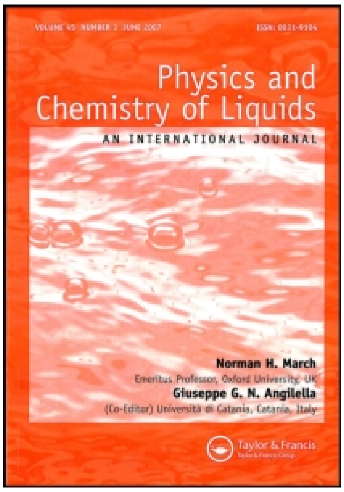

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Liquid–liquid equilibrium for system corn oil + oleic acid + ethanol + water

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Mixed solvent of (ethanol + 5% mass fraction of water) was studied as a possible extraction of oleic acid from corn oil at three temperatures (298.2, 308.2 and 318.2 K). The experimental liquid–liquid equilibrium data have been correlated using the UNIQUAC activity coefficient model to obtain the binary interaction parameters of these components. The UNIQUAC model satisfactorily correlated the equilibrium compositions. The partition coefficients and the selectivity factor of the mixed solvent systems were calculated and presented. From our experimental results, we conclude that increasing the temperature causes an increase in the distribution coefficient and a decrease in the selectivity factor. Considering the obtained partition coefficients and selectivity factors, 298.2 K may be suggested as an optimum temperature for an efficient extraction of oleic acid from corn oil by (ethanol + ethanol + 5% mass fraction of water).

Keywords: Corn oil; Distribution coefficient; Experimental data; Fatty acids; Liquid–liquid equilibrium; Selectivity

1. Introduction

Crude vegetable oils contain triacylglycerols (triglycerides) as their main components and free fatty acids (FFAs), with monoacylglycerols and diacylglycerols at lower concentrations. They are extracted mainly by solid–liquid extraction from oil seeds using hexane petroleum fractions as solvent [1,2]. The purification of crude vegetable oils involves removal of these impurities in several steps: solvent stripping, degumming, bleaching, deacidification and deodorization [3,4]. These processes are carried out by chemical and physical methods. Deacidification is the most important step in the refining processes [5]. Oil deacidification can be accomplished by chemical refining. In this method, FFAs are converted to soap and then separated by centrifuge, but this method causes loss of lot of oil. In the case of high acidity oils, physical processing techniques causes less loss of neutral oil but they have some disadvantages, including

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the consumption of large quantities of energy. Also, there is an adverse effect on color and stability of oils to oxidation [6].

Deacidification by solvent extraction has been receiving attention for its advantages in comparison to the physical and chemical refining. This method, based on the difference of the solubility of FFAs and triacylglycerols in an appropriate solvent, can be performed at low temperature and atmospheric pressure, reducing the energy consumption besides avoiding the formation of waste products. In addition, the solvent can be refined by distillation at low temperatures [7].

Kim *et al.* [8] and Kale *et al.* [9] tested the deacidification of crude rice bran oil by extraction with methanol. Turkay and Civelekoglu [10] studied the liquid–liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions.

In the present article, liquid–liquid equilibrium (LLE) data for the systems containing corn oil **(1)** + oleic acid **(2)** + ethanol **(3)** + water **(4)** at 298.15, 308.15 and 318.15 K are measured and reported. The mixture of (ethanol + 5% mass fraction of water) was considered as mixed solvent. The obtained LLE data were correlated using the UNIQUAC [11] activity coefficient model and the interaction parameters were presented.

2. Experimental

2.1. *Materials*

Edible Iranian corn oil (Glokozan Company, Iran) was used as a source of triglyceride, and commercial oleic acid of Ferak (Berlin, Germany) as the source of fatty acids. The chemical composition of these reagents was determined by gas chromatography. The fatty acid composition of the Iranian corn oil is presented in table 1.

The average molecular weight was 871.98 g mol^{-1} for the corn oil and 282.47 g mol^{-1} for the commercial oleic acid. The solvent used was ethanol (from Merck) with purity greater than 99.5%. Double distilled water was used to prepare the aqueous solvent.

2.2. *Procedure*

A glass equilibrium cell was used for the measurements. 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

Table 1. Mass fraction, w of fatty acid in Iranian corn oil.

Fatty acid		$100w$
Palmitic	C16 : 0	10.04
Stearic	C18 : 0	2.34
Oleic	C18 : 1	27.82
Linoleic	C18 : 2	58.29
Linolenic	C18 : 3	0.81
Ecosanoic	C20 : 0	0.47
Ecosenoic	C20 : 1	0.23

In $Cx:y$, x = number of carbons and y = number of double bonds.

uncertainty ±0.1°C). A thermometer with subdivisions of 0.1 K was used for monitoring the cell temperature. The masses of components were determined by a Sartorius analytical balance (Model A200 S, with an uncertainty ±0.0001 g). After several experiments and taking samples at time intervals from each phase, it was found that increasing the agitation time (minimum time 20 min) and rest time (minimum time 12 h) has no considerable effect on equilibrium phase compositions. Therefore, the mixture was stirred vigorously for 20 min at least and left to rest for 12 h. The oleic acid mass fraction was determined using potentiometric titration (Modified AOCS Method Ca 5a-40) [12] with a microburet; the solvent was determined by distillation in a vacuum oven (Model EIV-1). The water mass fraction was determined by Karl Fisher titration (Metrohm KF coulometer model 684). Having determined the amount of fatty acids, solvent and water, the oil mass fraction was obtained by taking the difference [13]. The uncertainties in the mass fraction were within ranges: 0.05–0.21% for oleic acid, 0.04–0.13% for ethanol, 0.02–0.11% for water and 0.06–0.23% for corn oil.

3. Results and discussion

Table 2 presents the overall experimental mass fractions of the mixtures and mass fractions of each component in the alcoholic and oil phase. The compositions expressed in units of mass fraction, w. The experimental LLE data were correlated using the UNIQUAC activity coefficient models. The adjustments were made by treating the system as a pseudo-quaternary one, 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 ethanol and water. The values of the molecular volume and surface area parameters r'_i and q'_i for the UNIQUAC model were calculated by the following relations [11,14,15]:

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

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

where $\bar{M}_i$ 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 and $\nu_k^{(i)}$ 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 waal's parameters obtained by the UNIFAC method [14,15]. The calculated r'_i and q'_i values are given in table 3.

The binary interaction parameters of the UNIQUAC activity coefficient model were calculated by using nonlinear regression analysis of Nelder–Mead [16]. The objective function used for correlating of experimental data by the UNIQUAC activity coefficient model was in the following form [17]:

$$\text{O.F.} = \sum_i \sum_j \sum_k \left(w_{ijk}^{\text{exptl}} - w_{ijk}^{\text{calcd}} \right)^2 \tag{3}$$

Table 2. Quaternary liquid–liquid equilibrium data for the system [corn oil (**1**) + commercial oleic acid (**2**) + ethanol (**3**) + water (**4**)] at $T = 298.2$, 308.2 and 318.2 K.

	Overall composition				Alcohol phase (II)				Oil phase (I)			
T	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
298.2 (K)	48.00	0.00	49.39	2.60	3.01	0.00	91.10	5.89	91.21	0.00	8.47	0.32
	47.22	2.54	47.73	2.51	2.87	2.58	89.3	5.25	87.65	2.48	9.49	0.38
	43.43	4.99	49.00	2.58	3.24	5.44	86.11	5.21	83.56	5.01	11.00	0.43
	39.26	9.88	48.32	2.54	6.23	10.47	78.42	4.88	74.34	9.80	15.23	0.63
	35.36	14.63	47.51	2.50	9.13	15.36	71.09	4.42	65.05	14.08	20.08	0.79
308.2 (K)	53.00	0.00	44.65	2.35	4.72	0.00	89.53	5.75	90.36	0.00	9.28	0.36
	45.70	2.55	49.16	2.59	4.30	2.92	87.65	5.13	86.72	2.79	10.09	0.4
	45.06	4.82	47.61	2.51	4.72	5.73	84.46	5.09	82.60	4.79	12.14	0.47
	41.37	9.31	46.85	2.47	9.12	9.98	76.32	4.58	74.86	8.71	15.84	0.59
	36.51	13.95	47.06	2.48	11.37	15.05	69.55	4.03	64.30	13.03	21.79	0.88
318.2 (K)	48.04	0.00	49.36	2.60	6.43	0.00	87.96	5.61	89.44	0.00	10.15	0.41
	45.63	2.54	49.24	2.59	7.68	3.17	84.16	4.99	84.71	2.61	12.21	0.47
	44.19	4.36	48.88	2.57	7.82	5.33	81.92	4.93	78.91	4.26	16.22	0.61
	40.87	9.25	47.39	2.49	9.79	11.55	74.28	4.38	71.38	9.39	18.45	0.78
	35.74	14.23	47.53	2.50	11.52	16.89	67.80	3.79	61.92	13.68	23.34	1.06

Table 3. Parameters r'_i and q'_i for system [corn oil (**1**) + commercial oleic acid (**2**) + ethanol (**3**) + water (**4**)].

Compound	r'_i	q'_i
Corn oil	0.044021	0.035671
Oleic acid	0.045147	0.037069
Ethanol	0.055905	0.056177
Water	0.051069	0.077713

Table 4. UNIQUAC parameters for the system [corn oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**)].

Pair *ij*	A_{ij}	A_{ji}
12	247.0	−190.0
13	385.0	140.0
14	3220.0	156.0
23	112.0	135.0
24	250.0	105.0
34	30.0	−505.0

where w^{exptl} and w^{calcd} 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 the agreement between the experimental data and the calculated values. The RMSD value is defined as follows [17]:

$$\text{RMSD} = \left(\sum_i \sum_j \sum_k \frac{(w_{ijk}^{\text{exptl}} - w_{ijk}^{\text{calcd}})^2}{6M} \right)^{1/2} \tag{4}$$

where, M is the total number of tie lines. The calculated RMSD values are: 0.035, 0.044 and 0.055 respectively for 298.2, 308.2 and 318.2 K. Therefore, it is concluded that the UNIQUAC activity coefficient model satisfactorily correlates the obtained experimental LLE data.

Table 4 shows the adjusted parameters of the UNIQUAC activity coefficient model. Figure 1 presents the fatty acid distribution coefficient at three temperatures for the studied systems. As it is seen by the increasing temperature, the fatty acid distribution coefficient increases. The distribution coefficient is calculated by the following equation:

$$K_2 = \frac{w_2^{\text{II}}}{w_2^{\text{I}}} \tag{5}$$

where, w_2^{II} and w_2^{I} are, respectively, the mass fractions of oleic acid (**2**) in solvent phase (II) and oil phases (I).

The solvent selectivity can be calculated by:

$$S = \frac{w_2^{\text{II}}/w_2^{\text{I}}}{w_1^{\text{II}}/w_1^{\text{I}}}. \tag{6}$$

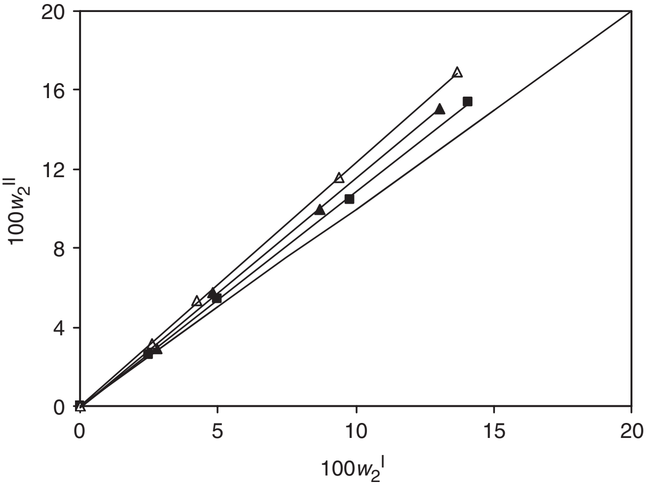

Figure 1. Experimental distribution coefficient data for systems of [corn oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**)] at: (■) 298.2 K, (▲) 308.2 K and (△) 318.2 K.

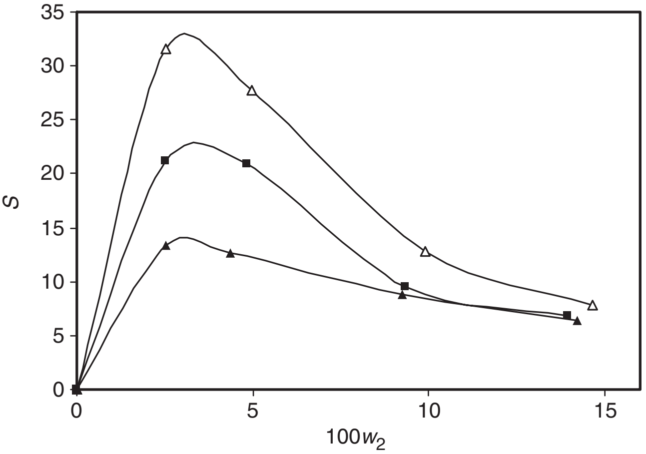

Figure 2. Experimental Selectivity data for systems of [corn oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**)] at: (△) 298.2 K, (■) 308.2 K and (▲) 318.2 K.

From figure 2, an increase in temperature results in a decrease in the solvent selectivity and at about 2.5% of FFA, the selectivity has a maximum in all studied systems.

4. Conclusion

LLE data for systems containing corn oil (**1**) + oleic acid (**2**) + ethanol (**3**) + water (**4**) were determined at $T = 298.2$, 308.2 and 318.2 K. The results confirm that at lower temperatures the selectivity (*S*), as a measure of ability of mixed solvent (ethanol + 5% mass fraction of water) for extraction of oleic acid from corn oil is higher but the distribution coefficient (K) as a measure of ratio of mixed solvent (ethanol + 5% mass fraction of water) to the feed required for the desired separation of oleic acid from corn oil is lower, therefore considering the obtained experimental selectivity and distribution coefficient, we suggest that $T = 298.2\,\mathrm{K}$ is an appropriate temperature for deacidification of corn oil by (ethanol + 5% mass fraction of water) mixture, since considering figure 1, $K > 1$ and the extraction is feasible and also, from figure 2, the selectivity is higher. The calculations based on the UNIQUAC activity coefficient model indicate a good fit of the representation of the tie line data for these systems.

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