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Liquid−Liquid Equilibrium Data for Systems Containing Palm Oil Fractions + Fatty Acids + Ethanol + Water

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ABSTRACT: Liquid−liquid extraction is an alternative method for the deacidification of vegetable oils. In contrast to traditional refining techniques, this alternative process minimizes the loss of neutral oil and preserves nutraceutical compounds originally present in crude edible oils. In this work liquid−liquid equilibrium data were measured at conditions that can be used for the deacidification of palm oil and its fractions. Crude palm oil was separated in two fractions, olein and stearin, and their compositions were characterized. Liquid−liquid equilibrium data were determined at 298.15 K and 318.15 K for systems containing palm olein + oleic acid + ethanol, anhydrous or with different water contents, and at 323.15 K for systems containing palm stearin + palmitic acid + ethanol, anhydrous or with different water contents. Other than their application in the design of liquid−liquid extractors for deacidification of palm oil fractions, these data are also of interest for the production of ethylic biodiesel since the same components are present in the two-phase systems that occur during part of the reactive and purification steps in the biofuel production.

INTRODUCTION

Crude palm oil is very rich in carotenes, tocopherols, and tocotrienols, natural compounds with antioxidant activity that exhibit a series of benefits to human health. Although these minor components would certainly enhance the nutritional value of the end product, most of their initial contents in the raw product are lost during the sequence of palm oil purification steps performed on the industrial scale. During palm oil refining, carotenes are thermally degraded, and significant amounts of tocopherols and tocotrienols are evaporated. Mayamol et al.[1] estimated that the amount of carotenes from palm oil degraded everyday on a worldwide scale corresponds to the suggested daily intake of vitamin A for the entire world population.

In the past decade different alternative techniques have been tested for refining palm oil to avoid the losses of carotenes and vitamin E.[1−3] The obtained final products known as red palm oil, or a fraction of it, the so-called red palm olein, are already being used in the formulation of functional foods.[2] Liquid−liquid extraction using hydrated ethanol as solvent is a promising technique for refining edible oils, including palm oil, without significant losses of natural antioxidants.[3−6] The addition of different amounts of water to ethanol makes possible to increase solvent selectivity, decreasing the losses of neutral oil during deacidification by liquid−liquid extraction. Some equilibrium data required for the appropriate design of liquid−liquid extractors used for palm oil deacidification have already been reported in the literature.[7]

Besides its direct use as a whole product, palm oil is also fractionated by crystallization, and its main fractions find different industrial applications. Palm stearin, the fraction of palm oil rich in triacylglycerols containing saturated fatty acids, is nowadays the most important trans fatty acid−free substitute for hydrogenated oils typically used as constituents in the formulation of several food products. Palm olein, the fraction of palm oil rich in triacylglycerols containing unsaturated fatty acids, is usually selected for producing biodiesel due to the appropriate cloud point and fusion behavior of the obtained biofuel. In fact, palm oil is considered the most promising oil source for biodiesel production due to its very high yield per hectare. Some agricultural varieties can attain yields 10 times higher than the corresponding yields obtained for soybean oil.[8] On the other hand, an alcoholic solvent can be applied for deacidifying vegetable oils that are afterward used for biodiesel production,[9] so that an advantageous integration of the oil refining and biofuel reactive steps would be possible. In this case equilibrium data involving oils + fatty acids + alcohols are required.

Despite the above-mentioned industrial interest, no equilibrium data are available in literature for the palm oil fractions. In the present work palm oil was separated by crystallization into two different fractions, olein and stearin, and liquid−liquid equilibrium data were measured for those fractions in mixtures with oleic or palmitic acids, ethanol, and water at temperatures ranging from (298.15 to 323.15) K. These data are of interest for the refining of palm oil fractions by liquid−liquid extraction, as well as for the production of ethylic biodiesel since these components are also present in the two−phase systems that occur during part of the reactive and purification steps of the biofuel production process. The measured liquid−liquid equilibrium data set was used for adjusting parameters of the nonrandom two-liquid (NRTL) model.

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Table 1. Fatty Acid Compositions of the Commercial Oleic Acid, Crude Palm Oil, Palm Olein, and Palm Stearin

		M^a	oleic acid	crude palm oil	palm olein	palm stearin
fatty acids	$Cx{:}y^b$	$g \cdot mol^{-1}$	100 x	100 x	100 x	100 x
lauric	C12:0	200.31		0.13	0.23	0.17
myristic	C14:0	228.37	0.55	0.91	0.88	1.03
palmitic	C16:0	256.42	4.75	43.91	38.88	51.45
palmitoleic	C16:1	254.40		0.17	0.16	0.12
margaric	C17:0	270.45		0.10		
margaroleic	C17:1	268.43		0.02		
stearic	C18:0	284.47	2.37	5.08	4.62	5.24
oleic	C18:1	282.46	78.72	39.49	43.76	33.75
linoleic	C18:2	280.44	13.61	9.46	10.66	7.58
linolenic	C18:3	278.43		0.27	0.32	0.23
arachidic	C20:0	312.53		0.34	0.34	0.33
gadoleic	C20:1	310.51		0.12	0.15	0.10

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

EXPERIMENTAL SECTION

Materials. The solvents used in this work were anhydrous ethanol from Merck (Germany), with a purity of 0.999 by mass, and aqueous ethanol with water mass fractions of 0.0546 and 0.1042 prepared by the addition of deionized water (Milli-Q, Millipore) to anhydrous ethanol. Commercial oleic acid, with purity greater than 0.78 by mass, was supplied by Merck (Germany), and palmitic acid, with purity greater than 0.99 by mass, was acquired from Sigma (USA). Crude palm oil was kindly supplied by Agropalma (Pará, Brazil), having been submitted only to the clarification process at the refinery, after oil extraction by pressing. Crude palm oil was separated in two fractions, the liquid fraction named palm olein and other semi-solid fraction denominated palm stearin.

All fatty reagents used in this work were analyzed by gas chromatography of the fatty acid methyl esters, according to the official method (162) of the American Oil Chemists' Society (AOCS).[10] Prior to the chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters according to Hartman and Lago.[11] The chromatographic analysis was carried out using a capillary gas chromatography system under the same experimental conditions shown in Lanza et al.[12] The fatty acid compositions of the commercial oleic acid, crude palm oil, palm olein, and palm stearin are presented in Table 1. Considering the chemical structure of the triacylglycerols, the average molar masses of palm oil, olein, and stearin can be calculated on the basis of the fatty acid compositions given in Table 1. The following results were obtained: 852.95 $g \cdot mol^{-1}$ for olein, 843.26 $g \cdot mol^{-1}$ for stearin, and 280.70 $g \cdot mol^{-1}$ for oleic acid. The chromatographic analysis also confirmed the above indicated purity of palmitic acid (> 0.99 by mass).

The free acidity of the olein and stearin palm oil fractions was determined according to the official method 2201 of the International Union of Pure and Applied Chemistry (IUPAC)[13] using the automatic titrator Titrando 808 (Metrohm, Switzerland). Palm olein presented a free acidity of 1.44 % by mass of oleic acid, and the acidity of stearin was 1.01 % by mass of palmitic acid.

Experimental Procedures. Crude palm oil was separated by dry fractionation[14] in a controlled temperature room at (293 ± 1) K. After crystallization the solid and liquid phases were separated by filtration under vacuum. The collected liquid phase corresponded to the palm olein fraction, and the semi−solid phase retained in the filter was the stearin fraction. Both fractions were characterized by gas chromatography and titration according to the information given above.

Equilibrium cells similar to those of Silva et al.[15] were used for measuring the liquid−liquid equilibrium data. The cell temperature was controlled with a thermostatic bath (Cole−Parmer, accurate to 0.1 K, model 12101-55, Chicago, USA). Thermometers (Incoterm, Porto Alegre/RS, Brazil) with subdivisions of 0.1 K were used for monitoring the cell temperature. The quantities of each component were determined by weighing on an analytical balance (Adam, accurate to 0.0001 g, model AAA 250 L, Milton Keynes, United Kingdom). The uncertainties of the systems' overall compositions were evaluated by error propagation, and the following values were obtained in mass fraction: from (0.06 to 0.12) % for oleic and palmitic acids, (0.01 to 0.10) % for ethanol, (0.01 to 0.03) % for water, and (0.06 to 0.20) % for palm olein and stearin. In each experimental run the mixture was stirred vigorously with a magnetic stirrer (Ika Werke, model RH-KT/C, Staufen, Germany) for 20 min and left to rest for at least 4 h. This led to the formation of two clear and transparent phases with a well-defined interface.

Equilibrium data for systems containing palm olein were measured at 298.15 K and 318.15 K using commercial oleic acid as the major source of free acidity. Palm stearin is semi-solid at room temperature and is only completely liquefied at temperatures close to 323.15 K. For this reason the palm stearin systems were measured at 323.15 K, using palmitic acid as the major source of free fatty acids. In both cases the uncertainty of the equilibrium temperature was not greater than 0.1 K. Anhydrous ethanol and hydro-alcoholic solutions containing mass fractions of (5.46 ± 0.02) % or (10.42 ± 0.05) % of water were used as solvents.

After equilibrium was attained, samples of both liquid phases were collected and analyzed. The fatty acid quantity was determined according to the official method 2201 of IUPAC[13] using the automatic titrator Titrando 808 (Metrohm, Switzerland), as previously indicated. The solvent (ethanol + water) quantity was determined by evaporation until reaching constant weight in a vacuum oven (Napco). Water quantity was determined by Karl Fisher titration, according to the AOCS method Ca 23-55.[16] Having determined the fatty acid, solvent, and water quantities, the triacylglycerol (palm olein or stearin) quantity was obtained by calculating the difference. In this work, all measurements were performed with at least three repetitions. Type A standard uncertainties[17] of the compositions varied within the following ranges in mass fraction: (0.08 to 0.16) % for oleic and palmitic acids, (0.03 to 0.19) % for ethanol, (0.01 to 0.05) % for water, and (0.12 to 0.40) % for palm olein and stearin, being the lowest figures obtained for the lowest compositions.

Calculation of the Deviations in the Mass Balance of the Phases. To test the quality of the experimental results, mass balances were performed according to the procedure developed by Marcilla at al.[18] and already applied to fatty systems by Rodrigues et al.[19] According to this procedure, relative deviations were calculated between the sum of the masses of both liquid phases obtained by mass balances and the overall mass initially fed into the equilibrium cell, estimating in this way a relative deviation for each experimental point. On the basis of this approach, n independent component balances should be written, with i being each component of the system:

$$m^{\mathrm{OC}} w_i^{\mathrm{OC}} = m^{\mathrm{SP}} w_i^{\mathrm{SP}} + m^{\mathrm{OP}} w_i^{\mathrm{OP}} \tag{1}$$

where m^{OC} is the mass of the overall composition (initial mixture fed into the equilibrium cell), m^{SP} and m^{OP} are the masses of the solvent and oil phases, respectively, w_i^{OC} is the mass fraction of component i in the initial mixture, and wi^{SP} and w_i^{OP} are the mass fractions of component i in the solvent and oil phases, respectively. With these n equations, it is possible to calculate the values for m^{SP} and m^{OP} from the experimental values w_i^{SP} and w_i^{OP} using a least-squares fitting. Thus, the values for m^{SP} and m^{OP} that minimize the mass balance errors of the previous system can be calculated. The sum of m^{SP} and m^{OP} can be compared to m^{OC} to estimate a relative deviation for the global mass balance (δ), expressed as:

$$\delta = \frac{|m^{\mathrm{OC}} - (m^{\mathrm{SP}} + m^{\mathrm{OP}})|}{m^{\mathrm{OC}}} \tag{2}$$

Thermodynamic Modeling. The experimental data determined in this work were used for adjusting binary interaction parameters of the NRTL model. The activity coefficient equations and the isoactivity criterion were used in the form reported by Rodrigues et al.,[20] with the compositions expressed in terms of mass fraction. The isoactivity criterion of phase equilibrium, developed on a molar fraction basis, can be expressed in the mass fraction scale as follows:

$$(\gamma_i x_i)^{\mathrm{SP}} = (\gamma_i x_i)^{\mathrm{OP}} \tag{3}$$

$$(\gamma_i^w w_i)^{\mathrm{SP}} = (\gamma_i^w w_i)^{\mathrm{OP}} \tag{4}$$

$$\gamma_i^w = \frac{\gamma_i}{M_i \sum_j^K \left(\frac{w_j}{M_j}\right)} \tag{5}$$

where γ_i is the activity coefficient of component i estimated according to the original NRTL model, γ_i^w is the corresponding activity coefficient expressed on a mass fraction scale, M_i is molar mass of component i, the subscript j stands for the other components, and K is the total number of components in the mixture.

Palm olein and palm stearin were treated as pseudocomponents, assuming that their different triacylglycerols behave similarly in the liquid–liquid systems investigated in the present work. In this case each triacylglycerol source, olein or stearin, can be adequately represented by a single triacylglycerol with the average physical–chemical properties of the corresponding palm oil fraction, including its average molar mass. The same behavior was also attributed to the commercial oleic acid. This approach was already used in prior works[21−23] for equilibrium data of vegetable oils and experimentally tested by Lanza et al.[24] in a similar system. In fact, Lanza et al.[24] proved the reliability of this hypothesis.

Estimation of the NRTL parameters was performed by minimizing an objective function of compositions, eq 6 below, according to the procedure suggested by Stragevitch and d'Ávila.[25]

$$\mathrm{OF}(w) = \sum_{m=1}^{D} \sum_{n=1}^{N} \sum_{i=1}^{K-1} \left[\left(\frac{w_{i,n,m}^{\mathrm{SP,exptl}} - w_{i,n,m}^{\mathrm{SP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{SP}}}} \right)^2 + \left(\frac{w_{i,n,m}^{\mathrm{OP,exptl}} - w_{i,n,m}^{\mathrm{OP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{OP}}}} \right)^2 \right] \tag{6}$$

where D is the total number of data groups, N is the total number of tie lines in the data group, K is the total number of components in the data group, w is the mass fraction, subscripts i, n, and m are the

Table 2. Liquid−Liquid Equilibrium Data for Systems Containing Palm Olein (1), Commercial Oleic Acid (3), Ethanol (5), and Water (6) at 298.15 K

	overall composition				solvent phase				oil phase			
$100\,w_{6S}$[a]	$100\,w_1$	$100\,w_3$	$100\,w_5$	$100\,w_6$	$100\,w_1$	$100\,w_3$	$100\,w_5$	$100\,w_6$	$100\,w_1$	$100\,w_3$	$100\,w_5$	$100\,w_6$
0.00	48.77	0.71	50.52	0.00	6.90	0.76	92.34	0.00	85.03	0.66	14.31	0.00
	46.93	2.68	50.39	0.00	7.88	3.20	88.92	0.00	78.57	2.23	19.20	0.00
	45.05	4.64	50.31	0.00	10.09	5.42	84.49	0.00	76.08	4.12	19.80	0.00
	43.22	6.61	50.17	0.00	12.65	7.58	79.77	0.00	71.39	5.92	22.69	0.00
	40.98	8.52	50.50	0.00	15.96	9.28	74.76	0.00	65.54	7.69	26.77	0.00
	38.99	10.47	50.54	0.00	22.64	11.13	66.23	0.00	57.44	9.49	33.07	0.00
5.46	49.10	0.72	47.44	2.74	2.00	0.75	91.32	5.93	90.39	0.71	8.66	0.24
	47.13	2.70	47.43	2.74	2.27	2.78	88.90	6.05	87.52	2.50	9.63	0.35
	45.11	4.65	47.50	2.74	2.22	4.80	86.91	6.07	84.20	4.42	10.95	0.43
	43.16	6.60	47.50	2.74	2.41	6.89	84.85	5.85	80.60	6.49	12.46	0.45
	41.14	8.56	47.55	2.75	3.52	8.84	81.92	5.72	77.53	8.24	13.63	0.60
	39.18	10.52	47.55	2.75	4.62	10.60	79.00	5.78	74.02	10.36	15.01	0.61

[a] w_{6S} = mass fraction of water in alcoholic solvent.

Table 3. Liquid−Liquid Equilibrium Data for Systems Containing Palm Olein (1), Commercial Oleic Acid (3), Ethanol (5), and Water (6) at 318.15 K

	overall composition				solvent phase				oil phase			
100 w_{6S}[a]	100 w_1	100 w_3	100 w_5	100 w_6	100 w_1	100 w_3	100 w_5	100 w_6	100 w_1	100 w_3	100 w_5	100 w_6
0.00	65.44	0.96	33.60	0.00	11.95	0.93	87.12	0.00	73.80	0.97	25.23	0.00
	49.03	0.72	50.25	0.00	11.53	0.87	87.60	0.00	78.40	0.71	20.89	0.00
	48.33	2.76	48.91	0.00	15.39	3.12	81.49	0.00	69.97	2.54	27.49	0.00
	45.04	4.64	50.32	0.00	19.39	4.94	75.67	0.00	62.65	4.38	32.97	0.00
5.46	48.89	0.71	47.65	2.75	2.04	0.76	90.99	6.21	90.12	0.66	8.71	0.51
	47.13	2.69	47.44	2.74	3.43	2.84	88.19	5.54	84.83	2.66	12.09	0.42
	44.95	4.64	47.66	2.75	4.09	4.78	85.85	5.28	80.92	4.52	14.07	0.49
	43.30	6.63	47.34	2.73	5.25	6.73	82.89	5.13	75.08	6.53	18.07	0.32
	41.13	8.56	47.56	2.75	4.75	8.87	81.52	4.86	71.79	8.11	19.71	0.39
	39.24	10.53	47.49	2.74	6.13	10.79	78.03	5.05	67.43	10.08	21.43	1.06
10.42	49.01	0.72	45.03	5.24	1.25	0.79	87.55	10.41	89.88	0.88	8.74	0.50
	46.95	2.69	45.11	5.25	1.50	2.55	86.00	9.95	85.62	2.97	10.95	0.46
	45.21	4.66	44.90	5.23	1.69	4.44	84.16	9.71	82.50	5.02	11.38	1.10
	43.20	6.61	44.96	5.23	2.15	6.33	81.71	9.81	78.79	7.15	13.22	0.84
	41.41	8.61	44.77	5.21	2.72	8.19	79.50	9.59	75.69	9.26	13.97	1.08
	39.40	10.58	44.81	5.21	3.19	9.99	77.42	9.40	71.76	11.18	15.97	1.09

[a] w_{6S} = mass fraction of water in alcoholic solvent.

Table 4. Liquid−Liquid Equilibrium Data for Systems Containing Palm Stearin (2), Palmitic Acid (4), Ethanol (5), and Water (6) at 323.15 K

	overall composition				solvent phase				oil phase			
100 w_{6S}[a]	100 w_2	100 w_4	100 w_5	100 w_6	100 w_2	100 w_4	100 w_5	100 w_6	100 w_2	100 w_4	100 w_5	100 w_6
0.00	32.27	0.33	67.40	0.00	11.20	0.37	88.43	0.00	73.70	0.30	26.00	0.00
	65.60	0.67	33.73	0.00	12.47	0.68	86.85	0.00	73.07	0.66	26.27	0.00
	48.52	0.49	50.99	0.00	11.12	0.58	88.30	0.00	74.19	0.41	25.40	0.00
	47.14	2.47	50.39	0.00	17.26	2.70	80.04	0.00	68.33	2.32	29.35	0.00
	45.24	4.43	50.33	0.00	25.82	4.72	69.46	0.00	62.97	4.40	32.63	0.00
5.46	49.14	0.50	47.61	2.75	2.90	0.52	90.84	5.74	86.46	0.48	12.61	0.45
	46.99	2.46	47.79	2.76	3.53	2.52	88.79	5.16	82.42	2.44	14.70	0.44
	45.22	4.43	47.60	2.75	4.20	4.54	85.96	5.30	78.72	4.25	16.37	0.66
	43.08	6.38	47.78	2.76	4.90	6.80	83.49	4.81	74.81	6.27	18.27	0.65
	41.54	8.39	47.33	2.74	6.51	8.76	79.73	5.00	70.84	8.22	20.21	0.73
	39.58	10.35	47.33	2.74	9.28	10.47	75.35	4.90	64.46	10.08	24.38	1.08
10.42	49.23	0.50	45.03	5.24	1.38	0.47	88.02	10.13	89.30	0.51	9.79	0.40
	47.16	2.47	45.12	5.25	1.72	2.31	86.78	9.19	86.37	2.63	10.49	0.51
	45.21	4.43	45.11	5.25	1.75	4.22	84.04	9.99	82.12	4.83	12.09	0.96
	43.12	6.39	45.23	5.26	2.56	6.08	82.63	8.73	79.08	6.84	13.28	0.80
	41.34	8.35	45.07	5.24	2.96	7.99	79.13	9.92	74.98	8.93	15.07	1.02
	39.13	10.23	45.36	5.28	4.06	9.87	76.97	9.10	71.47	10.67	16.71	1.15

[a] w_{6S} = water mass fraction in the alcoholic solvent.

component, tie line, and group numbers, respectively, and the superscripts SP and OP stand for the solvent and oil phases, respectively; exptl and calcd refer to experimental and calculated compositions. $\sigma_{w_{i,n,m}^{\mathrm{SP}}}$ and $\sigma_{w_{i,n,m}^{\mathrm{OP}}}$ are the standard deviations observed in the compositions of the two liquid phases.

In the case of some binary interactions, such as oleic acid and ethanol, oleic acid and water, and ethanol and water, NRTL parameters are already available in the literature,[21−23] and these values were used, being adjusted by the procedure described above only the remaining parameters. The average deviations between the experimental and the calculated compositions in both phases were calculated according to eq 7.

$$\Delta w = \sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{K}[(w_{i,n}^{\mathrm{SP,\,exptl}} - w_{i,n}^{\mathrm{SP,\,calcd}})^2 + (w_{i,n}^{\mathrm{OP,\,exptl}} - w_{i,n}^{\mathrm{OP,\,calcd}})^2]}{2NK}} \qquad (7)$$

■ RESULTS AND DISCUSSION

Tables 2, 3, and 4 show the overall phase compositions and the corresponding equilibrium data in mass fractions for pseudoternary systems containing palm olein/stearin + oleic/palmitic acids + ethanol and the pseudoquaternary systems containing palm olein/stearin + oleic/palmitic acids + ethanol + water. The following notations were used for the components: olein (1), stearin (2), commercial oleic acid (3), palmitic acid (4), ethanol (5), and water (6).

The average global mass balance deviations, calculated according to the procedure suggested by Marcilla et al.[18] for every phase diagram measured in the present work, varied within the range of (0.36 to 0.03) %, always lower than the highest acceptable value suggested by these authors. The low mass balance deviations as well as the low uncertainties of the experimental data confirm the good quality of the measured experimental data.

Table 5 gives the adjusted NRTL parameters, and Table 6 shows the average deviations between the experimental and the calculated compositions for each investigated system, estimated according to eq 7. Figures 1 and 2 show the experimental tie lines and those calculated using the NRTL model for systems containing palm olein (1) + commercial oleic acid (3) + ethanol (5) + water (6) at 298.15 K and 318.15 K, respectively. As can be seen in these figures and in the equilibrium data given in Tables 2 and 3, a temperature increase of 20 K had a large effect upon the size of the phase splitting region. In fact, it increases the mutual solubility of palm olein and ethanol, reducing the range of compositions in which two liquid phases coexist.

Table 5. NRTL Parameters for the Binary Interactions Between Palm Olein (1), Palm Stearin (2), Commercial Oleic Acid (3), Palmitic Acid (4), Ethanol (5), and Water (6)

T/K	pair ij	A_{ij}/K	A_{ji}/K	α_{ij}
298.15	1 3	−80.123	−250.66	0.20000
	1 5	190.15	1402.0	0.51531
	1 6	653.61	3622.8	0.20000
	3 5[a]	4800.0	−170.55	0.22957
	3 6[a]	1006.7	4210.6	0.10000
	5 6[a]	−10.984	−173.64	0.15018
318.15	1 3	4387.3	−278.24	0.20000
	1 5	153.27	1343.0	0.59907
	1 6	429.00	3264.8	0.20000
	3 5[b]	−376.26	172.46	0.57000
	3 6[b]	6962.8	7922.6	0.10000
	5 6[b]	−67.100	−255.04	0.47000
323.15	2 4	11484.0	−64.770	0.69943
	2 5	80.552	1306.5	0.62366
	2 6	1340.6	3616.8	0.20000
	4 5	4397.9	341.23	0.69471
	4 6	1204.7	2335.6	0.20000
	5 6[c]	32.990	2278.3	0.24000

[a] Parameters taken from Rodrigues et al.[21] [b] Parameters taken from Gonçalves and Meirelles.[22] [c] Parameters taken from Rodrigues et al. [23]

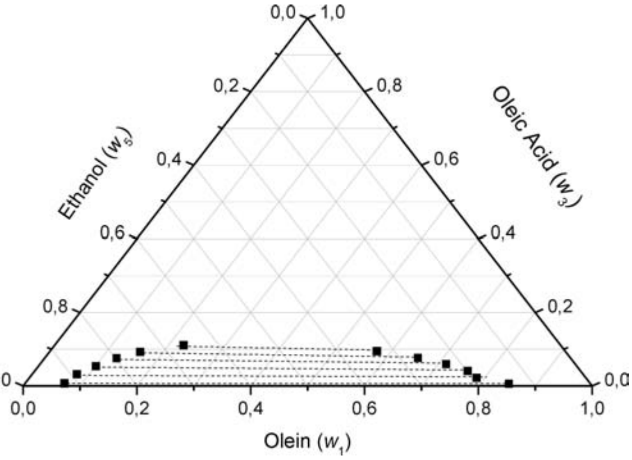

Figure 1. Liquid−liquid equilibrium for the pseudoternary system containing palm olein (1) + commercial oleic acid (3) + ethanol (5) at 298.15 K: ■, experimental data; - - -, calculated data by the NRTL model.

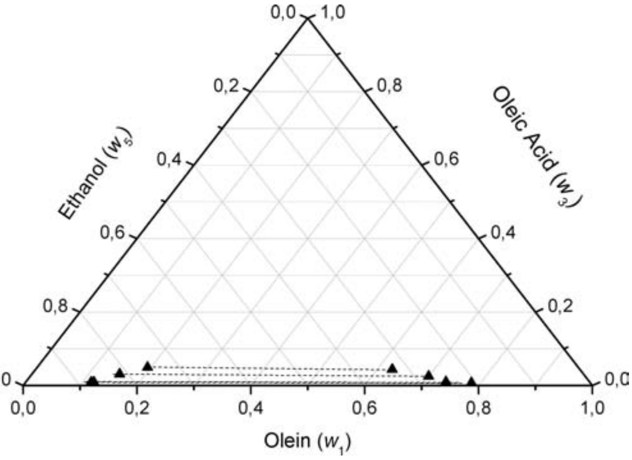

Figure 2. Liquid−liquid equilibrium for the pseudoternary system containing palm olein (1) + commercial oleic acid (3) + ethanol (5) at 318.15 K: ▲, experimental data; - - -, calculated data by the NRTL model.

Table 6. Average Deviations between Experimental and NRTL Calculated Phase Compositions

system	100 Δw
olein (1) + commercial oleic acid (3) + ethanol (5) at 298.15 K	0.68
olein (1) + commercial oleic acid (3) + ethanol (5) + water (6) (mass fraction of 5.46 % of water in anhydrous ethanol) at 298.15 K	0.34
olein (1) + commercial oleic acid (3) + ethanol (5) at 318.15 K	1.05
olein (1) + commercial oleic acid (3) + anhydrous ethanol (5) + water (6) (mass fraction of 5.46 % of water in anhydrous ethanol) at 318.15 K	0.69
olein (1) + commercial oleic acid (3) + anhydrous ethanol (5) + water (6) (mass fraction of 10.42 % of water in anhydrous ethanol) at 318.15 K	0.59
stearin (2) + palmitic acid (4) + ethanol (5) at 323.15 K	1.21
stearin (2) + palmitic acid (4) + ethanol (5) + water (6) (mass fraction of 5.46 % of water in anhydrous ethanol) at 323.15 K	0.84
stearin (2) + palmitic acid (4) + ethanol (5) + water (6) (mass fraction of 10.42 % of water in anhydrous ethanol) at 323.15 K	0.58

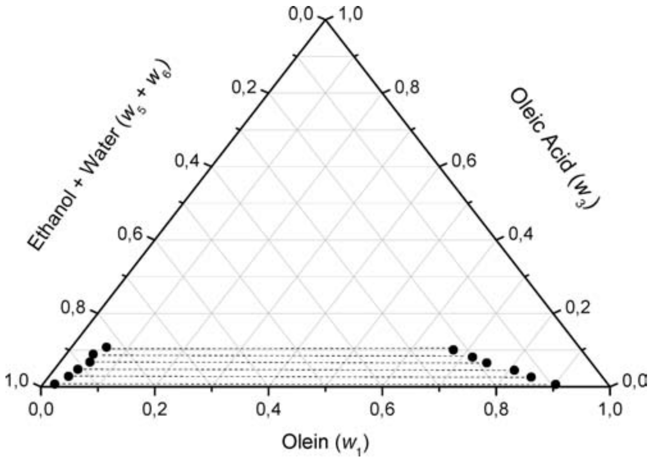

Figure 3. Liquid−liquid equilibrium for the pseudoquaternary system containing palm olein (1) + commercial oleic acid (3) + ethanol (5) + water (6) (mass fraction of 5.46 % of water in anhydrous ethanol) at 318.15 K: ●, experimental data; - - -, calculated data by the NRTL model.

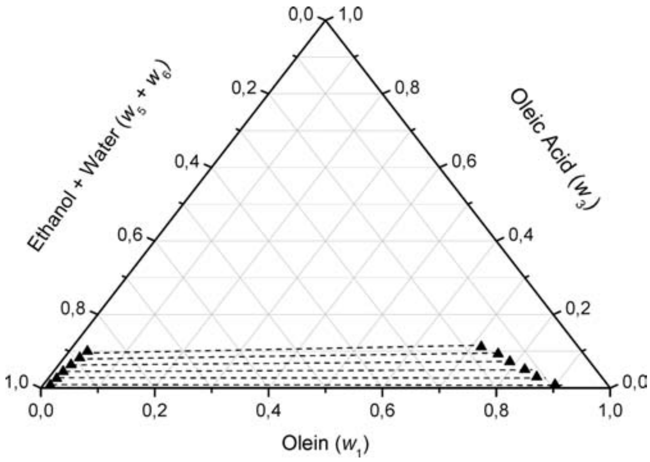

Figure 4. Liquid−liquid equilibrium for the pseudoquaternary system containing palm olein (1) + commercial oleic acid (3) + ethanol (5) + water (6) (mass fraction of 10.42 % of water in anhydrous ethanol) at 318.15 K: ▲, experimental data; - - -, calculated data by the NRTL model.

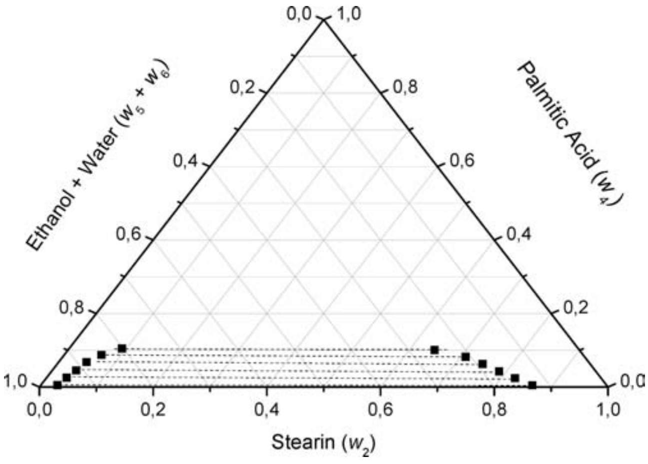

Figure 5. Liquid−liquid equilibrium for the pseudoquaternary system containing palm stearin (2) + palmitic acid (4) + ethanol (5) + water (6) (mass fraction of 5.46 % of water in anhydrous ethanol) at 323.15 K: ■, experimental data; - - -, calculated data by the NRTL model.

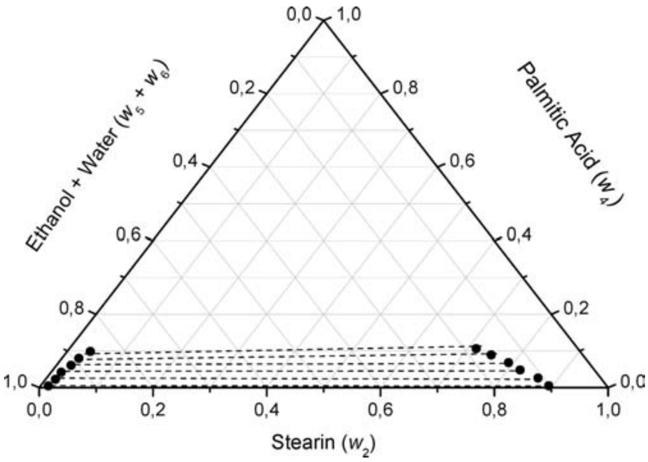

Figure 6. Liquid−liquid equilibrium for the pseudoquaternary system containing palm stearin (2) + palmitic acid (4) + ethanol (5) + water (6) (mass fraction of 10.42 % of water in anhydrous ethanol) at 323.15 K: ●, experimental data; - - -, calculated data by the NRTL model.

Figures 3 and 4 show the experimental data and those calculated by the NRTL model for systems containing palm olein (1) + commercial oleic acid (3) + ethanol (5) + water (6) at 318.15 K and different water mass fractions in the alcoholic solvent. As can be seen in these figures, increasing the water content in the solvent enlarges the phase splitting region as well as decreases the partition of the fatty acid to the alcoholic phase.

The above-described influences of temperature and water content in the alcoholic solvent upon the equilibrium data are similar to the behavior already reported in the literature by different authors who have measured the liquid−liquid equilibrium of fatty systems.[4,5,12,26]

Figures 5 and 6 provide the experimental data and the corresponding calculated values for systems containing palm stearin (2) + palmitic acid (4) + ethanol (5) + water (6) at 323.15 K and different water mass fractions in the alcoholic solvent. The behavior is similar to that described above for palm olein, with the addition of water to the solvent enlarging the region of two-phase coexistence. Comparing Figures 5 and 6 with Figures 3 and 4, and also based on the equilibrium data given in Tables 3 and 4, one can conclude that the systems with palm olein have a slightly larger phase splitting region than the palm stearin systems, probably a consequence of the somewhat higher temperature used in case of stearin.

Figures 1 to 6 also indicate that the selected thermodynamic model was able to accurately describe the phase compositions. This is further confirmed by the corresponding low deviations calculated for all systems, always within the range from (0.34 to 1.21) %, as shown in Table 6.

■ CONCLUSIONS

Phase equilibrium data for liquid−liquid systems containing palm olein/stearin + oleic/palmitic acids + ethanol + water were measured within the temperature range from (298.15 to 323.15) K. The low deviations obtained in the global mass balance indicate the good quality of the experimental data. The NRTL model was able to correlate the equilibrium data with very low deviations between experimental and calculated compositions. Increase in the water content of the solvent enlarges the phase splitting region as well as decreases the partition of fatty acids to the alcoholic phase. On the other hand, an increase in the temperature enhances the mutual solubility of the palm oil fractions and ethanol, reducing the range of compositions in which two liquid phases coexist. The experimental data measured in the present work are of interest for the refining of palm oil fractions by liquid−liquid extraction, as well as for the production of ethylic biodiesel.

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