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Liquid−Liquid Equilibrium in Mixtures Containing Propane-1,2,3-triol and Mixtures Containing Vegetable Oils at Atmospheric Pressure

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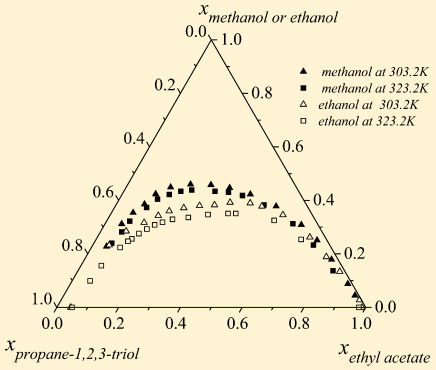
ABSTRACT: Mutual solubility of propane-1,2,3-triol with pentane, hexane, heptane, or ethyl acetate and mutual solubility between different vegetable oils (sunflower oil, soybean oil, corn oil, and olive oil) with methanol or ethanol have been reported at temperatures ranging from (298.2 to 348.2) K and atmospheric pressure. Furthermore, the binodal curves for ethyl acetate + methanol or ethanol + propane-1,2,3-triol at (303.2, 313.2, and 323.2) K have been explored. A higher solubility has been found in the system containing ethanol than the system containing methanol. The GCA-EoS model has been used to represent these mixtures. The distribution coefficient of alcohol and the selectivity of propane-1,2,3-triol in the ternary mixture of ethyl acetate + methanol or ethanol + propane-1,2,3-triol have been evaluated by GCA-EoS model. These results indicate a more effective use of propane-1,2,3-triol as separation agent by liquid−liquid extraction in the binary mixture of ethyl acetate + methanol than ethyl acetate + ethanol. On the other hand, regarding the mixtures containing vegetable oil, the mutual solubility of alcohol in the phase rich in vegetable oil is bigger than the mutual solubility of vegetable oil in the phase rich in alcohol.



1. INTRODUCTION

The liquid−liquid equilibium (LLE) has an important rol in the design and development of the separation process. The results obtained are of great importance in theoretical studies as well as in the application and parametrization of thermodynamics models. However, the experimental LLE available often shows discrepancies or is scarce. In this sense, this work presents LLE in mixtures including propane-1,2,3-triol and in mixtures including vegetables oils.

Propane-1,2,3-triol is a byproduct in the biodiesel production obtained from the transesterification of triglycerides from vegetable oils, animal fat, or microalgal oil in the presence of a short chain alcohol such as methanol or ethanol. This byproduct negatively impacts on the biofuel properties. Moreover, the benefits of its commercial sale reduced the costs of production improving the economic viability[1] of the process. The propane-1,2,3-triol is used in the fields of medicine, pharmacy, cosmetics, snuff, food processing, and as raw material in several chemical industries. For example in the production of acetals, amines, esters, ethers, mono and diglycerides, and urethane polymers.[2]

Mutual solubility of propane-1,2,3-triol + alkanes (pentane, hexane, heptane) and propane-1,2,3-triol + ethyl acetate binary systems has been explored in the temperatures ranging from (298.2 to 348.2) K. Comparable data has been found in the open literature for the mutual solubility between propane-1,2,3-triol and hexane[3] at 313.2 K with concordant results. As regards mutual solubility involving propane-1,2,3-triol, only with 2-propanone,[4] 2-butanone,[4] and pentanol[5] has been found.

Moreover, binodal curves for ethyl acetate + methanol or ethanol + propane-1,2,3-triol ternary systems in the temperatures ranging from (303.2 to 323.2) K have been explored. Regarding these kind of mixtures, no comparable data has been found in the open literature. The use of propane-1,2,3-triol as a separation agent by liquid−liquid extraction has been studied for isobutyl acetate + isobutyl alcohol,[6] 2-propanone + methanol, 2-butanone + ethanol and 2-butanone + 2-propanol[4] azeotropic binary mixtures. Cháfer et al.[6] shows the lack of ability of the propane-1,2,3-triol in the separation of isobutyl acetate + isobutyl alcohol, while Katayama et al.[4] consider propane-1,2,3-triol an interesting solvent in the separation of 2-propanone−methanol and 2-butanone−2-propanol by liquid−liquid extraction.

On the other hand, to understand the simulation and optimization of the transesterification reaction and the product recovery in the biodiesel production, knowledge about the complex phase behavior involved between the reagents (triglycerides, alcohol and catalyst) and products (biodiesel, propane-1,2,3-triol, unreacted or intermediate products, soap, and water) is essential.

According to Boocock et al.,[7] the transesterification reaction takes place in the alcohol phase, and therefore, the reaction rate depends in the intersolubility between the triglyceride and the alcohol. In this way, the mutual solubility for sunflower oil,

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soybean oil, corn oil and olive oil with methanol or ethanol in the temperatures ranging from (333.2 to 338.2) K are presented in this work.

The mutual solubility between different vegetable oils with methanol or ethanol has been reported for many researches because of its importance in the biodiesel production and they are summarized in Table 1.[1,8−22] Information available is more extensive for the systems with ethanol than for those with methanol. While methanol is the preferred alcohol short-chain, ethanol presents low toxicity and can be obtained from renewable raw materials.

Table 1. LLE of Vegetable Oils + Methanol or Ethanol Available in the Literature

alcohol	vegetable oil	T range /K[a] ref
methanol	mink oil	293−348[1]
	sunflower oil	293−348[1]
	rape seed oil	293−348[1]
	canola oil	293−303[8]
ethanol	avocado seed oil	298[9]
	babassu oil	303[10]
	canola oil	293−303,[8] 298−333,[11] 298,[12] 313−328[13]
	corn oil	298,[14] 298 −333,[11] 298[12]
	cottonseed oil	298,[15] 298,[12] 298−333[16]
	garlic oil	298[17]
	graped seed oil	298[17]
	j. curcas oil	298−333[11]
	macauba oil	298−333[11]
	palm oil	313−328,[13] 298−333[16]
	palm olein	298−333[16]
	peanut oil	298[9]
	rice bran	298−333,[16] 298−313[18]
	sesame oil	298[17]
	soybean oil	323,[19] 298−333,[16] 298,[12] 313−328,[13] 298[20]
	sunflower seed oil	298,[21] 298−333,[16] 313 K at 13 MPa and 333 K at 20 Mpa[22]

[a]At 0.1 Mpa, except when is specified.

2. EXPERIMENTAL SECTION

The materials used in this work together with the CAS number, purity and supplier are presented in Table 2. To reduce the water content in propane-1,2,3-triol, moderate temperature has been applied several days prior use. No further purification has been carried out for the remaining products.

Table 2. CAS Number, Purity and Supplier of the Reagents

compound	CAS no.	mass fraction purity	supplier
pentane	109-66-0	>0.98	Cicarelli
hexane	110-54-3	>0.96	Cicarelli
heptane	142-82-5	>0.95	Cicarelli
ethyl acetate	141-78-6	>0.995	Cicarelli
propane-1,2,3-triol	56-81-5	0.995	Biopack
methanol	67-56-1	>0.998	Cicarelli
ethanol	64-17-5	0.995	Biopack
sunflower oil		1.00	AGD S.A. Argentina
soybean oil		1.00	AGD S.A. Argentina
corn oil		1.00	Molino Cañuelas SACIFIA Argentina
olive oil		1.00	Agro Aceitunera S.A. Argentina

Table 3 presents the triglyceride compositions of sunflower oil, soybean oil,[23] corn oil, and olive oil analyzed by gas chromatography. The different oils have been subjected to alkaline saponification using 1N potassium hydroxide in methanol. Unsaponificable matter has been extracted with hexane. The fatty acids have been converted into methyl esters using 1 N H_2SO_4 in methanol and analyzed by gas chromatography (Perkin-Elmer, Shelton, CT, USA) via a fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) CP Wax 52 CB (Varian, Walnut Creek, CA, USA). The operation conditions are carrier gas N_2 at 1 mL/min, split ratio 100:1, column temperature programmed from 453.15 K (5 min) to 493.15 at 2 K/min, injector and detector (FID) temperatures at 523.15 K. The fatty acid methyl ester identification has been carried out by comparison and contrast of their retention times with those of reference compounds.

Table 3. Characterization and Chemical Composition of Triglycerides Oils

fatty acid composition (%)	sunflower oil	soybean oil[a]	corn oil	olive oil
hexadecanoic acid	5.19	10.9	10.57	18.06
cis 9-hexadecenoic acid	n.d.	n.d.	n.d.	2.15
octadecanoic acid	2.55	4.21	1.43	1.49
cis-9-octadecenoic acid	41.90	20.6	33.70	61.56
cis-9,*cis*-12-octadecadienoic acid	50.35	55.7	53.83	16.12
cis-9,*cis*-1, *cis*-15-octadecatrienoic acid	n.d.	7.84	0.47	0.61
cis-11-eicosenoic acid	n.d.	0.38	n.d.	n.d.
cis-13-docosenoic acid	n.d.	0.37	n.d.	n.d.

[a]Data obtained from Perillo and Maestri.,[23] n.d. not detected.

2.1. Mutual Solubility of Propane-1,2,3-triol with Alkanes or Ethyl Acetate. Mutual solubilities have been measured for different binary mixtures containing propane-1,2,3-triol: pentane + propane-1,2,3-triol, hexane + propane-1,2,3-triol, heptane + propane-1,2,3-triol, and ethyl acetate + propane-1,2,3-triol between (298.2 and 348.2) K. To obtain the binary mutual solubility, the two immiscible components have been added in an equilibrium vessel of 70 mL approximately at specific molar ratio at different temperatures. This vessel has been connected to a thermostatic water bath equipped with a temperature sensor that has been capable of maintaining the temperature within a fluctuation of ± 0.2 K.

The mixture has been stirred vigorously with a magnetic stirrer for 1 h and left to rest for 8 h. This led to the formation of two phases with a well defined interface. Finally, samples of the phases have been carefully collected for subsequent quantification of the components. The mass fraction w_i of the volatile compounds has been quantified from the sample by evaporation and the propane-1,2,3-triol has been calculated by difference. All weighing has been carried out in a Denver instrument APX-200 balance with an uncertainty of ± 10^{-4} g. With w_i and the molecular weight MW_i of each component, the molar fraction x_i of the binary systems have been calculated from:

$$x_i = \frac{w_i/MW_i}{\sum_i w_i/MW_i} \quad (1)$$

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For each sample and for each phase, four individual measurements have been performed and the average values are presented in Table 4.

Table 4. Mutual Solubility of Ethyl Acetate or Pentane or Hexane or Heptane + Propane-1,2,3-triol at Pressure p = 0.1 MPa[a]

	alkane/ethyl acetate phase	propane-1,2,3-triol phase
T/K	x_1	x_1
	pentane (1) + propane-1,2,3-triol (2)	
298.2	0.994	0.013
303.2	0.993	0.014
	hexane (1) + propane-1,2,3-triol (2)	
303.2	0.996	0.012
308.2		0.013
313.2	0.996	0.013
317.2	0.995	0.014
322.2	0.995	0.013
327.2	0.995	0.014
331.2	0.995	0.015
335.2	0.994	0.016
338.2	0.994	0.016
	heptane (1) + propane-1,2,3-triol (2)	
303.2		0.010
308.2	0.996	0.010
313.2	0.997	0.010
318.2	0.996	
323.2	0.997	0.010
328.2	0.996	0.011
333.2	0.996	0.011
	ethyl acetate (1) + propane-1,2,3-triol (2)	
301.2	0.989	
303.2	0.988	0.045
308.2	0.987	0.046
313.2	0.985	0.048
319.2	0.983	0.049
323.2	0.978	0.049
325.2	0.979	0.050
329.2	0.974	
334.2	0.970	0.052
343.2	0.966	0.053
348.2	0.962	0.054

[a]Standard uncertainties u are $u(T)$ = 0.2 K and $u(x)$ = 0.002.

2.2. Binodal Curve of the Ethyl Acetate + Methanol or Ethanol + Propane-1,2,3-triol Ternary System. Phase boundaries at (303.2, 313.2, and 323.2) K for ethyl acetate + methanol + propane-1,2,3-triol and ethyl acetate + ethanol + propane-1,2,3-triol have been obtained by turbidimetric analysis using the titration method under isothermal conditions following the procedure of Zhou et al.[2] The equilibrium vessel has been connected to the thermostatic water bath. Each component has been titrated using a syringe. An analytical balance has been used to quantify the weight before and after the titration procedure.

To obtain the phase rich in ethyl acetate, in the ethyl acetate + methanol + propane-1,2,3-triol ternary system, a known volume of ethyl acetate and methanol has been added to the vessel and titrated with propane-1,2,3-triol, with continuous stirring, until the mixture changed from transparent to turbid. In the case of the phase rich in propane-1,2,3-triol, a mixture of propane-1,2,3-triol and methanol has been titrated with ethyl acetate until the cloud point was visible. By titrating methanol, into a known mixture of ethyl acetate + propane-1,2,3-triol from a turbid to transparent solution, the data around the meeting point between the two branches of solubility curve has been obtained.

Knowing the weight of propane-1,2,3-triol, ethyl acetate and methanol used in the titrations, the corresponding solubility curve has been obtained at different temperatures.

The same procedure has been done for the ternary mixture of ethyl acetate + ethanol + propane-1,2,3-triol at (303.2, 313.2, and 323.2) K. This information is available in Table 5 for ethyl acetate + methanol + propane-1,2,3-triol and ethyl acetate + ethanol + propane-1,2,3-triol ternary mixtures.

Table 5. Binodal Curves in Molar Fraction of Ethyl Acetate + Methanol or Ethanol + Propane-1,2,3-triol at (303.2, 313.2, and 323.2) K and Pressure p = 0.1 MPa[a]

T = 303.2K		T = 313.2K		T = 323.2K	
x_1	x_2	x_1	x_2	x_1	x_2
ethyl acetate (1) + methanol (2) + propane-1,2,3-triol (3)					
0.943	0.045	0.888	0.092	0.826	0.137
0.898	0.088	0.811	0.163	0.714	0.233
0.800	0.179	0.701	0.256	0.608	0.313
0.717	0.251	0.598	0.325	0.479	0.383
0.637	0.309	0.482	0.389	0.392	0.418
0.521	0.378	0.383	0.426	0.341	0.430
0.415	0.423	0.300	0.441	0.295	0.434
0.336	0.447	0.236	0.448	0.217	0.439
0.270	0.458	0.196	0.448	0.210	0.438
0.203	0.460	0.153	0.440	0.184	0.434
0.144	0.449	0.114	0.413	0.153	0.422
0.108	0.424	0.095	0.384	0.124	0.404
0.091	0.386	0.073	0.348	0.104	0.373
0.070	0.354	0.065	0.313	0.075	0.322
0.054	0.312	0.058	0.267	0.069	0.282
0.047	0.228	0.054	0.220	0.058	0.240
ethyl acetate (1) + ethanol (2) + propane-1,2,3-triol (3)					
0.966	0.028	0.958	0.022	0.664	0.254
0.849	0.134	0.840	0.128	0.541	0.325
0.778	0.189	0.740	0.210	0.404	0.351
0.688	0.262	0.541	0.338	0.379	0.351
0.559	0.346	0.460	0.367	0.316	0.347
0.475	0.378	0.423	0.373	0.258	0.336
0.431	0.390	0.348	0.374	0.210	0.329
0.365	0.392	0.303	0.370	0.183	0.318
0.319	0.383	0.257	0.362	0.163	0.308
0.272	0.380	0.200	0.348	0.145	0.293
0.225	0.372	0.163	0.332	0.128	0.276
0.184	0.360	0.133	0.314	0.115	0.256
0.157	0.343	0.115	0.292	0.107	0.247
0.124	0.317	0.096	0.264	0.093	0.224
0.082	0.285	0.074	0.219	0.066	0.156
0.053	0.233	0.057	0.100	0.058	0.099

[a]Standard uncertainties u are $u(T)$ = 0.2 K and $u(x)$ = 0.002.

2.3. Mutual Solubility between Methanol or Ethanol with Vegetable Oils. The mutual solubility between sunflower oil, soybean oil, corn oil and olive oil with methanol or ethanol has been explored at atmospheric pressure in the temperatures ranging from (303.2 to 338.2) K. This data, reported in Table 6, has been obtained using the same

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procedure for the mutual solubility containing propane-1,2,3-triol, mentioned in section 2.1.

Table 6. Mutual Solubility of Methanol or Ethanol in Different Vegetable Oils at Pressure p = 0.1 MPa[a]

	alcohol phase	vegetable oil phase		alcohol phase	vegetable oil phase
T/K	w_1	w_1	T/K	w_1	w_1
methanol (1) + sunflower oil (2)			ethanol (1) + sunflower oil (2)		
303.2	0.994	0.041	303.2	0.935	0.160
313.2	0.991	0.043	308.2	0.922	0.171
319.2	0.990	0.053	313.2	0.913	0.196
323.2	0.990	0.053	318.2	0.906	0.211
328.2	0.989	0.059	323.2	0.889	0.231
333.2	0.988	0.059	328.2	0.868	0.286
			333.2	0.839	0.342
			338.2	0.812	0.440
methanol (1) + soybean oil (2)			ethanol (1) + soybean oil (2)		
303.2	0.992	0.057	303.2	0.934	0.161
308.2	0.992	0.060	308.2	0.928	0.166
313.2	0.992	0.066	313.2	0.923	0.176
318.2	0.991	0.070	318.2	0.899	0.202
323.2	0.990	0.075	323.2	0.881	0.226
328.2	0.988	0.081	328.2	0.855	0.284
333.2	0.986	0.088	331.2	0.812	0.302
			337.2	0.695	0.418
methanol (1) + corn oil (2)			ethanol (1) + corn oil (2)		
303.2	0.999	0.055	303.2	0.950	0.147
308.2	0.998	0.053	308.2	0.931	0.166
313.2	0.995		313.2	0.923	0.191
318.2	0.989	0.068	318.2	0.912	0.201
323.2	0.989	0.072	323.2	0.894	0.222
328.2	0.991	0.084	327.2	0.891	0.242
332.2	0.983	0.088	335.2	0.852	0.284
methanol (1) + olive oil (2)			ethanol (1) + olive oil (2)		
308.2	0.994	0.052	304.2	0.922	0.165
313.2	0.995	0.051	308.2	0.921	0.179
318.2	0.988		314.2	0.901	0.196
323.2	0.989	0.057	318.2	0.891	0.215
328.2	0.987	0.061	323.2	0.867	0.243
333.2	0.985	0.067	328.2	0.855	0.274
338.2	0.985	0.077	333.2	0.824	0.297
			337.2	0.799	0.320

[a]Standard uncertainties u are $u(T)$ = 0.2 K, $u(w)$ = 0.003, and $u(w)$ = 0.01 for systems with methanol and ethanol respectively.

As the high molecular weight of the vegetable oils produces an insignificant molar fraction of vegetable oils in the alcohol phase, the experimental and thermodynamic modeling of the mixtures containing vegetable oils has been performed in mass fraction.

3. THERMODYNAMICS MODELING

The group contribution equation of state GC-EoS has been proposed originally by Skjold-Jørgensen[24] with a later extension reported by Gros et al.[25] to take account the associative contributions to the residual properties. This model shows good predictive capabilities to represent vapor−liquid, liquid−liquid and vapor−liquid−liquid equilibria of highly asymmetric mixtures[26,27] and cover wide temperature range and pressures up to about 30 MPa.[28] This model has been employed to model the mixtures containing propane-1,2,3-triol and the mixtures containing vegetable oil reported in this work.

3.1. Mixtures Containing Propane-1,2,3-triol. These kinds of mixtures include the mutual solubility between propane-1,2,3-triol with pentane, hexane, heptane, and ethyl acetate and the binodal curve between ethyl acetate + methanol or ethanol + propane-1,2,3-triol. The dispersive force is quantified considering propane-1,2,3-triol, methanol and ethanol as molecular groups. Ethyl acetate is conformed by one CH_2COO ester group and two CH_3 paraffinic groups while the alkanes are represented by two CH_3 and 3, 4, and 5 CH_2 paraffinic groups for pentane, hexane, and heptane respectively.

Alcohol hydroxyl group (OH) and glycerol hydroxyl group (OH^{gly}) are the association group present in the alcohol and the propane-1,2,3-triol molecules with one and three associating groups respectively, while the ethyl acetate is represented by one associating ester group ($COOCH_2$).[29] Each OH and OH^{Gly} group has one electronegative O site and one electropositive H site. On the other hand, association in methyl ester is considered to take place through a single electron-donor site in the ester $COOCH_2$ functional group. The ester associating group does not self-associate, but can cross-associate with the electropositive site, of OH and OH^{Gly} groups. Andreatta et al.[29] describe the self- and cross-association models in this kind of mixture.

The binary systems of ethyl acetate + propane-1,2,3-triol and alkanes + propane-1,2,3-triol and the ternary system of ethyl acetate + methanol + propane-1,2,3-triol have been predicted from the parameters reported in Andreatta et al.,[29] while the ternary mixture of ethyl acetate + ethanol + propane-1,2,3-triol has been predicted with the parameters reported in Andreatta.[30]

3.2. Mixtures Containing Vegetable Oils. Espinosa[31] explains the characterization of vegetables oils from a pseudomolecule with a defined chemical structure, using the experimental information obtained from the saponification index and yodo index. The pseudomolecule of triacylglyceride proposed is the following:

$$[(CH_2COO)_2CHCOO](CH=CH)_n(CH_2)_m(CH_3)_3 \quad (2)$$

where the term in brackets represents the triglyceride functional group (TG), while m and n are the total number of CH_2 and CH═CH groups present in the vegetable oil. The average molecular weight $\overline{MW}_{oil}$, and the values m and n of the vegetable oil can be calculated from the sum of the molecular weight contribution of each group, the yodo index Y, and saponification index S as:

$$\overline{MW}_{oil} = Mw_{TG} + mMw_{CH_2} + nMw_{CH=CH} + 3Mw_{CH_3} \quad (3)$$

$$S = \frac{168270}{MW} \quad (4)$$

$$Y = \frac{25380n}{MW} \quad (5)$$

In this work, Y and S have been calculated by duplicating according to the methodology reported by Pearson[32] and Panreac Quimica S.A.[33] analytical methods in foods respectively. After calculation, the values m and n have been rounding to the nearest integer number to represent the amount of CH_2 and CH═CH respectively. All this information with the critical

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Table 7. $\overline{MW}_{oil}$, *S*, *Y*, Group Conformation and Critical Properties of the Different Vegetable Oils

				GCA-EoS model conformation				critical properties		
	$\overline{MW}_{oil}$	*S*	*Y*	TG	CH_2 (*m*)	CH=CH (*n*)	CH_3	T_c[a]/K	P_c[b]/MPa	d_c[c]/cm.mol^{-1}
sunflower oil	898.5	187.3	122.4	1	41	4	3	1047.1	0.233	11.88
soybean oil	889.2	189.2	134.5	1	39	5	3	1047.4	0.236	11.85
corn oil	888.2	189.5	120.9	1	40	4	3	1043.6	0.240	11.80
olive oil	876.8	191.9	89.6	1	41	3	3	1039.8	0.243	11.74

[a]Estimated by Fedors group contribution equation of state reported in Reid et al.[34] [b]Estimated by Joback group contribution approach reported in Poling et al. [35] [c]Estimated by Espinosa correlation [26] from van der Walls radio.

Table 8. Table of Parameters of GCA-EoS Model Used in Systems Containing Vegetable Oils[a]

pure group parameters						
group *i*	T_i*/K	q_i	g_i*	g_i'	g_i''	ref
CH_3	600.0	0.848	316910.00	−0.9274	0.0000	28
CH_2	600.0	0.540	356080.00	−0.8755	0.0000	28
CH_3OH	512.6	1.432	816116.00	−0.3877	0.0000	36
CH_3CH_2OH	514.0	1.972	479952.59	−0.7454	0.1544	30
TG	600.0	3.948	346350.00	−1.3460	0.0000	37
binary interaction parameters						
group *i*	group *j*	k_{ij}	k'_{ij}	α_{ij}	α_{ji}	ref
CH_3OH	CH_3	0.976	0.000	0.000	0.000	36
	CH_2	1.000	0.000	0.000	0.000	36
	TG	1.150	−0.050	1.000	0.000	this work
CH_3CH_2OH	CH_3	1.010	0.093	0.000	0.000	30
	CH_2	1.040	0.062	0.000	2.000	30
	TG	1.330	−0.001	0.800	4.400	This work
TG	CH_3/CH_2	0.860	0.000	0.000	0.000	37
association parameters						
		ϵ/k (*K*)	κ/cm^3·mol^{-1}			ref
self-association OH		2700.0	0.8621			36
cross-association OH−CCOO		2105.3	0.9916			36

[a]T*: characteristic reference temperature of each group, *q*: normalized van der Waals surface area, g*: surface energy parameter and g' and g'' its temperature dependence, k_{ij} and k'_{ij}: binary interaction parameter and its temperature dependence, α_{ij} and α_{ji}: non radomness parameters, ϵ/k and κ: energy and volume association parameters.

temperature, critical pressure and critical diameter estimated by Fedors,[34] Joback[35] and Espinosa,[26] respectively are presented in Table 7. This Table also brings the dispersive force quantification to represent the pseudomolecule of each vegetable oil with GCA-EoS model. As it can be seen in this Table, each vegetable oil contains between 3 and 5 CH=CH group. Due to the low concentration of the olefin group (CH=CH) in the vegetable oil molecules and the lack of parameters between this group with the remaining groups, the model has been simplified considering all saturated vegetables oils. The dispersive force for the remaining compounds is quantified by considering methanol and ethanol as molecular groups.

As regards the association contribution, the alcohol hydroxyl group (OH) defines the alcohol molecule with one associating group, while the triglyceride group is represented by three associating ester group ($COOCH_2$). As mentioned before, the association mechanism in this kind of mixture takes places between the electronegative site of ester group with the electropositive site of alcohol hydroxyl group.

The parameters between methanol and ethanol with TG have not been reported before and they have been obtained from the experimental mutual solubility between sunflower oil + methanol and sunflower oil + ethanol, respectively reported in Table 6. Table 8 reports the set of parameters and the bibliographic source[28,30,36,37] used in the modeling of the mixtures containing vegetables oils.

4. RESULTS

4.1. Mixtures Containing Propane-1,2,3-triol. Figure 1, shows the experimental mutual solubility for propane-1,2,3-triol + pentane, hexane, heptane or ethyl acetate regarding temperature along with the GCA-EoS predictions using the parameters reported in Andreatta et al.[29] A low solubility between the components is evident. From all these components, the ethyl acetate presents the highest mutual solubilty, while the heptane presents the lowest mutual solubility with propane-1,2,3-triol. The mutual solubility propane-1,2,3-triol + alkane increases with the decreasing of the length chain alkane. Reasonable results have been found with the GCA-EoS predictions.

Figure 2 shows the experimental binodal curve and the GCA-EoS predictions of the binodal curves and tie lines for the ethyl acetate + methanol + propane-1,2,3-triol and ethyl acetate + ethanol + propane-1,2,3-triol with the parameters reported in Andreatta et al.[29] and Andreatta[30] respectively. The pairs ethyl acetate/alcohol and propane-1,2,3-triol/alcohol are completely soluble, while the pair ethyl acetate/propane-1,2,3-triol is partially soluble. The alcohol is distributed between the phases of ethyl acetate and propane-1,2,3-triol. The solubility region

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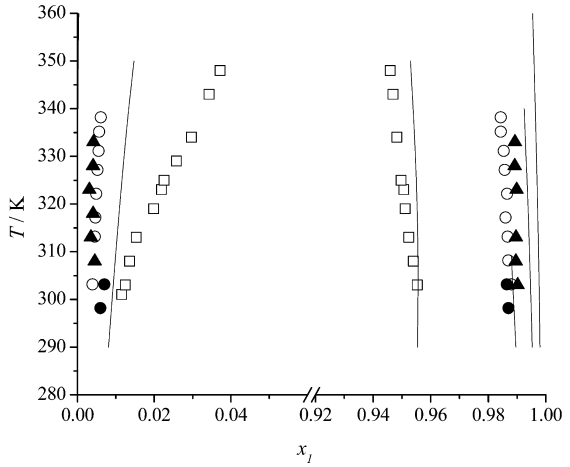

Figure 1. Experimental (symbols) and GCA-EoS predictions (lines) of mutual solubility in molar fraction of propane-1,2,3-triol (1) with ethyl acetate, □; pentane, ●; hexane, ○; and heptane, ▲ at 0.1 MPa.

increases slightly with the temperature. The system containing ethanol presents higher solubility than the system containing methanol, because ethyl acetate is more soluble in ethanol than in methanol.

The distribution coefficient of alcohol (K_2) has been defined as the ratio between the molar fraction of alcohol in the phase rich in propane-1,2,3-triol (GLY) and the molar fraction of alcohol in the phase rich in ethyl acetate (EA). From this definition, high values of K_2 mean high concentrations of alcohol in the propane-1,2,3-triol phase and low concentration of alcohol in the ethyl acetate phase.

$$K_2 = \frac{x_2^{\mathrm{GLY}}}{x_2^{\mathrm{EA}}} \tag{6}$$

According the GCA-EoS predictions, the tie lines for the ethyl acetate + methanol + propane-1,2,3-triol (Figure 2a), show a propane-1,2,3-triol phase richer in methanol than ethyl acetate phase. These results are in agreement with similar family components such as hexanoic acid methyl ester + methanol + propane-1,2,3-triol,[29] decanoic acid methyl ester + methanol + propane-1,2,3-triol[29] and methyl oleate + methanol + propane-1,2,3-triol.[36] This situation is related with high values in K_2 predicted by GCA-EoS as it can be seen from Figure 2c. By contrast, Figure 2b shows the GCA-EoS predictions for the tie lines of ethyl acetate + ethanol + propane-1,2,3-triol ternary mixture showing an ethyl acetate phase richer in ethanol than the propane-1,2,3-triol phase. These results are in concordance with those reported by Cháfer et al.[6] for isobutyl acetate + isobutyl alcohol + propane-1,2,3-triol ternary system. As a result, the GCA-EoS predicts K_2 values lower than one in wide range composition as it can be seen from Figure 2c. From this Figure, also can be predicted K_2 values higher for the systems containing methanol than for the one containing ethanol due a higher mutual solubility of ethanol with ethyl acetate and propane-1,2,3-triol than those of methanol systems.

The selectivity of the propane-1,2,3-triol (S_3)[38] in the ternary mixture of ethyl acetate (1) + methanol or ethanol (2) + propane-1,2,3-triol (3) has been defined as

$$S_3 = \frac{(x_2/x_1)^{\mathrm{GLY}}}{(x_2/x_1)^{\mathrm{EA}}} \tag{7}$$

where x_1 and x_2 are the molar fraction of ethyl acetate and alcohol in GLY and EA phases, respectively. In this case, this property indicates the suitability of propane-1,2,3-triol for separating ethyl acetate of methanol or ethanol by liquid−liquid extraction. The GCA-EoS predictions at 303.2 K show high values for S_3 in both ternary systems studied. These values decrease with increasing alcohol molar fraction because higher amounts of alcohol increase the mutual solubility of the propane-1,2,3-triol and ethyl acetate phases. Furthermore, these values are higher for the systems containing methanol than for the one containing ethanol as it can be seen from Figure 2c. No remarkable difference has been found with the temperature. According GCA-EoS predictions, the use of propane-1,2,3-triol as separation agent by liquid−liquid extraction would be more effective in ethyl acetate + methanol than ethyl acetate + ethanol binary mixtures due to their high values of K_2 and S_3.

4.2. Mixtures Containing Vegetable Oils. Figure 3 shows the mutual solubility for methanol and ethanol with sunflower oil reported in this work, and includes a comparison to the data available in the literature reported in Table 1 with agreement results. As it can be seen from this Figure, the solubility is bigger for the system containing ethanol than for

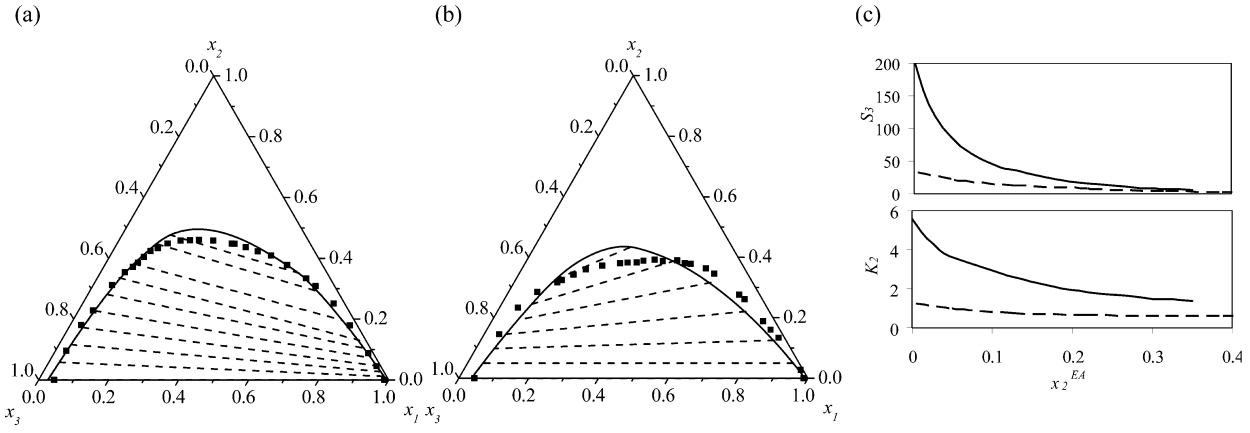

Figure 2. Experimental (symbols) and GCA-EoS predictions (lines) for LLE of ethyl acetate (1) + methanol (2) + propane-1,2,3-triol (3) (a) and ethyl acetate (1) + ethanol (2) + propane-1,2,3-triol (3) (b) at 303.2K. (c) GCA-EoS predictions for selectivity of propane-1,2,3-triol (S_3) and distribution coefficient of alcohol (K_2) in ethyl acetate + methanol + propane-1,2,3-triol (solid lines) and ethyl acetate + ethanol + propane-1,2,3-triol (dashed lines) ternary systems at 303.2 K. The values are reported in molar fraction.

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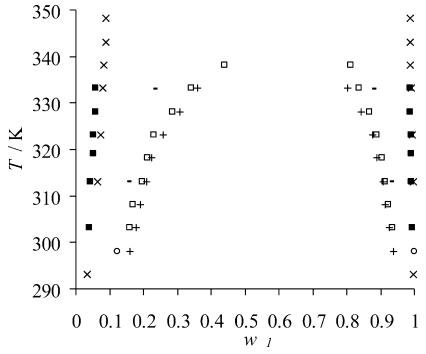

Figure 3. Comparison between experimental mutual solubility in mass fraction of methanol ■ (1) + sunflower oil (2) and ethanol □ (1) + sunflower oil (2) binary mixture obtained in this work and those available in the literature: methanol ×[1] and ethanol +,[16] o[21] and −[22] at (13 and 20) MPa respectively. The values are reported in mass fraction.

the one containing methanol, which contributes to have a biodiesel reaction in homogeneus phase in a broader concentration range. Figure 4a,b shows the experimental and GCA-EoS modeling of the mutual solubility for the different vegetable oils with methanol and ethanol respectively. Correlations have been obtained for the mixtures containing sunflower oil and predictions for remaining vegetable oils. It can be observed that this solubility increases with the temperature but the increase in temperature is lower for the system containing methanol than for the one containing ethanol. Furthermore, the mutual solubility of the alcohol in the vegetable oil phase is bigger than the mutual solubility of vegetable oil in the alcohol phase. Moreover, almost no difference can be observed in the solubility of the different vegetable oils dissolved in the methanol phase, as it is showed in Figure 4.a. These results are in agreement with those reported by Čerče et al.[1] According to the GCA-EoS modeling, the highest solubility of methanol in the vegetable oil has been found with the corn oil and olive oil, while the highest solubility of ethanol in the vegetable oil has been found in the sunflower oil and olive oil.

5. CONCLUSIONS

New experimental data have been reported for mutual solubility of propane-1,2,3-triol + alkanes or ethyl acetate and methanol or ethanol with sunflower oil, soybean oil, corn oil, and olive oil. Binodal curves for the ternary systems have been reported for ethyl acetate + methanol or ethanol + propane-1,2,3-triol ternary mixture at atmospheric pressure. All the mixtures involved in this study have been represented correctly by the GCA-EoS model. According to GCA-EoS predictions, the use of propane-1,2,3-triol as a separation agent by liquid−liquid extraction would be more effective in ethyl acetate + methanol than the ethyl acetate + ethanol binary mixtures.

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Notes

The authors declare no competing financial interest.

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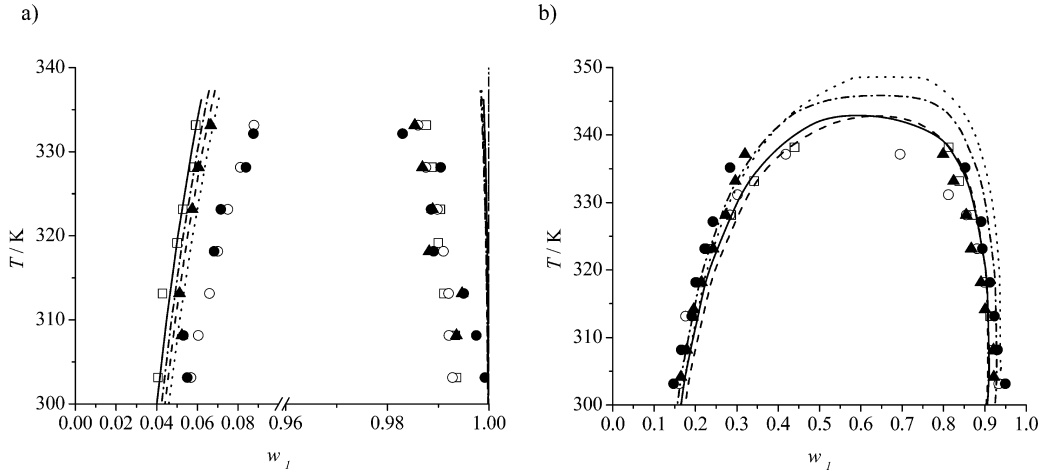

Figure 4. LLE of methanol (1) + vegetable oil (2) (a) and ethanol (1) + vegetable oil (2) (b). The vegetable oils are: □/—, sunflower oil, o/−·, soybean oil, ●/..., corn oil, ▲/---, olive oil. The symbols are the experimental data while the solid lines and dashes lines are the GCA-EoS correlations and predictions, respectively. The values are reported in mass fraction.

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