Liquid−Liquid Equilibrium for Systems of (Corn Oil + Oleic Acid + Methanol or Ethanol) at (303.15 and 313.15) K

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Liquid−liquid equilibrium data for the systems {corn oil + oleic acid + methanol} and {corn oil + oleic acid + ethanol} at (303.15 and 313.15) K are reported. The experimental liquid−liquid data were correlated using the UNIQUAC activity coefficient model, and the relevant parameters are presented. The experimental and calculated compositions of the equilibrium phases were compared, and the relative mean square deviations (rmsd) are reported. The results indicate applicability of the UNIQUAC activity coefficients model for liquid−liquid equilibrium calculations of the studied mixtures. The distribution coefficients and the selectivity factors of methanol and ethanol for the extraction of oleic acid from (corn oil + oleic acid) mixtures were calculated and presented. From our experimental and calculated results, we conclude that increasing the temperature causes an increase in the distribution coefficient but a decrease in the selectivity factor; therefore, considering economic and practical aspects, room temperature may be optimum for extraction of oleic acid from corn oil.

Introduction

Vegetable oils are a major feedstock in the pharmaceutical, surfactant, and especially food industries.[1] Crude vegetable oils consist predominantly of triacylglycerols and free fatty acids, with mono- and diacylglycerols present at a lower level. They are extracted mainly by mechanical pressing of oil seeds using filter press apparatus.[2,3] The residual can be extracted by solid−liquid operations using suitable solvents.[3−5] The basic refining processes of crude vegetable oils involve solvent stripping, degummimg, bleaching, deacidification, and deodorization.[6,7]

Edible vegetable oils such as corn oil are available in large amounts but can be chemically functionalized to generate hydroxyl fatty acids with more than one hydroxyl group.[1] The presence of these compounds can adversely affect oil quality and stability to oxidation. The medical and economical importance of the removal of free fatty acids (FFAs) from edible vegetable oils has caused many investigations on separation techniques such as chemical and physical refining processes.[8−11]

Although these refining processes can perform deacidification of oils, for oils with high acidity, chemical process causes high losses of neutral oil due to saponification and emulsification. The solvent extraction process is an appropriate physical method for the deacidification of edible vegetable oils.[2] The vegetable oils can be deacidified using various selective solvents such as acetone, furfural, ethyl acetate, propanol, 2-propanol, butanol, ethanol, methanol, and ethyl methyl ketone.[5] Turkay and Civelekoglu studied the solvent extraction of sulfur olive oil at room temperature and atmospheric pressure.[12] Solvent extraction has the advantages of avoiding formation of waste products and reducing the loss of neutral oil. Because of the high difference between the boiling points of the solvent, fatty acids, and triacylglycerols, solvent stripping from refined oil and solvent recovery from the extract stream can easily be carried out at relatively low temperatures.

In solvent extraction processes, suitable solvents play an important role from practical and economic viewpoints. By considering the role of the solvents in the extraction of fatty acids from edible oil mixtures, it is worthwhile to study the liquid−liquid equilibrium (LLE) of ternary systems of {edible oil (1) + fatty acid (2) + solvent (3)}. Therefore, the search for determining the optimum conditions of the deacidification of edible oils by solvent extraction is an ongoing study.[2]

Table 1. Mass Fraction (*w*) of Fatty Acid of Iranian Corn Oil

fatty acid		100 *w*	fatty acid		100 *w*
palmitic	C16:0[a]	10.04	linolenic	C18:3	0.81
stearic	C18:0	2.34	ecosanoic	C20:0	0.47
oleic	C18:1	27.82	ecosenoic	C20:1	0.23
linoleic	C18:2	58.29			

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

Design of industrial units for separation processes requires reliable phase equilibrium data of the different systems involved in a given process. Therefore, it is usual to measure the phase equilibrium properties of the ternary systems.

In the present paper, LLE data for the systems {corn oil (1) + oleic acid (2) + methanol (3)} and {corn oil (1) + oleic acid (2) + ethanol (3)} at (303.15 and 313.15) K are measured and reported. The obtained LLE data were correlated using the UNIQUAC activity coefficient model,[13] and the interaction parameters are presented.

Experimental Section

Chemicals. Edible Iranian corn oil and commercial oleic acid from Ferak (Berlin, Germany) were used as sources of triglyceride and fatty acids, respectively. The chemical compositions of corn oil and commercial oleic acid were determined by gas chromatography. The fatty acid composition of the Iranian corn oil is presented in Table 1.

The average molecular weight was 872 g·mol^{-1} for the corn oil and 282 g·mol^{-1} for the commercial oleic acid. The solvents used were ethanol and methanol, from Merck, with purity greater than 99.5 %.

Apparatus and Procedure. A glass equilibrium cell was used for the measurements. The schematic diagram of the equilibrium

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Table 2. Ternary Liquid−Liquid Equilibrium Data in Mass Fractions for the System Corn Oil (1) + Commercial Oleic Acid (2) + Methanol (3) at (303.15 and 313.15) K

	overall comp.			alcohol phase (II)			oil phase (I)		
	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
303.15 K	47.44	0.00	52.64	0.78	0.00	99.22	97.27	0.00	5.73
	44.12	3.17	52.72	0.83	3.49	95.68	89.30	3.59	7.12
	42.17	5.89	51.98	1.21	6.20	92.59	85.51	6.60	8.19
	42.75	9.28	47.96	2.04	9.62	88.34	79.20	9.78	10.62
	39.66	13.03	47.29	2.58	13.16	83.82	73.19	12.85	12.9
313.15 K	47.42	0.00	52.58	1.14	0.00	98.86	93.64	0.00	6.36
	44.14	3.18	52.72	1.67	3.46	95.51	88.72	3.60	7.68
	42.15	5.88	51.96	2.35	6.30	91.25	85.30	6.28	8.42
	42.77	9.33	47.98	2.8	9.22	87.90	79.38	9.04	11.58
	39.66	13.03	47.29	3.04	13.80	83.16	73.51	12.11	14.39

Table 3. Ternary Liquid−Liquid Equilibrium Data in Mass Fractions for the System Corn Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) at 303.15 and 313.15 K

	overall comp.			alcohol phase (II)			oil phase (I)		
	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
303.15 K	45.98	0.00	54.24	5.80	0.00	94.20	85.12	0.00	14.82
	46.63	1.28	52.17	6.69	1.94	91.37	81.82	1.82	16.37
	47.44	2.48	50.19	5.90	3.29	90.82	80.71	2.68	16.61
	45.83	3.30	50.87	7.41	4.16	88.44	79.82	3.22	16.96
	41.83	9.32	49.00	12.95	10.54	76.52	71.39	8.22	20.39
313.15 K	45.81	0.00	54.21	6.50	0.00	93.50	87.00	0.00	13.00
	46.62	1.26	52.17	6.85	1.54	92.06	83.59	1.42	14.99
	47.45	2.49	50.09	7.95	2.93	89.91	82.41	2.30	15.29
	45.85	3.30	50.87	8.23	3.95	87.82	81.42	3.10	15.48
	41.84	9.21	49.00	17.52	10.18	72.30	66.31	9.03	24.67

apparatus is presented in Figure 1. The cell has two partitions. The inner partition was for the sample, and water circulated around the sample via the outer partition. The cell temperature was controlled with a thermostatic bath (with an uncertainty ± 0.1 °C). A thermometer with subdivisions of 0.1 °C was used for monitoring the cell temperature. The mass of a component was determined by a Sartorius analytical balance (model A200 S, with an uncertainty ± 0.0001 g). The mixtures were prepared inside the cell and vigorously agitated with a magnetic stirrer. After several experiments and taking samples at different time intervals, it was found that increasing the agitation time (minimum time 30 min) and rest time (minimum time 12 h) has no considerable effect on equilibrium phase compositions. Therefore, the mixture was stirred for 30 min at least and then left to rest for 12 h. The samples of both equilibrium phases were collected and analyzed. The oleic acid compositions were determined using potentiometric titration (Modified AOCS Method Ca 5a-40)[14] with a microburet, and the mass of solvent was gravimetrically determined by weighing the total sample and then again after separating the volatile solvent by distillation in a vacuum oven (model EIV-1). Having determined the amount of fatty acids and solvent, the oil concentration was obtained by difference. The uncertainties in the concentrations were within ranges of (0.05 to 0.15) % for oleic acid, (0.05 to 0.10) % for ethanol and methanol, and (0.08 to 0.18) % for corn oil.

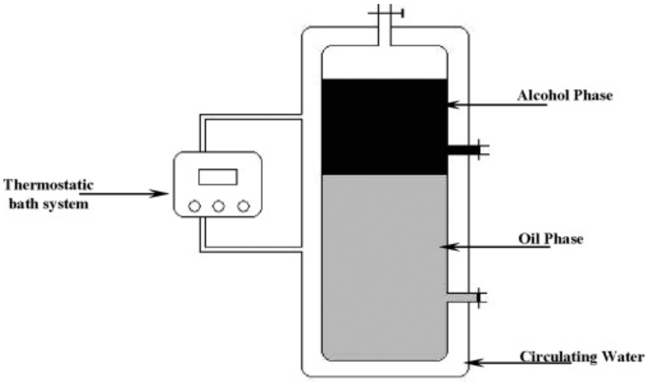

Figure 1. Schematic diagram of the equilibrium apparatus.

Results and Discussion

Tables 2 and 3 present the overall experimental mass fractions of the mixtures and mass fractions of each component in the alcohol and oil phase.

The experimental LLE data were correlated using the UNIQUAC activity coefficient model. Adjustments were made by treating the system as pseudo-ternary, composed of a single triacylglycerol having the corn oil average molecular weight, a representative fatty acid with the molecular weight of the commercial oleic acid and ethanol or methanol. The molecular volume and surface area parameters r'_i and q'_i for the UNIQUAC model were calculated by the following relations:[13,15,16]

$$r'_i = \frac{1}{\bar{M}_i} \sum_j^C x_j \sum_k^G \upsilon_k^{(i)} R_k \tag{1}$$

$$q'_i = \frac{1}{\bar{M}_i} \sum_j^C x_j \sum_k^G \upsilon_k^{(i)} Q_k \tag{2}$$

where $\overline{M}_i$ is the average molecular weight of the corn oil or the commercial oleic acid; x_j is the mole fraction of the triglycerides of the corn oil or the fatty acids of the commercial oleic acid; $\upsilon_k^{(i)}$ is the number of group 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_k and Q_k are the van der Waals parameters obtained by the UNIFAC method.[15,16] The calculated r'_i and q'_i values are given in Table 4. The binary interaction parameters of the UNIQUAC activity coefficient model were calculated by using nonlinear regression analysis of Nelder-Mead.[17] The objective function used for correlating

Table 4. Parameters r_i' and q_i' for the Studied Systems

compound	r_i'	q_i'
corn oil	0.04402	0.03566
oleic acid	0.04412	0.03748
methanol	0.05933	0.06392
ethanol	0.05591	0.05618

Table 5. UNIQUAC Parameters for the Studied Systems

pair $i-j$	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}
Corn Oil (1) + Oleic Acid (2) + Methanol (3)		
1−2	669.4	−1213.4
1−3	1631.8	836.8
2−3	481.2	564.8
Corn Oil (1) + Oleic Acid (2) + Ethanol (3)		
1−2	1037.6	−795.0
1−4	1255.2	836.8
2−4	481.2	564.8

Table 6. Calculated rmsd in Phase Composition (Mass Fractions) Correlations Using the UNIQUAC Model

solvent	T/K	rmsd
methanol	303.15	0.0249
	313.15	0.0238
ethanol	303.15	0.0492
	313.15	0.1168

of experimental data by the UNIQUAC activity coefficient model was in the following form:[18]

$$\mathrm{OF} = \sum_i \sum_j \sum_k (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2 \tag{3}$$

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. The root mean square deviation (rmsd) is a measure of agreement between the experimental and the calculated values. The rmsd value is defined as follows:[18]

$$\mathrm{rmsd} = [\sum_{n}^{i=1} \sum_{2}^{j=1} \sum_{M}^{k=1} (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2/2nM]^{1/2} \tag{4}$$

where n is the number of components and M is the total number of tie lines. The experimental equilibrium data for {corn oil (1) + oleic acid (2) + methanol (3)} and {corn oil (1) + oleic acid (2) + ethanol (3)} systems were used to calculate the parameters of the UNIQUAC model (see Table 5). Adjusted parameters of the UNIQUAC activity coefficient model[13] are shown in Table 6. Figures 2 and 3 show the experimental points and calculated tie lines for the systems {corn oil (1) + oleic acid (2) + methanol (3)} and {corn oil (1) + oleic acid (2) + ethanol (3)} at 303.15 K. These figures indicate that the UNIQUAC model provided a good representation of phase compositions. Figures 4 and 5, respectively, present the distribution coefficients of oleic acid (2) at (303.15 and 313.15) K for the studied systems. These figures indicate that the distribution coefficients for the system {corn oil (1) + oleic acid (2) + methanol (3)} are less than unity and for the system {corn oil (1) + oleic acid (2) + ethanol (3)} are higher than unity. The distribution coefficient was calculated by the following equation:

$$k_i = \frac{w_i^{\mathrm{II}}}{w_i^{\mathrm{I}}} \tag{5}$$

where w_i^{II} and w_i^{I} are respectively the mass fractions of component i in alcohol and oil phases.

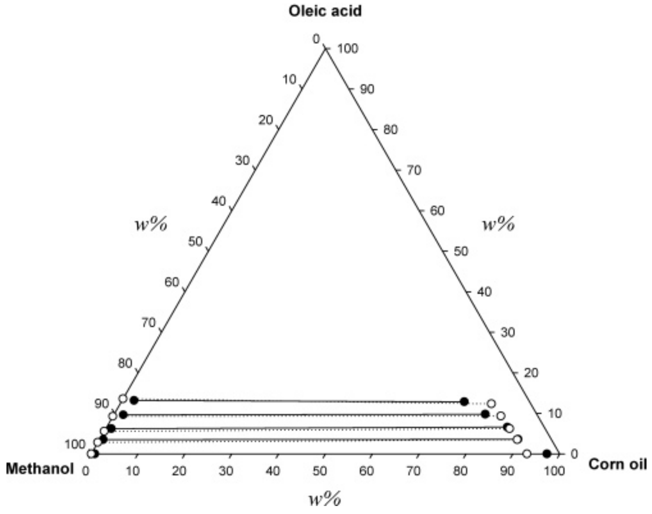

Figure 2. System of {corn oil (1) + oleic acid (2) + mthanol (3)} at 303.15 K: ●, experimental; ○, UNIQUAC.

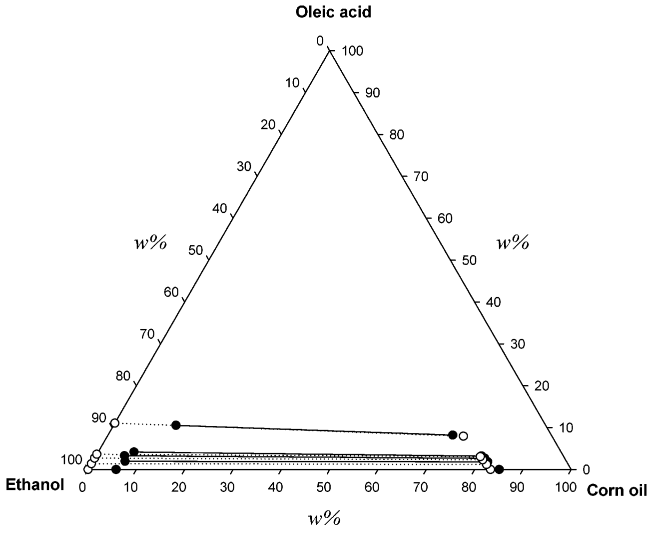

Figure 3. System of {corn oil (1) + oleic acid (2) + ethanol (3)} at 303.15 K: ●, experimental; ○, UNIQUAC.

The solvent selectivity factor was calculated by

$$S = \frac{k_2}{k_1} \tag{6}$$

Figure 6 shows the solvent selectivities of methanol and ethanol at (303.15 and 313.15) K for extraction of oleic acid from (oleic acid + corn oil) mixtures. According to this figure, the selectivity of methanol is higher than ethanol; however, temperature increases reduce the solvent selectivities for both methanol and ethanol.

Conclusions

LLE data for systems {corn oil (1) + oleic acid (2) + methanol (3)} and {corn oil (1) + oleic acid (2) + ethanol (3)} were determined at (303.15 and 313.15) K. The results indicated that, for both temperatures, methanol has the higher selectivity and lower distribution coefficient than ethanol for extraction of oleic acid from (oleic acid + corn oil).

The results confirm that at the lower temperature the selectivity (S), a measure of ability for extraction of oleic acid from corn oil, is higher but the distribution coefficient (K), a

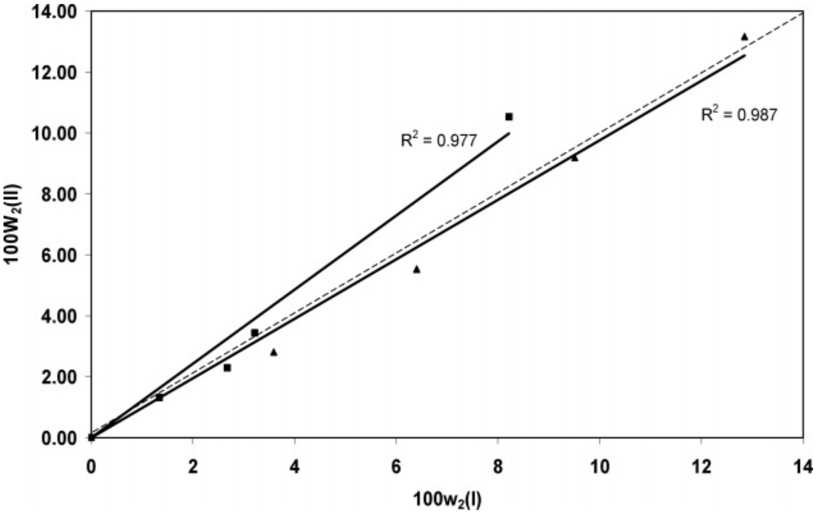

Figure 4. Distribution diagram for systems of ▲, {corn oil (1) + oleic acid (2) + methanol (3)}; ■, {corn oil (1) + oleic acid (2) + ethanol (3)} at 303.15 K.

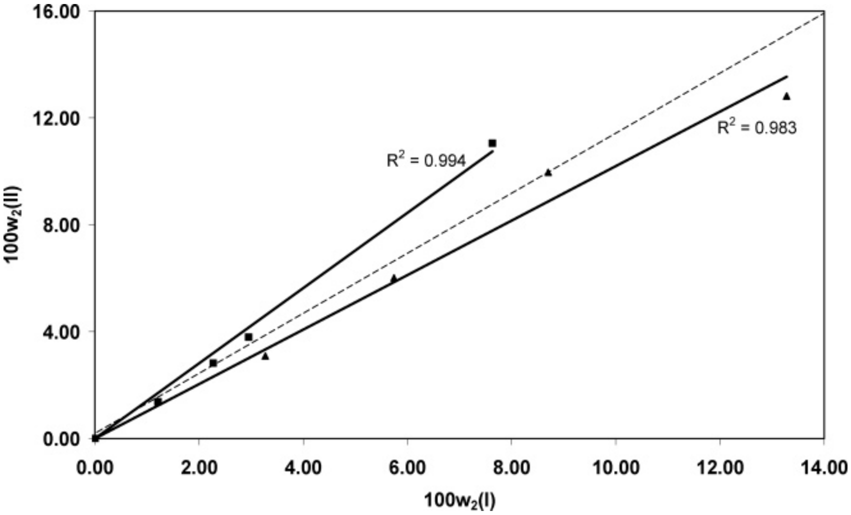

Figure 5. Distribution diagram for systems of ▲, {corn oil (1) + oleic acid (2) + methanol (3)}; ■, {corn oil (1) + oleic acid (2) + ethanol (3)} at 313.15 K.

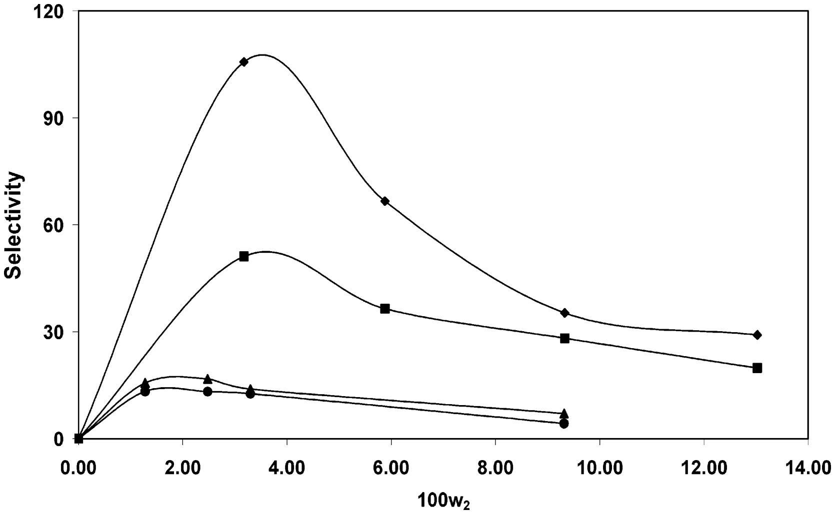

Figure 6. Experimental selectivity for systems of {corn oil (1) + oleic acid (2) + methanol (3)} at ◆, 303.15 K; ■, 313.15 K; and of {corn oil (1) + oleic acid (2) + ethanol (3)} at ▲, 303.15 K; ●, 313.15 K.

measure of ratio of methanol or ethanol to the feed required for the desired separation of oleic acid from corn oil, is slightly lower. We conclude that ethanol at 303.15 K is an appropriate solvent for deacidification of corn oil by solvent extraction. The calculations based on the UNIQUAC activity coefficient model indicate a good fit of the tie line data for these systems.

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