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ORIGINAL PAPER

Measuring and Modeling Liquid–Liquid Equilibria for a Soybean Oil, Oleic Acid, Ethanol, and Water System

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Abstract Vegetable oils can be deacidified by liquid–liquid extraction based on differences in polarity between triglycerides and fatty acids and differences in solubility. Information on the equilibrium between the phases of such systems is important for designing separation processes. The present paper reports experimental data for the extraction of fatty acid from soybean oil by (ethanol + water) as a mixed-solvent for system of soybean oil + oleic acid + ethanol + water at 30 °C at different water contents. The liquid–liquid equilibrium data of the systems were used to obtain interaction parameters in the universal quasi-chemical theory (UNIQUAC) activity coefficient model. These parameters can be used to predict equilibrium data of ternary and quaternary systems. The deviations between experimental and calculated compositions in both phases for each system using this model were calculated. The distribution coefficients and the selectivity factors of solvents for extraction of fatty acid from oil at 30 °C were calculated. Increasing of the water content as the co-solvent decreased the distribution coefficients and increased the selectivity factors of mixed-solvents, therefore considering the economical and practical aspects the optimum water content may be used for extracting oleic acid from soybean oil. We concluded that (ethanol + water) as a mixed-solvent can be used for extracting fatty acids from edible oils in a normal temperature.

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Introduction

Crude vegetable oils contain impurities, especially free fatty acids, and the presence of these compounds can adversely affect oil quality and oxidative stability. Most edible oils are produced by using alkali refining because it is a highly versatile process applicable to all crude vegetable oils; however, the process can result in considerable losses of neutral oil. The refining processes for crude vegetable oils involve solvent stripping, degumming, bleaching, deacidification, and deodorization [1, 2]. Removing free fatty acids (FFAs) is one of the most important steps in purifying edible oils, because the yield of neutral oil has a significant effect on refining costs [3].

Deacidification of oils is usually performed by chemical or physical procedures. For oils with high acidity, however, chemical refining causes high losses of neutral oil due to saponification and emulsification. Physical refining is an attractive process to deacidify highly acidic oils, because this process results in less neutral oil loss than does traditional alkali refining, but more energy is consumed. Moreover, in some cases, the refined oil is subject to undesirable changes in color and reduced stability to oxidation [4]. Thus, it is important to develop alternative processes to deacidify edible oils.

Deacidification of oils by liquid–liquid extraction using an appropriate solvent has been receiving attention due to advantages compared to physical and chemical refining. Kale et al. [5] studied the deacidification of crude rice bran oil by extraction with methanol. Turkay and Civelekoglu [6] investigated liquid–liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions. Shah and Venkatesan [7] tested aqueous isopropanol as a solvent to deacidify rice bran and groundnut oils. Pina and Meirelles [8] studied the deacidification of corn oil by continuous liquid–liquid extraction in a rotating disc column with solvent ethanol containing approximately 6% water. All of these studies showed decreased oil acidic value.

Araújo and Meireles [9] tested the ability of the Peng-Robinson equation of state to predict the vapor-liquid equilibrium of binary and ternary fatty systems. Equations of state are also used in the literature to calculate the equilibrium of alkane-vegetable oil mixtures [10, 11]. In the case of liquid–liquid equilibrium for fatty systems, the information is relatively scarce in the literature, yet such information is necessary to design separation processes involving fatty systems.

Liquid–liquid equilibrium data for fatty systems containing canola and corn oils have been reported by Batista et al. [12] and Gonçalves et al. [13], respectively. Batista et al. [14] predicted the liquid–liquid equilibrium using the UNIFAC and ASOG models. Rodrigues et al. [15] reported equilibrium data for the system of rice bran oil, fatty acids, ethanol and water.

Because liquid–liquid extraction can be carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is exposed to less harsh treatments. In addition, liquid–liquid extraction has the advantages of avoiding the formation of waste products and reducing neutral oil loss. Furthermore, solvent stripping from refined oil and solvent recovery from the extract stream can be easily carried out because of the high difference between the boiling points of the solvent, fatty acids, and triacylglycerols. These operations can be accomplished by evaporation or distillation at relatively low temperatures, in most cases lower than 80 °C [8].

The present work determined liquid–liquid equilibrium data for systems of soybean oil, oleic acid, ethanol, and water at 30 °C. The addition of water to the solvent reduced neutral oil loss and improved the solvent selectivity [8]. The experimental data set was used for adjusting the parameters of the UNIQUAC activity coefficient model.

Materials and Methods

Materials

Edible Iranian soybean oil was used as a source of triglycerides, and commercial oleic acid from Ferak (Berlin, Germany) was used as the source of fatty acids. The chemical compositions of soybean oil and commercial oleic acid were determined by gas chromatography of fatty acid methyl esters to determine the fatty acid composition, according to the official method of the AOCS [16]. The fatty acid composition of the soybean oil is presented in Table 1.

Table 1 Fatty acid composition of Iranian soybean oil

Fatty acid	C*x*:*y*[a]	Mass (%)
Palmitic	C16:0	11.43
Stearic	C18:0	3.90
Oleic	C18:1	26.24
Linoleic	C18:2	51.81
Linolenic	C18:3	6.40
Arachidonic	C20:4	0.22

[a] C*x*:*y*, *x* number of carbons, and *y* number of double bonds

The commercial oleic acid contained oleic, palmitoleic, linoleic, and palmitic acids as major components, and linolenic, stearic, arachidonic and myristic acids as minor components. The fatty acid compositions of the Ferak commercial oleic acid (Berlin, Germany) is presented in Table 2. The available commercial oleic fatty acid from Ferak was used as sources of fatty acids. Stearic, oleic, linoleic and linolenic fatty acids are isomers having the same numbers of carbon atoms (*x*) but different numbers of double bonds (*y*) (see Table 1). Therefore, they are expected to have similar solubility values in the mixed-solvent used.

The average molecular weight were 875 g/mol for the soybean oil and 282 g/mol for the commercial oleic acid. Ethanol with purity greater than 99.5% was used. Double-distilled water was used to obtain the aqueous solvent.

Procedures

Equilibrium cells were used to determine liquid–liquid equilibrium data. The cell temperature was controlled with a temperature-controlled bath (with ±0.1 °C uncertainty). The mixture was stirred vigorously for 20 min and allowed to stand for at least 12 h leading to the formation of two clear and transparent phases, with a well-defined interface.

Table 2 Fatty acid composition of Ferak commercial oleic acid

Fatty acid	C*x*:*y*[a]	Mass (%)
Palmitic	C16:0[a]	4.05
Palmitoleic	C16:1	5.85
Oleic	C18:1	83.13
Linoleic	C18:2	5.05
Others	–	1.92

[a] C*x*:*y*, *x* number of carbons, and *y* number of double bonds

After several experiments and taking samples at different time intervals, we found that increasing the agitation time (minimum time 20 min) and rest time (minimum time 12 h) had no effect on equilibrium phase compositions.

The quantity of oleic acid was determined by using potentiometric titration (Modified AOCS Method Ca 5a-40) [17] with a micro burette; the solvent was determined by evaporation in a vacuum oven. The water concentration was determined by using a Karl Fisher instrument (Metrohm KF coulometer model 684, Zurich, Switzerland). Having determined the amount of fatty acids, solvent and water, the triacylglycerols concentration was obtained by difference. The accuracy of the method had been checked in previous work [18] for corn oil + oleic acid + ethanol + water system. The uncertainties in the concentrations were within ranges of 0.04–0.23% for oleic acid, 0.03–0.11% for ethanol, 0.02–0.14% for water, and 0.03–0.24% for soybean oil.

Results and Discussion

Table 3 shows the compositions of the mixtures and the corresponding tie lines for the systems of interest. Due to the large difference in molecular weights of the components, mass fractions were used to express the compositions [12]. The results indicated that water content in the range 5% with ethanol as a mixed-solvent is appropriate for deacidifying by solvent extraction.

Modeling

The UNIQUAC activity coefficient model was used for correlating the compositions of liquid phases obtained at equilibrium. The equations for the UNIQUAC model are [12]:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{comb}} + \ln \gamma_i^{\mathrm{res}} \tag{1}$$

Table 3 Quaternary liquid–liquid equilibrium data for the system [soybean oil (**1**) + commercial oleic acid (**2**) + ethanol (**3**) + water (**4**)] at 30 °C

Water conc. in solvent (%)	Overall composition				Alcohol phase (II)				Oil phase (I)			
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
5	47.96	0.00	49.43	2.61	2.02	0.00	92.29	5.69	91.41	0.00	8.18	0.41
	47.22	2.53	47.74	2.51	2.63	2.86	89.28	5.23	87.21	2.64	9.63	0.52
	43.46	4.93	49.03	2.58	3.76	5.44	85.75	5.05	82.11	5.06	12.20	0.63
	40.38	9.63	47.49	2.50	5.85	10.35	78.99	4.81	74.31	9.76	14.99	0.94
	35.65	14.52	47.34	2.49	10.09	15.45	70.14	4.32	64.48	13.70	20.81	1.01
	29.6	20.34	47.56	2.50	17.10	20.68	58.56	3.66	52.96	19.23	26.53	1.28
10	50.03	0.00	44.98	4.99	1.75	0.00	87.55	10.70	93.39	0.00	6.29	0.32
	47.33	2.52	45.14	5.01	1.36	2.20	85.37	11.07	90.24	2.52	6.79	0.45
	45.64	4.98	44.44	4.94	1.49	4.22	88.03	10.76	85.66	5.20	8.56	0.58
	40.85	9.46	44.73	4.96	2.71	9.15	78.05	10.09	77.91	9.89	11.53	0.77
	34.96	14.92	45.12	5.00	4.98	14.54	71.31	9.17	67.73	15.71	15.53	1.03
	31.04	19.23	44.75	4.98	6.69	19.36	65.48	8.47	58.11	20.31	20.23	1.35
15	49.76	0.00	42.71	7.53	0.38	0.00	81.59	18.03	94.34	0.00	5.23	0.43
	47.39	2.45	42.64	7.52	0.53	1.85	79.77	17.85	90.98	2.96	5.51	0.55
	44.19	4.93	43.24	7.64	0.98	4.55	77.47	17.00	86.27	6.43	6.58	0.72
	37.88	9.15	45.02	7.95	1.07	6.82	75.4	16.71	78.41	11.66	9.08	0.85
	33.8	13.43	44.85	7.92	1.16	10.48	72.42	15.94	70.52	16.56	11.85	1.07
	30.66	18.51	43.21	7.62	1.73	15.27	68.06	14.94	62.22	22.04	14.37	1.37
18	50.50	0.00	40.59	8.91	0.36	0.00	79.7	19.94	95.43	0.00	3.97	0.60
	47.79	2.47	40.79	8.95	0.22	1.34	78.79	19.65	90.58	3.35	5.35	0.72
	44.58	4.81	41.5	9.11	0.32	3.18	77.01	19.49	86.52	6.47	6.22	0.79
	40.54	9.38	41.07	9.01	0.41	5.77	74.47	19.35	77.88	12.61	8.48	1.03
	35.52	14.51	40.97	9.00	0.40	9.39	70.99	19.22	67.65	19.51	11.38	1.46
	29.64	19.63	41.6	9.13	0.37	14.33	67.72	17.58	57.86	24.71	15.52	1.91

$$\ln \gamma_i^{\text{comb}} = \frac{\ln \Psi'_i}{\ln(w_i/\xi\overline{M_i})} + 1 - \frac{\xi\overline{M_i}\Psi'_i}{w_i} + \frac{z}{2}\overline{M_i}q'_i \ln\frac{\theta'_i}{\Psi'_i} - \frac{z}{2}\overline{M_i}q'_i\left(1 - \frac{\Psi'_i}{\theta'_i}\right) \tag{2}$$

where

$$\xi = \sum_{j=1}^{K} \frac{w_j}{\overline{\overline{M_j}}} \tag{3}$$

$$\theta' = \frac{q'_i w_i}{\sum_{j=1}^{K} q'_j w_j} \qquad \Psi'_i = \frac{r'_i w_i}{\sum_{j=1}^{K} r'_j w_j} \tag{4}$$

and

$$\ln\gamma_i^{\text{res}} = \overline{M_i}q'_i\left[1 - \ln\left(\sum_{j=1}^{K}\theta'_j\tau_{ji}\right) - \sum_{j=1}^{K}\left(\theta'_j\tau_{ji}\Big/\sum_{K=1}^{K}\theta'_K\tau_{Kj}\right)\right] \tag{5}$$

where

$$\tau_{ij} = \exp\left(-\frac{A_{ij}}{T}\right) \tag{6}$$

In Eqs. (2) to (6), $\ln\gamma_i^{\text{comb}}$ and $\ln\gamma_i^{\text{res}}$ represent the combinatorial and residual contributions, respectively. $\overline{M_i}$ is the average molecular weight of the soybean oil or the commercial oleic acid and w is the mass fraction. As usual in the UNIQUAC model, the lattice coordination number z was assumed to be equal to 10. A_{ij} and A_{ji} are the adjustable parameters. The adjustments were made by treating the system as a pseudo-quaternary one, composed of a single triacylglycerol having the soybean oil average molecular weight, a representative fatty acid with the molecular weight of the commercial oleic acid, ethanol and water. The values of r'_i and q'_i for the UNIQUAC model were calculated by using Eqs. (7) and (8):

$$r'_i = \frac{1}{\overline{M_i}}\sum_{j}^{C} x_j \sum_{k}^{G} \nu_k^{(i)} R_k \tag{7}$$

$$q'_i = \frac{1}{\overline{M_i}}\sum_{j}^{C} x_j \sum_{k}^{G} \nu_k^{(i)} Q_k \tag{8}$$

where x_j is the molar fraction of the triacylglycerols of the soybean oil or the fatty acids of the commercial oleic acid and $\nu_k^{(i)}$ is the number of groups k in molecule i. C is the number of components in the oil or in the commercial fatty acid, and G is the total number of groups. R_i and Q_i are the van der Waals parameters obtained from Magnussen et al. [19]. The calculated r'_i and q'_i values are shown in Table 4.

Table 4 UNIQUAC parameters r'_i and q'_i for [Soybean oil (**1**) + Oleic acid (**2**) + Ethanol (**3**) + Water (**4**)] system

Compound	r'_i	q'_i
Soybean oil	0.044019	0.035669
Oleic acid	0.045147	0.037069
Ethanol	0.055905	0.056177
Water	0.051069	0.077713

The experimental equilibrium data for the soybean oil, oleic acid, ethanol, and water system were used to calculate the parameters of the UNIQUAC models. The binary interaction parameters of the UNIQUAC activity coefficient model were calculated by using nonlinear regression analysis of Nelder-Mead [20]. The objective function used for correlating the experimental data is in the following form:

$$\text{OF} = \sum_{i}\sum_{j}\sum_{k}\left(w_{ijk}^{\text{exp}} - w_{ijk}^{\text{cal}}\right)^2 \tag{9}$$

where w^{exp} and w^{cal} are the experimental and calculated mass fractions and the subscripts i, j and k respectively designate, the component, the phase and the tie line.

Table 5 UNIQUAC interaction parameters for the [soybean oil (**1**) + commercial oleic acid (**2**) + ethanol (**3**) + water (**4**)] system at 30 °C

Pair ij	A_{ij}/K	A_{ji}/K
12	250.00	−180.00
13	390.55	−30.00
14	2702.00	151.80
23	100.00	140.00
24	240.00	55.64
34	20.00	−944.00

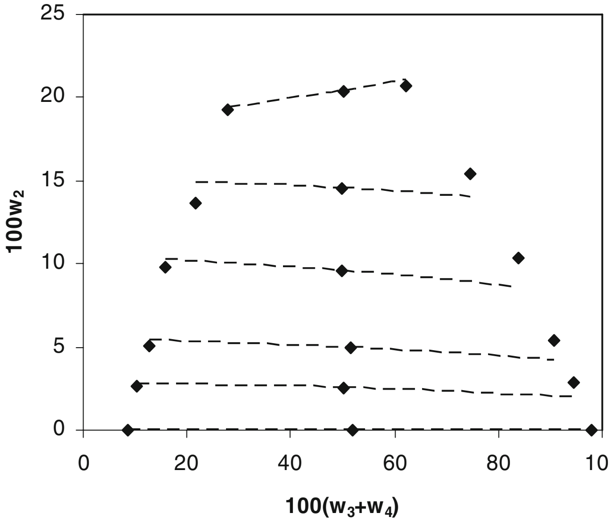

Fig. 1 System of soybean oil (**1**) + oleic acid (**2**) + aqueous solvent [ethanol (**3**) + 5% water (**4**)] at 30 °C (*filled diamonds*) experimental; (*dashed lines*) UNIQUAC

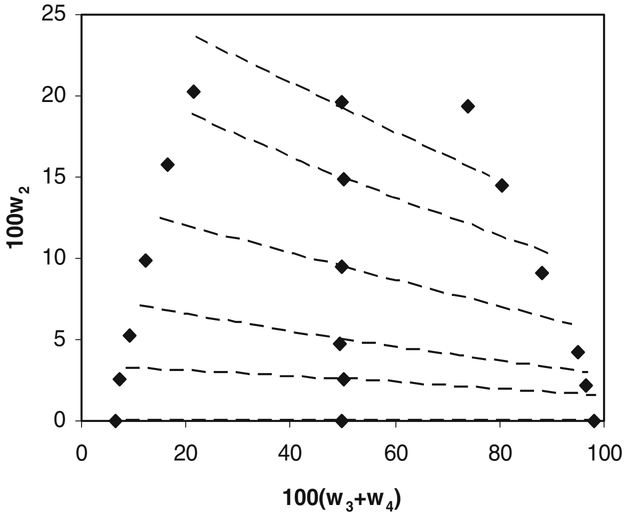

Fig. 2 System of soybean oil (**1**) + oleic acid (**2**) + aqueous solvent [ethanol (**3**) + 10% water (**4**)] at 30 °C. (*filled diamonds*) experimental; (*dashed line*) UNIQUAC

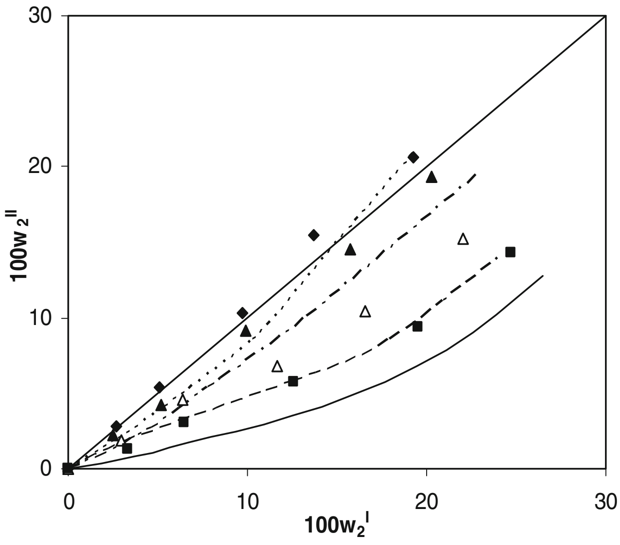

Fig. 3 The mass percent of oleic acid in alcohol-rich phase ($100w_2^{II}$) versus the mass percent of oleic acid in oil-rich phase ($100w_2^{I}$) for system of [soybean oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**)] with different ethanol + water mixed-solvents for mass percent of water: (*filled diamonds*) 5%; (*filled triangles*) 10%; (*open triangles*) 15%; (*filled squares*) 18%. Lines refer to calculated values by UNIQUAC model, (*solid line*) 5%; (*dotted line*) 10%; (*dot with dashed line*) 15%; (*dashed line*) 18%

Adjusted parameters of the UNIQUAC model are shown in Table 5. Figures 1 and 2 show the experimental data and the calculated tie lines for the soybean oil, oleic acid, and ethanol/5% water and the soybean oil, oleic acid, and ethanol/10% water systems. The equilibrium diagrams were plotted in triangular coordinates. For representing the pseudo- quaternary systems in triangular coordinates, ethanol and water were considered to be mixed-solvents. Figures 1 and 2 indicate that UNIQUAC model reasonably presented LLE experimental data for the mixed solvent (ethanol + water) in various concentration range of water. These figures also showed that the UNIQUAC model performed better for the systems with low oleic acid concentrations. Figure 3 presents the distribution coefficient at 30 °C. As was observed with the addition of water in the mixed solvent, the fatty acid distribution coefficient decreased. The distribution coefficient was calculated by using the following equation:

$$k_i = \frac{w_i^{II}}{w_i^{I}} \tag{10}$$

where $w_i$is the mass fractions of component i in phases I (oil-rich phase) and II (alcohol-rich phase), respectively. These results indicated that the addition of water increased solvent selectivity and consequently reduced the loss of neutral oil in solvent extraction. The solvent selectivity can be calculated by:

$$S = \frac{k_2}{k_1} \tag{11}$$

On addition of water a significant increase in the solvent selectivity was observed. Figure 4 presents the solvent

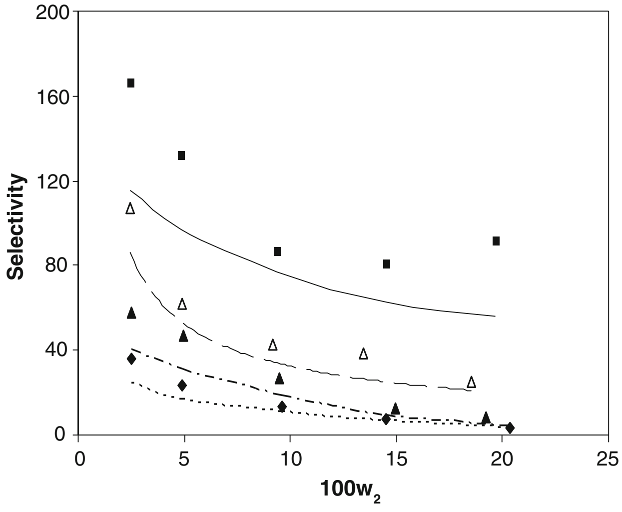

Fig. 4 Selectivity (*S*) versus mass percent of oleic acid ($100w_2$) for system of [soybean oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**)] with different ethanol + water mixed-solvents for mass percent of water: (*filled diamonds*) 5%; (*filled triangles*) 10%; (*open triangles*) 15%; (*filled squares*) 18%. Lines refer to calculated values by UNIQUAC model, (*dotted line*) 5%; (*dot with dashed line*) 10%; (*dashed line*) 15%; (*solid line*) 18%

Table 6 Mean deviations Δw in phase composition correlation for solvent water content (Mass %) by using the UNIQUAC model

Mass (%)	Δw (%)
5	7.15
10	5.43
15	4.56
18	3.83

selectivity at 30 °C. The deviations between experimental and calculated compositions in both phases for each system are shown in Table 6. These deviations were calculated according to Eq. (12):

$$\Delta w = \sqrt{\frac{\sum_n^N \sum_i^K \left[\left(w_{i.n}^{\mathrm{I.ex}} - w_{i.n}^{\mathrm{I.calc}} \right)^2 + \left(w_{i.n}^{\mathrm{II.ex}} - w_{i.n}^{\mathrm{II.calc}} \right)^2 \right]}{2NK}} \tag{12}$$

N is the total number of tie lines, and K is the total number of compounds or pseudocompounds. The subscripts i, n, are compound and tie line, respectively, and the superscripts I and II are the phases; ex and calc refer to experimental and calculated concentrations. Mean deviations Δw, calculated for the UNIQUAC model, confirm that this model was a good prediction for the equilibrium concentrations of components.

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