Extraction of Free Fatty Acids from Soybean Oil Using Ionic Liquids or Poly(ethyleneglycol)s

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The alternative solvents poly(ethyleneglycol)s (PEGs) with various molar masses and room temperature ionic liquids (RTILs) AMMOENG100 and 1-butyl-3-methylimidazolium dicyanamide (bmimDCA) were studied for the purpose of extraction of linoleic acid from soybean oil. Liquid-liquid phase equilibrium was measured for binary (PEG + soybean oil), (RTIL + soybean oil) as well as ternary (PEG + soybean oil + linoleic acid), (RTIL + soybean oil + linoleic acid) mixtures, as a function of temperature and composition. The influence on distribution coefficients and separation factor of temperature, initial acid content of the oil and solvent to oil ratio were studied. The effect of molar mass in the case of the PEGs was also examined. The experimental results were modeled using the Peng-Robinson cubic equation of state coupled with the Mathias-Klotz-Prausnitz mixing rule, with good results. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1344–1355, 2011
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Introduction

The presence of free fatty acids (FFAs) in vegetable oils is undesirable for both biodiesel and food oil productions. The most common way to produce biodiesel is through the transesterification of vegetable oils with an alcohol, yielding fatty acid alkyl esters and glycerol.[1] Commercial processes use alkaline catalysts NaOH or KOH, which are relatively inexpensive. However, vegetable oils contain a considerable quantity of FFAs that react with the alkaline catalyst to form soap, reducing the ester yield. In respect to fat containing food, the presence of FFAs is associated to an undesirable rancid flavor. The deacidification process determines the quality of oil, having, thus, a major economic impact on oil production. The removal of FFAs from crude oils represents the most important stage in their refining cycle.

Conventional methods for FFA removal present various limitations. A typical chemical deacidification may lead to an excessive loss of neutral oil with high FFA content as well as to production of low commercial value soap stock. Physical deacidification methods, although suitable for high FFA content oils, require pretreatments that are performed under very harsh conditions—high temperatures and high vacuum. The latter cause thermal polymerization and decomposition of high value oil constituents. According to Leibovitz and Ruckenstein,[2] chemical deacidification of crude

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corn oil with FFA content between 8.4 and 14% resulted in neutral oil loss of 15–25%, while for physical refining the loss of neutral oil varied between 11 and 20%.

These drawbacks associated with the conventional deacidification processes may be overcome by new approaches and their combination with current technologies. Bhosle and Subramanian[3] have reviewed alternative deacidification technologies reported in the literature, such as biological deacidification, solvent extraction, reesterification, supercritical fluid extraction, and membrane processing. Fixation of FFAs on an anion exchange resin was also proposed.[4] The authors succeed to efficiently reduce FFA content of synthetic oil. However, in the case of viscous oils, an organic solvent is necessary to use for dilution of the system. This implies subsequent recovery of free fatty acids from an organic phase. Nevertheless, these new approaches are possibly more environmentally acceptable and may reduce energy consumptions and oil losses.

The most studied extraction solvents for deacidification are short-chain alcohols. Meirelles and coworkers[5–10] have intensively studied the distribution coefficients of FFAs between oil- and alcohol-rich phase. Independently of temperature or chemical structures of vegetable oil, selected short-chain alcohol and FFA studied, the distribution coefficients of FFA have relatively low values (close to 1), indicating similar solubility of FFA in both oil-rich and solvent-rich phases. Presence of water in alcohols lowers losses of neutral oils but leads to slightly inferior FFA distribution coefficients compared with the case when dry alcohols were used.[11,12] Moreover, the solubility of tryglicerides (vegetable oils) increases proportionally to their FFA contents, thus leading to the loss of neutral oils.

The aim of this work was to explore the possibility of using alternative solvents for vegetable oil deacidification studies, using room temperature ionic liquids (RTILs) and poly(ethyleneglycol)s (PEGs). RTILs have appeared as alternative extraction solvents, reaction media, and catalysts[13,14] because of their practically null-volatility,[15] nonflammability,[16] comparative thermal stability,[17] and versatile solubility toward both polar and nonpolar solutes.[18] Combining different cations and anions, a variety of ionic liquids can be obtained with desired (“task specific”) solvent properties.[19] The incorporation of specific functional groups enhances solubility of specific solutes, such as polar substrates or catalysts,[20] or leads to unexpected antisolvent/co-solvent effects.[21] Therefore, RTILs offer wide potential in industrial applications.[22] Ionic liquids bmimDCA and Cocos alkyl pentaethoxi methyl ammonium methylsulfate (AMMOENG100) were chosen due to their extremely low miscibility with soybean oil, complete miscibility with FFA studied, and low viscosity and cost.

Liquid PEGs, are also nonvolatile, exhibit a very low toxicity (low enough for PEG to be approved as a food additive for humans) and biodegradability.[23] Moreover, PEGs and their aqueous solutions have already been widely used as sustainable medium for chemical reactions and liquid-liquid extractions (see Refs. 24 and 25 as well as references therein). In respect to solvent ability, PEGs form hydrogen bonds, because they are both proton donors and proton acceptors[26] but posses as well an aliphatic back bone that can provide van der Waals interactions.

In this work, liquid-liquid equilibrium (LLE) measurements on mixtures of soybean oil and several extraction solvents were used to evaluate the feasibility of FFA extraction. Two RTILs were used: bmimDCA and Cocos alkyl pentaethoxi methyl ammonium methylsulfate (AMMOENG100). Poly(ethylene glycol)s of average molar mass of 200, 400, 2000, and 4000 were also used. Linoleic acid was chosen as a model FFA. The effects of: concentration, temperature, polymer molar mass, water content, and solvent to oil ratio were scrutinized. The experimental LLE results were correlated using a model based on the Peng-Robinson cubic equation of state and Mathias-Klotz-Prausnitz mixing rule—the PR-MKP model, which showed very good results for all the studied systems.

Experimental

Materials

Refined soybean oil, anhydrous methanol (99.8%), and linoleic acid (99.5%, GC) were obtained from Sigma Aldrich, whereas diethyl ether and ethanol were purchased from Panreac. Analytical grade polyethylene glycols with molar mass, in g/mol, of 200 (PEG200), 400 (PEG400), 2000 (PEG2000), and 4000 (PEG4000) were supplied by Fluka. RTILs AMMOENG100 and bmimDCA were purchased from Solvent Innovation and IoLiTec, respectively. Water was distilled and deionized using a Milli-Q water filtration system from Millipore.

To reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa) and moderate temperature (60°C) were applied to the RTIL samples for at least 3 days immediately prior to their use.

To determine the fatty acid methyl ester composition of soybean oil, deacidification followed by transesterification were performed, according to a procedure in the literature.[27] Products of transesterified soybean oil were analyzed in a VARIAN CHROMPACK CP-3800 gas chromatograph equipped with a 30 m × 0.32 mm i.d. fused silica capillary column, coated with a 0.25 μm thickness film of 5% phenyl groups dissolved in dimethylpolysiloxane polymer, from Chrompack Company. The column temperature program started at 50°C for 1 min and went up to 185°C, with the heating rate of 20°C/min. The temperature was kept at 185°C for 2 min and then increased up to 250°C with the heating rate of 0.8°C/min. Volumes of injected samples were 0.5 μL. The carrier gas, helium, was delivered at 0.7 bar. The injector temperature and flame ionization detection temperature were 250 and 300°C, respectively. Methyl heptanoate in hexane was used as standard for GC analysis. Retention times in minutes were: methyl heptanoate 5.0; methyl palmitoleate 15.50; methyl palmitate 16.16; methyl linoleate 22.21; methyl oleate 22.5; and methyl stearate 23.71.

Model fatty systems were prepared by addition of known quantities of linoleic acid to a refined soybean oil. All liquid solutions were gravimetrically prepared to an estimated uncertainty of 0.02%.

Experimental procedure

Cloud points were determined by the cloud-point titration method in a temperature-controlled equilibrium cell, with a

Table 1. Fatty Acid Composition of Refined Soybean Oil Used in this Study (Source Sigma Aldrich)

Fatty Acid	Mass %
Linoleic acid (C18:2)	59
Oleic acid (C18:1)	20
Palmitic acid (C16:0)	16
Stearic acid (C18:0)	2
Palmitoleic acid (C16:1)	2
Others	1

magnetic stirrer inside. Each soybean oil + linoleic acid mixture of known composition was titrated by the solvent methanol or PEGs or ionic liquid, at constant temperature, with continuous stirring. The transition point is taken as the appearance/disappearance of turbidity in the solution, and it is defined as a cloud point. The liquid phase occupied almost the whole volume of the cell, to avoid corrections to composition due to vaporization. All experiments were performed at least twice. The temperature was controlled within ± 0.1 K and monitored by a calibrated mercury thermometer.

Liquid-liquid extractions were performed according to the following procedure: the model soybean oil mixtures containing from 2.62 to 17.3 mass % linoleic acid were mixed with the extraction solvent either PEG200, PEG400, PEG2000, PEG4000, bmimDCA, or AMMOENG100 in the ratios 1:1, 1:2, and 2:1 mass ratio at the temperatures 298.2, 323.2, and 343.2 K. Before commencing the work, the time taken to reach equilibrium was estimated by sampling the phases every 5 min until a few consecutive samples produced essentially the same result of the analysis. It was determined that 30 min were sufficient to reach equilibrium. After stirring, the mixtures were centrifugated and left still for at least 60 min at the given temperature, to allow a complete phase separation. Using a Hamilton syringe, the two liquid phases (oil- and solvent-rich) were carefully drawn to other vials and prepared for further analysis of the FFA content.

The concentrations of FFAs were determined by titration under dry nitrogen atmosphere. Approximately 2 g of sample were weighed and then 25 mL of (ethyl ether:ethyl alcohol 2:1(v:v)) mixture as well as two drops of phenolphthalein solution were added. These mixtures were titrated with 0.05 mol/L KOH in ethanol solution until solutions changed its color from transparent to light pink. In the case of experiments involving PEGs as extraction solvents, samples of both extract (PEG-rich) and raffinate (oil-rich) phases were titrated directly. Since RTILs are compounds composed of ions, the determination of FFAs concentration is not possible by alkali titration. In these experiments, only oil-rich phases washed with water (to remove traces of RTIL) and dried over Na_2SO_4 were analyzed for the FFA content. Afterward, the FFA content of the related RTIL-rich phase was calculated as a difference.

For those mixtures where concentrations of linoleic acid were measured for both phases in equilibrium, the cloud-point data were used to determine tie-lines. The cloud-point compositions were fitted by a linear equation in the ternary diagram at a certain temperature. The interception in the ternary diagram of the cloud-point line for each phase with the line corresponding to the measured concentration of linoleic acid in the same phase gave the equilibrium composition for that phase, including the concentration of the other two components (oil and solvent). As the overall composition of the mixture is known, the procedure could be validated by checking whether the tie-line connecting the equilibrium compositions thus determined passed through the point in the ternary diagram representing the overall composition. In all cases, the maximum deviations were below ± 0.001 mass fraction of linoleic acid.

Results

The determined composition of the soybean oil used in this study is shown in Table 1, allowing estimation of an average molar mass of 866.5 g/mol. The main constituents of the soybean triglycerides are tri-esters of linoleic, oleic and palmitic acid. Even though the oil is a mixture of various triglycerides, we considered it as a single component linoleic acid tri-ester (glyceryl trilinoleate). The concentration of FFAs in the refined oil is 0.14 mass %.

Chemical structures of solvents used for extraction of FFAs from soybean oil are shown in Figure 1. It should be noted that AMMOENG100 is an unknown isomer mixture where (*m* + *n*) varies from 4 to 14 while the cocos alkyl chain is a variable mixture of several fatty acid chains.

Table 2 presents the obtained cloud-point liquid-liquid equilibrium data for the pseudo-binary (extraction solvent + (soybean oil + linoleic acid)) systems using the following extraction solvents: PEG200, PEG400, PEG2000, PEG4000, AMMOENG100, bmimDCA, and methanol. The latter was chosen for comparison. Data in Table 2 show large immiscibility gaps with very steep binodal lines. This is also illustrated in Figure 2 for (oil + methanol), (oil + PEG) and (oil + RTIL) systems.

Although the mutual solubility of (soybean oil + methanol) mixture was reported in the literature,[28] it was not possible to quantitatively compare results as they are given solely in graphical form. However, the same data for the

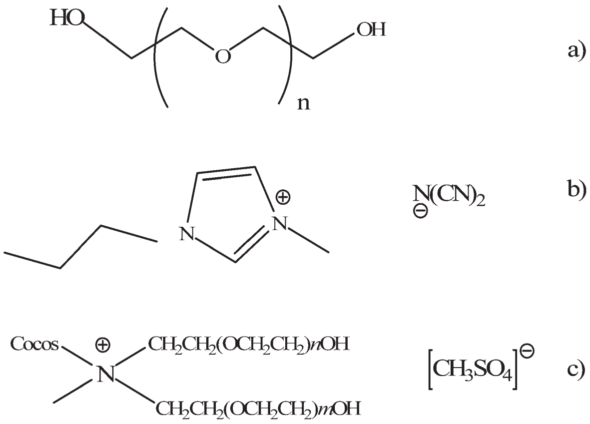

Figure 1. Structures of extraction solvents used in this study: (a) polyethylene glycol (PEG), (b) 1-butyl-3-methylimidazolium dicyanamide (bmimDCA), and (c) Cocos alkyl pentaethoximethyl ammonium methylsulfate (Ammoeng100).

Table 2. Cloud Point Data for {Extraction Solvent (sol) + Soybean Oil (oil) + Linoleic Acid (LA)} Systems, where Extraction Solvent Stands for either PEG200 or PEG400 or PEG2000 or PEG4000 or AMMOENG100 or bmimDCA or Methanol

Solvent	$w_{\mathrm{LA,init.}}$	$T = 298$ K		$T = 323$ K		$T = 343$ K		$T = 298$ K		$T = 323$ K		$T = 343$ K	
		$w_{\mathrm{sol}}^{\mathrm{oilrich}}$	$w_{\mathrm{sol}}^{\mathrm{sol.rich}}$	$w_{\mathrm{sol}}^{\mathrm{oilrich}}$	$w_{\mathrm{sol}}^{\mathrm{sol.rich}}$	$w_{\mathrm{sol}}^{\mathrm{oilrich}}$	$w_{\mathrm{sol}}^{\mathrm{sol.rich}}$	$x_{\mathrm{sol}}^{\mathrm{oilrich}}$	$x_{\mathrm{sol}}^{\mathrm{sol.rich}}$	$x_{\mathrm{sol}}^{\mathrm{oilrich}}$	$x_{\mathrm{sol}}^{\mathrm{sol.rich}}$	$x_{\mathrm{sol}}^{\mathrm{oilrich}}$	$x_{\mathrm{sol}}^{\mathrm{sol.rich}}$
PEG200	0.0014	0.0055	0.9991	0.0068	0.9991	0.0075	0.9991	0.0233	0.9998	0.0287	0.9998	0.0316	0.9998
	0.0572	0.0061	0.9990	0.0123	0.9990	0.0189	0.9990	0.0232	0.9997	0.0460	0.9997	0.0694	0.9997
	0.1554	0.0064	0.9989	0.0220	0.9989	0.0369	0.9989	0.0206	0.9997	0.0685	0.9997	0.1113	0.9997
PEG400	0.0014	0.0031	0.9989	0.0048	0.9989	0.0077	0.9989	0.0067	0.9995	0.0205	0.9995	0.0165	0.9997
	0.0572	0.0047	0.9988	0.0089	0.9988	0.0135	0.9988	0.0091	0.9994	0.0336	0.9994	0.0258	0.9997
	0.1554	0.0056	0.9987	0.0142	0.9987	0.0275	0.9987	0.0091	0.9992	0.0450	0.9992	0.0442	0.9996
PEG2000	0.0014	–*	–*	0.0004	0.9984	0.0009	0.9984	–*	–*	0.0017	0.9963	0.0004	0.9963
	0.0572	–*	–*	0.0009	0.9983	0.0012	0.9983	–*	–*	0.0035	0.9956	0.0005	0.9956
	0.1554	–*	–*	0.0014	0.9981	0.0017	0.9981	–*	–*	0.0046	0.9941	0.0006	0.9941
PEG4000	0.0014	–*	–*	–*	–*	0.0007	0.9987	–*	–*	–*	–*	0.0002	0.9940
	0.0572	–*	–*	–*	–*	0.0008	0.9986	–*	–*	–*	–*	0.0002	0.9928
	0.1554	–*	–*	–*	–*	0.0016	0.9983	–*	–*	–*	–*	0.0003	0.9899
AMMOENG100	0.0014	0.0028	0.9872	0.0052	0.9802	0.0060	0.9862	–†	–†	–†	–†		
	0.0572	0.0040	0.9864	0.0056	0.9786	0.0081	0.9859	–†	–†	–†	–†		
	0.1554	0.0082	0.9837	0.0087	0.9767	0.0093	0.9840	–†	–†	–†	–†		
bmimDCA	0.0014	0.0012	0.9987	0.0012	0.9987	0.0012	0.9987	0.0050	0.9997	0.0052	0.9997	0.0050	0.9997
	0.0572	0.0011	0.9986	0.0011	0.9982	0.0011	0.9982	0.0041	0.9996	0.0042	0.9995	0.0041	0.9995
	0.1554	0.0016	0.9984	0.0016	0.9983	0.0016	0.9983	0.0051	0.9995	0.0052	0.9995	0.0051	0.9995
MeOH	0.0014	0.0493	0.9963	0.0739	0.9929	0.0989	0.9885	0.5830	0.9999	0.6827	0.9997	0.7474	0.9996
	0.0565	0.0712	0.9966	0.1008	0.9940	0.1328	0.9889	0.6497	0.9999	0.7306	0.9998	0.7874	0.9995
	0.1551	0.1126	0.9967	0.1408	0.9943	0.1755	0.9896	0.7216	0.9998	0.7700	0.9997	0.8130	0.9995

$w_{\mathrm{LA,init.}}$ corresponds to the initial mass fraction of linoleic acid in soybean oil while cloud points $w_{\mathrm{sol}}^{\mathrm{oilrich}}$ and $w_{\mathrm{sol}}^{\mathrm{sol.rich}}$ are mass fractions of extraction solvent in the oil-rich and extraction solvent-rich sides, respectively. $x_{\mathrm{sol}}^{\mathrm{oilrich}}$ and $w_{\mathrm{sol}}^{\mathrm{sol.rich}}$ are mole fractions of extraction solvent in the oil-rich and extraction solvent-rich sides, respectively.

*PEG is solid at given temperature.

†Molar mass cannot be calculated since AMMOENG100 is an unknown isomer mixture.

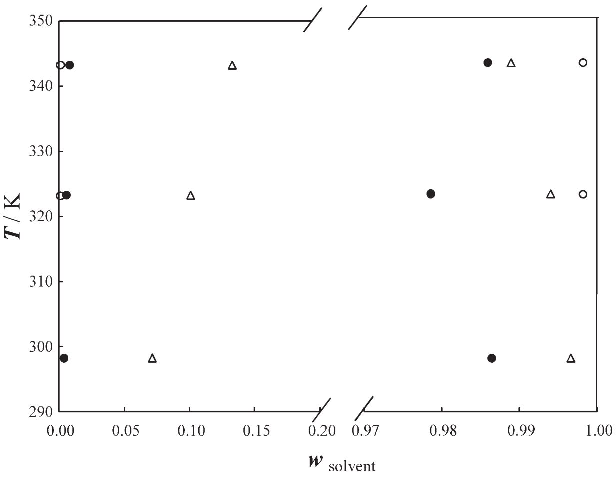

Figure 2. Temperature–mass fraction phase diagrams at atmospheric pressure of the pseudo-binary [extraction solvent + (soybean oil + linoleic acid)] mixtures.

Extraction solvent stands for either PEG2000 (empty cycles) or Ammoeng100 (filled cycles) or methanol (empty triangles). The initial compositions of the (soybean oil + linoleic acid) mixture in mass fraction of linoleic acid is 0.0572.

similar systems (sunflower oil + methanol), (canola oil + methanol), and (Jatropha curcas L. oil + methanol) have been reported by Mohsen-Nia and Khodayari,[29] Baptista et al.,[30] and Liu et al.,[31] respectively. Figure 3 shows the comparison of our results for (soybean oil + methanol) with the results for the aforementioned systems. It can be observed that the mutual solubilities in the studied systems are relatively similar, independently of the vegetable oil involved. In fact, this could be expected as the triglyceride compositions of soybean, sunflower, canola and Jatropha curcas L. oils are very much alike. All the studied solvents exhibited complete miscibility with free fatty (linoleic) acid in the studied range of temperatures.

Ternary LLE data for all the studied (linoleic acid + soybean oil + extraction solvent) systems as function of temperature, initial linoleic acid content of oil ($w_{\mathrm{LA,init.}}$) and oil to solvent ratio (L) are given in Table 3. The compositions of both solvent-rich and oil-rich phases—the tie-lines—are presented. Furthermore, Table 4 reveals the distribution of the linoleic acid between soybean oil and solvents—RTILs and PEGs containing 10 mass % of water as a function of initial linoleic acid content, at 298.2 K.

Calculations

The tie-line compositions can be used to calculate distribution coefficients, according to the relation:

$$K_i = \frac{w_i^{\text{solvent phase}}}{w_i^{\text{oil phase}}} \tag{1}$$

where $w_i^{\text{solvent phase}}$ and $w_i^{\text{oil phase}}$ are mass fractions of component i (i = linoleic acid or soybean oil) in the solvent-rich and the oil-rich phase, respectively. The separation factor α of linoleic acid and soybean oil is given as the ratio of their distribution coefficients:

$$\alpha = \frac{K_{\text{linoleic acid}}}{K_{\text{soybean oil}}} = \frac{w_{\text{LA}}^{\text{solvent phase}}}{w_{\text{oil}}^{\text{oil phase}}} \cdot \frac{w_{\text{oil}}^{\text{oil phase}}}{w_{\text{LA}}^{\text{oil phase}}} \tag{2}$$

where $w_{\text{LA}}^{\text{solvent phase}}$, $w_{\text{LA}}^{\text{oil phase}}$, $w_{\text{oil}}^{\text{solvent phase}}$ and $w_{\text{oil}}^{\text{oil phase}}$ are the mass fractions of linoleic acid (LA) and soybean oil (oil) in the respective phases. Table 3 includes the calculated values of the distribution coefficients and separation factors according to Eqs. 1 and 2 as well as the corresponding values of natural oil loss (NOL) for the given temperature expressed as:

$$\text{NOL} = \frac{w_{\text{oil}}^{\text{solvent phase}}}{L} \cdot 100 \tag{3}$$

where $w_{\text{oil}}^{\text{solvent phase}}$ and L are mass fraction of oil in solvent-rich phase and mass ratio of soybean oil and solvent used, respectively. It presents a percentage of oil taken by solvent-rich phase.

Discussion

Considering the oil with the lowest acid content studied (0.0014 mass fraction of linoleic acid) it can be concluded from Table 2 that the relative affinity of soybean oil to the various solvents follows the order methanol > PEG200 > PEG400 > AMMOENG100 > bmimDCA > PEG2000 > PEG4000. This order stands for both mass and mole fractions [in the case of AMMOENG100, mole fractions cannot be calculated, because the exact molar mass is not available due to its undefined cation alkyl chain structure (Private Communication with *Solvent Innovation*)]. Although methanol has the highest polarity of all the studied solvents it is

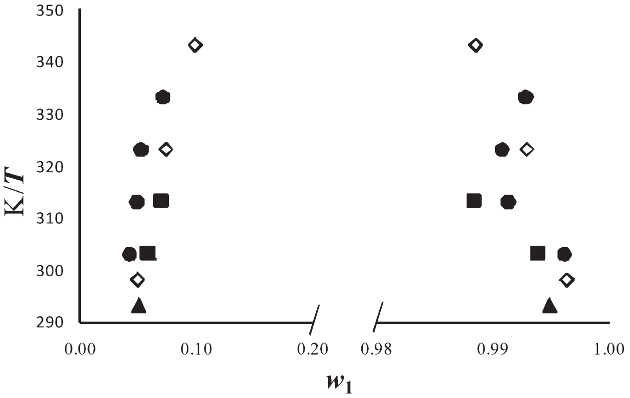

Figure 3. Temperature–mass fraction phase diagram of the (methanol + sunflower oil) mixture taken from Mohsen-Nia and Khodayari[29] (filled squares), (methanol + canola oil) mixture taken from Batista et al.[30] (filled triangles), (methanol + Jatropha curcas L. oil) taken from Liu et al.[31] (filled cycles) and (methanol + soybean oil) mixture–data from this work (empty diamonds).

Table 3. Ternary Liquid-Liquid Equilibrium Data for {Soybean Oil (Oil) + Linoleic Acid (LA) + Extraction Solvent (Sol)} Systems as Function of Temperature, Initial Linoleic Acid Mass Fraction ($w_{LA,init.}$) and Oil to Solvent Mass Ratio (L)

			Overall Composition			Oil-Rich Phase			Solvent-Rich Phase						
Solvent	L	$w_{LA,init.}$	w_{sol}	w_{oil}	w_{LA}	w_{sol}	w_{oil}	w_{LA}	w_{sol}	w_{oil}	w_{LA}	K_{LA}	K_{oil}	α	NOL
T = 298 K															
PEG 200	0.815	0.0263	0.5443	0.4437	0.0120	0.0060	0.9777	0.0163	0.9905	0.0015	0.0080	0.4908	0.0015	327.2	0.1840
	0.999	0.0515	0.4870	0.4865	0.0265	0.0060	0.9585	0.0355	0.9823	0.0020	0.0157	0.4423	0.0021	210.6	1.5716
	1.001	0.1145	0.4693	0.4699	0.0608	0.0062	0.9111	0.0827	0.9643	0.0032	0.0325	0.3930	0.0035	112.3	0.3197
	1.001	0.1733	0.4523	0.4528	0.0949	0.0063	0.8658	0.1279	0.9484	0.0042	0.0474	0.3706	0.0049	76.4	0.4195
	1.671	0.0265	0.3681	0.6152	0.0167	0.0060	0.9735	0.0205	0.9878	0.0017	0.0105	0.5122	0.0017	301.3	0.1017
	0.553	0.0263	0.6378	0.3527	0.0095	0.0060	0.9799	0.0141	0.9921	0.0014	0.0065	0.4610	0.0014	329.3	0.2532
T = 323 K															
	1.835	0.0264	0.3467	0.6361	0.0172	0.0087	0.9711	0.0202	0.9878	0.0017	0.0105	0.5198	0.0017	305.8	0.0093
	0.823	0.0238	0.5426	0.4465	0.0109	0.0082	0.9765	0.0153	0.9905	0.0015	0.0080	0.5228	0.0015	348.5	0.1820
	0.543	0.0265	0.6419	0.3486	0.0095	0.0080	0.9791	0.0129	0.9916	0.0014	0.0070	0.5426	0.0014	387.6	0.2578
T = 343 K															
	1.835	0.0264	0.3467	0.6361	0.0172	0.0119	0.9683	0.0198	0.9868	0.0017	0.0115	0.5808	0.0018	322.7	0.0926
	0.818	0.0264	0.5434	0.4445	0.0121	0.0112	0.9725	0.0163	0.9905	0.0015	0.0080	0.4908	0.0015	327.2	0.1834
	0.553	0.0265	0.6377	0.3527	0.0096	0.0105	0.9768	0.0127	0.9911	0.0014	0.0075	0.5906	0.0014	421.9	0.253
T = 298 K															
PEG 400	0.815	0.0263	0.5443	0.4437	0.012	0.0033	0.9837	0.0130	0.9871	0.0021	0.0108	0.8308	0.0021	389.2	0.2577
	0.973	0.0515	0.4936	0.4803	0.0261	0.0036	0.9678	0.0286	0.9747	0.0032	0.0221	0.7727	0.0033	234.2	0.3415
	0.999	0.1145	0.4699	0.4694	0.0607	0.0042	0.9273	0.0685	0.9486	0.0054	0.0460	0.6715	0.0058	115.8	0.5405
	0.997	0.1733	0.4534	0.4519	0.0947	0.0048	0.8868	0.1084	0.9263	0.0074	0.0663	0.6116	0.0083	73.7	0.7422
	1.839	0.0265	0.3462	0.6365	0.0173	0.0034	0.9783	0.0183	0.9807	0.0027	0.0166	0.9071	0.0028	333.0	0.1468
	0.576	0.0263	0.6283	0.3619	0.0098	0.0033	0.9862	0.0105	0.9889	0.0020	0.0091	0.8667	0.0020	433.4	0.3472
T = 323 K															
	1.840	0.0264	0.3462	0.6365	0.0173	0.0058	0.9768	0.0174	0.9813	0.0026	0.0161	0.9253	0.0027	342.7	0.1413
	0.818	0.0238	0.5441	0.4451	0.0108	0.0054	0.9830	0.0116	0.9870	0.0021	0.0109	0.9397	0.0021	447.5	0.2567
	0.539	0.0265	0.6437	0.3469	0.0094	0.0053	0.9853	0.0094	0.9889	0.0020	0.0091	0.9681	0.0020	484.0	0.3711
T = 343 K															
	1.853	0.0264	0.3444	0.6383	0.0173	0.0099	0.9731	0.0170	0.9802	0.0027	0.0171	1.0059	0.0028	359.3	0.1457
	0.821	0.0264	0.5425	0.4454	0.0121	0.0093	0.9788	0.0120	0.9857	0.0022	0.0121	1.0083	0.0022	458.3	0.2680
	0.546	0.0265	0.6407	0.3498	0.0095	0.0090	0.9812	0.0098	0.9883	0.0020	0.0097	0.9898	0.0020	494.9	0.3663
T = 343 K															
PEG 2000	1.001	0.0271	0.4929	0.4934	0.0137	0.0010	0.9863	0.0127	0.9817	0.0039	0.0144	1.1339	0.0040	283.5	0.3896
	0.999	0.0542	0.4864	0.4858	0.0278	0.0010	0.9716	0.0274	0.9674	0.0059	0.0267	0.9745	0.0061	159.8	0.5906
	1.002	0.1053	0.4717	0.4727	0.0556	0.0012	0.9426	0.0562	0.9412	0.0095	0.0493	0.8772	0.0101	86.6	0.9481
	1.026	0.1665	0.4482	0.4599	0.0919	0.0013	0.9119	0.0868	0.9034	0.0148	0.0818	0.9424	0.0162	58.1	1.4425
T = 343 K															
PEG 4000	1.060	0.0271	0.4786	0.5073	0.0141	0.0004	0.9869	0.0127	0.9797	0.0050	0.0153	1.2047	0.0051	236.2	0.4717
	1.005	0.0542	0.4849	0.4872	0.0279	0.0005	0.9725	0.0270	0.9647	0.0080	0.0273	1.0111	0.0082	123.3	0.7960
	1.003	0.1053	0.4714	0.4729	0.0557	0.0007	0.9441	0.0552	0.9362	0.0136	0.0502	0.9094	0.0144	63.2	1.3559
	1.013	0.1665	0.4514	0.4573	0.0913	0.0010	0.9135	0.0855	0.8965	0.0214	0.0821	0.9602	0.0234	41.0	2.11
T = 298 K															
bmimDCA	0.833	0.0263	0.5389	0.449	0.0121	0.0012	0.9844	0.0144	0.9884	0.0017	0.0099	0.6875	0.0017	404.4	0.2041
	1.007	0.0515	0.4851	0.4884	0.0265	0.0012	0.9673	0.0315	0.9777	0.0022	0.0201	0.6381	0.0023	277.4	0.2185
	1.001	0.1145	0.4693	0.4699	0.0608	0.0014	0.9238	0.0748	0.9572	0.0030	0.0398	0.5321	0.0032	166.3	0.3000
	0.989	0.1733	0.4553	0.4503	0.0944	0.0015	0.8812	0.1173	0.9409	0.0037	0.0554	0.4723	0.0042	112.5	0.3471
	1.732	0.0265	0.3598	0.6232	0.0170	0.0012	0.9783	0.0205	0.9880	0.0017	0.0103	0.5024	0.0017	295.5	0.0982
	0.554	0.0263	0.6374	0.3531	0.0095	0.0011	0.9867	0.0122	0.9906	0.0016	0.0078	0.6393	0.0016	399.6	0.2889
T = 323 K															
	1.829	0.0264	0.3474	0.6354	0.0172	0.0012	0.9796	0.0192	0.9786	0.0082	0.0132	0.6875	0.0084	81.8	0.4483
	0.848	0.0238	0.5351	0.4538	0.0111	0.0012	0.9853	0.0135	0.9854	0.0059	0.0087	0.6444	0.0060	107.4	0.6958
	0.562	0.0265	0.6340	0.3563	0.0097	0.0011	0.9869	0.0120	0.9863	0.0056	0.0081	0.6820	0.0057	120.4	0.9964
T = 343 K															
	1.802	0.0264	0.3508	0.6321	0.0171	0.0012	0.9806	0.0182	0.9760	0.0091	0.0149	0.8187	0.0093	88.1	0.5050
	0.841	0.0264	0.5366	0.4512	0.0122	0.0012	0.9850	0.0138	0.9825	0.0069	0.0106	0.7681	0.0070	109.7	0.8205
	0.557	0.0265	0.6361	0.3543	0.0096	0.0011	0.9871	0.0118	0.9862	0.0056	0.0082	0.6949	0.0057	121.9	1.0054
T = 298 K															
AMMOENG100	1.012	0.0263	0.4904	0.4962	0.0134	0.0026	0.9943	0.0031	0.9632	0.0134	0.0234	7.5484	0.0135	559.1	1.324
	1.002	0.0515	0.4863	0.4872	0.0265	0.0027	0.9908	0.0065	0.9410	0.0139	0.0451	6.9385	0.0140	495.6	1.3872
	0.998	0.1145	0.4701	0.4692	0.0607	0.0031	0.9802	0.0167	0.8873	0.0151	0.0976	5.8443	0.0154	379.5	1.5030
	0.998	0.1733	0.4530	0.4522	0.0948	0.0036	0.9668	0.0296	0.8404	0.0162	0.1434	4.8445	0.0153	316.6	1.6232
	1.839	0.0265	0.3462	0.6365	0.0173	0.0026	0.9925	0.0049	0.9466	0.0138	0.0396	8.0900	0.0139	582.0	0.7504
	0.542	0.0263	0.6424	0.3482	0.0094	0.0025	0.9961	0.0014	0.9734	0.0131	0.0135	9.6429	0.0132	730.5	2.4170
T = 323 K															
	1.835	0.0264	0.3467	0.6361	0.0172	0.0050	0.9893	0.0057	0.9423	0.0197	0.0380	6.6667	0.0199	335.0	1.0736
	0.841	0.0238	0.5372	0.4518	0.011	0.0049	0.9925	0.0026	0.9624	0.0198	0.0178	6.8461	0.0199	344.0	2.3543
	0.559	0.0265	0.6352	0.3551	0.0097	0.0049	0.9931	0.0020	0.9665	0.0198	0.0137	6.8500	0.0199	344.2	3.5420
T = 343 K															
	1.822	0.0264	0.3483	0.6345	0.0172	0.0065	0.9873	0.0062	0.9452	0.0180	0.0368	5.9355	0.0182	326.1	0.9879
	0.839	0.0264	0.5371	0.4507	0.0122	0.0064	0.9909	0.0027	0.9643	0.0158	0.0199	7.3704	0.0159	463.5	1.8832
	0.560	0.0265	0.6348	0.3555	0.0097	0.0064	0.9915	0.0021	0.9714	0.0150	0.0136	6.4762	0.0151	428.9	2.6786

K_{LA} and K_{oil} correspond to distribution coefficients of linoleic acid and soybean oil, respectively. α stands for separation factor while NOL is natural oil loss.

Table 4. Linoleic Acid Distribution Between Soybean Oil and Solvent Containing 10 Mass% of Water Phases as a Function of Initial Linoleic Acid Content at 298.2 K

	Overall Composition					Oil-Rich Phase	Solvent-Rich Phase	
Solvent	$w_{LA,init.}$	w_{solv}	w_{oil}	w_{LA}	w_{water}	w_{LA}	w_{LA}	K_{LA}
PEG200 + 10%H_2O	0.0262	0.4553	0.4861	0.0131	0.0455	0.0114	0.0017	0.1474
	0.0514	0.4511	0.4779	0.0259	0.0451	0.0231	0.0028	0.1197
	0.1145	0.4574	0.4400	0.0569	0.0457	0.0513	0.0056	0.1090
	0.1731	0.4559	0.4122	0.0863	0.0456	0.0791	0.0072	0.0914
PEG400 + 10%H_2O	0.0262	0.4615	0.4790	0.0129	0.0466	0.0098	0.0030	0.3089
	0.0514	0.4557	0.4727	0.0256	0.0460	0.0204	0.0053	0.2582
	0.1145	0.4545	0.4424	0.0572	0.0459	0.0468	0.0104	0.2233
	0.1733	0.4543	0.4132	0.0866	0.0459	0.0721	0.0145	0.2014
PEG2000 + 10%H_2O	0.0298	0.4482	0.4854	0.0149	0.0515	0.0093	0.0057	0.6109
	0.0571	0.4492	0.4712	0.0286	0.0510	0.0182	0.0104	0.5722
	0.1075	0.4480	0.4459	0.0537	0.0524	0.0349	0.0189	0.5409
	0.1527	0.4480	0.4251	0.0766	0.0504	0.0502	0.0265	0.5272
PEG4000 + 10%H_2O	0.0298	0.4501	0.4849	0.0149	0.0502	0.0089	0.0060	0.6787
	0.0571	0.4474	0.4725	0.0286	0.0515	0.0177	0.0109	0.6145
	0.1075	0.4504	0.4449	0.0536	0.0511	0.0333	0.0203	0.6112
	0.1527	0.4485	0.4243	0.0765	0.0507	0.0488	0.0277	0.5672
bmimDCA+ 10%H_2O	0.0261	0.4450	0.4964	0.0133	0.0453	0.0111	0.0022	0.2016
	0.0514	0.4540	0.4741	0.0257	0.0462	0.0220	0.0037	0.1681
	0.1145	0.4568	0.4399	0.0569	0.0464	0.0497	0.0071	0.1433
	0.1731	0.4537	0.4136	0.0866	0.0461	0.0777	0.0089	0.1145
AMMOENG 100 + 10%H_2O	0.0262	0.4450	0.4863	0.0131	0.0456	0.0015	0.0116	7.8980
	0.0515	0.4536	0.4752	0.0258	0.0454	0.0036	0.0222	6.2388
	0.1144	0.4544	0.4429	0.0572	0.0455	0.0099	0.0474	4.7828
	0.1732	0.4529	0.4148	0.0869	0.0454	0.0177	0.0692	3.9207

The oil to solvent mass ratio is 1:1.

the most soluble in nonpolar soybean oil. The long-chain PEGs are the least soluble while the studied ionic liquids, though being ionic compounds, are in the middle. Obviously, polarity does not count much and the presence of higher polymer chain lengths has not improved the van der Waals interactions with the corresponding aliphatic chains in triglycerides.

The increase of the acid content in the soybean oil increases its mutual solubility with the studied extraction solvents as presented in Figure 2. This effect is more pronounced in the case methanol. On the contrary, in the case of higher molar mass PEGs and ionic liquids, the mutual solubility does not change significantly with oil's acidity.

It is interesting that the temperature–composition phase diagram of the (AMMOENG100 + soybean oil) system shows an hour-glass shape, which shrinks as the acid content increases. Eventually, this would lead to the formation of both Upper Critical Solution Temperature and Lower Critical Solution Temperature if an oil with high enough acid content were used.

Table 2 and Figure 2 show that the mutual solubility of soybean oil with each of the studied alternative solvents, except AMMOENG100, is considerably lower than that with methanol, thus making them very promising media to carry out deacidification with lower losses of vegetable oil. As it can be observed from Table 2, solubility of soybean oil ($w_{LA,init.} = 0.0014$) in solvent phase at 343 K are 0.09, 0.11, 1.98, 0.13, and 0.71%, for PEG200, PEG400, Ammoeng100, bmimDCA, and methanol, respectively. On the other hand, the studied solvents are completely miscible with free fatty (linoleic) acid. It was shown in the literature[32] that, at a given temperature, the mutual solubility of triglycerides increases with an increase of the alcohol carbon chain length. The aforementioned facts apparently indicate that the alternative solvents proposed here show better potentials for the deacidification purposes than short-chain alcohols, which are considered as the best solvents in this respect.

Relatively low solubilities of ionic liquids and PEGs solvents in oil phase ($w_{sol}^{oil\ rich}$) were observed, ranging from 0.09 to 0.93 mass % depending on solvent and conditions. Eventual removal of these solvents from oil should be addressed in future studies.

Considering the values of K and α given in Table 3, it can be observed that the efficiency of the extraction—deacidification was, to some extent, influenced by temperature in the studied range. It indicates that increasing the temperature enhanced K_{LA}. On the other hand the distribution coefficient of linoleic acid decreases with increasing the initial linoleic acid content—Figure 4, which can be attributed to the enhancement of the oil-solvent mutual solubility at higher temperatures. In the case of higher molar mass PEGs (PEG2000 and PEG4000), it appears that there is a minimum of the initial value of the w_{LA}—approximately 0.10. However, there are not enough data points to prove this trend. Also, it is clear that using the higher molar mass PEGs resulted in the enhanced distribution of linoleic acid between the phases. Conversely—see Figure 5—the influence of molar mass on the separation factor α is not that straightforward. For the soybean oil with the initial mass fractions smaller than 0.1, the separation factor decreased in the order: PEG400 > PEG200 > PEG2000 > PEG4000. Deacidification of the oils with higher acid concentration ($w_{LA,init.} > 0.10$) gave similar value of separation factor whether PEG200 or PEG400 were used, while PEG2000

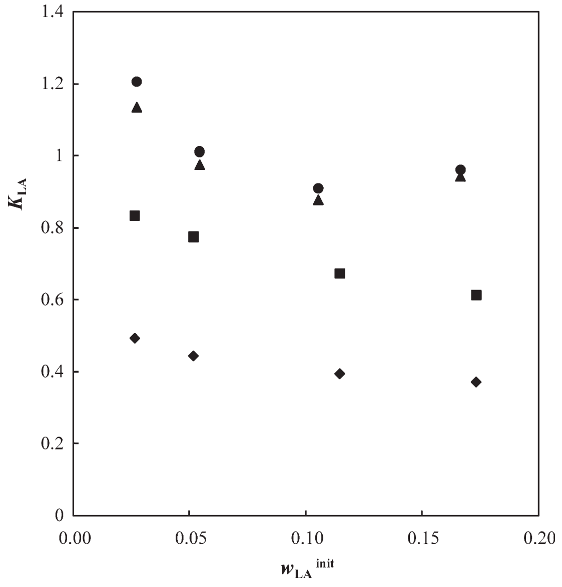

Figure 4. The influence of initial acid content of soybean oil on distribution of linoleic acid between phases using PEG200 (diamonds), PEG400 (squares), PEG2000 (triangles), and PEG4000 (cycles) for mass ratio of soybean oil and solvent (L) 1:1 at 298.2 K.

demonstrated a higher separation factor in comparison to PEG4000.

Considerably high distribution coefficients of linoleic acid between oil-rich and solvent-rich phase were obtained for AMMOENG100, ranging from approximately 5 to 8. To the best of our knowledge, these present the highest values ever reported in literature in the case of deacidification of oils by solvent extraction. The great affinity between linoleic acid and AMMOENG may be explained by the fact that AMMOENG100 ionic liquid originates from fatty acids—the COCOS alkyl chain in AMMOENG100 is a mixture having approximately 50 mass % of lauric acid alkyl chain (Private communication with solvent innovation). Somewhat smaller values were obtained using bmimDCA, as presented in Figure 6. As expected, K_{LA} and α decreased as initial acid content of oil increased.

When compared with the most studied extraction solvents, short chain alcohols, PEGs, and ionic liquids showed favorable values of neutral oil loss (NOL) which present another

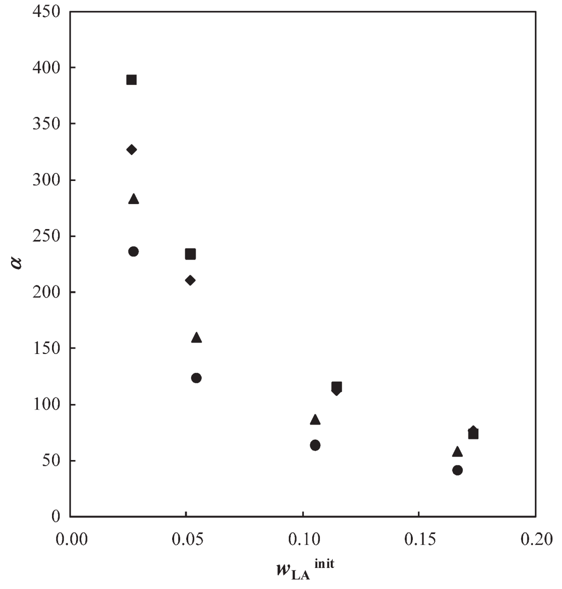

Figure 5. The influence of initial acid content of soybean oil on separation factor, using PEG200 (diamonds), PEG400 (squares), PEG2000 (triangles), and PEG4000 (cycles) for mass ratio of soybean oil and solvent (L) 1:1 at 298.2 K.

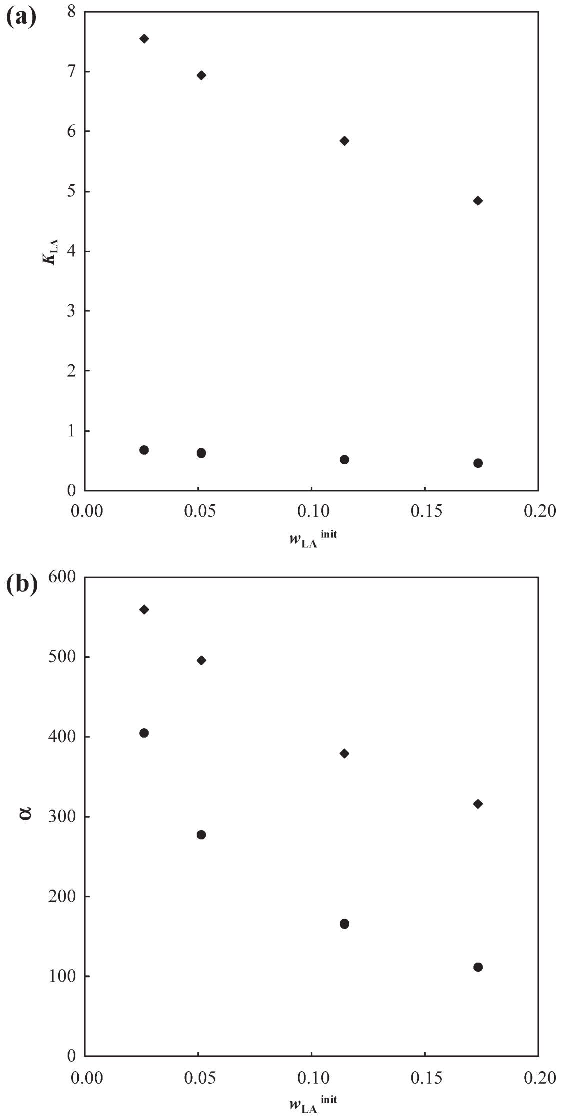

Figure 6. The influence of initial acid content of soybean oil on distribution of linoleic acid between phases (a) and on separation factor (b), using ionic liquids as extraction solvents, Ammoeng100 (diamonds) and bmimDCA (cycles) for mass ratio of soybean oil and solvent (L) 1:1 at 298.2 K.

Table 5. Normal Boiling Points, Critical Temperatures and Acentric Factors of the Components of the Studied Mixtures

	T_b/K	T_c/K	P_c/MPa	ω
AMOENG100-1 ($m + n = 4$, $M_w = 561$)	1275.1	1549.4	11.30	1.1109
AMOENG100-2 ($m + n = 6$, $M_w = 649$)	1411.4	1754.7	9.72	0.7482
AMOENG100-3 ($m + n = 8$, $M_w = 737$)	1547.8	1997.6	8.53	0.3768
[C$_4$mim][DCA]	783	1035.8	24.4	0.8419
PEG 200	565.5	726.6	2.43	1.1467
PEG 400	685.7	839.4	1.02	0.9844
PEG 2000	1260	1800	10	0‡
PEG 4000	1260	1800	10	0‡
Linoleic acid tri-methyl ester (C18:2)*	826.8	958.8	0.344	0.4461
Linoleic acid (C18:2)†	626.8	798.4	1.29	0.7749

*This ester was taken as a pseudo-component that represents a complex mixture of esters that constitute the deacidified soybean oil used in this study—see Table 1.

†This acid was taken as a major one that influences the acid number of the studied soybean oil.

‡Higher values of the acentric factor ($\omega = 0.5$; $\omega = 2.0$, and $\omega = 2.5$) have not given better correlation results.

important parameter for the extraction process design decisions. On average, the NOL in this study is 0.10%, having the highest value of 3.51% for AMMOENG100 at 323.2 K (Table 3). The typical NOL loss when using short chain alcohols is 5%.[33]

In this work, the influence of water addition to the extraction solvents was investigated as well. Table 4 presents the distribution of linoleic acid between the two phases at 298.2 K, as a function of initial mass fraction of linoleic acid, when the solvent containing 10 mass % of water is used. The distribution coefficient of linoleic acid decreases with increasing the initial acid content. As in the case of the pure solvents, water containing PEGs show the same influence of molar mass on K_{LA}. However, higher distribution coefficients were obtained using aqueous higher molar mass PEGs. It is possible to compare the results when 10% water containing solvents were used with pure solvents (Table 3). The presence of water in studied extraction solvents demonstrated unfavorable influence on related distribution coefficients. This effect was also observed in the case of short-chain alcohols by Rodrigues and Meirelles.[32]

Modeling

Experimental liquid-liquid equilibria (LLE) results of the studied ternary mixtures were correlated using the Peng-Robinson equation of state[34] coupled with the Mathias-Klotz-Prausnitz (MKP) mixing rule[35]—the PR-MKP model (for the related equations see Appendix). The correlations were carried out using the program PE 2000 developed by Pfohl et al.[36]

Normal boiling points, critical temperatures, and acentric factors of the pure components are presented in Table 5. In this respect, a few clarifications should be given. Ionic liquid AMOENG100 does not have a completely defined structure, due to two reasons[30]: (i) the total number ($m + n$) of ethylene-oxide units in the cation varies from 4 to 14 (Figure 1); (ii) since this ionic liquid originates from fatty acids the cocos alkyl chain is a variable mixture of several fatty acid alkyl chains, with that of the lauric acid having the major presence (50%). Consequently, we calculated critical parameters and acentric factors for three cases of AMOENG100, having distinct total number of ethylene-oxide units ($m + n = 4$, 6, 8). However, to simplify the calculations it was assumed that the Cocos alkyl chain is represented only by lauric acid. After such assumptions, the critical parameters and acentric factor for AMOENG100 were obtained applying the modified Lydersen-Joback-Reid method given by Valderrama and Robles.[37–39] For the ionic liquid [bmim][DCA], these values were taken directly from literature.[37] In the case of PEG200, PEG400, soybean oil, and fatty acids the boiling point, critical temperature and pressure were calculated using the method of Gani and coworkers[40,41] as in the case of other substances of high molar masses.[42,43] For soybean oil—a mixture of triglycerides—a pseudo-component had to be introduced to simplify the calculation of critical parameters. According to Table 1, we have chosen linoleic acid tri-methyl ester (C18:2) to represent the mixture. For fatty acids, linoleic acid was chosen as a major one. The acentric factor for PEG200 was obtained using the Lee-Kesler equation,[44] while for PEG400 the method of Gani had to be applied, because otherwise the optimization could not converge. For PEG2000 and PEG4000, we assumed critical temperature and pressure that were suggested as universal for all polymers,[45] $T_c = 1800$ K and $P_c = 1$ MPa. The boiling point of these polymers was estimated using the usual ratio of $T_b/T_c \approx 0.7$ for hydrogen bonding substances. In respect to acentric factor, it was accepted to be zero because this assumption gave very good correlations, which was not the case when the higher values were tried—see Table 5.

The obtained binary interaction parameters and average absolute deviations of the calculations are given in Table 6. It can be concluded that the PR-MKP model correlated very well with the presented experimental LLE ternary data, in the temperature range of 298.15–343.15 K. This conclusion stands even more if one takes into consideration that the studied systems are quite complex consisting of components that (i) posses versatile solvent properties (ionic liquids[46]), (ii) provide strong hydrogen bonds both as proton donors and proton acceptors (PEG200 and PEG400—see Ref. 25), (iii) allow van der Waals interactions due to long aliphatic chains (FFAs), and (iv) are real polymers for which the calculation of critical parameters and acentric factors is still open to discussion.[47–49] Even more, some of the components are mixtures themselves and had to be represented by a pseudo-component (see above). Consequently, the fact that the mixtures could not be well represented by using only a simple, quadratic mixing rule indicates the presence of diverse, specific interactions—thus, the values of the MKP mixing rule interaction parameter λ_{ij} are quite different from zero, in most of the studied cases. However, it has to be

Table 6. Binary Interaction Parameters of the PR MKP Model and Average Absolute Deviations of the Compositions in the Solvent- (δ') and the Oil-Rich Phase (δ'') for the Ternary Systems Free Fatty Acid (1) + Soybean Oil (2) + Solvent (3)

T/K	k_{12} l_{12} λ_{12}	k_{13} l_{13} λ_{13}	k_{23} l_{23} λ_{23}	δ'	δ''
Fatty acid (1) + Soybean oil (2) + AMOENG100-1 (3)					
298.15	−0.080679	0.048278	0.083427	0.00290	0.00596
	0.095925	0.045103	−0.200556		
	0.095585	0.042606	0.424885		
323.15	−0.461921	0.033590	−0.009857	0.00506	0.008290
	0.040503	0.023489	0.004162		
	0.027374	0.011237	0.009886		
343.15	−0.223727	−0.120178	−0.155206	0.000239	0.006795
	0.403410	0.079153	−0.230815		
	0.331274	0.143916	0.720764		
Fatty acid (1) + Soybean oil (2) + AMOENG100-2 (3)					
298.15	0.252106	0.064883	0.030915	0.000859	0.000558
	0.325086	0.048310	0.228311		
	−0.084222	0.003034	0.226023		
323.15	0.469544	−0.080976	0.095072	0.000353	0.000018
	0.364355	−0.086013	0.288399		
	−0.283796	−0.169117	0.298793		
343.15	−0.143485	−0.140293	−0.056889	0.000268	0.007790
	0.481890	0.073047	−0.243582		
	0.355085	0.138382	0.629935		
Fatty acid (1) + Soybean oil (2) + AMOENG100-3 (3)					
298.15	0.094244	−0.048970	0.203600	0.000656	0.000410
	0.330985	0.067419	0.263382		
	−0.119958	0.052020	0.219077		
323.15	−0.004996	0.069252	−0.035413	0.000059	0.000013
	0.071652	0.031504	0.045370		
	0.003001	0.014846	0.018845		
343.15	0.014076	0.119657	−0.023001	0.000330	0.000265
	0.114103	0.057382	0.054430		
	0.080054	−0.008207	0.036962		
Fatty acid (1) + Soybean oil (2) + [C$_4$MIM][DCA] (3)					
298.15	−0.154756	0.040381	−0.346614	0.000325	0.000612
	0.053152	0.050819	0.069408		
	0.012959	−0.051495	0.007826		
323.15	0.048013	0.002231	−0.190083	0.000075	0.001056
	0.072684	−0.004880	0.170321		
	0.048825	0.012348	0.004079		
343.15	−0.191719	0.380312	−0.366503	0.000092	0.000391
	0.223361	0.450290	0.086141		
	−0.301898	−0.015471	−0.224926		
Fatty acid (1) + Soybean oil (2) + PEG200 (3)					
298.15	−0.042238	0.012890	−0.068378	0.000444	0.000654
	0.009003	−0.015330	0.173410		
	0.018525	0.014626	−0.001475		
323.15	−0.035614	0.010621	−0.059516	0.000663	0.000225
	0.031411	−0.015234	0.145775		
	0.119937	0.039394	0.025993		
343.15	−0.043676	−0.270756	−0.135644	0.000414	0.000361
	−0.343123	−0.126524	0.048414		
	−0.000013	0.661582	0.118408		
Fatty acid (1) + Soybean oil (2) + PEG400 (3)					
298.15	−0.402695	−0.023196	−0.032593	0.000699	0.000806
	−0.068364	−0.004347	0.193910		
	0.062236	0.018193	0.011458		
323.15	−0.586571	−0.093307	0.324492	0.000268	0.000124
	0.225287	0.118454	0.478780		
	−0.455892	−0.241950	0.165539		
343.15	0.119944	0.095394	−0.143479	0.000094	0.000104
	0.110471	−0.030535	0.066055		
	0.110471	−0.036407	−0.053556		
Fatty acid (1) + Soybean oil (2) + PEG2000 (3)					
343.15	0.041918	0.109927	−0.138994	0.001642	0.003613
	0.041650	−0.000350	−0.189530		
	0.032137	−0.091010	−0.164828		
Fatty acid (1) + Soybean oil (2) + PEG4000 (3)					
343.15	−0.030897	0.121900	0.113515	0.000503	0.001929
	0.089043	0.106737	0.015657		
	0.139119	0.010579	−0.218234		

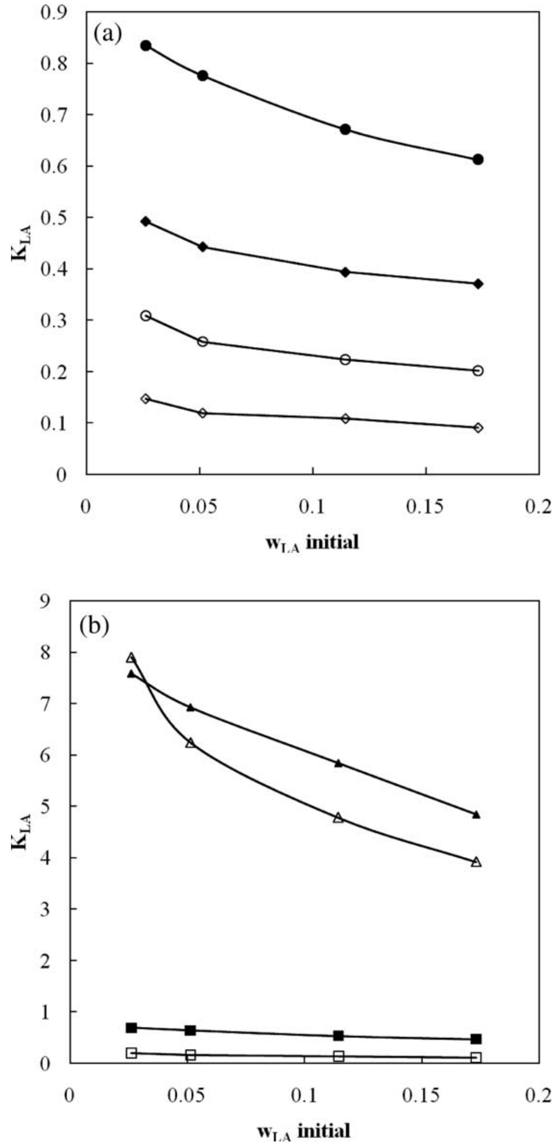

Figure 7. Comparison of partition coefficient as a function of initial linoleic acid content using oil to solvent ration of 1:1 at 298.2 K for

(a) pure PEG200 (filled diamonds), 0.9 mass fraction PEG200 + 0.1 mass fraction water (empty diamonds), pure PEG400 (filled cycles) and 0.9 mass fraction PEG400 + 0.1 mass fraction water (empty cycles); (b) pure bmimDCA (filled squares), 0.9 mass fraction bmimDCA + 0.1 mass fraction water (empty squares), Ammoeng100 (filled triangles) and 0.9 mass fraction Ammoeng + 0.1 mass fraction water (empty triangles).

mentioned that the prediction of data using the parameters obtained at 298.15 K—temperature independent parameters—did not give such good results, with the maximum absolute deviations between 0.02 and 0.03. Thus, the PR-MKP model did not exhibit fine predictive abilities.

Conclusions

PEGs ($M_w = 200$, 400, 2000, and 4000 g/mol) and RTILs, AMMOENG100 and [bmim][DCA], were tested as the alternative solvents for the deacidification of soybean oil. Liquid-liquid phase equilibrium experimental data of the binary and ternary mixtures (PEG + soybean oil), (RTIL + soybean oil), (PEG + soybean oil + linoleic acid) and (RTIL + soybean oil + linoleic acid) were obtained. All the studied solvents exhibited complete miscibility with free fatty (linoleic) acid and a very low solubility in soybean oil. Thus, they appeared as promising media for the deacidification, causing lower losses of natural oil. The highest values of linoleic acid distribution coefficient were obtained when ionic liquid AMMOENG100 was employed as extraction solvent. The partition coefficient of linoleic acid between oil-rich and solvent-rich phases is enhanced by increasing temperature and molar mass of PEG. On the other hand, the distribution of linoleic acid decreases as initial linoleic acid content increases (Figure 7).

A model based on the Peng-Robinson cubic equation of state coupled with the Mathias-Klotz-Prausnitz mixing rule showed good results in the correlation of the experimental results for the ternary studied mixtures.

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Appendix A

Peng-robinson Equation of State

$$p = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{A1}$$

$$a_i(T) = 0.45724\frac{R^2T_c^2}{P_c}[1 + (0.37464 + 1.54226\Omega - 0.266992\Omega^2)(1 - \sqrt{T_r})]^2 \tag{A2}$$

$$b_i = 0.0778\frac{RT_c}{P_c} \tag{A3}$$

Mathias-Klotz-Prausnitz Mixing Rule

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) + \sum_{i=1}^{N} x_i \left[\sum_{j=1}^{N} x_j(\sqrt{a_i a_j}\lambda_{ij})^{1/3}\right]^3 \tag{A4}$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \tag{A5}$$

$$b_{ij} - \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{A6}$$

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