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Phase equilibria of glycerol containing systems and their description with the Cubic-Plus-Association (CPA) Equation of State

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ABSTRACT

Biodiesel is nowadays in Europe the most used biofuel for road transportation. During its production, different separation and purification processes are required for the glycerol rich streams such as the recovery of the unreacted alcohol and the removal of water. The adequate design of the recovery and purification steps requires the knowledge about the vapour–liquid equilibria data for water + glycerol and alcohol + glycerol systems that are surprisingly scarce. To overcome this lack of information, experimental measurements for 5 alcohol + glycerol systems were performed. These data were used to evaluate the capability of the Cubic-Plus-Association Equation of State (CPA EoS) to model systems containing glycerol.

To achieve a good description of the experimental data a new association scheme is proposed for the glycerol molecule. It is shown that a very good description of the VLE data with average deviations inferior to 1% for the bubble point temperatures is obtained. Two different cross-associating combining rules were tested with similar results.

Furthermore the predictive performance of the model is evaluated for multicomponent systems. Good liquid–liquid equilibria predictions are obtained for the ternary system methanol + glycerol + methyl oleate at four different temperatures.

1. Introduction

Biodiesel is now being seen as a promising and sustainable short-term alternative fuel, as the continuous increase in crude oil prices, scarce resources of fossil energies and environmental concerns limit the use of petroleum-based fuels. It consists of a blend of fatty acid alkyl esters that can be mixed in all proportions with regular diesel, is made from renewable sources and presents several environmental and economical benefits [1]. For instance, it is easily biodegradable, has a more favourable combustion profile, and offers no significant storage or transport problems.

The transesterification of vegetable oils and animal fats is the most used method to produce biodiesel, generating a by-product with commercial value, glycerol [1]. A typical biodiesel production and purification facility contains three major processing sections: a transesterification unit, a biodiesel purification section and a glycerol recovery section [2]. The purification steps of the transesterification reaction are extremely important in order to provide the fuel with the quality levels required by the standards for alternative fuels. The glycerol recovery section is incorporated in order to remove as much glycerol as possible from biodiesel, since the maximum free glycerol value admissible according to the European Standard EN 14214 is 0.02 wt% [3]. Glycerol impacts negatively on the fuel properties [2,4] and profits from selling it into the commercial glycerol market reduces biodiesel production costs in 22–36% [2], improving the economic viability of biodiesel. Glycerol has several different potential uses in medical, pharmaceutical (drugs) and personal care preparations (cosmetics and toothpastes), tobacco and food processing (as a food additive, solvent, sweetener or a component of food packaging materials) and as a raw material in different chemical industries, for example, in the production of acetals, amines, esters and ethers, mono- and di-glycerides and urethane polymers [5].

The transesterification takes place in a multiphase reactor where oil reacts with an alcohol, usually in presence of a catalyst such as NaOH, to form fatty acid esters and glycerol. Commonly used alcohols are methanol or ethanol although higher chain alcohols have been suggested [6,7]. The glycerol formed separates from the oil phase and at the outlet of the reactor two liquid phases co-exist: one of them rich in glycerol and the other in fatty acid methyl esters. The unreacted alcohol is distributed between these two liquid phases [2].

A better understanding and prediction of the phase equilibria of the ternary system FAME + glycerol + methanol is required for the design and optimization of the reactor and separation unit if the reaction rate, selectivity and yield are to be improved. However

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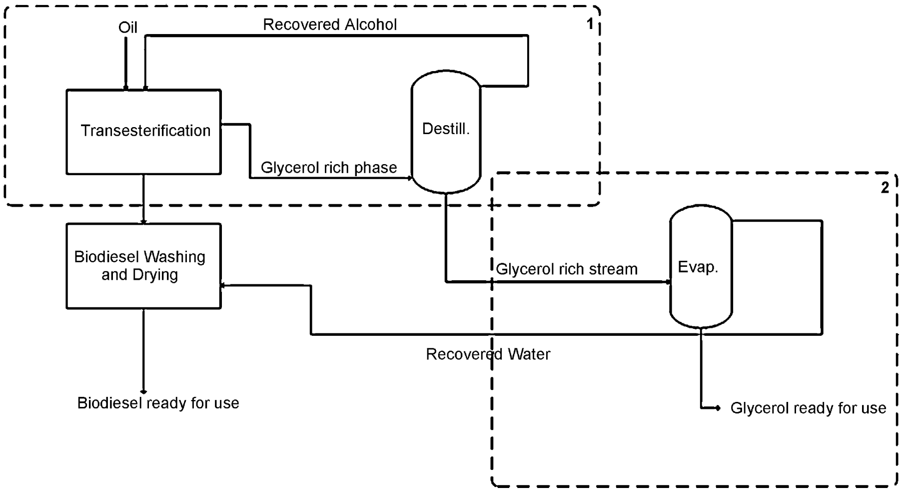

Fig. 1. Biodiesel production simplified flowsheet.

equilibria data for the products of the transesterification unit only recently became available [8–14].

After the reactor, the glycerol rich phase is sent to the alcohol recovery section where it is recovered by distillation and recycled into the reactor of the transesterification section (Fig. 1 (1)). The glycerol-rich stream from the bottom of the distillation column is then evaporated to decrease its water content [2], and to meet the specifications for sale in the glycerol market (Fig. 1 (2)). The accurate knowledge of the vapour–liquid equilibria of glycerol + alcohol and glycerol + water systems is thus essential for the design of the separation and purification processes of the glycerol recovery section.

Isobaric or isothermal vapour–liquid equilibria data are not available in the literature for binary systems with glycerol and alcohols greater than methanol. For that reason, in this work, new VLE measurements at atmospheric pressure were performed for binary systems with glycerol and alcohols up to C_4.

As glycerol, water and alcohols are associating molecules, equations of state that do not explicitly describe association interactions are expected to perform poorly for these systems. The SAFT EoS had already been successfully applied to the description of the vapour–liquid equilibria of the binary system water + glycerol and to the ternary water/1,3-propanediol/glycerol, in the work of Li and Englezos [15], with binary interaction parameters obtained from experimental data of the binary subsystems. The difficulty of the description of the water + glycerol system can be hinted from this work by the fact that among the several binary systems studied only the glycerol + water system requires two temperature dependent binary interaction parameters in order to obtain an adequate description of the data.

Another association equation of state is the Cubic-Plus-Association Equation of State. It combines the cubic Peng–Robinson or Soave–Redlich–Kwong equations of state for describing the physical interactions with the association contribution proposed by Wertheim. This equation of state has already shown to be able to describe the mutual solubilities of binary mixtures of water and hydrocarbons [16–18]. It was also successfully applied to systems with cross-associating components such as water + alcohol [19,20], and can take into account the solvation phenomena occurring between water and aromatic hydrocarbons [21,22], olefinic hydrocarbons [22], aromatic perfluorocarbons [23] and esters [24]. Concerning polyols the CPA EoS has been successfully applied to systems containing glycols + aromatic or olefinic hydrocarbons [22], glycols + *n*-alcohols [25] and glycols + water [26], but never to glycerol containing systems.

In previous works we have shown that the CPA EoS can be successfully applied to model systems of interest for the biodiesel production such as the water solubility in biodiesels [24], and the mutual solubilities of water and fatty acids [27]. In this work, the CPA EoS is extended to other systems of interest for the biodiesel production process, in particular to systems containing glycerol. A new association scheme with 6 association sites is implemented in order to adequately describe the glycerol molecule. Results using this association scheme are compared with those obtained for the four-site (4C) scheme. This scheme was selected for comparison since it had already been successfully applied to glycols with the CPA EoS [28], as will be discussed more extensively later in the model section.

A discussion about the most appropriate CPA pure component parameters for glycerol is presented. Two associating combining rules are evaluated for the description of the VLE data for glycerol + alcohol systems. Using the glycerol description here proposed derived from the VLE data, the predictive performance of the CPA EoS for the description of the LLE of the ternary system methanol + glycerol + methyl oleate at four different temperatures and atmospheric pressure is attempted.

2. Experimental

2.1. Chemicals

Glycerol (SIGMA, ≥99%, water content: 241 ppm), methanol (FLUKA, ≥99.8%, water content: 32 ppm), ethanol (Riedel-de-Haen, ≥99.8%, water content: 173 ppm), 1-propanol (FLUKA, ≥99.8%, water content: 538 ppm), 2-propanol (FLUKA, ≥99.8%, water content: 147 ppm) and 1-butanol (Carlo Erba, ≥99.5%, water content: 133 ppm) were stored with zeolite 4A to minimize their water content and were used without further purification. The water content was determined using a Metrohm 831 Karl–Fischer (KF) coulometer.

2.2. Apparatus and procedures

Isobaric VLE data (T, x) at atmospheric pressure was measured using the ebuliometer presented in Fig. 2. The ebuliometer is composed of a boiling still with a port for liquid sampling/injection and a condenser. The temperature control is done using a thermostatic bath. The pressure was kept constant trough a vacuum line with a calibrated Baratron Heated Capacitance Manometer 728A MKS, with an accuracy of 0.50%. The total volume of the still was

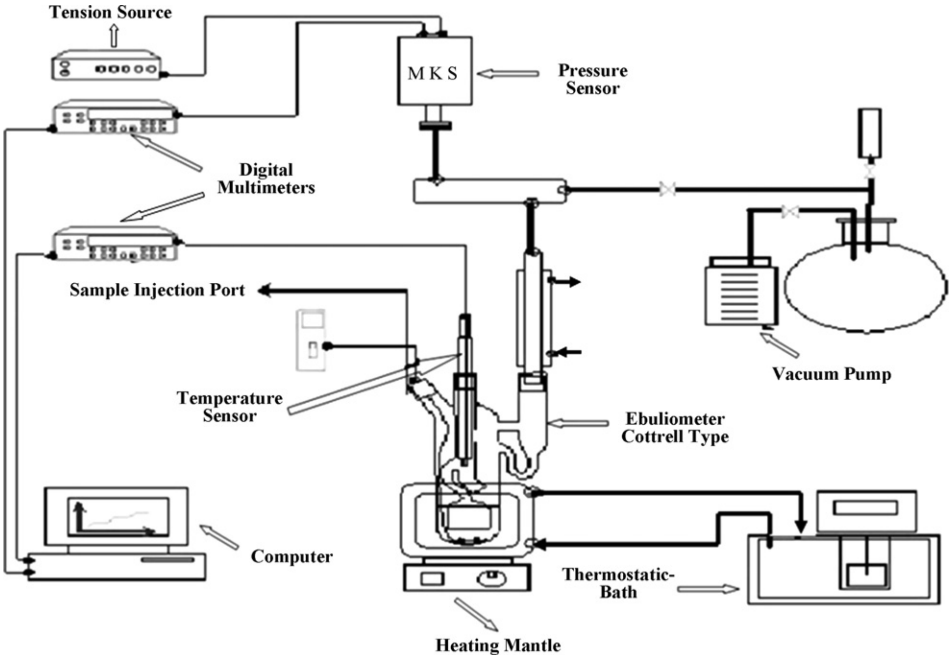

Fig. 2. Description of the ebuliometer.

about 50 ml, of which about 30 ml was occupied by the liquid solution.

In the measurements a liquid solution rich in glycerol was introduced into the boiling still and heated to its boiling point while mixing with a magnetic stirrer. The temperature was measured using a calibrated Pt100 temperature sensor with an uncertainty of 0.05 K, and the liquid phase sampled and its composition measured. Subsequently fixed amounts of water or alcohol were introduced into the ebuliometer to change the mixture composition and the procedure repeated. Refractive index measurements were used for analyzing the composition of the binary liquid mixtures in the boiling still, using an Abbe type refractometer, with an uncertainty of 1×10^{-4}. The adequacy of the apparatus for these measurements was demonstrated with measurements of vapour–liquid equilibrium data for the binary system water + glycerol, as will be shown in Section 4.1.

3. Model

The simplified CPA EoS version, proposed by Kontogeorgis et al. [29,30], combines a physical contribution (in this work from the Soave–Redlich–Kwong (SRK) EoS) with an association contribution, originally proposed by Wertheim and used in other associating equations of state such as SAFT, accounting for intermolecular hydrogen bonding and solvation effects [17,31,32]. In terms of the compressibility factor the CPA EoS can be expressed as:

$$Z = Z^{\text{phys.}} + Z^{\text{assoc.}} = \frac{1}{1-b\rho} - \frac{a\rho}{RT(1+b\rho)} - \frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1-X_{Ai}) \quad (1)$$

where a is the energy parameter, b the co-volume parameter, ρ is the molar density, g a simplified hard-sphere radial distribution function, X_{Ai} the mole fraction of pure component i not bonded at site A and x_i is the mole fraction of component i.

The pure component energy parameter of CPA is given by a Soave-type temperature dependency, while b is temperature independent:

$$a(T) = a_0\left[1 + c_1\left(1 - \sqrt{T_r}\right)\right]^2 \quad (2)$$

where a_0 and c_1 are regressed from pure component vapor pressure and liquid density data.

X_{Ai} is related to the association strength $\Delta^{A_iB_j}$ between sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{Ai} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}} \quad (3)$$

where

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right] b_{ij}\beta^{A_iB_j} \quad (4)$$

where $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are the association energy and the association volume, respectively.

The simplified radial distribution function, $g(\rho)$ is given by:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \text{where} \quad \eta = \frac{1}{4}b\rho \quad (5)$$

For non-associating components, such as esters, CPA has three pure component parameters (a_0, c_1 and b) while for associating components like water, glycerol and alcohols it has five (a_0, c_1, b, ε, β). In both cases, these parameters are regressed simultaneously from pure component experimental data using the following objective function:

$$\text{OF} = \sum_i^{NP}\left(\frac{P_i^{\text{exp.}} - P_i^{\text{calc.}}}{P_i^{\text{exp.}}}\right)^2 + \sum_i^{NP}\left(\frac{\rho_i^{\text{exp.}} - \rho_i^{\text{calc.}}}{\rho_i^{\text{exp.}}}\right)^2 \quad (6)$$

When CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (7)$$

Table 1
VLE experimental results at atmospheric pressure for several alcohol + glycerol systems and water + glycerol.

Glycerol + water		Glycerol + methanol		Glycerol + ethanol		Glycerol + 1-propanol		Glycerol + 2-propanol		Glycerol + 1-butanol	
X_{water}	T_b/K	$x_{methanol}$	T_b/K	$x_{ethanol}$	T_b/K	$x_{1\text{-propanol}}$	T_b/K	$x_{2\text{-propanol}}$	T_b/K	$x_{1\text{-butanol}}$	T_b/K
0.1219	480.59	0.0329	451.78	0.0107	453.99	0.0418	481.69	0.0064	468.93	0.0086	485.36
0.1810	433.33	0.0487	435.40	0.0168	438.00	0.0474	467.41	0.0079	459.08	0.0219	477.97
0.2880	429.24	0.0671	423.42	0.0244	427.23	0.0559	452.42	0.0222	443.27	0.0286	467.63
0.3561	418.62	0.0911	411.38	0.0541	416.50	0.0629	435.93	0.0293	425.27	0.0353	453.44
0.4140	410.83	0.1144	399.25	0.0759	406.82	0.0698	425.04	0.0405	415.17	0.0486	444.20
0.4571	405.29	0.1590	390.55	0.0902	399.89	0.0920	415.69	0.0503	404.17	0.0671	433.81
0.5051	400.99	0.1947	382.21	0.1114	392.95	0.1111	407.05	0.0777	395.31	0.0883	425.91
0.5464	397.90	0.2325	377.27	0.1321	388.91	0.1380	402.35	0.0980	389.81	0.1068	420.02
0.5761	394.60	0.2637	373.72	0.1646	385.67	0.1646	398.25	0.1297	385.01	0.1344	416.12
0.9172	392.50	0.2914	370.57	0.1791	382.72	0.1881	395.05	0.1478	380.51	0.1540	413.02
0.6415	391.00	0.3147	368.03	0.1974	379.88	0.2088	392.21	0.1821	377.96	0.1737	410.62
0.6685	389.11	0.3426	365.28	0.2229	377.68	0.2418	390.31	0.2106	375.56	0.1997	408.82
0.6924	388.01	0.3633	361.28	0.2479	376.19	0.2606	388.51	0.2252	373.96	0.2193	407.13
0.7098	386.71	0.3932	359.38	0.2902	372.84	0.2730	387.26	0.2492	373.06	0.2349	406.63
0.7304	385.51	0.4218	358.83	0.3149	369.90	0.3001	386.16	0.2787	371.56	0.2375	406.01
0.7443	384.71	0.4447	357.24	0.3546	368.10	0.3207	385.36	0.2915	370.71	0.2764	405.38
0.7586	384.01	0.4651	356.34	0.3434	366.25	0.3339	384.71	0.3121	370.01	0.2971	404.63
		0.4848	354.49	0.4246	364.91	0.3518	383.96	0.3189	369.81	0.3036	404.23
		0.5055	353.24	0.4493	364.21	0.3753	383.41	0.3347	369.11	0.3165	403.93
		0.5216	352.14	0.4754	363.51	0.3928	383.01	0.3580	368.41	0.3294	403.33
		0.5434	351.34			0.4044	382.56			0.3553	403.19
		0.5578	350.54			0.4273	382.26			0.3682	402.93
		0.5740	349.84			0.4410	381.96			0.3876	402.53

and

$$b = \sum_i x_i b_i \tag{8}$$

For a binary mixture composed by a self-associating and a non-associating compound, the binary interaction parameter k_{ij} is the only adjustable parameter.

For extending the CPA EoS to mixtures containing cross-associating molecules, combining rules for the cross-association energy, ε^{ij}, and cross-association volume, β^{ij} (or the cross-association strength, $\Delta^{A_iB_j}$) are required. Different sets of combining rules have been proposed by several authors [33–35,20] being the CR-2 and the CR-4, as noted below, the most commonly used:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_i} + \varepsilon^{B_j}}{2}, \quad \beta^{A_iB_j} = \sqrt{\beta^{A_i}\beta^{B_j}} \tag{9}$$

which is referred as the CR-2 set [20]

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \tag{10}$$

which is referred as the CR-4 set (or Elliot rule) [20]

For the estimation of the k_{ij} parameter, the objective function employed was:

$$\mathrm{OF} = \sum_i^{NP} \left(\frac{T_b^{\text{calc.}} - T_b^{\text{exp.}}}{T_b^{\text{exp.}}} \right)^2 \tag{11}$$

In the particular case of ester + associating compound systems, cross-association occurs even if the ester itself is not a self-associating molecule. To account for solvation, the cross-association energy ($\varepsilon^{A_iB_j}$) is taken as half the associating compound association energy and the cross-association volume ($\beta^{A_iB_j}$) is left as an adjustable parameter, fitted to equilibrium data, as proposed before by Folas et al. [22]. This approach was already successfully applied to water + esters mixtures of importance for biodiesel production [24].

The association term depends on the number and type of association sites. For water, a four-site (4C) association scheme was adopted, considering that hydrogen bonding occurs between the two hydrogen atoms and the two lone pairs of electrons in the oxygen of the water molecule. For alcohols, the two-site (2B) or the three-site (3B) association schemes may be applied. The results from Huang and Radosz [36] and from Kontogeorgis et al. [30] suggest the use of the 2B scheme for alcohols, which proposes that hydrogen bonding occurs between the hydroxyl hydrogen and one of the lone pairs of electrons from the oxygen atom of another alcohol molecule.

For the ester family a single association site is considered (the ester group) that solvates (cross-associate) only with associating compounds such as water or alcohols.

The CPA EoS was previously applied to the smallest polyol, ethylene glycol, using the associating schemes 4C and 2B. It was shown that the 4C scheme produced better results, suggesting that the polyol could be considered equivalent to two alcohol molecules [28]. For others glycols (diethylene glycol and triethylene glycol) the same association scheme was selected based on the choice for ethylene glycol [28]. The 4C association scheme performed well while modelling the VLE, LLE and VLLE of systems containing ethylene glycol, water and methane [29,37], the SLE of water + MEG system [38], and the LLE of glycol + hydrocarbons systems [28].

For glycerol, the 4C associating scheme and a new one, that considers the glycerol molecule as having three similar alcohol groups, with two association sites for each OH group, therefore with 6 associating sites (3 × 2B), are investigated in this work. The use of a two-site model for each hydroxyl group for glycerol was previously suggested by Li et al. within the framework of SAFT EoS [15,39].

4. Results and discussion

4.1. Experimental results

Experimental isobaric VLE data of the binary systems glycerol + alcohols (methanol, ethanol, 1-propanol, 2-propanol and 1-butanol) and glycerol + water at atmospheric pressure are reported in Table 1.

Only for the glycerol + water system isobaric VLE data was previously available in the literature [40]. In Fig. 3 it is shown that the data measured in this work are in good agreement with the existing data, showing the adequacy of the experimental set up used for measuring the VLE of glycerol + alcohol systems. For mixtures poor in glycerol their boiling temperature does not change significantly

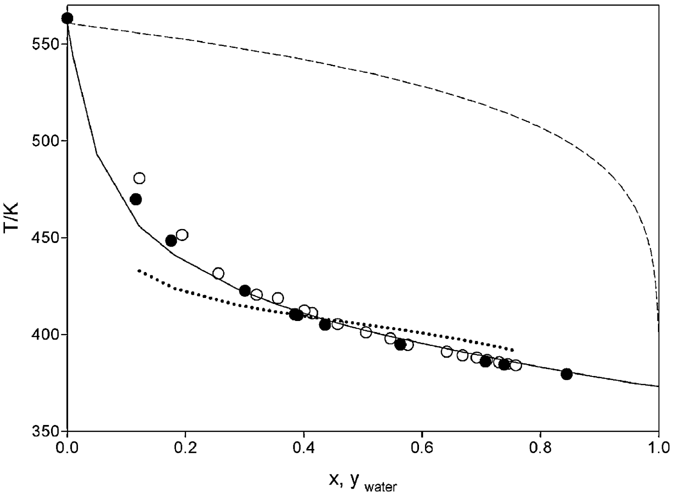

Fig. 3. CPA results for the VLE of water + glycerol using the 3 × 2B scheme (set 1 of parameters (. . .) and set 2 of parameters (liquid phase (—), vapor phase (- - -)). Experimental data (this work (○) and literature (●) [40]).

and since our intention is to study glycerol rich systems, important to characterize glycerol recovery processes in the biodiesel production, no measurements were performed for mixtures with a mole fraction of glycerol lower than 0.2.

4.2. *Correlation of the CPA pure compound parameters*

The compounds studied for the VLE in this work, are self-associating and thus five CPA pure compound parameters must be estimated. These parameters are obtained by a simultaneous regression of selected vapor pressure and saturated liquid density data, collected from the DIPPR database [41], covering the range of reduced temperatures from 0.45 to 0.85, using the objective function presented in Eq. (6). The CPA parameters for n-alcohols have been proposed in a previous work [42] while those for 2-propanol were here estimated. Their values are reported in Table 2 along with the parameters for the other compounds here studied.

For glycerol, two different association schemes (4C and 3 × 2B) were investigated. When using the 4C scheme, only one set of pure compound parameters providing a reasonable description of the liquid density and vapor pressures was obtained, with global average deviations of 1.4% and 1.1%, respectively, for the vapor pressure and liquid density. With the 3 × 2B scheme, two sets of parameters are obtained, with global average deviations inferior to 0.8% for the vapor pressure and to 1.5% for the liquid density. Results are presented in Table 2.

The parameter values are rather uniform in the two sets, except for the a_0 parameter and for the association energy parameter, ε.

The prediction performance of the model depends on the pure compound parameters, therefore the best set of parameters for glycerol will be selected based also on their suitability for modeling the VLE of binary mixtures of glycerol with alcohols from C_1 to C_4. It will be shown that the best set is the one obtained using as first estimates the ethylene glycol's CPA parameters available in the literature [28] (set 2).

4.3. *Correlation of the vapor–liquid equilibria*

To obtain a good vapour–liquid equilibria description, the fitting of the binary interaction parameter k_{ij} in Eq. (7) is required. The new experimental data obtained in this work were used for the binary interaction parameter optimization, using the objective function presented in Eq. (11). Results for the k_{ij} values and global average deviations for the bubble temperatures for the different association schemes and combining rules used are presented at Tables 3 and 4.

For glycerol, the association schemes 4C and the two 3 × 2B sets of parameters in Table 2 were evaluated.

Two combining rules, CR-2 and CR-4 (Eqs. (9) and (10)), are used in order to evaluate their correlation performance for isobaric VLE

Table 2
CPA pure compound parameters and modelling results.

Compound	T_c (K)	T_{range} (K)	a_0 (J m^3 mol^{-2})	c_1	b × 10^5 (m^3 mol^{-1})	ε (J mol^{-1})	β	AAD %	
								P^σ	ρ
Methanol	512.7	275–434	0.43	0.75	3.22	20859	0.034	0.29	0.14
Ethanol	514.7	274–436	0.68	0.94	4.75	21336	0.019	0.35	0.51
1-propanol	536.8	284–370	1.14	0.90	6.38	21913	0.008	0.13	0.34
2-propanol	508.2	235–425	1.01	1.00	6.37	21048	0.011	0.18	0.56
1-butanol	562.9	274–412	1.80	0.99	8.13	20069	0.004	0.4	0.61
Methyl oleate	764.0	384–643	10.70	1.86	33.39			4.81	
Water	647.3	291–518	0.12	0.67	1.45	16655	0.069	0.73	0.82
Glycerol									
4C			2.28	1.18	7.06	14036	0.025	1.42	1.07
3 × 2B									
Set-01	766.1	341	2.63	1.29	7.05	4794	0.007	0.53	0.56
Set-02		–651	1.21	1.06	6.96	19622	0.009	0.77	1.49

Table 3
CPA VLE results for several alcohol + glycerol systems and water + glycerol and binary interaction parameters using the CR-4 combining rule.

	k_{ij}			AAD %		
	4C	3 × 2B set 1	3 × 2B set 2	4C	3 × 2B set 1	3 × 2B set 2
Water	−0.280	−0.395	−0.229	1.16	2.13	0.72
Methanol	−0.041	−0.117	0.014	0.32	0.60	0.27
Ethanol	−0.025	−0.106	0.060	1.97	1.52	1.55
1-propanol	−0.007	−0.031	0.002	1.00	0.92	1.06
2-propanol	−0.048	−0.118	0.049	1.90	1.76	1.36
1-butanol	−0.019	−0.049	0.015	0.93	1.08	0.60
Global AAD %				1.21	1.33	0.93

Table 4
CPA VLE results for several alcohol + glycerol systems and binary interaction parameters using the CR-2 combining rule.

	CR-2 and 3 × 2B set 2	
	k_{ij}	AAD %
Methanol	0.037	0.30
Ethanol	0.066	1.55
1-propanol	0.005	1.09
2-propanol	0.048	1.35
1-butanol	0.017	0.59
Global AAD %		0.97

of glycerol + alcohol systems, using the 3 × 2B association scheme and the second set of parameters.

Very similar results are obtained when using the two rules especially for systems with the heavier alcohols. For the binary mixtures with ethanol and methanol the binary interaction parameters are slightly higher when using the CR-2 combining rule. Still the obtained global average deviations for the bubble temperatures are very similar, as seen in Tables 3 and 4. This similar behavior of the combining rules was previously observed for the VLE of the monoethylene glycol + water system [25].

As the deviations are slightly superior for the CR-2 combining rule, as well as the majority of the binary interaction parameters, and taking advantage of its increase in computational speed, the CR-4 combining rule was adopted in this work.

The results are strongly dependent on the choice of the glycerol parameters when using the 3 × 2B scheme. The first set of 3 × 2B parameters for glycerol has been found to give large and negative binary interaction parameters and higher global average deviations when modelling the VLE data for glycerol + alcohol systems. For the water + glycerol system this set of parameters fails to correlate the phase equilibrium, with a large binary interaction and produces a poor description of the VLE curve (Fig. 3).

With the second set of pure compound parameters for glycerol, positive and small binary interaction parameters are required to obtain a description of the bubble point curves with global average deviations inferior to 1% for the glycerol + alcohol systems. VLE results are depicted in Figs. 4 and 5. For methanol, 1-propanol and 1-butanol, very satisfactory results are obtained with pure predictions ($k_{ij} = 0$) with global average deviations inferior to 1.1%. For the water + glycerol mixture, a correct description of the equilibrium curve is achieved, although at the expense of a slightly larger (negative) k_{ij}. A global average deviation inferior to 0.7% for the bubble point curve was obtained for this mixture.

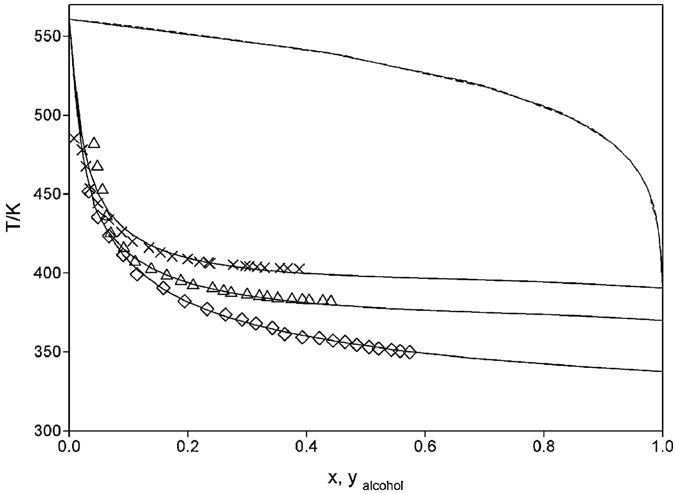

Fig. 4. VLE for alcohol + glycerol systems. Experimental (methanol + glycerol (◇), 1-propanol + glycerol (△), 1-butanol + glycerol (×)) and CPA results with 3 × 2B scheme and set 2 of parameters (liquid phase (—), vapor phase (- - -)).

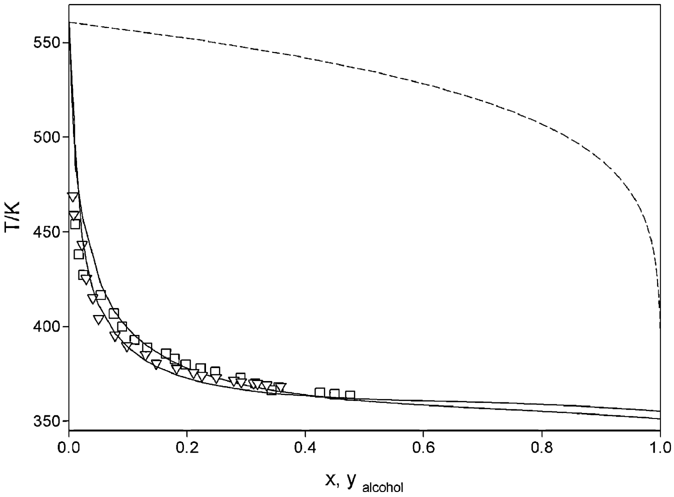

Fig. 5. VLE for alcohol + glycerol systems. Experimental (ethanol + glycerol (□), 2-propanol + glycerol (▽)) and CPA results with 3 × 2B scheme and set 2 of parameters (liquid phase (—), vapor phase (- - -)).

Using the CPA EoS with the 4C scheme for glycerol, the binary interaction parameters are higher (and negative), when compared with the results obtained when using the second set of binary interaction parameters of the 3 × 2B scheme, for the glycerol + alcohol systems. Also, global average deviations in the bubble point temperatures are higher, about 1.2%.

Positive and small binary interaction parameters when using the 3 × 2B scheme suggests that the right interactions between unlike molecules are being considered and that apparently, cross-association between glycerol and alcohols is not underestimated, what happens when using the simpler 4C scheme.

For the water + glycerol system a negative and large value for the binary interaction parameter is required for both association schemes, suggesting that the strong polar interactions between water and glycerol are underestimated by CPA.

Nevertheless, the CPA EoS performs better than the SAFT model in correlating this binary system. In the work of Li et al. [15], referred in the preceding introduction section, good results are only obtained increasing the model complexity, using two (and temperature dependent) binary interaction parameters, the binary interaction parameter for the dispersion interactions, k_{ij}, and the bonding volume parameter for the association interactions, k_{ij}^{AB}. In this work, the CPA EoS provided very good binary VLE results, requiring only a single and temperature independent k_{ij} keeping the general predictive character of the model.

The results support the choice of the 3 × 2B associating scheme for glycerol and the option for the second set of parameter values, presented in Table 2.

4.4. LLE description of the ternary system methanol + glycerol + methyl oleate

To further test the capability of the CPA EoS in predicting systems containing glycerol and alcohols the description of the LLE for the ternary system methanol + glycerol + methyl oleate was performed. Data for this ternary system were available in the literature at four different temperatures from 313 to 373 K, and at atmospheric pressure [8,9]. The CPA pure compound parameters for methyl oleate were taken from literature [24] and are presented at Table 2. The modeling was based only on binary interaction parameters of the constituent binary subsystems. Since no binary

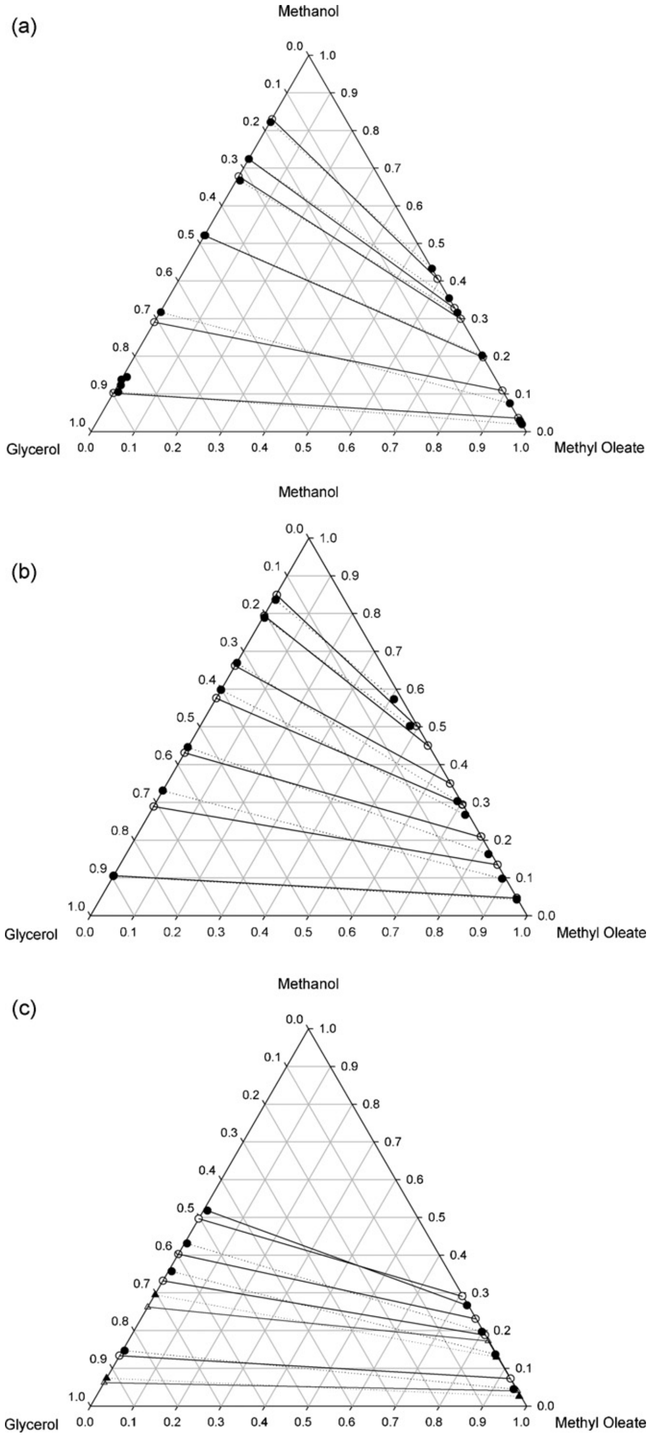

Fig. 6. (a) LLE for methanol + glycerol + methyl oleate at 313 K. CPA results ((○) and solid lines) and experimental results ((●) and dashed lines). (b) LLE for methanol + glycerol + methyl oleate at 333 K. CPA results ((○) and solid lines) and experimental results ((●) and dashed lines). (c) LLE for methanol + glycerol + methyl oleate at 353 K (CPA results ((○) and solid lines) and experimental results ((●) and dashed lines)), and at 373 K (CPA results ((△) and solid lines) and experimental results ((▲) and dashed lines)).

data were available for methyl oleate + methanol, neither for methyl oleate + glycerol it was necessary to adjust these binary interaction parameters. The CR-4 combining rule and the second set of parameters obtained with the 3 × 2B association scheme for glycerol were used. Methanol was modeled with the 2B association scheme and methyl oleate was considered to have a single site that cross-associate (solvates) with associating molecules.

Before comparing the calculated values with the literature experimental data it should be noticed that in both papers where experimental data of this ternary system were reported [8,9], the methyl oleate used was of technical grade (stated purity > 70%). Negi et al. [9] reported that 85% methyl oleate was found on their technical grade methyl oleate and that major impurities were different unsaturated and saturated C18 acids, all of these making about 97% of the technical grade methyl oleate. The modeling was carried assuming that the methyl oleate was pure.

As no equilibrium data for the methyl oleate + methanol binary are available in the literature, to consider solvation between these components the same value for β_{ij} employed before for water + fatty acid esters systems, ($\beta_{ij} = 0.201$) [24] was used. A higher value for this parameter does not seem to be adequate since the cross-association phenomena happening in methyl oleate + methanol mixtures is weaker than in water + ester systems. It was used the k_{ij} of the binary glycerol + methanol from Table 3, regressed from VLE data, and for the system methyl oleate + methanol the tuned k_{ij} was -0.027. No interaction parameters were considered for the system methyl oleate + glycerol as the methyl oleate–glycerol solubility is very low, and the addition of this parameter had no influence in the results.

Good results were obtained at all the four temperatures. The immiscibility between glycerol and methyl oleate and the methanol concentration in both phases are adequately predicted. Results are presented in Fig. 6(a–c).

In both papers where the experimental data was found, group contribution models (the original UNIFAC, the UNIFAC Dortmund, the A-UNIFAC and the GCA–EoS) were applied to the description of the reported ternary system, also considering each OH group to have two associating sites, with a reasonable agreement with the experimental data.

The CPA model was here extended to the description of the ternary mixture methyl oleate + methanol + glycerol at four different temperatures. A good description of the experimental data was obtained considering that limited data is available for optimizing the binary interaction parameters and that the available data presents considerable uncertainties in what concerns the sample composition. The results are quite encouraging in the description of the LLE of ternary or multicomponent mixtures present in biodiesel production and this will be object of future studies using the CPA EoS towards the description of the phase equilibria present in the biodiesel production process.

5. Conclusions

New experimental measurements for the vapour–liquid equilibria of glycerol + alcohol systems from methanol to 1-butanol are presented, which are of interest for the biodiesel production and purification process. The measured data for the system water + glycerol are in good agreement with previously available measurements. For the other binaries no literature data was found.

The CPA EoS was here extended to the modelling of VLE of glycerol systems. Two similar sets of CPA pure component parameters for glycerol, in terms of the good description of vapor pressure and liquid densities were obtained when using the new association scheme. VLE results were taken into account for the selection of the most adequate set of parameters for glycerol.

Two different models for glycerol, the well-known four-site (4C) and a new one suggesting 6 association sites, 3 × 2B, have been considered for the correlation of the new experimental data. The 3 × 2B scheme proved to be best for modelling the VLE data, with the smallest global average deviations, and positive and lower binary interaction parameters. Even good pure predictions ($k_{ij} = 0$) were achieved with the 3 × 2B scheme.

Also, two different combining rules were tested, CR-2 and CR-4 that showed to have similar performances.

A single, temperature independent, binary interaction parameter was enough to provide excellent description of the VLE data measured, with global average deviations inferior to 1%.

This model was extended to model the ternary mixture methyl oleate + methanol + glycerol at four different temperatures. A good description of the experimental data was obtained considering that limited data is available for optimizing the binary interaction parameters and that the available data presents considerable uncertainties in what concerns the sample composition.

List of symbols

a	energy parameter in the physical term
a_0, c_1	parameters for calculating a
A_i	site A in molecule i
b	co-volume
g	simplified hard-sphere radial distribution function
k_{ij}	binary interaction parameter
P	vapor pressure
R	gas constant
T	temperature
x	mole fraction
X_{A_i}	fraction of molecule i not bonded at site A
Z	compressibility factor

Greek symbols

β	association volume
ε	association energy
η	reduced fluid density
ρ	mole density
Δ	association strength

Subscripts

b	bubble
c	critical
i,j	pure component indices
r	reduced

Superscripts

assoc.	association
phys.	physical

List of abbreviations

AAD	average absolute deviation (%AAD = $\frac{1}{NP}\sum_{i=1}^{NP}\mathrm{ABS}\left[\frac{\mathrm{exp}_i-\mathrm{calc}_i}{\mathrm{exp}_i}\right]\times 100$)
CPA	Cubic-Plus-Association
CR	combining rule
EoS	equation of state
FAME	fatty acid methyl ester
VLE	vapor–liquid equilibria
SAFT	statistical associating fluid theory
SRK	Soave–Redlich–Kwong
UNIQUAC	universal quasi-chemical activity coefficient model
UNIFAC	universal functional activity coefficient model
NRTL	non-random two liquid model

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