Brazilian Journal of Chemical Engineering (2020) 37:783–794
https://doi.org/10.1007/s43153-020-00051-9

ORIGINAL PAPER

Deacidification of Amazonian Pracaxi (*Pentaclethra macroloba*) and Patawa (*Oenocarpus bataua*) oils: experimental and modeling of liquid–liquid extraction using alcoholic solvents

Ericsem Pereira[1] · **Débora Tamires Vitor Pereira**[1] · **Marcela C. Ferreira**[2] · **Julian Martínez**[1] · **Antonio J. A. Meirelles**[1] · **Guilherme J. Maximo**[1]

Received: 3 April 2020 / Revised: 11 July 2020 / Accepted: 17 July 2020 / Published online: 27 July 2020

Abstract

This paper presents a study about the deacidification of typical Amazonian oils, namely, patawa and pracaxi oils. The liquid–liquid extractions were carried out using three alcoholic solvents: anhydrous ethanol, azeotropic ethanol, and azeotropic isopropanol at 298.15 K and atmospheric pressure. Liquid–liquid equilibrium data for the oils + oleic acid + solvents systems were determined. The azeotropic ethanol was found to be the best extractant for removing free fatty acids (FFAs) since its use provided the highest selectivity values (from 62.98 to more 1.53×10^3), reasonable distribution coefficients (from 1.06 to 1.47), and reduced loss of neutral oil (oil concentrations lower than 1.49 wt% in the alcoholic phases). Moreover, the obtained experimental data were correlated using the nonrandom two-liquid (NRTL) and universal quasi chemical (UNIQUAC) activity coefficient models. The deviations between calculated and experimental values ranged from 0.39 to 1.22 and from 0.28 to 1.10 for the various studied systems using the UNIQUAC and the NRTL models, respectively. Such results indicate the positive perspective of using the liquid–liquid extraction technique for patawa and pracaxi oils refining and the feasibility of using ethanol as an FFA extractant.

Keywords Phase equilibrium · Ethanol · Isopropanol · Oil refining process

Introduction

Oilseeds are the primary source for the production of edible oils, an essential component of the human diet since it is the primary source of dietary lipids, the most concentrated source of metabolic energy (Vaisali et al. 2015). According to the United States Department of Agriculture (USDA), the annual global production of the major vegetable oils amounted to 203.84 Mt in 2018/19 (USDA 2019). These vegetable oils have been primarily produced in these large amounts for food purposes (O'Brien 2009). However, oils of vegetable origin are not only suitable for food purposes, but around 20% of the annually produced oils are also processed into biofuels and other chemical products (Biermann et al. 2011). In countries like Brazil, the use of vegetable oils in the energy sector is supported and encouraged by national programs and policies (Sampaio Neto et al. 2020).

Thus, given the high demand for vegetable oils, the oil industry's attention has been brought to alternative matrices. Since the Brazilian Amazonian region presents several species with high oil content that have not been adequately studied yet, some groups have driven their research focus to the products typically cultivated in that region (Santos et al. 2013; Penha et al. 2015; Rosa et al. 2016; Vidoca et al. 2020).

In a previous publication of our group, physicochemical and nutraceutical properties of vegetable oils produced by Brazilian Amazonian oleaginous plant species have been identified (Pereira et al. 2019a). Such species as Pracaxi (*Pentaclethra macroloba*) and Patawa (*Oenocarpus bataua*),

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s43153-020-00051-9) contains supplementary material, which is available to authorized users.

✉ Guilherme J. Maximo
maximo@unicamp.br

[1] School of Food Engineering, University of Campinas, Monteiro Lobato Street, 80, Campinas, São Paulo 13083-862, Brazil

[2] School of Technology, University of Campinas, Pascoal Marmo Street, 1888, Limeira, São Paulo 13484-332, Brazil

are of particular interest. The former produces fruits containing seeds from which is extracted oil with a high content of ω6 (from 12 to 13 wt% of linoleic acid) and ω9 (from 47 to 53 wt% of oleic acid) fatty acids and is considered a natural source of behenic acid (dos Santos Costa et al. 2014; Pereira et al. 2019a). In turn, the patawa oil, extracted from patawa fruit pulp, has a healthy FA content, presenting a ratio of 18.5/81.5 (w/w) saturated/unsaturated FA, in which the oleic acid represents more than 70 wt%. Although both of these oils are widely used in the cosmetic industry to prepare formulations of hair and skin products (Pereira Lima et al. 2017), their use might be further explored in the food industry.

The primary constituents of crude oils, such as patawa and pracaxi oils, are triacylglycerols (TAGs), partial acylglycerols, free fatty acids (FFAs), and variable amounts of non-glyceride compounds (such as phosphatides, fat-soluble vitamins, and pigments). The refining of edible oils makes seed oils obtained by extraction more palatable for human consumption, and usually refers to the operations of deacidification, bleaching, and deodorization (Dijkstra and Segers 2007). Because the presence of FFAs in vegetable oils is undesirable for biodiesel and edible oil production, the deacidification process determines its quality, having a significant economic impact on oil production (Manic et al. 2011).

The deacidification step is usually performed by chemical or physical refining. However, for oils with a high content of FFAs, the chemical refining may cause high losses of the neutral oil, while physical refining methods lead, in some cases, to undesirable alterations in color and oxidative stability reductions (Leibovitz and Ruckensteins 1983; Antoniassi et al. 1998). Considering the oils selected for this study, chemical or physical refining might affect the final product's quality. Because of harvesting and oil extraction conditions, these oils can often present FFA contents higher than the maximum acid value of 4.00 mg KOH/g oil, recommended for cold-pressed and virgin oils (Codex Alimentarius 1999). In this context, the liquid–liquid extraction technique is an alternative to the traditional processes. This technique is based on the difference of solubility of FFAs and neutral TAGs in an appropriate solvent (Thomopoulos 1971).

The liquid–liquid deacidification can be conducted using short-chain alcohols, such as ethanol and isopropanol, as solvents (Bhattacharyya et al. 1987; Rodrigues et al. 2004; Casas et al. 2014). Moreover, study publications using this liquid–liquid or solvent extraction at room temperature and atmospheric pressure have shown that it reduces the energy consumption of oil refining, minimizes the losses of nutraceutical compounds, and avoids the formation of side products (Sengupta and Bhattacharyya 1992; Rodrigues et al. 2014).

On the other hand, the liquid–liquid extraction approach's development demands a systematic study of the phase equilibrium involving fatty compounds and solvent. Thus, more experimental data relating to the equilibrium of systems composed by vegetable oils + fatty acids + solvents are necessary for designing industrial-scale equipment, expand the liquid–liquid equilibrium (LLE) databank for fatty systems containing vegetable oils, and to develop feasible liquid–liquid extraction oil refining processes.

Therefore, the present work aimed to investigate the LLE behavior of the following systems at 298.15 K and atmospheric pressure: patawa oil + oleic acid + anhydrous ethanol; pracaxi oil + oleic acid + anhydrous ethanol; pracaxi oil + oleic acid + azeotropic ethanol (6.02 wt% of water); pracaxi oil + oleic acid + azeotropic isopropanol (13.07 wt% of water). The reliability of the measured LLE data was tested using mass balance equations (Marcilla et al. 1995) and the Othmer–Tobias correlation (Othmer and Tobias 1942). Furthermore, the nonrandom two-liquid—NRTL (Renon and Prausnitz 1968) and universal quasi chemical—UNIQUAC (Abrams and Prausnitz 1975) models were used to correlate the experimental data and to obtain binary interaction parameters for the studied systems.

Material and methods

Materials

Crude patawa and pracaxi oils used in this study were kindly supplied by Amazon Oil Industry (Ananindeua, Brazil). Patawa and pracaxi oils presented initial acidity values of 0.49% and 1.62%, respectively, expressed as the mass fraction of oleic acid and determined according to the method Cd 3d-63 (AOCS 2009). Commercial oleic acid was acquired from Sigma-Aldrich (USA) with a purity of 90.76%. The solvents used in this work were anhydrous ethanol from Merck (Germany) with purity greater than 99.5%, and isopropanol from Merck (Germany) with purity greater than 99.8%. Purities provided by the manufacturer, no further purification methods were employed. The aqueous azeotropic solvents were gravimetrically prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol (6.02 wt%) and isopropanol (13.07 wt%).

Fatty acid composition characterization

The fatty acid compositions of patawa and pracaxi oils were taken from the previous publication of this group about the physico-chemical characterization of these products (Pereira et al. 2019a). The commercial oleic acid was analyzed by gas chromatography (GC), according to the AOCS official method Ce 1–62 (AOCS 2009). The conversion of FA to fatty acid methyl esters (FAME) was conducted according to the method described by Hartman and Lago (1973). GC analyses were performed in a Clarus 600 gas chromatograph (PerkinElmer, USA) equipped with a flame ionization detector (FID) and a DB-WAX capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm; Agilent Technologies, USA), in the following operating conditions: Helium (carrier gas) at a flow rate of 1.78 mL min^{-1}, FID temperature of 250 °C, injector at 250 °C, injection volume of 1 µL, column temperature ramp from 50 °C to 250 °C at 10 °C min^{-1}. Individual FAME peaks were identified by comparing retention times to an external standard (FAME mix C8–C24; Sigma-Aldrich, USA). Retention times and peak areas were evaluated via Total Chrom software (version 6.3.2, PerkinElmer, USA). Results were expressed as relative percentages of the mass of total FA.

Triacylglycerol profile

In order to calculate the average molar mass of patawa and pracaxi oil TAGs, the procedure described by Antoniosi Filho et al. (1995) was used to obtain the probable TAG profile of the oils. This combinatorial analysis method uses the oils' FA compositions, previously obtained by Pereira et al. (2019a), using the same analytical method described in the subtopic 2.1.2, as analytical input data to proceed the calculations based in a non-random model, which considers the preferences for FAs sterification positions.

The Antoniosi Filho et al. (1995) computational method takes into account that the most highly unsaturated FA preferentially acylates at the *sn*-2 position, taking the place of the radicals R^2, as shown in Fig. 1. Subsequently, the remaining acids, including any unsaturated FA not requested at the *sn*-2 position, will be placed on the *sn*-1,3 positions of the glycerol backbone, replacing the R^1 or R^3 radicals (Fig. 1). Regarding *sn*-1,3 positions, the *sn*-3 position will contain the remaining FA with the highest degree of unsaturation and the *sn*-1 position the other. Finally, if *sn*-1,3 positions contain FAs with the same degree of unsaturation, then that one with the longer carbon chain length is preferentially acylated at the *sn*-3 position, thus replacing the R^3 radical of Fig. 1.

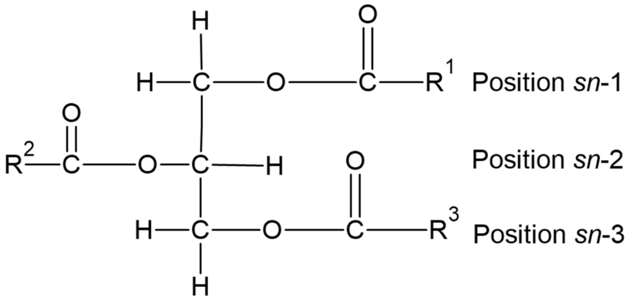

Fig. 1 Structure of the triacylglycerol molecule and *sn* stereospecific numbering positions

The probable TAG profiles of patawa and pracaxi oils can be found at Tables S1 and S2, respectively, in the Supporting information material. While the most representative TAG of patawa oil is the triolein (39.83 mol%) with a molecular mass of 885.45 g mol^{-1}, the most abundant triglycerides of pracaxi oil are also triolein (14.02 mol%) and a TAG molecule comprised by two oleic acids e one behenic acid (14.92 mol%) with a molecular mass of 943.57 g mol^{-1}.

Experimental procedure

Model fatty systems containing FAs and TAGs were prepared by adding known quantities of commercial oleic acid to patawa and pracaxi oils. While the liquid–liquid extraction using anhydrous ethanol solvent was performed for both oils, azeotropic ethanol and isopropanol were used only with the pracaxi oil.

The acidic oil was obtained by mixing the patawa and pracaxi oils with up to 10.98 and 15.02 wt% of commercial oleic acid, respectively, in the case of systems containing anhydrous ethanol. For the systems with ethanol and isopropanol plus water, the amounts of oleic acid dissolved in the pracaxi oil were up to 14.06 wt% and 18.03 wt%, respectively. The model fatty systems were mixed with the solvents, in the mass ratio oil:solvent 1:1 at 298.15 K, for determination of LLE data. It is worth noting that, aiming at better evaluate the performance of the liquid–liquid extraction technique, oleic acid concentrations selected for the evaluation of all model systems ranged from the initial free FA concentration of each oil to the maximum level where the addition of commercial oleic acid has not generated phase split.

The components were weighed using an analytical balance (model XT220A, Precisa, Switzerland) with an uncertainty of $\pm 2.10^{-4}$ g in the measurement. Weighted components were introduced in glass cells connected to a thermostatic circulating bath (Cole Parmer, USA) and vigorously stirred using a magnetic stirrer (Fisatom, Brazil) for at least 60 min at 298.15 K, to obtain good contact between both phases. Then all systems were left to rest for at least 24 h at a constant temperature in a thermostatic bath. Two clear layers and a well-defined interface were formed when the systems reached the equilibrium state. For the sake of this study, we prepared one equilibrium cell for each evaluated system, performing quantification analyses in triplicate.

Samples of both phases were collected for the quantification of the components. For the collection, we used syringes that were carefully inserted into side holes of the glass cells properly designed to collect both the bottom and top phases. First of all, the collection was performed in the top phase in order to cause the least perturbation in the system. Afterward, the bottom phase is collected, taking the same care to avoid the destabilization of the remaining system. It is worthy to note that the amounts of sample needed to immediately perform all measurements in triplicates were taken at once. This method was thoroughly tested and described in previous publications of this research group (Rodrigues and Meirelles 2008; Ferreira et al. 2018a, b).

The concentration of FFAs was determined by titration, according to the official AOCS method Cd 3d-63 (AOCS 2009) using an automatic titrator (model 848 Titrino plus, Methrom, Switzerland). The total solvent concentration, in oil and alcoholic phases, was determined by evaporation at 343.15 K in an oven with air circulation and renewal (Marconi, model MA 035/3, Brazil) until constant mass. The water concentration was determined by Karl Fischer titration, according to AOCS method Ca 2e-84 (AOCS 2009) with a KF Titrino plus (model 870, Metrohm, Switzerland). The TAG concentration was determined by difference. In this study, all measurements were performed at least in triplicate, and standard deviations were used as the uncertainties of experimental phase compositions.

The procedure developed by Marcilla et al. (1995), was used to test the validity of the experimental LLE data gathered. In this approach, the total mass used in the experiment (*MOC*) is compared with the sum of calculated oil and alcoholic phase masses (*MOP* and *MAP*, respectively). This procedure permits the calculation of the mass of each phase based on the experimental values by the least square fitting. Thus the relative deviation of the mass balance for each component is calculated, taking into account the mass fraction of each component of the system. The overall mass balance relative deviation (δ) is calculated by Eq. 1:

$$\delta(\%) = \frac{\left[\left(M^{OP} + M^{AP}\right) - M^{OC}\right]}{M^{OC}} \times 100. \tag{1}$$

The reliability of the experimental tie-lines of the systems was also verified by applying the Othmer–Tobias correlation. The procedure described by Othmer and Tobias (1942) is an empirical method used to assure the consistency of the experimental data through the linearity of the graphic. This correlation is given by Eq. 2.

$$ln\left(\frac{100 - w_{ab}}{w_{ab}}\right) = A + Bln\left(\frac{100 - w_{ot}}{w_{ot}}\right), \tag{2}$$

where w_{ab} and w_{ot} stand for the mass percentages of alcohol in the bottom phase and the mass percentage of oil in the top phase, respectively. The values of A and B are dependent on individual systems.

Thermodynamic modeling

In this study, the experimental equilibrium data sets determined for the systems were used to adjust the interaction parameters of the NRTL (Renon and Prausnitz 1968) and UNIQUAC (Abrams and Prausnitz 1975) models. In both models, the mass fraction was used as the concentration unit because of the great contrast in the molecular mass of the components in the system. In liquid phases where the molecular weights of some compounds are much larger than that of solvent, the mole fraction may not be suitable for use as a unit of concentration (Batista et al. 1999). Therefore, toward applying the activity coefficient models, the equations had to be modified, as suggested by Oishi and Prausnitz (1978).

The adjustments were made by treating the patawa or pracaxi oil + oleic acid + anhydrous ethanol as pseudo-ternary systems and the pracaxi oil + oleic acid + ethanol or isopropanol + water as pseudo-quaternary systems. Therefore, systems were considered as composed by a single TAG having the patawa or pracaxi oil average molar mass, a representative FA with the molar mass of the commercial oleic acid, ethanol, or isopropanol, and water.

The values of UNIQUAC interaction (Eq. 3) and structural parameters (Eqs. 4, 5), and NRTL interaction parameters (Eqs. 6, 7) were calculated and adjusted by the following equations:

$$\psi_{mn} = exp - \left(\frac{a_{mn}}{T}\right), \tag{3}$$

$$r_i = \frac{1}{M_i} \sum_{j}^{C} x_j \sum_{k}^{G} v_k^{(j)} R_k, \tag{4}$$

$$q_i = \frac{1}{M_i} \sum_{j}^{C} x_j \sum_{k}^{G} v_k^{(j)} Q_k, \tag{5}$$

$$\tau_{ji} = \frac{\left(g_{ji} - g_{ii}\right)}{RT}, \tag{6}$$

$$G_{ji} = \rho_{ji} exp\left(-\alpha_{ji}\tau_{ji}\right), \tag{7}$$

where r_i and q_i are structural volume and area parameters, respectively, of the UNIQUAC activity coefficient model; x_j is the mole fraction of the TAG of the pracaxi oil or commercial oleic acid; $v_k^{(j)}$ is the number of groups k in molecule j; M_i is the average molar mass of the pracaxi oil or commercial oleic acid; C is the number of compounds in the oil or FA; G is the total number of groups; R_k and Q_k are van der Waals parameters established in the literature (Magnussen et al. 1981) and more recently updated in the publication by Kang et al. (2015), where the authors present updates of the parameter matrix which reflects the information of a vast phase equilibrium data set.; τ_{ji} is a coefficient defined by the ratio between the difference of energies of interactions between a j–i pair of molecules (g_{ji}); G_{ji} is a coefficient defined by the constant ρ_{ji} and the non-randomness constant for binary j–i interactions (α_{ji}).

The estimation of interaction parameters of the NRTL model, as well as the calculus of the phase compositions, were based on the minimization of the objective function of composition (Eq. 8) developed by Stragevitch and D'Ávila (1997).

$$S=\sum_{m}^{D}\sum_{n}^{N}\sum_{i}^{C-1}\left[\left(\frac{\omega_{inm}^{OP,exp}-\omega_{inm}^{OP,calc}}{\sigma_{\omega_{inm}^{OP}}}\right)^{2}+\left(\frac{\omega_{inm}^{AP,exp}-\omega_{inm}^{AP,calc}}{\sigma_{\omega_{inm}^{AP}}}\right)^{2}\right], \tag{8}$$

where D is the total number of groups of data; N is the total number of tie lines; C is the total number of components or pseudo compounds in the group of data (m); w is the mass fraction; the subscripts i, n, and m are component, tie line, and group number, respectively; the superscripts OP and AP stand for oil and alcoholic phases, respectively; exp and $calc$ refer to experimental and calculated concentrations, respectively; $\sigma\omega_{inm}{}^{OP}$ and $\sigma\omega_{inm}{}^{AP}$ are the standard deviations, or estimated experimental uncertainties, observed in the compositions of the oil and alcoholic liquid phases, respectively.

The estimation of the UNIQUAC interaction parameters was based on the minimization of the Rachford and Rice (1952) equation (Eq. 9), described by Walas (1985), and implemented using the MATLAB software (MathWorks, USA), as described in the literature (Pereira et al. 2019b).

$$f_{(\beta)}=\sum\frac{z_i}{\beta+K_i(1-\beta)}-1, \tag{9}$$

where β is the fraction of the total material that is present in the first liquid phase, K_i is the distribution ratio between the activity coefficient of component i in the first liquid phase (I) by its activity coefficient in the second one (II) given by $K_i=\gamma_i^I/\gamma_i^{II}$, and z_i is the overall composition of component i provided by $z_i=\beta x_i^I+(1-\beta)x_i^{II}$. The solution of Eq. 9 to obtain the phase fractions is carried out by Newton–Raphson iteration. Subsequently, the obtained phase fractions are used to calculate new compositions. Next, new values of distribution constants (K_i) are calculated with the appropriate phase equilibrium equation. Finally, these new K_i values are compared to the previous ones, and if the tolerance of 10^{-3} is not observed, the equation is solved again for phase fractions, using the new values. These calculations are repeated until the convergence is obtained. If the value of β is not between 0 and 1, it is considered that the calculation has not resulted in a phase split.

The deviations between experimental and calculated compositions in both phases (Δw), using UNIQUAC and NRTL models, were calculated according to Eq. 10:

$$\Delta w=100\sqrt{\frac{\sum_{n}^{N}\sum_{i}^{C}\left[\left(\omega_{inm}^{OP,exp}-\omega_{inm}^{OP,calc}\right)^{2}+\left(\omega_{inm}^{AP,exp}-\omega_{inm}^{AP,calc}\right)^{2}\right]}{2NC}}, \tag{10}$$

where N is the total number of tie lines; C is the total number of components or pseudo compounds in the group of data.

Results and discussion

Table 1 shows that oleic and behenic acids are the most important FAs present in pracaxi oil. Meanwhile, as one may notice by Table 1, the oleic acid is the major FA of the patawa oil.

Tables 2 and 3 present the experimental composition of the corresponding tie lines for the systems: pracaxi oil (1) + oleic acid (2) + anhydrous ethanol (3); patawa oil (4) + oleic acid (2) + anhydrous ethanol (3); pracaxi oil (1) + oleic acid (2) + ethanol (3) + water (5); pracaxi oil (1) + oleic acid (2) + isopropanol (4) + water (5). All concentrations are given as mass percentages. As one may notice by Table 3, while the water concentration, determined by Karl Fischer titration, in the alcoholic phase was found to be constant in both pracaxi oil + azeotropic alcohol systems, it was found to be negligible in the oil phase.

In order to test the quality of the equilibrium data and evaluate the reliability of the results, the procedure developed by Marcilla et al. (1995), and already applied to fatty systems by several authors (Rodrigues et al. 2005a, 2006b; Reipert et al. 2011; Hirata et al. 2013) was used. The global mass balance deviations for all systems studied varied within the range from 0.01 to 0.53%, ensuring proper alignment between the experimental data relative to both overall and phase concentrations. The overall composition of the mixtures can be found on Tables S3 and S4 of the supporting information material.

The Othmer-Tobias, given in Eq. 2, was used to verify the consistencies of the tie-lines data. The constants (A and B) and the regression coefficients (R^2) are given in Table 4. For the systems evaluated here, the values of the regression coefficients were superior to 0.97, indicating the high reliability of the experimental data.

Commercial oleic acid, pracaxi, and patawa oils treated as pseudo components in this paper with average molar masses, as well as volume and area parameters values, shown in Table 5. The values found for UNIQUAC structural parameters in this work are in coherence with those found in the literature for water, ethanol, ispropanol, and commercial oleic acid molecules (Batista et al. 1999; Rodrigues et al. 2005b). It is worth noting that the representative TAGs considered for the modeling procedures are pseudo components with average molar masses calculated by pondering molar masses of the

Table 1 Fatty acid composition of patawa and pracaxi oils, and commercial oleic acid

Symbol	Fatty acid[a]		M[b] g/mol	Patawa oil Mass %	Pracaxi oil Mass %	Commercial oleic acid Mass %
L	Lauric	C12:0	200.32	1.37 ± 0.03	1.20 ± 0.07	–
M	Miristic	C14:0	228.38	0.94 ± 0.01	0.71 ± 0.05	–
P	Palmitic	C16:0	256.43	11.04 ± 0.03	1.95 ± 0.09	0.31 ± 0.01
S	Stearic	C18:0	284.49	3.06 ± 0.19	2.92 ± 0.18	1.97 ± 0.00
Po	Palmitoleic	C16:1	254.41	0.41 ± 0.01	–	–
S	Stearic	C18:0	284.48	5.09 ± 0.06	–	–
O	Oleic	C18:1	282.47	74.18 ± 0.08	47.57 ± 3.27	90.51 ± 0.02
Li	Linoleic	C18:2	280.45	5.97 ± 0.07	12.08 ± 0.40	6.66 ± 0.02
Ln	Linolenic	C18:3	278.44	0.51 ± 0.01	1.07 ± 0.01	–
A	Arachidic	C20:0	312.54	0.50 ± 0.02	1.34 ± 0.12	0.57 ± 0.01
Be	Behenic	C22:0	340.59	–	17.88 ± 2.14	–
Er	Erucic	C22:1	338.57	–	0.82 ± 0.11	–
Lg	Lignoceric	C24:0	368.63	–	12.49 ± 1.92	–

[a] In *Cx:y*, x = number of carbons and y = number of double bonds

[b] M = fatty acid molar mass.

Table 2 Liquid–liquid equilibrium data for the system pracaxi oil (1) or patawa oil (4) + oleic acid (2) + anhydrous ethanol (3) at 298.15 ± 0.5 K and atmospheric pressure

Alcohol phase			Oil phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
3.75 ± 0.01	0.81 ± 0.05	95.44 ± 0.16	87.21 ± 0.06	0.64 ± 0.05	12.15 ± 0.26
3.86 ± 0.01	3.46 ± 0.10	92.68 ± 0.04	83.71 ± 0.22	2.61 ± 0.06	13.68 ± 0.30
5.65 ± 0.11	6.85 ± 0.25	87.50 ± 0.13	80.57 ± 0.04	5.09 ± 0.22	14.34 ± 0.21
5.39 ± 0.03	9.80 ± 0.15	84.80 ± 0.34	77.17 ± 0.08	7.48 ± 0.41	15.36 ± 0.28
9.52 ± 0.01	11.99 ± 0.08	78.49 ± 0.07	70.98 ± 0.11	9.37 ± 0.16	19.65 ± 0.40
13.26 ± 0.05	16.67 ± 0.55	70.07 ± 0.17	60.53 ± 0.50	14.29 ± 0.36	25.18 ± 0.15
$100w_4$	$100w_2$	$100w_3$	$100w_4$	$100w_2$	$100w_3$
5.79 ± 0.00	0.37 ± 0.00	93.84 ± 0.56	98.86 ± 0.03	0.30 ± 0.10	0.84 ± 0.14
6.08 ± 0.01	0.92 ± 0.02	93.00 ± 0.38	98.36 ± 0.20	0.73 ± 0.04	0.91 ± 0.05
5.65 ± 0.01	1.68 ± 0.02	92.67 ± 0.39	97.49 ± 0.12	1.49 ± 0.16	1.02 ± 0.19
5.56 ± 0.03	5.68 ± 0.03	88.76 ± 0.66	94.17 ± 0.02	4.61 ± 0.05	1.22 ± 0.19
5.35 ± 0.00	8.46 ± 0.06	86.19 ± 0.20	91.50 ± 0.05	7.11 ± 0.05	1.40 ± 0.21
4.24 ± 0.01	11.50 ± 0.01	84.26 ± 0.32	88.32 ± 0.15	10.17 ± 0.07	1.51 ± 0.10

actual triglycerides found in pracaxi and patawa oils and their percentage mole fractions in the samples.

The adjusted interactions parameters of the UNIQUAC and NRTL models for the systems evaluated here are presented in Table 6. The set of interaction parameters obtained in this study are coherent with those values reported in the publication by Rodrigues and Meirelles (2008), where the authors also employed the UNIQUAC and NRTL equations for modeling the LLE data of systems containing peanut and avocado seed oils + ethanol + water. Besides, UNIQUAC and NRTL interaction parameters of the same magnitude for studies evaluating de LLE behavior of systems composed by vegetable oils + free fatty acids + alcoholic solvents can be found elsewhere (Reipert et al. 2011; Homrich and Ceriani 2016).

Figure 2 shows the experimental points and the tie lines calculated using the NRTL model for the system patawa oil + oleic acid + anhydrous ethanol. Figures 3, 4, and 5 show the experimental points and the tie lines calculated using the NRTL and UNIQUAC models for the systems: pracaxi oil + oleic acid + anhydrous ethanol; pracaxi oil + oleic acid + ethanol + water; pracaxi oil + oleic

Table 3 Liquid–liquid equilibrium data for the system pracaxi oil (1) + oleic acid (2) + ethanol (3) or isopropanol (4) + water (5) at 298.15 K ± 0.5 K and atmospheric pressure

Alcoholic solvent	Alcohol phase				Oil phase			
	$100w_1$	$100w_2$	$100w_3$	$100w_5$	$100w_1$	$100w_2$	$100w_3$	$100w_5$
Ethanol (6 mass % water)	1.49 ± 0.02	0.57 ± 0.02	91.26 ± 0.44	6.68 ± 0.38	92.40 ± 0.10	0.56 ± 0.00	6.55 ± 0.00	0.49 ± 0.02
	0.86 ± 0.03	3.08 ± 0.56	90.48 ± 0.06	5.58 ± 0.06	90.08 ± 0.24	2.10 ± 0.04	7.29 ± 0.00	0.53 ± 0.01
	0.54 ± 0.11	6.69 ± 0.10	87.33 ± 0.06	5.44 ± 0.44	85.85 ± 0.02	6.33 ± 0.12	7.28 ± 0.27	0.55 ± 0.05
	0.02 ± 0.00	8.91 ± 1.03	84.82 ± 0.46	6.25 ± 0.03	83.02 ± 0.07	7.82 ± 0.06	8.59 ± 0.10	0.58 ± 0.11
	0.10 ± 0.03	10.68 ± 0.13	84.14 ± 0.04	5.08 ± 0.04	80.27 ± 0.21	9.95 ± 0.11	9.35 ± 0.01	0.43 ± 0.01
	0.05 ± 0.02	14.19 ± 0.12	80.70 ± 0.02	5.06 ± 0.20	76.89 ± 0.13	12.90 ± 0.17	9.84 ± 0.20	0.37 ± 0.03
	$100w_1$	$100w_2$	$100w_4$	$100w_5$	$100w_1$	$100w_2$	$100w_4$	$100w_5$
Isopropanol (13 mass % water)	0.85 ± 0.02	0.64 ± 0.07	85.83 ± 0.14	12.68 ± 1.08	90.02 ± 0.30	0.95 ± 0.14	8.66 ± 0.23	0.38 ± 0.03
	0.01 ± 0.03	3.52 ± 0.13	83.35 ± 0.03	13.12 ± 0.70	84.79 ± 0.04	3.65 ± 0.03	9.99 ± 0.17	1.57 ± 0.35
	0.71 ± 0.11	5.49 ± 0.16	80.00 ± 0.10	13.80 ± 0.70	81.39 ± 0.21	6.32 ± 0.10	11.09 ± 0.00	1.20 ± 0.17
	0.78 ± 0.00	7.46 ± 0.27	78.68 ± 0.20	13.08 ± 0.30	76.38 ± 0.17	9.38 ± 0.20	12.97 ± 0.09	1.27 ± 0.31
	0.75 ± 0.03	10.49 ± 0.08	75.14 ± 0.11	13.62 ± 0.54	72.24 ± 0.33	12.54 ± 0.11	14.03 ± 0.10	1.19 ± 0.10
	0.89 ± 0.02	15.03 ± 0.14	72.00 ± 0.15	12.08 ± 0.50	67.81 ± 0.14	15.05 ± 0.15	15.84 ± 0.08	1.29 ± 0.08
	0.30 ± 0.02	18.24 ± 0.04	69.40 ± 0.02	12.06 ± 0.34	63.44 ± 0.10	17.74 ± 0.02	17.25 ± 0.43	1.57 ± 0.08

Table 4 Othmer–Tobias constants and regression coefficients

Systems	A	B	R^2
Patawa oil + oleic acid + anhydrous ethanol at 298.15 K	− 0.7255	0.4598	0.9777
Pracaxi oil + oleic acid + anhydrous ethanol at 298.15 K	1.0905	1.9593	0.9785
Pracaxi oil + oleic acid + azeotropic ethanol at 298.15 K	− 0.2793	0.8263	0.9750
Pracaxi oil + oleic acid + azeotropic isopropanol at 298.15 K	− 0.1129	0.7623	0.9702

Table 5 Average molar masses (M) and structural parameters (r_i and q_i)

Compound	M G mol^{-1}	r_i	q_i
Patawa oil[a]	842.46	–	–
Pracaxi oil	925.97	0.049	0.045
Commercial oleic acid	282.42	0.046	0.041
Ethanol	46.07	0.058	0.054
Isopropanol	60.09	0.056	0.049
Water	18.02	0.136	0.096

[a] Systems containing patawa oil and anhydrous ethanol were submitted to the NRTL modeling procedures only

acid + isopropanol + water, respectively. In the phase diagrams, ethanol + water and isopropanol + water were admitted as mixed solvents.

As can be observed from Fig. 3, the deviations of the mass balance tend to increase with the oleic acid concentration. However, as shown by the Othmer–Tobias correlation (Table 4), the obtained regression coefficient for this ternary system was higher than 0.97, which ascertains the consistency of the tie-lines data. One may also notice that the use of mixed solvents such as ethanol + water (Fig. 4) and isopropanol + water (Fig. 5), resulted in slighter tie-lines inclinations. These inclination reductions indicate that by adding water to the alcoholic solvent, the ability for extracting free FA is also reduced, as observed by Rodrigues et al. (2005a).

Figures 2, 3, 4 and 5 show that both thermodynamic models studied described the phase compositions of the systems investigated with accuracy. The calculated tie lines using the structural and interaction parameters obtained here for UNIQUAC and NRTL models were compared with experimental data. Mean deviations in phase compositions, calculated according to Eq. 10, are shown in Table 7. Furthermore, it can be observed by Figs. 1, 2, 3 and 4 that the tie lines calculated for FFA concentrations almost overlapped experimental data, which indicates a good representation of LLE in the range of composition evaluated.

One may also notice by Figs. 3, 4 and 5 that the water content of ethanol expanded the heterogeneous region, in which alcoholic and oil phases are immiscible. The widening of this region has a beneficial effect on the oil refining

Table 6 UNIQUAC and NRTL interaction parameters for the systems with Patawa* and Pracaxi Oils at 298.15 K

Pair ij[a]	UNIQUAC		NRTL		
	Aij[b] K	*Aji*[c] K	*Aij*[b] K	*Aji*[c] K	α_{ij}[d]
13	285.70	− 228.20	− 8752.80	20,515.00	0.27
14	3987.00	− 58.10	375.52	1568.70	0.49
15	29,719.00	− 68.00	41.97	2925.80	0.28
16	250.50	− 145.90	− 46.19	2696.00	0.27
23	–	–	− 124.47	11,914	0.10
24	–	–	− 31.97	− 301.32	0.11
23	197.40	− 90.50	27,128.00	− 8257.40	0.15
24	30.00	413.00	4352.10	− 1362.00	0.10
25	68.70	154.40	4851.30	7.76	0.21
35	318.20	− 307.60	− 30.26	44.76	0.39
45	923.00	− 384.00	1995.80	101.75	0.32

Systems containing patawa oil and anhydrous ethanol were submitted to the NRTL modeling procedures only

[a] Pracaxi oil (1), Patawa oil (2), oleic acid (3), ethanol (4), isopropanol (5), and water (6)

[b] *Aij* is the interaction parameter between the pair *i*–*j* of molecules

[c] *Aji* is the interaction parameter between the pair *j*–*i* of molecules

[d] α_{ij} is the non-randomness constant for binary *i*–*j* interactions from the NRTL model

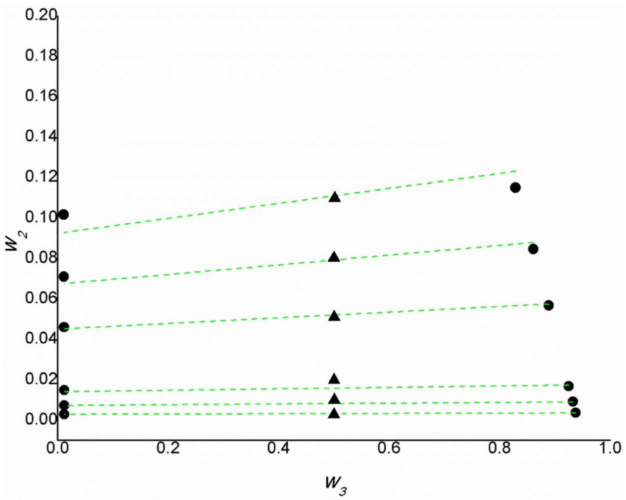

Fig. 2 System of patawa oil (1) + oleic acid (2) + anhydrous ethanol (3) at 298.15 K: (triangle) represents experimental feed compositions; (circle) represents phase compositions experimental points, green dashed lines represent calculated tie lines with NRTL model

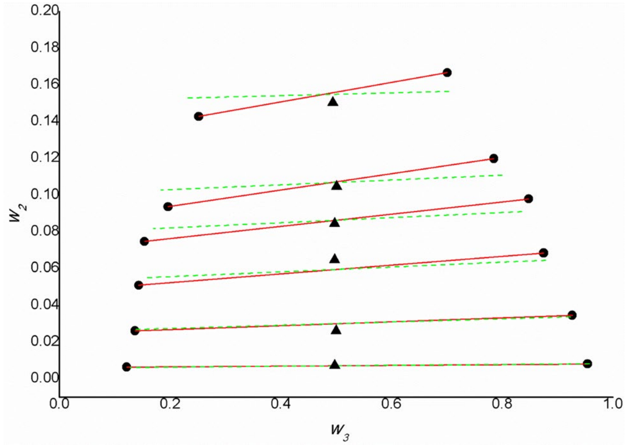

Fig. 3 System of pracaxi oil (1) + oleic acid (2) + anhydrous ethanol (3) at 298.15 K: (triangle) represents experimental feed compositions; (circle) represents phase compositions experimental points, solid red lines and green dashed lines represent calculated tie lines with UNIQUAC and NRTL models, respectively

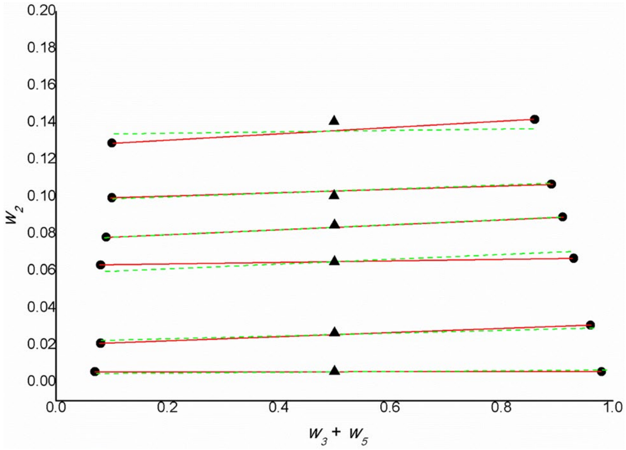

Fig. 4 System of pracaxi oil (1) + oleic acid (2) + aqueous solvent [ethanol (3) + water (5)] at 298.15 K: (triangle) represents experimental feed compositions; (circle) represents phase compositions experimental points, solid red lines and green dashed lines represent calculated tie lines with UNIQUAC and NRTL models, respectively

process, while it allows the deacidification of highly acidic oils. The broadest phase splitting region is observed in Fig. 5 in which the mixed solvent [isopropanol + water] is used. This positive effect of water on the performance of solvents has been observed in various publications in the literature (Gonçalves and Meirelles 2004; Dalmolin et al. 2009; Ansolin et al. 2013). It can also be observed that while the UNIQUAC model more closely captured the correct slope of the curves, the NRTL model presented higher deviations between the experimental and calculated values near the plait point of the systems, which is where the overall systems' oleic acid concentrations varied up to 14, 11, 14, and 18 wt% in Figs. 2, 3, 4 and 5, respectively. Likewise, deviations values were also found to be higher near the plait point in publications regarding the LLE of ternary systems

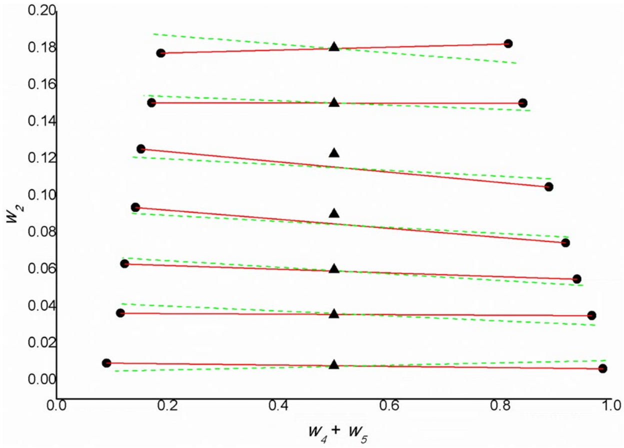

Fig. 5 System of pracaxi oil (1) + oleic acid (2) + aqueous solvent [isopropanol (4) + water (5)] at 298.15 K: (triangle) represents experimental feed compositions; (circle) represents phase compositions experimental points, solid red lines and green dashed lines represent calculated tie lines with UNIQUAC and NRTL models, respectively

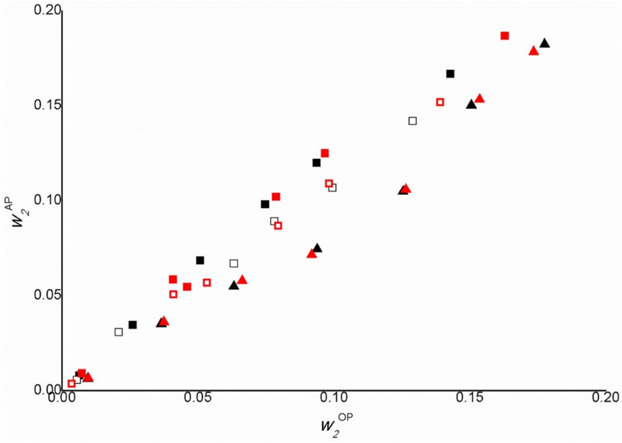

Fig. 6 Distribution diagram at 298.15 K for systems: filled square, pracaxi oil (1) + oleic acid (2) + anhydrous ethanol (3); open square, pracaxi oil (1) + oleic acid (2) + ethanol (3) + water (5); triangle, pracaxi oil (1) + oleic acid (2) + isopropanol (4) + water (5); black symbols represent experimental points and red symbols represent UNIQUAC model calculations

containing fatty compounds and alcoholic solvents (Follegatti-Romero et al. 2010).

Losses of neutral oil to the alcoholic phase and of the solvent to the oil phase were also minimized. This result can be explained by the decrease of mutual solubility between oil and solvent by the presence of water in the system. The reduction in neutral oil and solvent losses can be seen in the baseline of the figures and the data shown in Tables 2 and 3. On the other hand, Fig. 6 shows that the addition of water reduces the solvent capacity of extracting FFAs from the oil phase. It is also worth noting in this figure, the excellent performance of the UNIQUAC model to describe the distribution of fatty compounds between the liquid phases.

Figure 7 shows experimental and model estimated distribution coefficients (k_2) and selectivity ($S_{1/2}$) for the pracaxi systems evaluated here as a function of acidity level in the oil (w_2), which is the mass fraction of oleic acid dissolved in the oil to obtain model fatty systems containing FAs and TAGs. Distribution coefficients and selectivity values were calculated according to Eqs. 11 and 12, respectively, where the subscript i represents oleic FA, and j is the pracaxi oil.

$$k_i = \frac{\omega_i^{AP}}{\omega_i^{OP}} \tag{11}$$

$$S_{i/j} = \frac{k_i}{k_j} \tag{12}$$

It can be observed from data showed in Fig. 7 that azeotropic ethanol and isopropanol provided higher selectivity values than anhydrous solvent. The addition of water could decrease the neutral oil loss. On the other hand, anhydrous ethanol showed the highest distribution coefficients of up to 1.47. Therefore, despite the addition of water increase the selectivity, decreasing the neutral oil loss, the FA distribution coefficient was found to be lower in the presence of water.

Table 7 Mean Deviations in Phase Compositions

System	Δ*w* (%)	
	UNIQUAC	NRTL
Patawa oil + oleic acid + anhydrous ethanol[a]	–	0.28
Pracaxi oil + oleic acid + anhydrous ethanol	0.43	1.10
Pracaxi oil + oleic acid + aqueous solvent [ethanol + water]	0.39	0.42
Pracaxi oil + oleic acid + aqueous solvent [isopropanol + water]	1.22	0.47
Global	0.68	0.66

[a] Systems containing patawa oil and anhydrous ethanol were submitted to the NRTL modeling procedures only

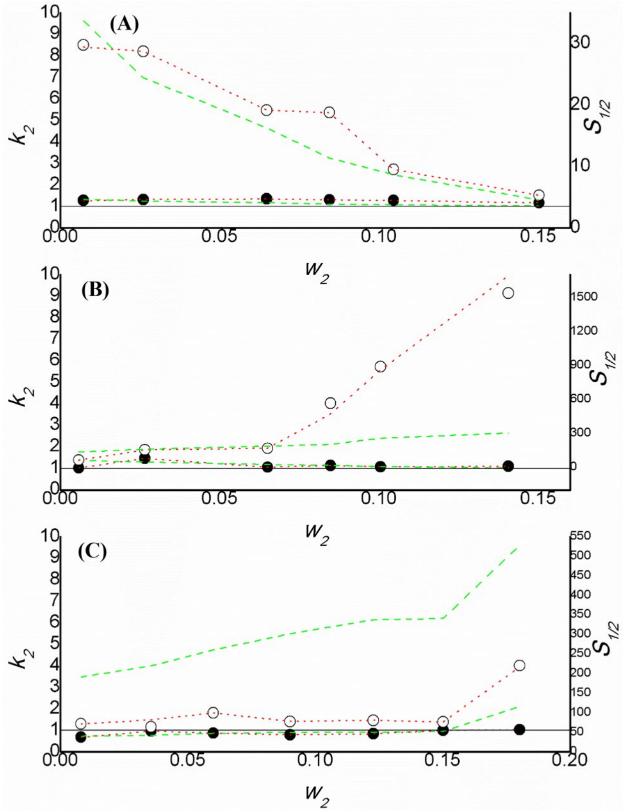

Fig. 7 Experimental fatty acid distribution coefficients (filled circle) and selectivity (○) for the systems: (A) pracaxi oil (1) + oleic acid (2) + anhydrous ethanol (3); (B) pracaxi oil (1) + oleic acid (2) + ethanol (3) + water (5); (C) pracaxi oil (1) + oleic acid (2) + isopropanol (4) + water (5); solid red lines and green dashed lines represent calculated tie lines with UNIQUAC and NRTL models, respectively

The azeotropic isopropanol system showed the lowest FFA distribution coefficients. This result implies that, since free FA showed a preference for the oil phase, this mixed solvent [isopropanol + water] may not be effective in removing free FA from pracaxi oil. As observed by Rodrigues et al. (2006a), low FA distribution coefficients demand a higher number of theoretical stages to deacidify the oil in an industrial operation totally.

Results also indicated that the UNIQUAC model presents a better description of the selectivity values. NRTL model provides reasonable descriptions of selectivity for the system represented in Fig. 7a. However, the NRTL model description fails mainly for the experimental points of systems described in Fig. 7b, c. Possibly, the higher experimental uncertainties recorded in these systems affected the performance of the NRTL model. Regarding the oleic acid distribution coefficients, both models provided good calculations.

Conclusions

In this paper, phase equilibrium data for liquid–liquid systems containing patawa or pracaxi oil + oleic acid + solvent (anhydrous ethanol, azeotropic ethanol [ethanol + 6.02 wt% of water], and azeotropic isopropanol [ispropanol + 13.07 wt% of water]) were measured at 298.15 K. Results obtained here showed that the addition of water to the solvent phase resulted in a substantial increase of selectivity values and broader phase splitting regions for both azeotropic alcohols evaluated here, which allow the use of these solvents to deacidify highly acidic vegetable oils. However, in the case of azeotropic isopropanol, the low values of FFA distribution coefficients suggested that this solvent may not be effective in removing this compound from the oil phase. On the other hand, despite azeotropic ethanol showed slightly lower FFA distribution coefficients when compared to anhydrous ethanol, its high selectivity values suggested that it could be a good solvent for deacidification of either patawa or pracaxi oils.

The NRTL and UNIQUAC models were used to describe the LLE behavior of systems, exhibiting mean deviations of 0.68% and 0.66%, respectively. Accordingly, the results shown in this paper corroborate to the expansion of the use of deacidification technique by liquid–liquid extraction of vegetable oils. This paper shows the feasibility of using ethanol as an FFA extractant and confirms previous evidence of the superiority of this solvent above other short-chain alcohols in the liquid–liquid extraction. Finally, we showed a positive perspective of using the liquid–liquid extraction technique for pracaxi oil refining.

Acknowledgements Ericsem Pereira and Débora Tamires Vitor Pereira thank the São Paulo Research Foundation (FAPESP), Brazil, Grants #2017/16979-7, and #2018/15737-2 for the scholarship and financial support. The authors thank the São Paulo Research Foundation (FAPESP), Brazil, Grants #2014/21252-0, #2016/08566-1, and #2017/23670-2, and the National Council for Scientific and Technological Development (CNPq), Brazil, Grants #305870/2014-9 and #406963/2016-9 for their financial support and scholarships. This study was also financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brazil (CAPES)—Finance Code 001.

Funding This work was supported by the São Paulo Research Foundation (FAPESP) [Grant numbers 2014/21252-0, 2016/08566-1, 2017/23670-2, 2017/16979-7, and 2018/15737-2]; the National Council for Scientific and Technological Development (CNPq) [Grant numbers 305870/2014-9 and 406963/2016-9]; and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) [Grant number 001].

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Abrams DS, Prausnitz JM (1975) Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J 21:116–128. https://doi.org/10.1002/aic.690210115

Ansolin M, Basso RC, de Meirelles AJA, Batista EAC (2013) Experimental data for liquid–liquid equilibrium of fatty systems with emphasis on the distribution of tocopherols and tocotrienols. Fluid Phase Equilib 338:78–86. https://doi.org/10.1016/j.fluid.2012.09.033

Antoniassi R, Esteves W, de Almeida Meirelles AJ (1998) Pretreatment of corn oil for physical refining. J Am Oil Chem Soc 75:1411–1415. https://doi.org/10.1007/s11746-998-0191-8

Antoniosi Filho NR, Mendes OL, Lanças FM (1995) Computer prediction of triacylglycerol composition of vegetable oils by HRGC. Chromatographia 40:557–562. https://doi.org/10.1007/BF02290268

AOCS (2009) Official methods and recommended practices of the AOCS, 6th edn. American Oil Chemists' Society, Urbana

Batista E, Monnerat S, Kato K, Stragevitch L, Meirelles AJA (1999) Liquid−liquid equilibrium for systems of canola oil, oleic acid, and short-chain alcohols. J Chem Eng Data 44:1360–1364. https://doi.org/10.1021/je990015g

Bhattacharyya AC, Majumdar S, Bhattacharyya DK (1987) Refining of high FFA rice bran oil by isopropanol extraction and alkali neutralisation. Oleagineux 42:431–433

Biermann U, Bornscheuer U, Meier MAR, Metzger JO, Schäfer HJ (2011) Oils and fats as renewable raw materials in chemistry. Angew Chemie Int Ed 50:3854–3871. https://doi.org/10.1002/anie.201002767

Casas A, Rodríguez JF, Del Peso GL, Rodríguez R, Vicente G, Carrero A (2014) Liquid–liquid phase equilibria for soybean oil methanolysis: experimental, modeling, and data prediction. Ind Eng Chem Res 53:3731–3736. https://doi.org/10.1021/ie403927c

Codex Alimentarius (1999) Codex standard for named vegetabel oils. In: Codex stan 210, pp 1–13

Dalmolin I, Lanza M, Meirelles AJA, Batista EAC (2009) Liquid−liquid equilibrium data for systems containing refined rice bran oil, anhydrous ethanol, water, and hexane. J Chem Eng Data 54:2182–2188. https://doi.org/10.1021/je900234u

Dijkstra AJ, Segers JC (2007) Production and refining of oils and fats. In: Gunstone FD, Harwood JL, Dijkstra AJ (eds) The lipid handbook, third. CRC Press, Boca Raton, pp 143–251

dos Santos Costa MNF, Muniz MAP, Negrão CAB, da Costa CEF, Lamarão MLN, Morais L, Silva Júnior JOC, Ribeiro Costa RM (2014) Characterization of *Pentaclethra macroloba* oil. J Therm Anal Calorim 115:2269–2275. https://doi.org/10.1007/s10973-012-2896-z

Ferreira MC, Bessa LCBA, Abreu CRA, Meirelles AJA, Caldas Batista EA (2018a) Liquid–liquid equilibrium of systems containing triolein + (fatty acid/ partial acylglycerols/ester) + ethanol: experimental data and UNIFAC modeling. Fluid Phase Equilib 476:186–192. https://doi.org/10.1016/j.fluid.2018.07.030

Ferreira MC, Bessa LCBA, Meirelles AJA, Batista EAC (2018b) Liquid–liquid equilibrium during ethanolysis of soybean oil. Fluid Phase Equilib 473:286–293. https://doi.org/10.1016/j.fluid.2018.06.020

Follegatti-Romero LA, Lanza M, Batista FRM, Batista EAC, Oliveira MB, Coutinho JAP, Meirelles AJA (2010) Liquid−liquid equilibrium for ternary systems containing ethyl esters, anhydrous ethanol and water at 298.15, 313.15, and 333.15 K. Ind Eng Chem Res 49:12613–12619. https://doi.org/10.1021/ie101611j

Gonçalves CB, Meirelles AJA (2004) Liquid–liquid equilibrium data for the system palm oil + fatty acids + ethanol + water at 318.2 K. Fluid Phase Equilib 221:139–150. https://doi.org/10.1016/j.fluid.2004.05.002

Hartman L, Lago RCA (1973) Rapid preparation of fatty acid methyl esters from lipids. Lab Pract 22:475–476

Hirata GF, Abreu CRA, Bessa LCBA, Ferreira MC, Batista EAC, Meirelles AJA (2013) Liquid–liquid equilibrium of fatty systems: a new approach for adjusting UNIFAC interaction parameters. Fluid Phase Equilib 360:379–391. https://doi.org/10.1016/j.fluid.2013.10.004

Homrich POB, Ceriani R (2016) Liquid–liquid equilibrium data for the pseudoternary model system of refined sunflower seed oil + (n -hexanal, or 2-nonenal, or 2,4-decadienal) + anhydrous ethanol at 298.15 K. J Chem Eng Data 61:3069–3076. https://doi.org/10.1021/acs.jced.6b00152

Kang JW, Diky V, Frenkel M (2015) New modified UNIFAC parameters using critically evaluated phase equilibrium data. Fluid Phase Equilib 388:128–141. https://doi.org/10.1016/j.fluid.2014.12.042

Leibovitz Z, Ruckensteins C (1983) Our experiences in processing maize (corn) germ oil. Fette, Seifen, Anstrichm 85:538–543

Magnussen T, Rasmussen P, Fredenslund A (1981) UNIFAC parameter table for prediction of liquid–liquid equilibria. Ind Eng Chem Process Des Dev 20:331–339. https://doi.org/10.1021/i200013a024

Manic MS, Najdanovic-Visak V, da Ponte MN, Visak ZP (2011) Extraction of free fatty acids from soybean oil using ionic liquids or poly(ethyleneglycol)s. AIChE J 57:1344–1355. https://doi.org/10.1002/aic.12349

Marcilla A, Ruiz F, García AN (1995) Liquid–liquid–solid equilibria of the quaternary system water–ethanol–acetone–sodium chloride at 25 °C. Fluid Phase Equilib 112:273–289. https://doi.org/10.1016/0378-3812(95)02804-N

O'Brien RD (2009) Fats and oils: formulating and processing for applications, third. CRC Press, Boca Raton

Oishi T, Prausnitz JM (1978) Estimation of solvent activities in polymer solutions using a group-contribution method. Ind Eng Chem Process Des Dev 17:333–339. https://doi.org/10.1021/i260067a021

Othmer D, Tobias P (1942) Liquid–liquid extraction data—the line correlation. Ind Eng Chem 34:693–696. https://doi.org/10.1021/ie50390a600

Penha FM, Rezzadori K, Proner MC, Zin G, Fogaça LA, Petrus JCC, de Oliveira JV, Di Luccio M (2015) Evaluation of permeation of macauba oil and n-hexane mixtures through polymeric commercial membranes subjected to different pre-treatments. J Food Eng 155:79–86. https://doi.org/10.1016/j.jfoodeng.2015.01.020

Pereira E, Ferreira MC, Sampaio KA, Grimaldi R, de Meirelles AJA, Maximo GJ (2019a) Physical properties of Amazonian fats and oils and their blends. Food Chem 278:208–215. https://doi.org/10.1016/j.foodchem.2018.11.016

Pereira E, Junqueira FT, de Meirelles AJA, Maximo GJ (2019b) Prediction of the melting behavior of edible fats using UNIFAC and UNIQUAC models. Fluid Phase Equilib 493:58–66. https://doi.org/10.1016/j.fluid.2019.04.004

Pereira Lima R, Souzada Luz PT, Braga M, dos Santos Batista PR, Ferreira da Costa CE, Zamian JR, Santos do Nascimento LA, da Rocha Filho GN (2017) Murumuru (*Astrocaryum murumuru* Mart.) butter and oils of buriti (*Mauritia flexuosa* Mart.) and pracaxi (*Pentaclethra macroloba* (Willd.) Kuntze) can be used for biodiesel production: physico-chemical properties and thermal and kinetic studies. Ind Crops Prod 97:536–544. https://doi.org/10.1016/J.INDCROP.2016.12.052

Rachford HH, Rice JD (1952) Procedure for use of electronic digital computers in calculating flash vaporization hydrocarbon equilibrium. J Pet Technol 4:19–23. https://doi.org/10.2118/952327-G

Reipert ÉCD, Rodrigues CEC, Meirelles AJA (2011) Phase equilibria study of systems composed of refined babassu oil, lauric acid, ethanol, and water at 303.2K. J Chem Thermodyn 43:1784–1790. https://doi.org/10.1016/j.jct.2011.05.039

Renon H, Prausnitz JM (1968) Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J 14:135–144. https://doi.org/10.1002/aic.690140124

Rodrigues CEC, Filipini A, Meirelles AJA (2006a) Phase equilibrium for systems composed by high unsaturated vegetable oils + linoleic acid + ethanol + water at 298.2 K. J Chem Eng Data 51:15–21. https://doi.org/10.1021/je0495841

Rodrigues CEC, Gonçalves CB, Marcon EC, Batista EAC, Meirelles AJA (2014) Deacidification of rice bran oil by liquid–liquid extraction using a renewable solvent. Sep Purif Technol 132:84–92. https://doi.org/10.1016/j.seppur.2014.05.009

Rodrigues CEC, Meirelles AJA (2008) Extraction of free fatty acids from peanut oil and avocado seed oil: liquid−liquid equilibrium data at 298.2 K. J Chem Eng Data 53:1698–1704. https://doi.org/10.1021/je7007186

Rodrigues CEC, Onoyama MM, Meirelles AJA (2006b) Optimization of the rice bran oil deacidification process by liquid–liquid extraction. J Food Eng 73:370–378. https://doi.org/10.1016/j.jfoodeng.2005.02.004

Rodrigues CEC, Pessôa Filho PA, Meirelles AJA (2004) Phase equilibrium for the system rice bran oil + fatty acids + ethanol + water + γ-oryzanol + tocols. Fluid Phase Equilib 216:271–283. https://doi.org/10.1016/j.fluid.2003.11.008

Rodrigues CEC, Reipert ÉCD, de Souza AF, Filho PAP, Meirelles AJA (2005a) Equilibrium data for systems composed by cottonseed oil + commercial linoleic acid + ethanol + water + tocopherols at 298.2 K. Fluid Phase Equilib 238:193–203. https://doi.org/10.1016/j.fluid.2005.09.027

Rodrigues CEC, Silva FA, Marsaioli A, Meirelles AJA (2005b) Deacidification of Brazil nut and macadamia nut oils by solvent extraction: liquid−liquid equilibrium data at 298.2 K. J Chem Eng Data 50:517–523. https://doi.org/10.1021/je049687j

Rosa MTMG, Silva EK, Santos DT, Petenate AJ, Meireles MAA (2016) Obtaining annatto seed oil miniemulsions by ultrasonication using aqueous extract from Brazilian ginseng roots as a biosurfactant. J Food Eng 168:68–78. https://doi.org/10.1016/j.jfoodeng.2015.07.024

Sampaio Neto OZ, Gonçalves D, de Bergara SF, Batista EAC, de Meirelles AJA (2020) Oil extraction from semi-defatted babassu bagasse with ethanol: liquid–liquid equilibrium and solid–liquid extraction in a single stage. J Food Eng 276:109845. https://doi.org/10.1016/j.jfoodeng.2019.109845

Santos OV, Corrêa NCF, Carvalho RN, Costa CEF, Lannes SCS (2013) Yield, nutritional quality, and thermal-oxidative stability of Brazil nut oil (*Bertholletia excelsa* H.B.K) obtained by supercritical extraction. J Food Eng 117:499–504. https://doi.org/10.1016/j.jfoodeng.2013.01.013

Sengupta R, Bhattacharyya DK (1992) A comparative study between biorefining combined with other processes and physical refining of high-acid mohua oil. J Am Oil Chem Soc 69:1146–1149. https://doi.org/10.1007/BF02541052

Stragevitch L, D'Ávila SG (1997) Application of a generalized maximum likelihood method in the reduction of multicomponent liquid–liquid equilibrium data. Braz J Chem Eng 14:41–52. https://doi.org/10.1590/S0104-66321997000100004

Thomopoulos C (1971) Méthode de desacidification des huiles par solvant sélectif. Rev Fr des Corps Gras 18:143–150

United States Department of Agriculture (2019) Oilseeds: World Markets and Trade. In: Data Anal. https://www.fas.usda.gov/data/oilseeds-world-markets-and-trade. Accessed 16 SepT 2019

Vaisali C, Charanyaa S, Belur PD, Regupathi I (2015) Refining of edible oils: a critical appraisal of current and potential technologies. Int J Food Sci Technol 50:13–23. https://doi.org/10.1111/ijfs.12657

Vidoca LP, de Almeida ES, Cardoso MF, Otavio L, Valadares LF, Monteiro S (2020) Extraction of carotene from crude hybrid palm oil using polymeric resin. J Food Eng 278:109944. https://doi.org/10.1016/j.jfoodeng.2020.109944

Walas SM (1985) Phase equilibria in chemical engineering. Butterworth-Heinemann, Stoneham