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Extraction of Free Fatty Acids from Peanut Oil and Avocado Seed Oil: Liquid−Liquid Equilibrium Data at 298.2 K

Christianne E. C. Rodrigues[*,†] **and Antonio J. A. Meirelles**[‡]

Department of Food Engineering (ZEA-FZEA), University of São Paulo (USP), P.O. Box 23, 13635-900, Pirassununga, São Paulo, Brazil, and EXTRAE, Department of Food Engineering (DEA-FEA), State University of Campinas (UNICAMP), P.O. Box 6121, 13083-862 Campinas, São Paulo, Brazil

The present paper reports phase equilibrium experimental data for two systems composed by peanut oil or avocado seed oil + commercial oleic acid + ethanol + water at 298.2 K and different water contents in the solvent. The addition of water to the solvent reduces the loss of neutral oil in the alcoholic phase and improves the solvent selectivity. The experimental data were correlated by the NRTL and UNIQUAC models. The global deviations between calculated and experimental values were 0.63 % and 1.08 %, respectively, for the systems containing avocado seed oil. In the case of systems containing peanut oil those deviations were 0.65 % and 0.98 %, respectively. Such results indicate that both models were able to reproduce correctly the experimental data, although the NRTL model presented a better performance.

Introduction

The production of vegetable oils consists in its extraction from oilseeds, bran, nut, or fruit pulps using mainly hexane petroleum fractions as solvent.[1,2] Crude vegetable oils obtained from solid−liquid extraction operations contain variable amounts of nonglyceride impurities, such as free fatty acids, phosphatides, and pigments that are detrimental to the quality of the final product and must be removed.

A variety of procedures may be involved in the conversion of crude vegetable oils to edible products such as solvent stripping, degumming, bleaching, deacidification, and deodorization.[3,4] The deacidification step, or removal of free fatty acids, is usually performed by chemical or physical refining. However, for oils with high content of free fatty acids, chemical refining causes high losses of the neutral oil due to saponification and emulsification and generates considerable quantities of effluent.[5] Physical refining is also a feasible process for deacidification of highly acidic oils since it results in less loss of neutral oil than the chemical 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]

Liquid−liquid extraction technique has been considered as an alternative to the classical processes such as chemical and physical refining.[5,7,8] This alternative process is based on the difference of solubility of free fatty acids and neutral triacylglycerols (main components of vegetable oils) in an appropriate solvent[9] and can be performed under milder conditions (temperatures close to room temperature and atmospheric pressure) when compared to traditional methods. Besides, the liquid−liquid extraction has the advantages of avoiding the formation of waste products and reducing the losses of neutral oil and nutraceutical compounds.[10–12]

References related to such extraction studies show a decrease of free fatty acid contents in the vegetable oils.[13–16] The development of this approach for a future commercial application demands a systematic study of the phase equilibrium that involves fatty compounds and solvent.[17–22] Liquid−liquid equilibrium data for fatty systems containing several vegetable oils (canola, corn, palm, rice bran, macadamia nut, Brazil nut, cottonseed, grape seed, garlic, sesame seed, and soybean oils) have been reported by our research group always using short-chain alcohols as solvent.[10,11,23–30]

The aim of this work was to extend the phase equilibrium data bank investigating the liquid−liquid equilibrium for systems containing peanut oil or avocado seed oil, artificially acidified with commercial oleic acid, and a solvent (ethanol with different contents of water) at 298.2 K. The experimental data were correlated by the NRTL and UNIQUAC equations and the adjusted interaction parameters enable the modeling and simulation of liquid−liquid extractors.

Experimental Section

Materials. Refined peanut oil and refined avocado seed oil used in this work were kindly supplied by Campestre (São Paulo/SP, Brazil). These oils presented acidity values of (0.13 ± 0.01) % and (0.38 ± 0.02) %, respectively, expressed as mass fraction of oleic acid.

All reagents, the refined vegetable oils, and commercial oleic acid from Merck (Germany) were analyzed by gas chromatography of fatty acid methyl esters to determine the fatty acid composition, according to the official method (1-62) of the AOCS.[31] The fatty samples were prepared in the form of fatty acid methyl esters according to the official method (2-66) of the AOCS.[32] An HP5890 gas chromatograph with a flame ionization detector was used under the following experimental conditions: fuse silica column of cyanopropylsiloxane 0.25 μm, 60 m × 0.32 mm i.d.; hydrogen as the carrier gas at a rate of 2.5 $\text{mL}\cdot\text{min}^{-1}$; injection temperature of 548.2 K; column temperature of (448.2 to 498.2) K (rate of 1.3 $\text{K}\cdot\text{min}^{-1}$); and detection temperature of 578.2 K. The fatty acid methyl esters were identified by comparison with external standards purchased from Nu Check Inc. (Elysian, MN).

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[*] To whom correspondence should be addressed.E-mail: chrisrodrigues@usp.br. Fax: + 55-19-3565-4284.
[†] University of São Paulo (USP).
[‡] State University of Campinas (UNICAMP).

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

Experimental Procedure. Model fatty systems containing fatty acids and triacylglycerols were prepared by the addition of known masses of commercial oleic acid to refined vegetable oils. In the case of systems containing anhydrous ethanol, the source of the acidic oil was obtained by mixing peanut or avocado seed oils with up to 20.45 mass % or 11.56 mass % of oleic acid, respectively. For the systems with ethanol plus water as solvent, the amounts of commercial oleic acid dissolved in the peanut or avocado seed oils were up to 40.48 mass % or 37.99 mass %, respectively. The model fatty systems were mixed with the ethanolic solvents in the mass ratio oil/solvent 1:1 at (298.2 ± 0.1) K for determination of liquid−liquid equilibrium data used to adjust NRTL and UNIQUAC parameters. Commercial oleic acid was added to both systems and ethanolic solvents containing mass fractions of (0, 6, and 12) % of water were used as extractants.

The equilibrium data were determined using polypropylene centrifuge tubes (50 mL) (Corning Inc., Lowell/MA, USA). The components were weighed on an analytical balance (Adam, model AAA 250L, Milton Keynes, United Kingdom) with a precision of 0.0001 g. The tubes were vigorously stirred for at least 15 min at room temperature (quite close to 298 K), centrifuged for 10 min at 4500 *g* at (298.2 ± 1.5) K (Jouan Centrifuge, model BR4i, equipped with a temperature controller, Saint-Herblain, France), and left to rest for 2 h in a thermostatic bath at (298.2 ± 0.1) K (Cole Parmer, model 12101-05, Chicago, IL). This contact time was stated based on a previous study that showed the equilibrium phase was attained after 1 h of rest.[10]

After this treatment, the two phases became clear with a well-defined interface, and the composition of both phases was measured. The concentration of free fatty acids was determined by titration (official method 2201 of IUPAC[33]) with an automatic burette (Metrohm, model Dosimat 715, Herisan, Switzerland). The total solvent concentration was determined by evaporation at 313.2 K in a vacuum oven (Napco model 5831, New York). The water concentration was determined by Karl Fischer titration, according to AOCS method Ca 23-55[31] with a KF Titrino (Metrohm, model 701, Herisan, Switzerland). The triacylglycerol concentration was determined by difference.

In this work, all measurements were performed at least in triplicate. The uncertainties of the concentrations varied within the following mass fractions ranges: (0.01 to 0.27) % for oils, (0.02 to 0.23) % for oleic acid, (0.02 to 0.11) % for ethanol, and (0.01 to 0.26) % for water, being the lowest figures obtained for the lowest mass fractions.

Modeling Approach. In the present work, the experimental data measured for the model systems were used to adjust the NRTL and UNIQUAC interaction parameters between each vegetable oil and the other components of the system (commercial oleic acid, ethanol, and water). The parameters concerning the interaction between these other components with each other were taken from our prior work.[10]

Mass fraction was used to express composition due to the large difference in molar mass of the components of the system.[10,11,23–30] Rodrigues et al.[11] show the activity coefficient equations, expressed in mass fractions, according to the NRTL and UNIQUAC models.

The adjustments were made by treating the model systems composed by vegetable oils + commercial oleic acid + anhydrous ethanol as a pseudoternary one and the systems composed by vegetable oils + commercial oleic acid + ethanol + water as pseudoquaternary ones. Each system was considered as composed by a single triacylglycerol having the corresponding vegetable oil average molar mass, a representative fatty acid with the molar mass of the commercial oleic acid, ethanol, and water.

The values of r_i' and q_i', volume and area parameters necessary for the UNIQUAC model, were calculated via eq 1, where x_j is the mole fraction of the triacylglycerols of the vegetable oils or the fatty acids of the commercial oleic acid, $\nu_k^{(j)}$ is the number of groups k in molecule j, $\bar{M}_i$ is the average molar mass of the vegetable oils or the fatty acids, C is the number of compounds in the oil or in the fatty acid, G is the total number of groups, and R_i and Q_i are van der Waals parameters taken from Magnussen and co-workers.[34]

$$r'_i = \frac{1}{\bar{M}_i}\sum_{j}^{C} x_j \sum_{k}^{G} \nu_k^{(j)} R_k \; ; \qquad q'_i = \frac{1}{\bar{M}_i}\sum_{j}^{C} x_j \sum_{k}^{G} \nu_k^{(j)} Q_k \quad (1)$$

The interaction parameters estimation was based on the minimization of the objective function of composition (eq 2), following the procedure developed by Stragevitch and d'Avila. [35]

$$S = \sum_{m}^{D}\sum_{n}^{N}\sum_{i}^{K-1}\left[\left(\frac{w_{\text{inm}}^{\text{OP}} - w_{\text{inm}}^{\text{OP,calc}}}{\sigma_{w_{\text{inm}}^{\text{OP}}}}\right)^2 + \left(\frac{w_{\text{inm}}^{\text{AP}} - w_{\text{inm}}^{\text{AP,calc}}}{\sigma_{w_{\text{inm}}^{\text{AP}}}}\right)^2\right] \quad (2)$$

where D is the total number of groups of data, N is the total number of tie lines, and K is the total number of components or pseudocompounds in the group of data m. w is the mass fraction, the subscripts i, n, and m are component, tie line, and group number, respectively, and the superscripts OP and AP stand for oil and alcoholic phases, respectively; calc refers to calculated mass fractions. $\sigma_{w_{\text{inm}}}^{\text{OP}}$ and $\sigma_{w_{\text{inm}}}^{\text{AP}}$ are the standard deviations observed in the compositions of the two liquid phases.

The deviations between experimental and calculated compositions in both phases were calculated according to eq 3.

$$\Delta w = \sqrt{\frac{\sum_{n}^{N}\sum_{i}^{K}\left[\left(w_{i,n}^{\text{OP}} - w_{i,n}^{\text{OP,calc}}\right)^2 + \left(w_{i,n}^{\text{AP}} - w_{i,n}^{\text{AP,calc}}\right)^2\right]}{2NK}} \quad (3)$$

where N is the total number of tie lines, and K is the total number of components or pseudocompounds in the group of data.

Results

The fatty acid compositions of peanut oil, avocado seed oil and commercial oleic acid from Merck are presented in Table 1.

As Table 1 shows, oleic and linoleic acids are the most important fatty acids present in peanut and avocado seed oils. The results obtained for peanut oil are in accordance with the values of fatty acid composition reported in the literature for this oil.[36,37] It can be emphasized that the avocado oil used in this work was extracted from avocado seeds, not from the fruit pulp. Avocado oils extracted from seeds and from pulp exhibit some differences in their fatty acid compositions. In a general way, avocado oil from pulp presents a major content of oleic acid (around of 60 %) and lower content of linoleic acid (10 %) than the avocado seed oil composition presented in Table 1.[36,38]

Table 1. Fatty Acid Mole Fractions *x* and Mass Fractions *w* of the Refined Vegetable Oils and Commercial Oleic Acid

			M^a	peanut oil		avocado seed oil		commercial oleic acid	
symbol	fatty acid		g·mol^{-1}	100*x*	100*w*	100*x*	100*w*	100*x*	100*w*
Cp	Caproic	C8:0^b	144.22	0.90	0.48				
C	Capric	C10:0	172.27	0.69	0.44				
L	Lauric	C12:0	200.32	8.03	5.97	2.21	1.61	1.58	1.13
M	Miristic	C14:0	228.38	2.50	2.12	0.81	0.67	1.09	0.89
P	Palmitic	C16:0	256.43	11.60	11.04	15.77	14.66	5.83	5.36
Po	Palmitoleic	C16:1	254.42					0.13	0.12
S	Stearic	C18:0	284.49	3.39	3.58	2.83	2.92	1.39	1.42
O	Oleic	C18:1	282.47	26.69	27.97	38.21	39.12	77.05	78.02
Li	Linoleic	C18:2	280.45	39.65	41.25	37.31	37.93	11.91	11.97
Le	Linolenic	C18:3	278.44	4.29	4.43	1.22	1.23	0.49	0.50
A	Arachidic	C20:0	312.54	0.63	0.73	0.93	1.06	0.53	0.59
Ga	Gadoleic	C20:1	310.52	0.44	0.51	0.71	0.80		
Be	Behenic	C22:0	340.59	1.18	1.49				

^{a} *M* = molar mass. ^{b} In C*x*:*y*, *x* = number of carbons and *y* = number of double bonds

Table 2. Probable Triacylglycerol Mole Fractions *x* and Mass Fractions *w* of Refined Vegetable Oils

		M^a	peanut oil		avocado seed oil	
group main	triacyl glycerol	g·mol^{-1}	100*x*	100*w*	100*x*	100*w*
42:1^b	LOL	721.17	0.78	0.66		
42:2	LLiL	719.15	1.16	0.98		
44:1	LOM	749.22	0.56	0.49		
44:2	LLiM	747.21	1.04	0.91		
44:3	CpOLi	745.19	0.75	0.66		
44:4	CpLiLi	743.17	0.57	0.50		
46:1	LOP	777.28	1.75	1.60	0.81	0.72
46:2	LLiP	775.26	2.76	2.53	0.79	0.70
46:3	COLi	773.24	0.80	0.73		
48:1	MOP	805.33	1.04	0.99		
48:2	LOO	803.31	3.51	3.32	1.53	1.43
48:3	LOLi	801.30	6.10	5.77	2.16	2.05
48:4	LLiLi	799.28	5.05	4.76	1.12	1.06
48:5	LLiLe	797.27	0.95	0.90		
50:1	POP	833.37	1.45	1.42	2.96	2.84
50:2	PLiP	831.35	2.82	2.76	3.32	3.19
50:3	MOLi	829.35	2.18	2.13	0.92	0.88
50:4	MLiLi	827.34	1.58	1.54		
52:1	POS	861.45	0.91	0.92	1.09	1.09
52:2	POO	859.40	4.22	4.28	8.89	8.80
52:3	POLi	857.39	8.74	8.85	15.40	15.24
52:4	PLiLi	855.37	7.30	7.37	8.00	7.90
52:5	PLiLe	853.38	1.38	1.39		
54:2	SOO	887.46	1.36	1.42	2.12	2.17
54:3	SOLi/OOO^c	885.44	4.45	4.65	8.48	8.67
54:4	OOLi	883.43	10.00	10.43	17.33	17.68
54:5	OLiLi	881.41	12.92	13.44	16.12	16.40
54:6	LiLiLi	879.43	8.33	8.64	6.07	6.16
54:7	LiLiLe	877.38	2.01	2.08		
56:2	PLiBe/OOA	915.53	0.60	0.65	0.58	0.62
56:3	OLiA	913.52	0.64	0.69	1.25	1.30
56:4	LiLiA/OLiGa	911.51	0.66	0.71	1.06	1.10
58:3	OLiBe	941.57	0.89	0.99		
58:4	LiLiBe	939.55	0.74	0.84		

^{a} *M* = molar mass. ^{b} In *x*:*y*. *x* = number of carbons (except glycerol carbons) and *y* = number of double bonds. ^{c} In the case of peanut oil SOLi is the main triacylglycerol in the isomer set 54:3. For avocado seed oil the main triacylglycerol is OOO.

Table 3. Average molar masses *M*, and Structural parameters r_i' and q_i'

compound	M^a/g·mol^{-1}	r_i'	q_i'
peanut oil (1)	847.53	0.04399	0.03568
avocado seed oil (2)	865.98	0.04406	0.03572
commercial oleic acid (3)	278.96	0.04513	0.03714
ethanol (4)	46.07	0.05591	0.05618
water (5)	18.02	0.05107	0.07771

^{a} Oil average molar masses calculated using the composition estimated according to the procedure suggested by Antoniosi Filho et al.[37]

From this fatty acid composition, it was possible to determine the probable triacylglycerol composition of the vegetable oils (Table 2) by using the algorithm suggested by Antoniosi Filho et al.[39] In Table 2, the main triacylglycerol represents the component of largest concentration in the isomer set with *x* carbons and *y* double bonds.

The values of molar masses obtained for the pseudo components and components, as well as volume and area parameter values, calculated by eq 1, are presented in Table 3. Peanut oil, avocado seed oil, and commercial oleic acid were treated in this work as pseudocompounds with the average molar masses indicated in Table 3.

Experimental equilibrium data reported for similar systems[26,40] indicated that fatty compounds may partition selectively between both alcoholic and oil phases. Nevertheless, the observed differences in the partition behavior are restricted to a narrow range of compositions, so that the pseudo component approach can be considered as approximately valid.

Tables 4 and 5 present the overall experimental composition of the mixtures and the corresponding tie lines for the pseudoternary (anhydrous ethanol as solvent) and pseudoquaternary (aqueous ethanol as solvent) model systems. All concentrations are given as mass percentages.

To test the validity of experimental results obtained, the procedure developed by Marcilla et al.[41] and tested in our prior works[27–30] was followed. The proposed approach compare the amount of the initial mixture (M_{OC}) with the sum of oil and alcoholic phase amounts (M_{OP} and M_{AP}) calculated by mass balance taken into account the mass fraction of each component of the system. The deviation between the sum ($M_{OP} + M_{AP}$) and M_{OC}, calculated according to $(|(M_{OP} + M_{AP}) - M_{OC}|/M_{OC})\cdot 100$, was always lower than 0.5 %, indicating the good quality of the experimental data.

Figures 1 and 2 show the experimental points and calculated tie lines for the systems peanut oil + commercial oleic acid + ethanol with 6.22 % mass fraction of water and peanut oil + commercial oleic acid + ethanol with 12.27 % mass fraction of water, respectively. The equilibrium diagrams are plotted in triangular coordinates. To represent the pseudoquaternary systems in triangular coordinates, ethanol + water were admitted as a mixed solvent. Figures 1 and 2 indicate that both thermodynamic models studied are able to describe with accuracy the phase compositions for the systems investigated. It is important to emphasize that the phase equilibrium concerning to the systems composed by

Table 4. Liquid-Liquid Equilibrium Data for the System Peanut Oil (1) + Commercial Oleic acid (3) + Solvent [Ethanol (4) + Water (5)] at (298.2 ± 0.1) K

	OC[b]				OP[c]				AP[d]			
$100w_5^{solv}$ [a]	$100w_1$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_3$	$100w_4$	$100w_5$	$100w_1$	$100w_3$	$100w_4$	$100w_5$
0	49.99	0.00	50.01	0.00	85.2	0.00	14.8	0.00	7.7	0.00	92.3	0.00
	48.96	1.05	49.99	0.00	84.25	0.92	14.83	0.00	7.99	1.23	90.78	0.00
	47.67	2.35	49.98	0.00	81.23	2.04	16.73	0.00	9.2	2.71	88.09	0.00
	46.57	3.35	50.08	0.00	79.79	2.96	17.25	0.00	9.64	3.89	86.47	0.00
	45.02	5.16	49.82	0.00	74.49	4.58	20.93	0.00	11.75	5.87	82.38	0.00
	39.62	10.25	50.13	0.00	56.89	9.45	33.66	0.00	26.99	10.95	62.06	0.00
6.22	50.01	0.00	46.88	3.11	94.44	0.00	5.17	0.39	1.82	0.00	91.31	6.87
	49.35	0.65	46.89	3.11	93.67	0.73	5.14	0.46	0.53	0.65	91.21	6.57
	48.80	1.22	46.87	3.11	92.78	1.22	5.66	0.34	1.83	1.23	91.76	6.49
	47.76	2.26	46.87	3.11	91.57	2.23	5.91	0.29	1.95	2.30	89.20	6.67
	46.66	3.35	46.88	3.11	88.76	3.38	7.35	0.51	2.80	3.43	88.84	5.78
	44.64	5.36	46.91	3.09	85.83	5.30	8.36	0.51	1.20	5.40	85.47	6.33
	40.20	10.00	46.68	3.12	75.34	9.90	14.04	0.72	3.36	10.16	78.88	6.71
	34.83	15.10	47.00	3.07	65.58	14.85	18.70	0.87	5.23	15.49	72.36	5.12
	29.77	20.12	46.96	3.15	53.61	19.65	25.34	1.40	9.47	20.57	62.01	4.53
12.27	50.01	0.00	43.86	6.13	94.50	0.00	5.16	0.34	0.59	0.00	87.69	11.72
	49.21	0.81	43.67	6.31	93.38	1.02	5.23	0.37	0.43	0.71	86.84	12.02
	48.91	1.14	43.82	6.13	92.75	1.45	5.39	0.41	0.32	1.11	86.11	12.46
	47.75	2.21	43.90	6.14	91.36	2.74	5.63	0.27	0.40	1.96	85.01	12.63
	46.54	3.46	43.87	6.13	89.27	3.95	6.32	0.46	0.35	2.86	84.20	12.59
	44.81	5.15	43.72	6.32	87.00	6.00	6.41	0.59	0.60	4.33	82.56	12.51
	39.70	10.19	44.02	6.09	76.87	12.01	9.82	1.30	2.57	8.46	76.96	12.01
	29.72	20.21	43.99	6.08	58.61	22.31	17.33	1.75	3.80	18.35	66.32	11.53

[a] w_5^{solv} = mass fraction of water in the ethanolic solvent. [b] OC = overall composition. [c] OP = oil phase. [d] AP = alcoholic phase.

Table 5. Liquid-Liquid Equilibrium Data for the System Avocado Seed Oil (2) + Commercial Oleic acid (3) + Solvent [Ethanol (4) + Water (5)] at (298.2 ± 0.1) K

	OC[b]				OP[c]				AP[d]			
$100w_5^{solv}$ [a]	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	$100w_2$	$100w_3$	$100w_4$	$100w_5$
0	50.01	0.00	49.99	0.00	86.20	0.00	13.80	0.00	7.30	0.00	92.70	0.00
	48.83	1.18	49.99	0.00	84.02	1.07	14.91	0.00	7.07	1.27	91.66	0.00
	47.74	2.25	50.01	0.00	81.58	1.97	16.45	0.00	7.27	2.48	90.25	0.00
	46.73	3.28	49.99	0.00	79.82	2.86	17.32	0.00	8.49	3.68	87.83	0.00
	46.50	3.33	50.17	0.00	74.42	4.56	21.02	0.00	11.75	5.86	82.39	0.00
	44.88	5.19	49.93	0.00	56.37	9.76	33.87	0.00	27.22	10.62	62.16	0.00
6.22	49.98	0.00	46.91	3.11	94.44	0.00	5.17	0.39	1.82	0.00	91.31	6.87
	49.14	0.86	46.89	3.11	93.74	0.82	5.02	0.42	1.71	0.88	91.02	6.39
	48.45	1.55	46.89	3.11	91.53	1.49	6.52	0.46	1.84	1.55	90.04	6.57
	47.62	2.31	46.96	3.11	90.89	2.29	6.48	0.34	1.79	2.34	89.38	6.49
	46.67	3.29	46.93	3.11	88.94	3.20	7.57	0.29	1.99	3.39	87.95	6.67
	44.69	5.30	46.90	3.11	85.83	5.30	8.23	0.64	2.80	5.40	85.43	6.37
	37.90	10.09	46.99	3.15	75.34	9.90	13.87	0.89	4.25	10.16	80.01	5.58
	37.90	15.23	43.75	3.12	65.58	14.85	18.66	0.91	7.03	15.49	72.23	5.25
	32.91	20.16	43.87	3.06	53.61	19.65	25.54	1.20	12.89	20.57	61.53	5.01
12.27	50.01	0.00	43.86	6.13	96.50	0.00	3.16	0.34	0.59	0.00	87.69	11.72
	49.16	0.84	43.86	6.14	95.46	0.96	3.10	0.48	0.53	0.69	87.17	11.61
	48.79	1.20	43.87	6.14	94.05	1.45	4.09	0.41	0.32	1.11	86.11	12.46
	47.60	2.36	43.90	6.14	92.26	2.74	4.73	0.27	0.40	1.96	85.01	12.63
	46.61	3.40	43.86	6.13	90.05	3.95	5.54	0.46	0.35	2.86	84.20	12.59
	44.79	5.20	43.87	6.14	87.94	6.01	5.11	0.94	0.67	4.36	83.12	11.85
	39.66	10.28	43.98	6.08	76.87	12.01	9.92	1.20	2.98	8.46	76.55	12.01
	29.71	20.29	43.93	6.07	58.61	22.31	17.28	1.80	3.80	18.35	66.76	11.09

[a] w_5^{solv} = mass fraction of water in the ethanolic solvent. [b] OC = overall composition. [c] OP = oil phase. [d] AP = alcoholic phase.

avocado seed oil (2) + commercial oleic acid (3) + ethanol (4) + water (5) present a similar behavior to the Figures 1 and 2. For fatty systems with avocado seed oil both thermodynamic equations present a good representation of the phase equilibrium.

Figure 3 presents the distribution of oleic acid between the phases for the system containing peanut oil. In this figure, the experimental data correspond to different levels of water in the ethanolic solvents and w_5^{solv} indicates the water mass fraction in the mixture ethanol + water.

It can be observed that the addition of water reduces the solvent capacity of extracting free fatty acids. The results shown in Figure 3 indicate that the NRTL model provided a good representation of fatty acid distribution between the two liquid phases.

Table 6 presents the adjusted parameters of the UNIQUAC and NRTL models for the systems containing peanut and avocado seed oils. The deviations between experimental and calculated compositions in both phases were calculated according to eq 3 and are shown in Table 7. It should be emphasized that only parameters between each vegetable oil and the others compounds of the systems were adjusted, that is, pairs 13, 14, 15 and 23, 24, 25 (see the definitions in Table 3).

Figure 4 shows the partition coefficient of refined avocado seed oil (k_2) and commercial oleic acid (k_3) as a function of acidity level in the oil (w_3^{oil}). The distribution coefficient was calculated according to eq 4. In fact, the acidity level in the oil (w_3^{oil}) is the mass fraction of commercial oleic acid dissolved

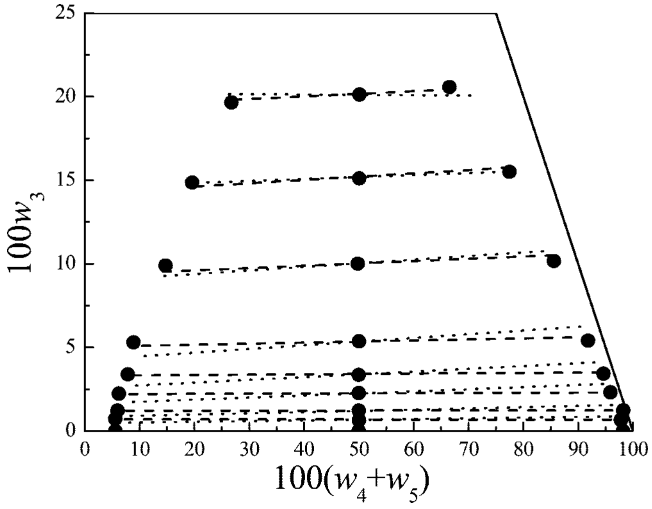

Figure 1. System of peanut oil (1) + commercial oleic acid (3) + aqueous solvent [ethanol (4) + water (5), where mass fraction of water in the solvent w_5^{solv} = 6.22 %] at (298.2 ± 0.1) K: ●, experimental; - - -, NRTL; •••••, UNIQUAC.

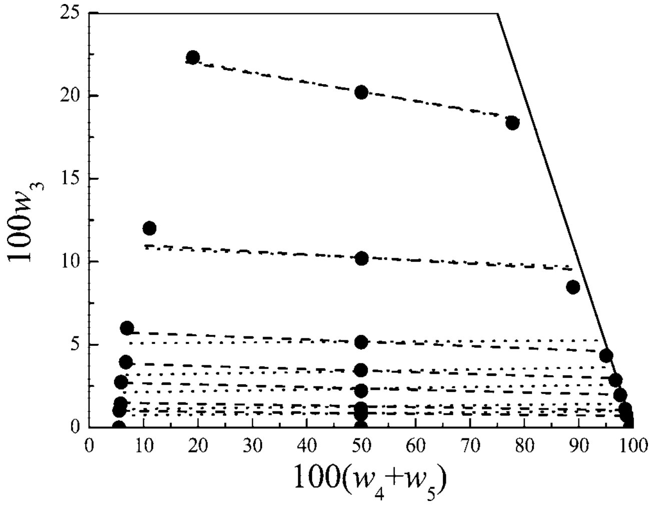

Figure 2. System of peanut oil (1) + commercial oleic acid (3) + aqueous solvent [ethanol (4) + water (5), where w_5^{solv} = 12.27 %] at (298.2 ± 0.1) K: ●, experimental; - - -, NRTL; •••••, UNIQUAC.

in the oil to obtain model fatty systems containing fatty acids and triacylglycerols.

$$k_i = \frac{w_i^{\mathrm{AP}}}{w_i^{\mathrm{OP}}} \qquad (4)$$

where k_i is the distribution coefficient of fatty compound i; w is the mass fraction, and the superscripts OP and AP stand for oil and alcoholic phases, respectively.

It can be observed that higher free fatty acid contents in the system increases the oil partition coefficient. This can be attributed to the increase of the oil and solvent mutual solubility at higher free fatty acid concentration. On the other hand, the loss of neutral oil in the alcoholic phase is largely suppressed by the water content in the solvent. In Figure 4, it can be noted the good performance of the NRTL model for describing the distribution of fatty compounds between the two liquid phases.

Figure 5 shows experimental and estimated selectivities (S) for the systems composed by avocado seed oil (2) + commercial oleic acid (3) + ethanol (4) + water (5). Selectivity was calculated according to eq 5 below, where k is the distribution coefficient of commercial oleic acid (3) or avocado seed oil (2).

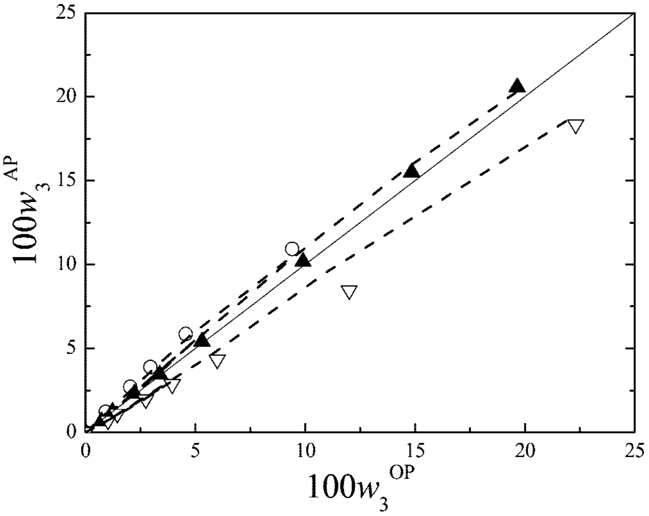

Figure 3. Fatty acids distribution diagram at (298.2 ± 0.1) K for systems of peanut oil (1) + commercial oleic acid (3) + ethanol (4) + water (5): ○, w_5^{solv} = 0 %; ▲, w_5^{solv} = 6.22 %; ▽, w_5^{solv} = 12.27 %; - - -, NRTL.

Table 6. UNIQUAC and NRTL Parameters for the Systems with Peanut Oil, and Avocado Seed Oil at (298.2 ± 0.1) K

	UNIQUAC Model		NRTL Model		
pair ij [a]	A_{ij}/K	A_{ji}/K	A_{ij}/K	A_{ji}/K	α_{ij}
13	294.27	−218.01	−318.70	−121.02	0.70
14	260.11	−59.48	375.92	1355.20	0.53
15	1463.20	−103.57	−1249.80	4565.20	0.13
23	300.90	−220.06	−175.05	−165.72	0.72
24	261.06	−59.96	249.71	1403.30	0.50
25	8539.50	−108.30	−1356.10	3737.50	0.12
34[b]	67.64	−88.95	4800.00	−170.55	0.23
35[b]	191.68	157.03	1006.70	4210.60	0.10
45[b]	337.46	−279.92	−10.98	−173.64	0.15

[a] Peanut oil (1), avocado seed oil (2), commercial oleic acid (3), ethanol (4), and water (5). [b] Parameters taken from Rodrigues and co-workers[10] and Gonçalves and co-workers.[25]

Table 7. Mean Deviations in Phase Compositions for the Systems with Peanut Oil and Avocado Seed Oil at (298.2 ± 0.1) K

		100Δw [b]	
system	100w_5^{solv} [a]	UNIQUAC	NRTL
peanut oil	0	0.98	0.56
	6.22	1.07	0.55
	12.27	0.86	0.74
	global deviation of the correlation	0.98	0.65
avocado seed oil	0	1.26	0.68
	6.22	1.16	0.51
	12.27	0.99	0.71
	global deviation of the correlation	1.08	0.63

[a] w_5^{solv} = mass fraction of water in the ethanolic solvent. [b] Calculated according to eq 3.

$$S = \frac{k_3}{k_2} \qquad (5)$$

As can be seen in Figure 5, the addition of water causes a significant increase in the solvent selectivity. On the other hand, it can be observed that higher free fatty acid contents in the system diminish the selectivity of the solvent.

The results presented in Figure 5 show that NRTL model provides a reasonable description of selectivity. The model description fails mainly for the experimental points with w_5^{solv} = 12.27 %. For this system, the oil concentration in the alcoholic

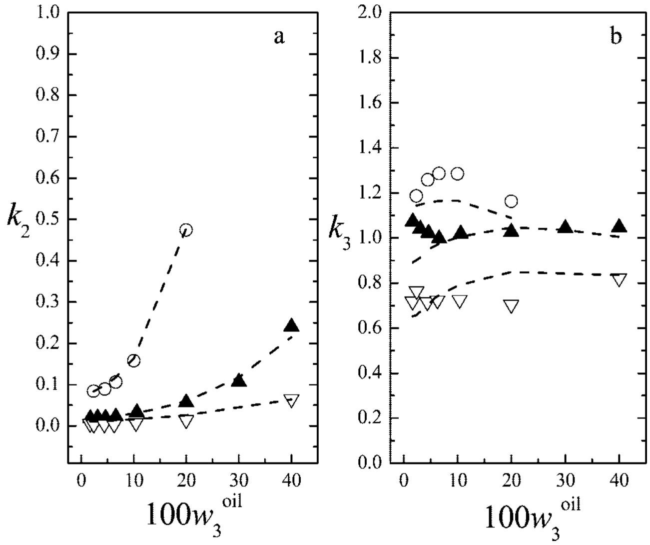

Figure 4. Distribution coefficients (k) at (298.2 ± 0.1) K: ○, $w_5^{solv} = 0$ %; ▲, $w_5^{solv} = 6.22$ %; ▽, $w_5^{solv} = 12.27$ %; - - -, NRTL. (a) avocado seed oil (k_2); (b) commercial oleic acid (k_3).

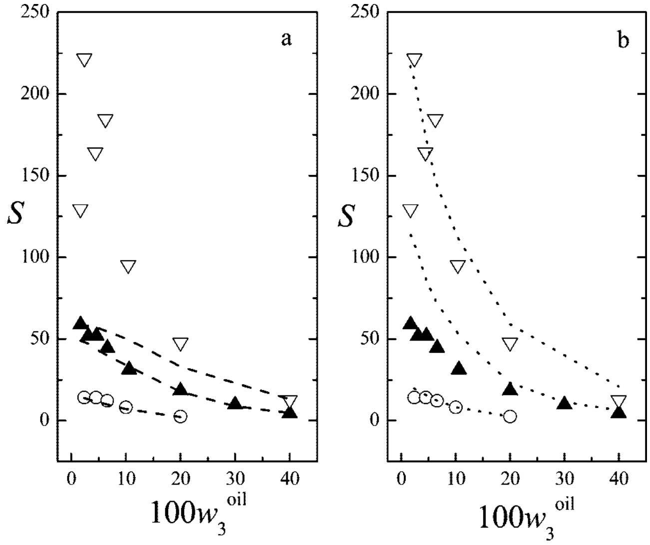

Figure 5. Selectivities (S) for systems of avocado seed oil (2) + commercial oleic acid (3) + ethanol (4) + water (5) at (298.2 ± 0.1) K: ○, $w_5^{solv} = 0$ %; ▲, $w_5^{solv} = 6.22$ %; ▽, $w_5^{solv} = 12.27$ %. (a) - - -, NRTL; (b) ·····, UNIQUAC.

phase is very low and exhibits a relatively high experimental uncertainty, which influences the uncertainties of the oil experimental distribution coefficient and the corresponding solvent selectivity. The higher experimental uncertainties affect the performance of the NRTL model.

In relation to UNIQUAC model, it can be noted that equation presents a better description of selectivity for the system with $w_5^{solv} = 12.27$ %. In fact, the UNIQUAC model super estimates free fatty acids partition coefficients mainly for systems with $w_5^{solv} = 6.22$ % and $w_5^{solv} = 12.27$ % and low contents of acidity.

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

Conclusions

In recent years, our research group has worked on phase equilibrium of edible oils to improve the oil deacidification technique by liquid−liquid extraction. In the presented paper, experimental equilibrium data for systems containing peanut or avocado seed oils were measured. It can be observed that by adding water to the ethanolic solvents there is a large increase in the heterogeneous region and on the selectivity with a slight decrease of the oleic acid distribution coefficient. Despite the complexity of the studied systems, the estimated parameters of the NRTL and UNIQUAC models are representative, since the description of the liquid−liquid equilibrium exhibit mean deviations of 0.65 % and 0.98 %, respectively, for the systems with peanut oil and mean deviations of 0.63 % and 1.08 %, respectively, for the systems with avocado seed oil. With the help of these parameters it is possible to model and simulate, with good accuracy, liquid−liquid extractors for vegetable oil deacidification.

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