their estimations of the fatty acid distribution coefficient are significantly different (Figure 4). Such a result confirms that the NRTL model provided a better description of the fatty acid concentrations. The selectivity values estimated by the NRTL model are close to the experimental results, except for aqueous ethanol containing 18 wt % water. In this last case, the uncertainty of the experimental selectivity, calculated by error propagation, is very high (see the error bars in Figure 4). In fact, for such a system (18 wt % water in the solvent), 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 solvent selectivity.

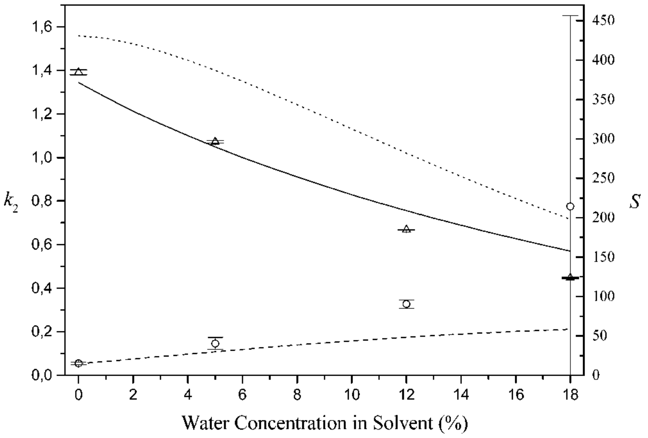

Figure 4. Fatty acid distribution coefficient and selectivities for systems of corn oil (1) + oleic acid (2) + ethanol (3) + water (4): (—) calculated k_2 by the NRTL model; (- - -) calculated k_2 by the UNIQUAC model; (— — —) calculated S by the NRTL model; (△) experimental k_2; (○) experimental S.

Conclusion

Liquid—liquid equilibrium data for systems containing corn oil + oleic acid + ethanol + water were experimentally determinated at 298.15 K. The addition of water in the solvent causes a decrease in the fatty acid distribution coefficient and an increase in the selectivity.

Despite the complexity of the studied systems, the estimated parameters for 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 1.39% in relation to the experimental data. These parameters enable the modeling and simulation of liquid—liquid extractors using the proposed solvents.

Moreover, the results obtained allow one to conclude that a water content in the range 4—6 wt % in the aqueous ethanol is appropriate for deacidification by solvent extraction, as it still provides values of fatty acid distribution coefficient around unity, and high values for the solvent selectivity (larger than 25).

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