



Phase equilibria description of biodiesels with water and alcohols for the optimal design of the production and purification process



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HIGHLIGHTS

- The soft-SAFT EoS was applied to assist the design of biodiesel purification units.
- Phase behavior of ester + water/alcohol mixtures were described, in broad T/P ranges.
- Ester–water/alcohol solvation explicitly considered through a new association scheme.
- Only one binary parameter ξ is used for all ester–water/alcohol mixtures.
- Water solubility in biodiesels is predicted from the ester–water binary systems.

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ABSTRACT

The water solubility in fatty acid esters and biodiesels and the vapor–liquid equilibria (VLE) of fatty acid ester + methanol/ethanol systems, formed at biodiesel production and purification industrial units, were modeled in this work to complete the development and application of the soft-SAFT equation of state (EoS) to the design and optimization of biodiesel production plants.

The soft-SAFT EoS is able to accurately describe the water solubility and the VLE of methanol and ethanol with a large number of binary systems, composed of a variety of esters, in wide ranges of temperature, including near/supercritical conditions, with the use of just one binary interaction parameter. This parameter is chain length dependent for the water systems, while it is constant for the methanol and the ethanol binary mixtures.

An entirely predictive scheme is proposed for the soft-SAFT EoS water solubility in biodiesels description, being only necessary to know the biodiesel fatty acid esters composition to determine the required molecular and binary interaction parameters. A new association scheme to explicitly consider the solvation phenomenon between esters and water/alcohols is also proposed.

The results obtained in this work with soft-SAFT are clearly superior, regarding qualitative and quantitative agreement with the experimental data and predictive ability of the model, to those obtained with other similar modeling approaches, namely with the Cubic-plus-Association equation of state (CPA EoS) and other SAFT-type EoSs, as discussed throughout the work.

The soft-SAFT EoS is shown here as a valuable tool to assist the design of biodiesel purification units, specifically for applications in the biodiesel washing, drying and alcohol removal, in order to obtain the biodiesel with the quality specifications required by the international standards.

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1. Introduction

The development of reliable thermodynamic models able to properly predict the phase equilibria of associating and non-associating pure compounds and their mixtures, in wide ranges of temperature, pressure and composition, is essential for the

proper design, optimization and operation of production facilities. For the biodiesel production industry, this thermodynamic characterization is important in order to produce the biodiesel in accordance with the quality standards established by the American Society of Testing and Materials (ASTM) D6751 [1] in North America, by the EN 14214 [2] in Europe, and by the RANP 07/08 [3] in Brazil.

Two of these imposed biodiesel quality standards are the alcohol and the water contents. Water and alcohol are introduced during the biodiesel production. Biodiesel, a blend of alkyl

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monoesters of fatty acids, is produced through a transesterification of vegetable oils with short-chain alcohols. The basic catalyzed reaction takes place in a multiphase reactor where oil reacts with an alcohol, usually in presence of a catalyst, to form fatty acid esters and glycerol. 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 (FAMES). The unreacted alcohol is distributed between these two liquid phases. The methyl ester stream leaving the transesterification reactor is then washed with acidified water to neutralize the catalyst and to convert any existing soaps to free fatty acids [4].

Higher contents of these compounds alter the biofuel properties and cause engine problems. An excess of alcohol will originate a decrease of the biodiesel densities, viscosities and flash points, and the use of the biodiesel with high amounts of alcohol on its composition will result on the deterioration of the natural rubber seals and on the corrosion of Al and Zn pieces of the engine [5,6].

Unlike diesel fuels, biodiesel is hydrophilic causing problems in the storage and use of biodiesels. Water is introduced during the biodiesel production, as explained above, and is also typically present in the distribution and storage, being even used in tanks as cleaner and ballast. However, water decreases the oxidation stability of the biodiesel, and oxidation products will be formed during long storage periods [7,8]. The presence of water in biodiesel will also cause biological growth during storage, namely yeast, fungi, and bacteria. The resulting biodiesel with a high content of water will, in the long term, originate the engine corrosion and block the injection system due to the formation of sludges and slimes [6].

The control of the amount of alcohol and water present in the biodiesel, to meet the quality standards imposed by the different norms, is carried out in the biodiesel production facility in purification units. After being washed with water, the fatty acid esters are dried to produce biodiesel with an acceptable water content [9]. Evaporations and/or distillation units are also used to remove excess alcohol from the fatty acid ester stream coming out of the transesterification reactor [9,10].

The development of modeling tools to accurately predict the water solubility in fatty acid esters and biodiesels and the VLE of fatty acid ester + alcohol systems is essential for the biodiesel production and purification processes, since they allow the choice of the best raw materials, as well as the correct design and optimization of the washing, drying and alcohol removal units and storage facilities, in order to obtain the biodiesel with the required quality. However, that is a quite difficult task since the association, solvation phenomena and sometimes the size asymmetry between the compounds, make these mixtures highly non-ideal [11–14].

A wide variety of theoretically based thermodynamic models have already been used for the description of the phase equilibria of these systems in the literature. Considering activity coefficient models, Rostami et al. [15,16] used the UNIQUAC method to successfully describe the water solubility in four biodiesels from palm, soya, corn and frying oil, with parameters regressed from the experimental data presented in the same work. Tu et al. [17] used the Margules, Wilson, NRTL and UNIQUAC models to satisfactorily describe the isobaric vapor–liquid equilibria data of the binary mixtures of methanol with methyl acetate and methyl acrylate. The same models plus the van Laar equation were used by Resa et al. [18,19] to correlate the isobaric vapor–liquid equilibria for methanol binary mixtures containing ethyl butyrate and ethyl propionate. Ortega et al. [20,21] chose the UNIFAC and the ASOG models to describe the isobaric vapor–liquid equilibria of methyl butanoate and propyl butanoate with ethanol binary systems. Using two versions of the UNIFAC model, Soto et al. [22] successfully described the isobaric vapor–liquid equilibrium data of the binary system composed of ethanol and ethyl methanoate.

Methods based on quantum mechanical (chemical) calculations have also been applied. Moderately successful results were found by Shah and Yadav [23] for the water solubility in fatty acid esters predictions with the COSMO-SAC model. Güzel and Xu [24] presented results for the prediction of the VLE of fatty acid ester + methanol/ethanol systems with the COSMO-RS model. Although the results for the ethanol systems are in agreement with the experimental data, improvements are still necessary for the description of the methanol systems.

Considering equations of state (EoSs) approaches, the high pressure vapor–liquid equilibria of methanol/ethanol + fatty acid methyl ester systems were described by Shimoyama et al. [25,26] using the Peng-Robinson (PR) EoS with different mixing rules. Results in agreement with the experimental data were obtained, nevertheless with the expense of using quite large and temperature dependent binary interaction parameters regressed from experimental data.

Equations of state that explicitly consider the effect of short-range association interactions are one of the most appropriate choices for modeling the water solubility in fatty acid esters and biodiesels and the VLE of fatty acid ester + alcohol systems. Ferreira et al. [27] used the group contribution with association equation of state (GCA-EoS) to describe ester + alcohol systems; however their study was focused only in small esters systems. The PR EoS with and without an association term was used by Arvelos et al. [28] for the description of the high pressure VLE data of the methanol/ethanol + fatty acid methyl ester systems, with the classical van der Waals mixing rules. Similar good results were obtained, but with the necessity of using temperature dependent binary interaction parameters in both approaches.

The first effort to apply an association EoS for a global and exhaustive description of fatty acid esters systems containing alcohols and water, in wide ranges of temperature and pressure, was performed by Oliveira et al. using the Cubic-Plus-Association equation of state (CPA EoS) [11–14,29]. Although in general quite good results were obtained, there is still room for improvements on the description of the water solubility in biodiesels as well as on the model predictive power for describing the VLE of ester + alcohol systems.

Improvements are expected when using more refined EoSs, such as EoSs based on statistical mechanics concepts. Among them, the Statistical Association Fluid Theory (SAFT) and its variants, which explicitly take into account the effects of molecular shape, dispersion forces and molecular association, represent an excellent choice to model those challenging systems.

Even though there is a growing interest in the description of the phase equilibria of systems of relevance for the biodiesel industry, few works have been devoted to the use of SAFT type EoSs for that purpose. Perdomo et al. [30] used the SAFT-VR equation for the description of the reactive equilibrium of the lauric acid esterification, involving the prediction of the phase equilibria of different multicomponent mixtures with acid lauric, methyl laurate, water and methanol. The same authors [31] have also used this model to describe the LLE of ternary systems composed of the fatty acid esters methyl palmitate, methyl linoleate and methyl oleate.

To our knowledge, the application of SAFT type equations to the description of water + fatty acid ester/biodiesel and methanol/ethanol + fatty acid ester systems, of key relevance for the biodiesel production and purification, has not been previously attempted. The closer contribution is the work of NguyenHuynh et al. [32], who used the polar-GC-SAFT EoS considering three different versions of SAFT, the SAFT-0, the SAFT-VR and the PC-SAFT, to describe the VLE of ester + 1-alkanol systems, but only small esters systems were considered.

In this contribution, we expand the work initiated in a previous publication [33], where a molecular model within the soft-SAFT

EoS framework was developed for 24 fatty acid methyl and ethyl esters, from C8:0 to C24:0, performing a complete and systematic thermodynamic study concerning fatty acid esters and biodiesels thermophysical properties, such as high pressure density, surface tension, speed of sound and viscosity [33]. It is our purpose to extend the excellent ability of the soft-SAFT EoS to describe fatty acid esters to the modeling of the complex phase equilibria of their binary mixtures with water, methanol and ethanol. The complex solvation interaction between esters and water/methanol/ethanol will be explicitly taken into account with the soft-SAFT EoS through a new solvation scheme here proposed.

The work is organized as follows: the next section includes a brief review of the features of soft-SAFT relevant for this work. In the results section, the molecular models for each compound and the solvation scheme proposed for mixtures are described. After that, the first mixtures addressed are the water systems followed by the alcohol systems. Mixtures composed of fatty acid esters that are major components of biodiesels are investigated and, in order to provide a systematic soft-SAFT study in what concerns cross-association and binary interaction parameters values, mixtures of methanol/ethanol with small esters are also studied, taking advantage of the available literature experimental data. The following section is focused on the description of the near/supercritical VLE of methanol and ethanol binary systems with fatty acid esters, for application on the biodiesel production process using supercritical alcohols. The final section of this work is devoted to the application of the soft-SAFT to the description of real systems through the prediction of the water solubility in four biodiesels produced from different oil sources. All the information gathered while describing pure fatty acid methyl esters [33] and their binary mixtures with water is used to propose an entirely predictive procedure, which only requires the knowledge of the biodiesel fatty acid methyl esters composition to describe the water solubility.

2. Theory

The Statistical Association Fluid Theory (SAFT) equation of state [34] is a well-established equation based on the first order thermodynamic perturbation (TPT1) of Wertheim [35–37]. It is expressed as a sum of contributions to the total free energy of the system, where different intermolecular effects are separated and quantified. Due to its accurate results when dealing with complex systems, it has become very popular in the chemical engineering field and also for practical industrial applications. There are several variants of the SAFT EoS, depending on the type of reference fluid adopted. The original version developed by Chapman et al. [34] uses a hard-sphere as the reference fluid; Gil-Villegas et al. [38] developed the SAFT-VR using a square-well with a variable range; the soft-SAFT, developed by Blas and Vega [39,40] and applied in this work, uses a Lennard–Jones as a reference fluid; and the PC-SAFT, proposed by Gross and Sadowski [41], uses a hard-chain. Other more recent and complex approaches have combined the spirit of these variants with Group-Contribution methods [42,43].

Soft-SAFT is written in terms of a sum of contributions to the total Helmholtz free energy of the system:

$$a^{res} = a - a^{id} = a^{ref} + a^{chain} + a^{assoc} + a^{polar} \quad (1)$$

where a^{res} and a^{id} are the residual Helmholtz free energy and the ideal contribution respectively. Subsequently, *ref*, *chain*, *assoc* and *polar* represent the reference term, the chain formation, the association and the polar interactions. In order to establish the simplest and more transferable model that can capture the main features of the molecule, and to facilitate its use in a practical application, the polar term for esters was omitted here. This assumption is supported by the results from a previous work [33], where fatty

acid esters thermodynamic properties were described in wide ranges of temperature and pressure using this simpler approach. The absence of a polar term can also be supported by looking to previous contributions where other thermodynamic models were applied to the description of pure fatty acid esters and their systems. For instance, Perdomo et al. [30,31,44] with the SAFT-VR, Ferreira et al. [45] and Andreatta et al. [46] with the GCA EoS, and Oliveira et al. [29] with the CPA EoS, were able to properly describe pure fatty acid esters and their binary and ternary mixtures without the inclusion of a polar term.

For the reference term, soft-SAFT uses a Lennard–Jones (LJ) spherical fluid taking into account the repulsive and the attractive interactions of the monomers forming the chain. This term defines the LJ monomer using two molecular parameters: the segment diameter, σ_{ii} , and the dispersive energy between segments, ε_{ii} [39]. The reference term is considered using the equation of Johnson et al. [47]. Since this expression is originally written for a pure fluid, the extension to mixtures is given by the van der Waals one-fluid theory with the modified Lorentz–Berthelot (LB) mixing rules for the size σ_{ij} and energy ε_{ij} parameters:

$$\sigma_{ij} = \eta_{ij} \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (2)$$

$$\varepsilon_{ij} = \xi_{ij} (\varepsilon_{ii} \varepsilon_{jj})^{1/2} \quad (3)$$

η_{ij} and ξ_{ij} are two binary parameters used to adjust the cross-segment diameter and cross-dispersive energy of the mixtures studied when the compounds have a very different structure. Values of 1 mean predictions of mixtures are obtained from pure component molecular parameters.

The chain and association terms derive directly from Wertheim's theory [35–37]:

$$a^{chain} = \rho k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (4)$$

$$a^{assoc} = \rho k_B T \sum_i x_i \sum_{\alpha} \left(\ln X_i^{\alpha} - \frac{X_i^{\alpha}}{2} \right) + \frac{M_i}{2} \quad (5)$$

being ρ the molecular density, k_B the Boltzmann constant, T the temperature, m the chain length parameter indicating the number of monomers forming the chain, x_i the molar fraction of component i , and g_{LJ} the radial distribution function at density $\rho = m \rho_{monomer}$ of a LJ spheres fluid. The description of g_{LJ} is given by fitted computer simulation data, as a function of density and temperature [48].

In the association term, X_i^{α} is the fraction of pure component i not bonded at site α , while M_i is the number of association sites of type α in component i . X_i^{α} is given by:

$$X_i^{\alpha} = \frac{1}{1 + N_{avog} \rho \sum_j x_j \sum_{\beta} X_j^{\beta} \Delta_{\alpha\beta,ij}} \quad (6)$$

The specific site-site function, $\Delta_{\alpha\beta,ij}$, includes two additional parameters describing the size and strength of the association interactions: $K_{\alpha\beta,ij}$, which is the site-site bonding-volume, and $\varepsilon_{\alpha\beta,ij}^{HB}/k_B$, which defines the site-site association energy.

The reader is referred to the original soft-SAFT papers [39,40] for more details of the different terms of the equation.

In summary, within the soft-SAFT framework, non-associating molecules are defined by three molecular parameters: the chain length, m_i , the segment diameter, σ_{ii} , and the dispersive energy between segments, ε_{ii} . For associating molecules, the site-site association energy, $\varepsilon_{\alpha\beta,ij}^{HB}$, and the site-site bonding-volume of association, $K_{\alpha\beta,ij}$ are also included to characterize the associating interactions.

3. Results and discussion

3.1. Molecular models for esters, water and alcohols

The choice of an appropriate coarse-grained model that can represent the basic physical characteristics of a fluid is fundamental for an accurate modeling of the thermodynamic properties of pure compounds and their mixtures with molecular based equations of state.

Water has been successfully addressed in several contributions with soft-SAFT, and the same approach is here adopted: it is considered to be a single spherical Lennard–Jones (LJ) monomer ($m_{\text{H}_2\text{O}} = 1$) with four associating sites, in which hydrogen bonding is occurring between the two hydrogen atoms and the two lone pairs of electrons in the oxygen of the water molecules [49].

Methanol and ethanol were previously considered by Pàmies [50] and Lovell et al. [51] as homonuclear chainlike molecules of equal diameter σ and the same dispersive energy ε . The hydroxyl group in alkanols is mimicked by two square-well sites embedded off-centre in one of the LJ segments. The molecular parameters for water and alkanols were taken from these previous publications [50–51].

Esters are considered with soft-SAFT to be non-self-associating fluids described as homonuclear chainlike molecules composed of m LJ segments of equal diameter, σ , and dispersive energy, ε , bonded tangentially to form the chain. This was the approach followed in a very recent work where the soft-SAFT was used to describe 24 fatty acid methyl and ethyl esters, from C8:0 to C24:0 [33]. As referred in the Introduction section, besides investigating the phase equilibria of aqueous and alcohol mixtures with the fatty acid esters usually present in biodiesel systems, binary mixtures of methanol/ethanol with small esters and belonging to different esters families are also here investigated. This will help to provide a systematic study on the modeling strategy by identifying parameter trends with the molecular weight of the analyzed esters.

Different approaches were applied for computing the molecular parameters of the new esters considered in this work, those not addressed in the previous publication. For the already modeled fatty acid methyl esters, from methyl caprylate (C8:0) to methyl linoleate (C24:0), the pure compound parameters previously proposed [33] were used. It was already observed in the previous work that the fatty acid methyl esters molecular parameters followed linear trends with the molecular weight, and several correlations were proposed. As a first attempt, these correlations were here used for computing the molecular parameters of the small methyl esters, methyl ethanoate, methyl butanoate, methyl hexanoate and methyl heptanoate. Using this approach, acceptable agreement was obtained for the density, while more important deviations were observed for the vapor pressures, when compared to experimental data. This is mainly caused by the fact the correlations were parameterized from longer fatty acids with very low vapor pressure values and a certain degree of uncertainty, that were only given 20% weight in the optimization process. Hence, the extrapolation of data from these conditions seems not to be accurate enough. Since one of the main goals of this work is the precise description of the VLE of esters systems, highly dependent on the quality of the description of the pure components vapor pressures, we decided to refine the previous correlations with the esters molecular weight, by including the small saturated esters (inferior to C8) for which experimental data were available. These correlations are now established using the previously gathered information for the saturated FAMES from C₈ to C₂₄ [33] (unsaturated compounds have been excluded from the regression) and adding the molecular parameters values for methyl butanoate and methyl ethanoate, regressed from pure saturated liquid densities and vapor pressures [52]:

$$m = 0.0108M_W + 2.29 \quad (7)$$

$$m\sigma^3 (\text{\AA}^3) = 1.8608M_W - 36.872 \quad (8)$$

$$m\varepsilon/k_B B (\text{K}) = 5.017M_W + 392.8 \quad (9)$$

The new correlations are in fact very close to those presented in Ref. [33]. However, the minor modifications produce important enhancements when dealing with binary systems. The predictive ability of these correlations is tested in this work through the description of the methyl hexanoate and methyl heptanoate + water solubility.

In this same work [33], it was also possible to use the molecular parameters correlations proposed for FAMES to successfully predict several FAMES thermophysical properties, such as densities, surface tensions and viscosities. Nevertheless, significant deviations had also been noticed for vapor pressures, due to the same reasons explained above. This is also expected to happen to the small ethyl esters considered here, ethyl methanoate, ethyl propanoate and ethyl butanoate, if the correlations proposed above are used for the prediction of these compounds molecular parameters. Again, aiming at providing the best description of the VLE of esters systems, the small ethyl esters molecular parameters were also regressed from available pure component vapor pressure and saturated liquid density data [52]. The same procedure was applied to hexyl acetate, belonging to an ester subfamily different than the other compounds here studied.

The results of the optimizations provided an overall deviation

(OARD)
$$\text{OARD} (\%) = \frac{\sum_{i=1}^{N_{\text{compounds}}} \sum_{j=1}^{N_{\text{Datapoints}}} \left| \frac{\text{calc}_j - \text{exp}_j}{\text{exp}_j} \right|}{N_{\text{Datapoints}}} \times 100$$
 of only 0.50% for the liquid density and of 1.43% for the vapor pressure. The sets of molecular parameters for the studied esters are presented in Table 1. For an easier identification of the esters considered in this work, their chemical structures are also depicted in Table 1. Table 2 presents the molecular parameters sets for methanol, ethanol and water.

The temperature–density and pressure–temperature diagrams for the small esters are depicted in Fig. 1a and b. For the heavier esters density and vapor pressure results, the reader is referred to our previous work [33].

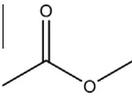
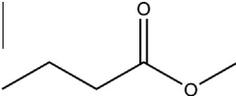
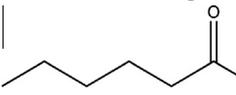
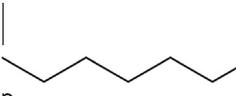
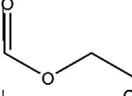
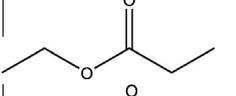
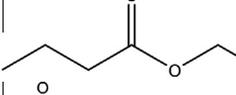
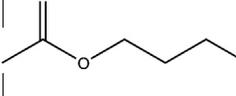
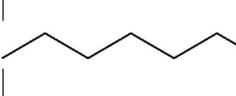
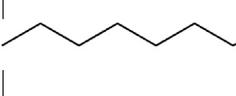
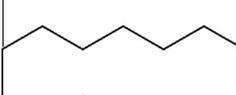
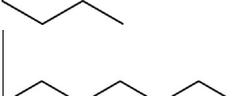
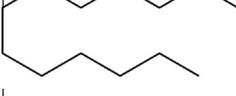
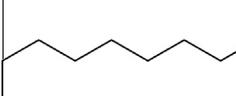
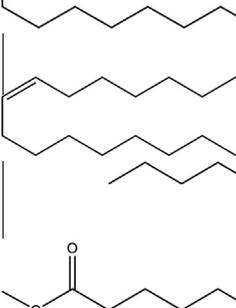
As mentioned, it is possible to observe that the molecular parameters determined in this work still follow trends with the ester molecular weight similar to those previously found for the heavier fatty acid methyl esters [33], as presented in Fig. 2, although these tiny differences cause an important impact on the vapor pressure calculations.

3.2. Water solubility in fatty acid esters description with the soft-SAFT

Once the molecular parameters of each compound are established, it is then possible to describe the phase equilibria of the binary systems. Firstly, water + fatty acid methyl ester systems are addressed, with particular focus on describing the water solubility in the ester rich phase, necessary for a correct design and operation of the biodiesel purification units. Binary systems composed of several saturated (methyl hexanoate, methyl heptanoate, methyl octanoate, methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate, and methyl octadecanoate), and unsaturated (methyl oleate and methyl linoleate) esters, were modeled here.

In the particular case of the mixtures of esters with polar compounds, only cross-association occurs even if esters are themselves non-self-association molecules [53,54]. This is a special case and different from the classical cross-association examples for which the common mixing rules can be applied. This specific issue has

Table 1
Soft-SAFT molecular parameters for the compounds considered in this work^a.

Chemical structure	Compound	m_i	σ_{ii} (Å)	ε_{ii}/k_B (K)
	Methyl ethanoate ^b	3.051	3.241	247.500
	Methyl butanoate ^b	3.419	3.546	260.437
	Methyl hexanoate ^c	3.703	3.798	285.918
	Methyl heptanoate ^c	3.853	3.902	292.647
	Ethyl methanoate ^b	2.680	3.413	261.869
	Ethyl propanoate ^b	3.595	3.492	251.410
	Ethyl butanoate ^b	3.153	3.865	280.767
	Hexyl acetate ^b	3.917	3.889	283.669
	Methyl caprylate [33]	4.043	3.986	293.900
	Methyl laurate [33]	4.568	4.291	320.831
	Methyl myristate [33]	4.940	4.374	328.605
	Methyl palmitate [33]	5.221	4.472	339.425
	Methyl stearate [33]	5.562	4.542	348.794
	Methyl oleate [33]	5.551	4.508	342.101
	Methyl linoleate [33]	5.260	4.556	343.349

^a One association site is considered for all the esters. Self-association is not permitted. Solvation is only considered through cross-association between the site of the ester and the sites representing the hydrogens of water (two) and alcohol (one) molecules.

^b Regressed in this work from VLE data.

^c Obtained from the correlations proposed in this work.

Table 2
Soft-SAFT molecular parameters for methanol, ethanol and water.

Compound	m_i	σ_{ii} (Å)	ε_{ii}/k_B (K)	$\varepsilon_{ii}^{HB}/k_B$ (K)	K_{ii}^{HB} (Å ³)
Methanol [50]	1.491	3.375	220.400	3213	4847
Ethanol [50]	1.740	3.635	234.800	3387	2641
Water [49]	1.000	3.154	365.000	2388	2932

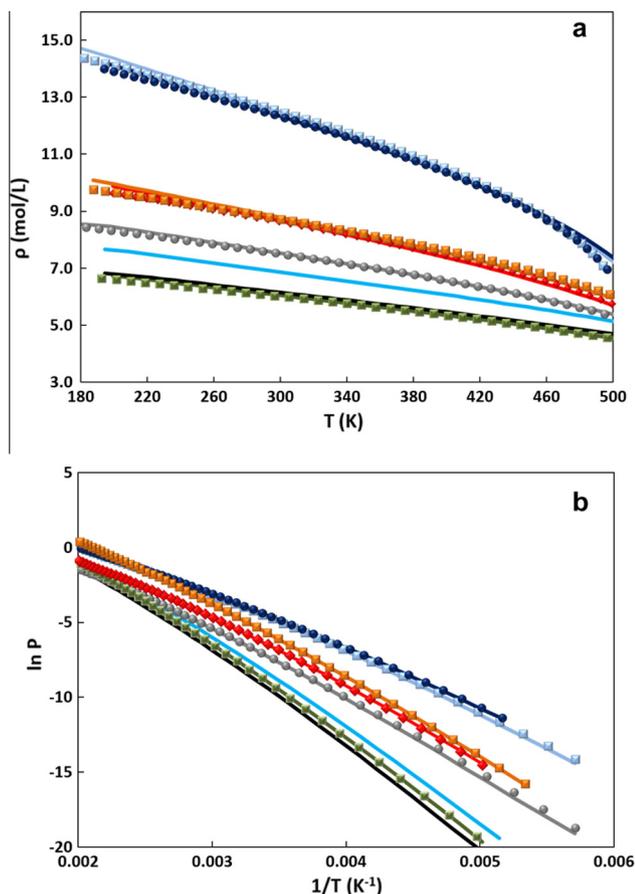


Fig. 1. Phase equilibrium properties of small esters. (a) Saturated liquid density vs. temperature and (b) vapor pressure vs. temperature. Symbols represent experimental data [52] (■, methyl ethanoate; ●, ethyl methanoate; ◆, ethyl propanoate; ■, methyl butanoate; ●, ethyl butanoate; ■, hexyl acetate) and lines are the soft-SAFT results (—, methyl hexanoate; —, methyl heptanoate).

been previously addressed with association equations of state and can be solved by adding sites to the non-associating fluid, ensuring that only cross-association is allowed. In previous work with the CPA EoS, one site was added in the ester molecule to cross-associate with the other compound (water or alcohol); the cross-association energy was taken as half of the value of the association compound energy, while the cross-association volume was regressed from phase equilibria experimental data [11,12]. In the contribution of NguyenHuynh and coworkers, the polar GC-SAFT model, using three different versions of SAFT, considered several sites with the cross-association parameters values equal to those of the associating compound. A study using this equation was also reported analyzing the number of associating sites of the ester. They concluded that one associating site provided the best results [32].

In this work using the soft-SAFT EoS, several possibilities were also evaluated. In a preliminary attempt, no cross-association between the esters and water was considered, fitting the data using only the binary parameters η and ξ , related to the size and

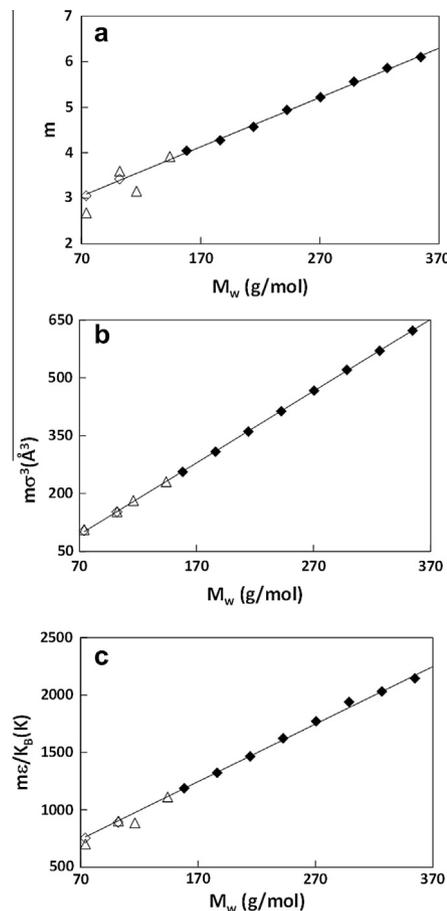


Fig. 2. Trends of the molecular parameters with the molecular weight of the compounds: for the methyl esters, this work (◇) and Oliveira et al. [33] (◆), and for the ethyl esters and hexyl acetate, this work (△): (a) Parameter m vs. molecular weight. (b) Parameter $m\sigma^3$ vs. molecular weight. (c) Parameter $m\varepsilon/k_B$ vs. molecular weight. Lines represent the proposed correlations with the molecular weight (Eqs. (7)–(9)).

dispersive energy of the monomers forming the molecule. The results showed that the cross-association phenomenon needs to be explicitly considered with the model. Taking the methyl laurate system as an example, reasonable results were only obtained using two very far from unity interaction parameters, $\eta = 0.650$ and $\xi = 2.42$ (consider that unity is an ideal case, where the values are predicted by the classical LB rules). While the value of η could still be justified, as similar values have been found in other liquid–liquid equilibria systems involving water and hydrocarbons [49] and water and ionic liquids [55,56] with soft-SAFT, the ξ value is physically unsound, representing an incredibly high cross-dispersive energy. In addition, and as depicted in Fig. 3a, the soft-SAFT temperature dependency of the water solubility does not follow the pattern than the one from the experimental data (see the dashed black line). One of the advantages of using a molecular-based equation of state, such as soft-SAFT, is the physical meaning of the parameters. This applies in this case as well. η and ξ are binary parameters to take into account the differences in size and energy of the monomers forming the molecules, but are van der Waals forces, while the interaction between the esters and the hydrogen-bonding water molecules are stronger and more localized (short-ranged), belonging to cross-associating forces in a coarse grained model. Soft-SAFT is able to consider these forces in an explicit manner.

Several options were then considered and tested for the cross-association parameters values, including the use of both, or only

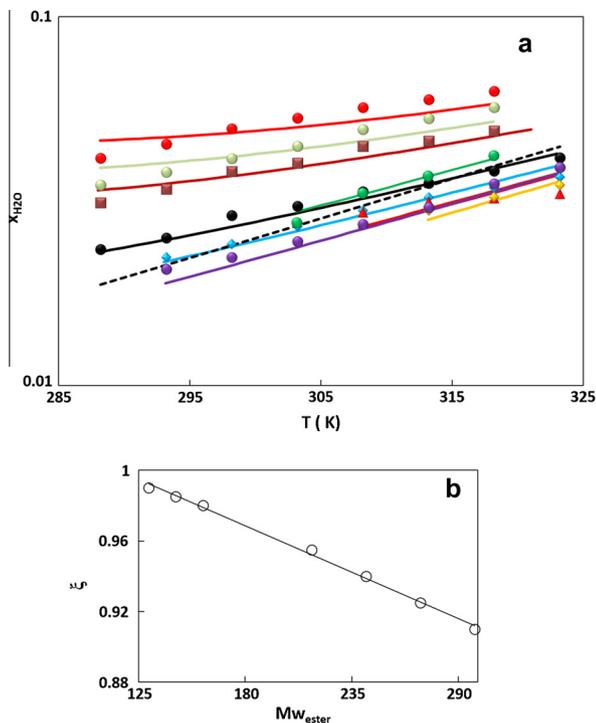


Fig. 3. (a) Water solubility in fatty acid esters at atmospheric pressure. Symbols represent experimental data [11,12] (●, methyl hexanoate; ●, methyl heptanoate; ■, methyl caprylate; ●, methyl laurate; ◆, methyl myristate; ▲, methyl palmitate; ◆, methyl stearate; ●, methyl oleate; ●, methyl linoleate) and the curves are the soft-SAFT results (full lines consider cross-association, while the dashed line is an example if cross-association between methyl laurate and water is not considered). (b) Please on Figure 3 caption, move " , methyl heptanoate" to the place between, methyl hexanoate and , methyl caprylate. It should appear as : , methyl hexanoate; , methyl heptanoate; , methyl caprylate as a function of saturated fatty acid esters molecular weight.

one, binary interaction parameters. In all cases, it was assumed an association site in the ester, following the recommendation of NguyenHuhn et al. [32] and the results from Oliveira et al. [11,12]. The best choice, providing an excellent description of the water solubility, including the correct description of the solubility temperature dependency, was achieved by considering the cross-association volume to be half of the water value (Eq. (10)) and the cross-association energy to be equal to the water value (Eq. (11)), while using only one binary interaction parameter regressed from experimental data, ξ .

$$K_{ij}^{HB} = \frac{K_{water}^{HB}}{2} \quad (10)$$

$$\varepsilon_{ij}^{HB} = \varepsilon_{water}^{HB} \quad (11)$$

The approach considered by NguyenHuynh et al. [32] with the polar GC-SAFT versions (the cross-association parameters values being equal to those of the associating compound, $K_{ij} = K_{water}$; $\varepsilon_{ij}^{HB} = \varepsilon_{water}^{HB}$) was also tested. Although providing satisfactory results, the enhancement of the qualitative and quantitative agreement with the experimental data provided by using the cross-association volume as half of the water value justifies its use in this work. Notice that the values are constant for all the esters studied, making this approach transferable to other fatty acid – water systems.

The binary parameter ξ , accounting for differences in the cross-dispersive energy between monomers, was fitted to reach quantitative agreement in all the systems considered here. The solubility of water in the nine systems here studied using the soft-SAFT EoS is presented in Fig. 3a. Deviations between the experimental data and the modeling results are also presented in Table 3.

Table 3

Average Absolute Deviation (AAD%) of the CPA EoS [11–13] and the soft-SAFT EoS modeling results for the systems considered in this work.

Compound	CPA AAD %	Soft-SAFT AAD %
<i>Water solubility in FAMES^a</i>		
Methyl hexanoate	7.38	6.76
Methyl heptanoate	6.00	6.28
Methyl octanoate	7.52	4.57
Methyl dodecanoate	7.39	2.92
Methyl tetradecanoate	6.44	3.29
Methyl hexadecanoate	9.35	7.80
Methyl octadecanoate	3.10	3.30
Methyl oleate	4.27	4.45
Methyl linoleate	3.40	2.51
OARD %	6.09	4.65
<i>VLE ester + methanol^b</i>		
Ethyl propionate	0.15	0.07
Methyl acetate	0.03	0.10
Hexyl acetate	0.41	0.62
Ethyl butanoate	0.54	0.36
Methyl laurate	0.27	0.36
Methyl myristate	0.39	0.59
Methyl oleate	0.41	0.42
OARD %	0.31	0.36
<i>VLE ester + ethanol^b</i>		
Ethyl methanoate	0.17	0.10
Methyl butanoate	0.15	0.89
Hexyl acetate	0.53	0.60
Methyl laurate	0.33	0.28
Methyl myristate	0.11	0.83
Methyl oleate	0.34	0.78
OARD %	0.27	0.58
<i>Water solubility in biodiesels^a</i>		
Rapeseed	10.5	14.0
Soybean	3.9	4.5
Palm	6.3	2.0
Sunflower	9.4	2.2
OARD %	7.5	5.7

^a Deviations in the mole fraction water solubility.

^b Deviations in temperature.

It is worth to remark that for the systems containing saturated esters (from methyl hexanoate to methyl octadecanoate), the binary interaction parameter ξ decreases when increasing the molecular weight of the compound, following a linear trend with the ester molecular weight, as shown in Fig. 3b and described by Eq. (12). This means that the cross-dispersive energy is overestimated when the fatty acid becomes heavier and requires a smaller binary parameter to be corrected. However, the fact that a correlation can be established facilitates this task for heavier compounds of the same family.

$$\xi_{ij} = -4.763 \times 10^{-4} M_w + 1.054 \quad (12)$$

Conversely, ξ values for the methyl oleate and methyl linoleate systems, although still of the same order than the rest (0.920 and 0.945, respectively), do not follow the above linear correlation, suggesting that unsaturated methyl esters systems need specific interaction parameters values and cannot be predicted using this correlation. This may be related with the enhanced interactions that the unsaturated bonds have with water.

The adequacy of the molecular parameters correlations with the ester molecular weight previously proposed (see Eqs. (7)–(9)) is clearly seen through the soft-SAFT results for the water solubility in methyl hexanoate and methyl heptanoate.

As expected, when using a more theoretical equation such as the soft-SAFT, improvements are observed when comparing with the results obtained with the simpler association CPA EoS [11,12]. Examples are shown in Fig. 4 for methyl laurate, methyl

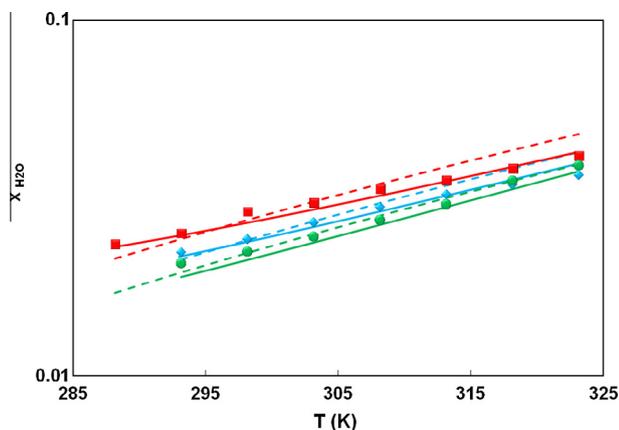


Fig. 4. Comparison between the modeling results of the CPA (dashed lines) and the soft-SAFT (solid lines) EoSs for the water solubility in methyl laurate (■) methyl myristate (◆) and methyl oleate (●) at atmospheric pressure. Symbols represent experimental data [11,12].

myristate and methyl oleate, and deviations from the experimental data are compared in Table 3. As observed in Fig. 4, and corroborated when comparing the global average deviation of both approaches depicted in Table 3, the qualitative and quantitative agreement with the experimental data provided by soft-SAFT overcomes the already good results provided by the CPA EoS, using only one binary interaction parameter regressed from experimental data. Since the association terms of both equations are similar, the differences observed are due to the reference and chain terms of the equations, a van der Waals based equation with the CPA EoS, and a Lennard–Jones reference fluid with the soft-SAFT. The use of a more detailed intermolecular potential, realistically considering monomer interactions and their molecular size through physically meaningful molecular parameters, as in soft-SAFT, allows a clear improvement of the description of the phase equilibria of these highly non-ideal aqueous systems.

3.3. Modeling of VLE of ester + methanol or ethanol systems with the soft-SAFT EoS

The second type of binary systems to be addressed are those composed of fatty acid esters and methanol/ethanol, found at the biodiesel production and purification facilities in the units used to remove/recover the excess alcohol from the fatty acid ester stream coming out of the reactor. As done for the water systems, binary mixtures of methanol/ethanol with small esters and from other ester families different than the fatty acid methyl esters were also investigated for completeness.

The same approach explained and considered for the aqueous systems was adopted here to take into account the interactions between esters and methanol or ethanol: the cross-association volume is taken as half of the alcohol self-association volume value and the cross-association energy is considered to be equal to the alcohol value (see Eqs. (10) and (11)). Again, the adjustable ξ energy parameter was fitted to the experimental data.

The first binary systems considered were those containing methanol with methyl ethanoate, ethyl propanoate, ethyl butanoate, hexyl acetate, methyl laurate, methyl myristate and methyl oleate. In Fig. 5a, the vapor–liquid equilibrium (VLE) of methanol with ethyl butanoate and hexyl acetate are plotted. When modeling these equilibria, it was noticed that very similar values of ξ were obtained for both systems. Hence, we decided to use the same value to describe all methanol systems, in order to develop a procedure as predictive and transferable as possible, without

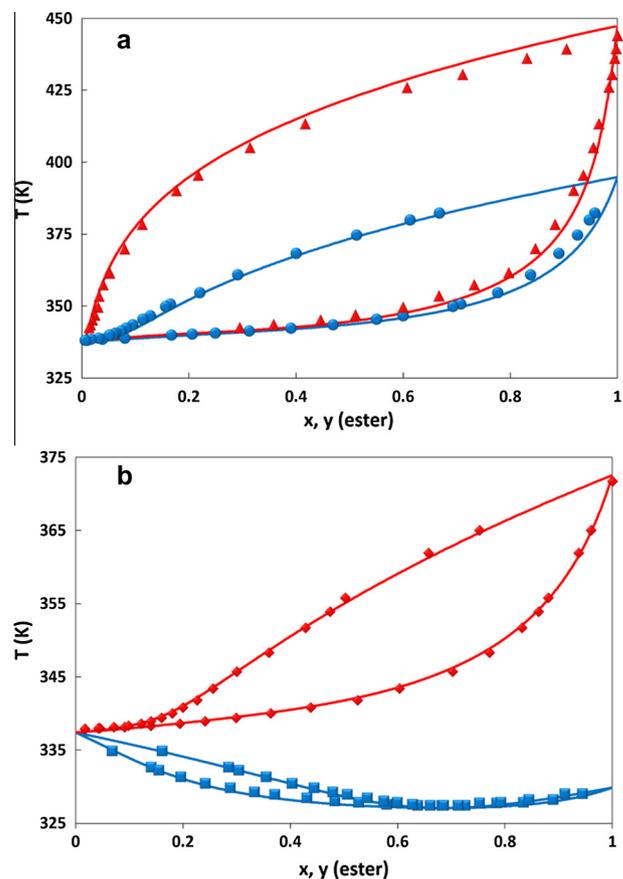


Fig. 5. (a) VLE at atmospheric pressure for the methanol + ethyl butanoate [19] (●) and methanol + hexyl acetate systems [58] (▲). (b) VLE at atmospheric pressure for methanol + methyl ethanoate [17] (■) and methanol + ethyl propanoate systems [18] (◆). Symbols are experimental data [17–19,58], while the lines depict the soft-SAFT EoS results.

losing accuracy. As a result, ξ was fitted to these two systems (ethyl butanoate and hexyl acetate). A value of $\xi = 0.960$ was found to correlate the data in very good agreement with the experimental information. Using this constant value the soft-SAFT EoS was able to properly predict the rest of considered systems, dealing with a large range of different esters in what concerns chain length and type, as shown in Figs. 5 and 6. These results are excellent for the purpose of having a tool with the ability to predict the behavior of similar systems with other esters involved.

The same procedure of the soft-SAFT EoS was applied for the ethanol systems considered, containing the esters ethyl methanoate, methyl butanoate, hexyl acetate, methyl laurate, methyl myristate and methyl oleate. In a first attempt, the ξ from the methanol systems was transferred to describe the VLE of ethanol mixtures. Although reasonable agreement was achieved for all cases, some systematic overprediction in the solubility was observed for all systems. Considering that a compromise between transferability and accuracy must be achieved, ξ was refitted to correlate the data of one selected ethanol mixture (ethanol + methyl butanoate) and transferred to the other systems to predict the VLE. A slight modification of the original methanol value ($\xi = 0.970$) was enough to accurately describe not only the ethanol + methyl butanoate, but also to predict the VLE of the different ethanol systems, independently of the length and type of ester. Results are depicted in Figs. 7 and 8. The fact that the ξ value is so close to that for methanol systems suggests that similar patterns are observed for both cases. In addition, a value close to unity means that the predicted LB rule would provide reasonable agreement with the experimental data,

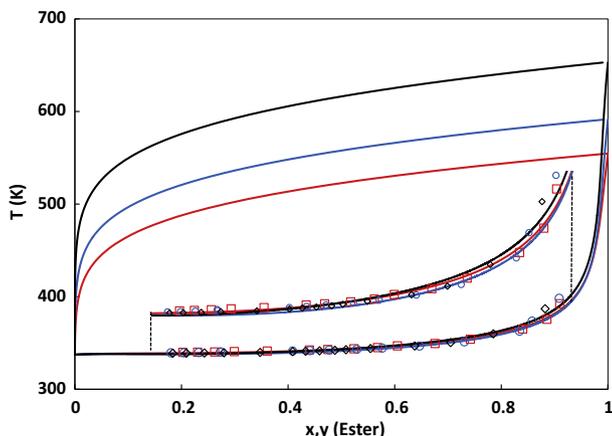


Fig. 6. VLE at atmospheric pressure for the methanol + methyl laurate (\square), methanol + methyl myristate (\circ) and methanol + methyl oleate (\diamond) systems. Symbols are experimental data [13]. Lines depict the soft-SAFT EoS results.

even if we deal here with compounds with different structures coming from different organic chemical families (alcohols and esters). This also suggests that the key issue for having a good description of these mixtures remains in the fact that the cross-association phenomena is explicitly considered.

As mentioned, the advantage of using an EoS with a sound statistical mechanics framework, properly taking into account the molecular shape and interactions of the molecules with the use of a low number of physical parameters, is patent in the results obtained for the VLE of the alcohol systems. Compared to the CPA EoS, similar results are obtained, as the deviations reported in Table 3 show. However, the performance of soft-SAFT is considered to be superior because of a better transferability of the molecular parameters, as CPA required chain length binary interaction parameters regressed from experimental data to describe these systems [13].

In what concerns the comparison with other SAFT type EoSs, the three versions of the polar-GC-SAFT (SAFT-0, VR-SAFT and PC-SAFT) also provided good results for the same small ester + alcohol systems considered in this work [32]. Nevertheless, and in contrast to the simple approach adopted here with the soft-SAFT to describe esters, NguyenHuynh et al. [32] applied a more complex method for the pure esters and mixtures description. As referred above, the polar term was added, with the correspondent dipole moment, making necessary the use of an extra parameter for the pure esters description. Then, for the VLE calculation of esters mixtures with alcohols, it was also necessary to explicitly consider the ester–alcohol

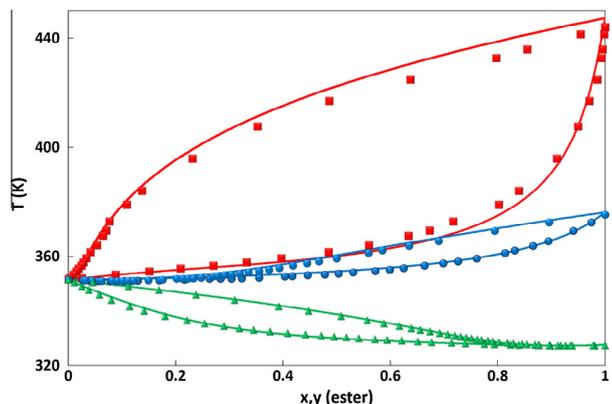


Fig. 7. VLE at atmospheric pressure for the ethanol + hexyl acetate (\blacksquare) [58], ethanol + methyl butanoate (\bullet) [21] and ethanol + ethyl methanoate systems (\blacktriangle) [22]. Symbols are experimental data [21,22,58]. Lines depict the soft-SAFT EoS results.

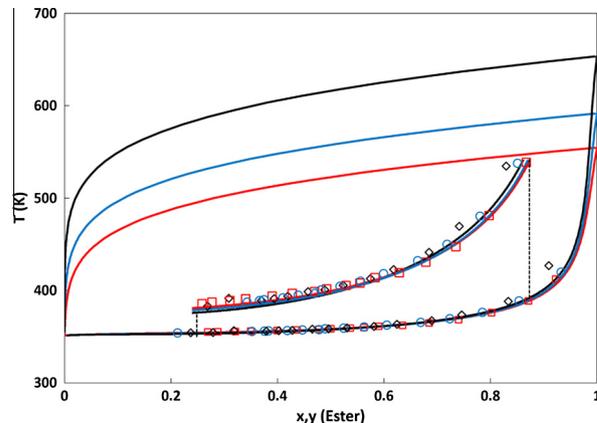


Fig. 8. VLE at atmospheric pressure for the ethanol + methyl laurate (\square), ethanol + methyl myristate (\circ) and ethanol + methyl oleate systems (\diamond). Symbols are experimental data [13]. Lines depict the soft-SAFT EoS results.

interactions. This was achieved through the addition of a cross-association term, as done here, characterized by the inclusion of one association site in the ester and the use of a cross-association scheme. The inclusion of cross-association was shown by NguyenHuynh et al. [32] to be mandatory for a good description of the ester + alcohols VLE systems. Consequently, the polar term seems not to have a significant impact in achieving an accurate description of the esters–alcohol systems. This confirms the observation shown in the present work: the cross-association is the key term for a successful description of ester + associating systems.

3.4. High pressure VLE of fatty acid ester + alcohols with the soft-SAFT EoS

Another important application is the description of the VLE of fatty acid ester + methanol/ethanol systems at higher pressure ranges, from 2 to 16 MPa. This is of particular importance for the design of biodiesel production methods using supercritical conditions. This non-catalytical method can overcome some of the limitations of the conventional process of biodiesel production [14].

High pressure VLE data were available for methanol systems containing methyl laurate, methyl myristate and methyl oleate [26,57], while for ethanol systems, data with methyl laurate and methyl myristate, at three different temperatures, were also found [25].

The modeling procedure adopted is exactly the same described in the previous section, with the cross-association volume and energy values determined from the alcohols self-association parameters, following Eqs. (10) and (11). Concerning the fitted ξ parameter, we were unable to find good agreement using the values found in the previous section, so unfortunately the values could not be transferred. However, it was still possible to use constant values for ξ (although different than before) for the calculation of the phase equilibria of the methanol and ethanol systems.

As done before, a particular system (methanol with methyl laurate) at an intermediate temperature (523 K) was used to fit the ξ parameter. Once an optimal value was found ($\xi = 1.030$), the rest of the isotherms were predicted using the same value, which was also transferred to the other methanol + ester systems. The modeling of three mixtures, two saturated and a third unsaturated, is depicted in Fig. 9. The soft-SAFT calculations can describe the VLE of the different systems in quantitative agreement with the experimental data, with an overall deviation inferior to 4%, as depicted in Table 4.

For ethanol systems, only data for mixtures containing saturated esters were available [25]. Similar results to those reported

for the methanol systems were observed: using a constant value of $\xi = 1.070$ (correlated to the methyl laurate mixture at 523 K), the high pressure VLE of the systems containing methyl laurate and methyl myristate at three different temperatures is accurately predicted with the soft-SAFT EoS (see the results in Fig. 10). Global deviations inferior to 3% were obtained (Table 4). A final remark concerning the binary ξ parameter is the fact that it is higher than unity, contrasting with the previous results. In other words, the crossed-energy van der Waals interactions were underpredicted and it was necessary to use a value higher than unity. Note that, as far as the cross-association values were kept the same as before, the effect of the pressure on the interactions is effectively accounted through ξ . It may be possible that a pressure increase also increases the cross-association. As we are always keeping the same

Table 4

Average Absolute Deviation (AAD%) of the soft-SAFT EoS modeling results for the high pressure VLE of the ester + alcohol systems.

	T/K	AAD %
<i>Methanol</i>		
Methyl laurate	493	1.15
	523	0.41
	543	1.13
Methyl myristate	493	3.20
	523	3.40
	543	2.09
Methyl oleate	523	1.50
	548	1.89
	573	18.73
OARD %		3.72
<i>Ethanol</i>		
Methyl laurate	493	1.66
	523	2.33
	543	2.64
Methyl myristate	493	3.07
	523	3.29
	543	3.40
OARD %		2.73

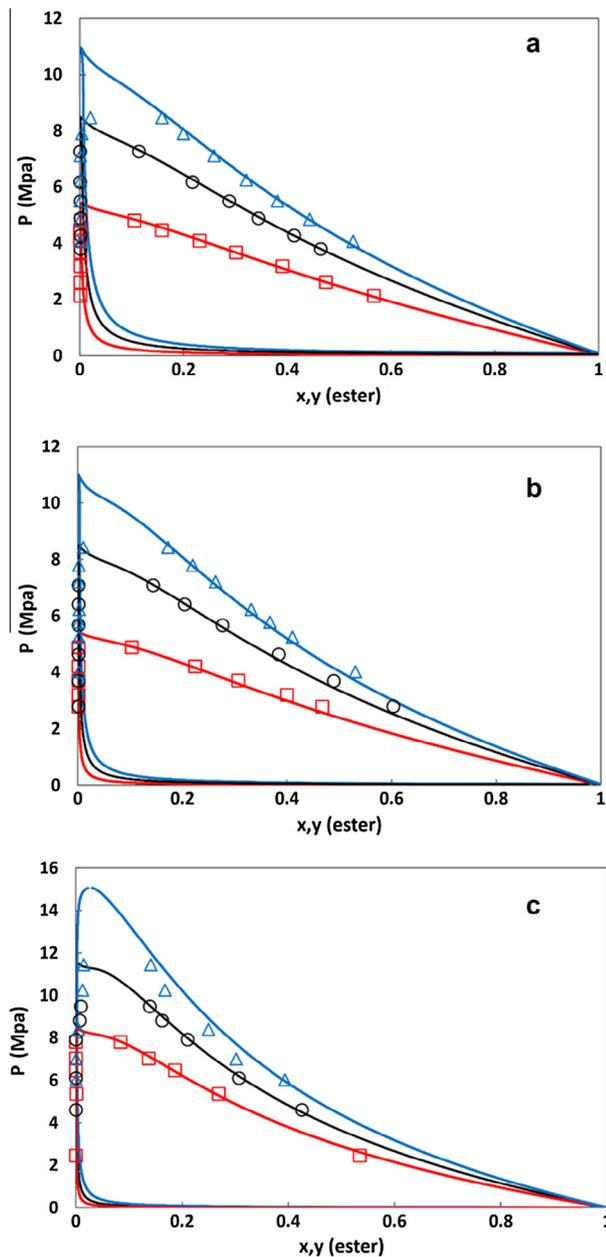


Fig. 9. (a) VLE for the methanol + methyl laurate system at \square , 493 K; \circ , 523 K; and \triangle , 543 K. (b) VLE for the methanol + methyl myristate system at \square , 493 K; \circ , 523 K; \triangle and 543 K. (c) VLE for the methanol + methyl oleate system at \square , 523 K; \circ , 548 K; and \triangle , 573 K. For all Figures, symbols are experimental data [26,57], while lines depict the soft-SAFT EoS results.

values (in order to preserve transferability), this effect has been entirely accounted by ξ . Still, with this limitation in mind, the soft-SAFT equation is powerful enough to provide a precise description of a wide variety of systems at different conditions.

3.5. Prediction of the water solubility in biodiesels with the soft-SAFT EoS

The final test of the use of soft-SAFT as a modeling tool in the biodiesel process is its application to the description of the water

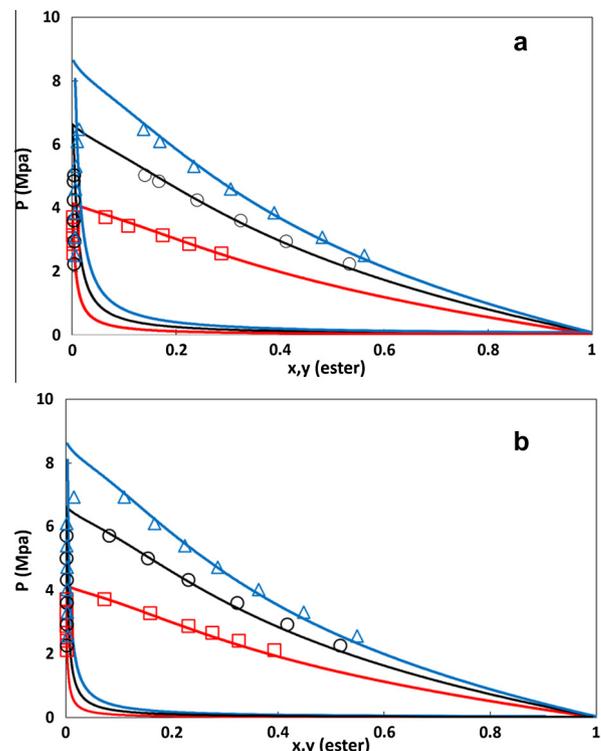


Fig. 10. (a) VLE for the ethanol + methyl laurate system at \square , 493 K; \circ , 523 K; and \triangle , 543 K. (b) VLE for the ethanol + methyl myristate system at \square , 493 K; \circ , 523 K; and \triangle , 543 K. For both Figures, symbols represent experimental data [25] and lines depict the soft-SAFT EoS results.

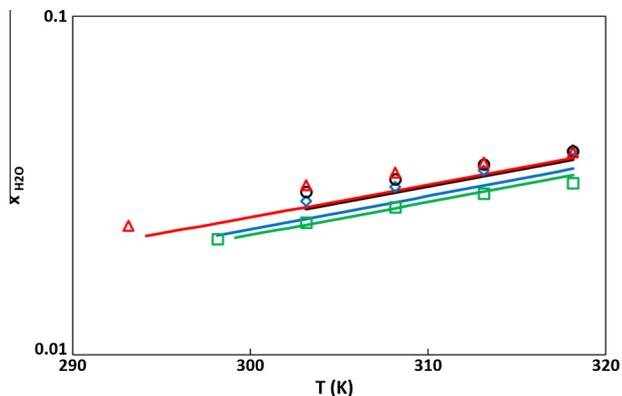


Fig. 11. Water solubility in biodiesels. Symbols are the experimental data [12] (\diamond , Soybean; \square , Palm; \circ , Rapeseed; \triangle , Sunflower) and lines the soft-SAFT EoS predictions.

solubility in real systems, i.e. biodiesels (mixtures of fatty acid esters).

In a recent work [33], it was shown that the soft-SAFT provides very good predictions for the density and viscosity in a wide range of pressure and temperature of several biodiesels produced from different oil sources, as well as their binary and ternary mixtures (among biodiesels).

Using the available water solubility experimental data for the methylic biodiesels from Soybean, Rapeseed, Palm and Sunflower oils in the temperature range 288.15–318.15 K [12], the soft-SAFT is used to describe these data using only the information gathered for the pure fatty acid methyl esters and their binary mixtures with water studied above.

In order to model these mixtures, we have decided to treat the biodiesel as a pseudo-pure fluid, assuming that all the compounds form a quasi-ideal mixture where no adjustable binary parameters are needed. The validity of this assumption is supported by the results presented in the previous work [33], where no binary parameters were needed to describe several multicomponent mixtures of fatty acids. In order to compute the biodiesel, it is necessary to use averaged molecular soft-SAFT parameters that simulate an “averaged” fluid which has the same thermodynamic properties of the mixture. This can be done by using the van der Waals one fluid mixing rules, which are already used in soft-SAFT to compute the reference term. The corresponding expressions to obtain σ and ε are:

$$\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \sigma_{ij}^3}{(\sum_i x_i m_i)^2} \quad (13)$$

$$\varepsilon \sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \varepsilon_{ij} \sigma_{ij}^3}{(\sum_i x_i m_i)^2} \quad (14)$$

The effective chain length of the conformal fluid is given by:

$$m = \sum_i x_i m_i \quad (15)$$

where i refers to each component of the mixture.

The considered biodiesels were composed of up to 14 fatty acid methyl esters from C10 to C24 and with up to three unsaturated bonds. Their detailed composition can be found in the work where the water solubilities were experimentally measured [12]. This information, along with the FAMES pure compound parameters previously proposed [33], allow the estimation of the biodiesels molecular parameters through the van der Waals one fluid mixing rules.

Having the biodiesels molecular parameters, it is then possible to treat the biodiesel-water as a binary mixture and to follow the same procedure done in previous sections. Again, only one association site is considered in the biodiesel, and the cross-association volume and energy values are calculated using Eqs. (10) and (11).

In the same way as done for the binary mixtures of fatty acid esters and water, only one binary interaction parameter, ξ , is used for the biodiesel systems description. In order to develop a predictive methodology to calculate these mixtures, the ξ value was not fitted, but computed as an average ξ from the biodiesel FAMES composition and the correspondent ξ value previously obtained for each FAME + water system:

$$\xi = \sum_{\text{FAME}} x_{\text{FAME}} \xi_{\text{FAME+water}} \quad (16)$$

where FAME refers to each ester composing the biodiesel.

For the FAMES for which no aqueous binary system had been previously studied, the linear correlation with the ester molecular weight for ξ proposed when studying the aqueous binary mixtures with FAMES was used. For C16:1, C22:1 and C18:3 the same ξ values than for C16, C22 and C18:2 were used. This last assumption was previously used with the CPA EoS with good results [12]. Results are depicted in Fig. 11 for the four biodiesels considered. Very good agreement with the experimental data is achieved in all cases, with the highest deviations for the case of the Rapessed biodiesel, as observed in Table 3.

The calculation method here described is completely predictive since correlations with the ester molecular weight are available for the pure compounds and binary interaction parameters. The soft-SAFT EoS is able to provide an accurate description of the water solubility in any biodiesel whatever its raw material is, just from the knowledge of the biodiesel composition in fatty acid methyl esters. As in the case of the description of the water solubilities in fatty acid esters, soft-SAFT also performs better than the CPA EoS for the majority of the biodiesels here considered, presenting smaller overall deviations (see Table 3).

4. Conclusions

A robust modeling with a transferable approach based on the soft-SAFT equation of state was used here to describe the phase behavior of esters mixtures with water and alcohols for biodiesel production. The solvation phenomenon between the non-self associating esters and the associating water and alcohols was considered for the first time within the soft-SAFT framework, through the description of the water solubility and the vapor-liquid equilibria of esters binary mixtures with small alcohols. Considering one association site in the ester, the cross-association volume was taken as half of the value of the volume of the associating compound and the cross-association energy was considered to be equal to the correspondent value of the associating compound (either water or alcohol) in all cases.

In a first stage, improved molecular parameters correlations with the ester molecular weight were proposed including small saturated methyl esters. The refined correlations allowed the prediction of methyl hexanoate and methyl heptanoate parameters without the need of experimental data. Then, nine fatty acid ester + water systems were studied, containing methyl esters from C₆ to C₁₈ and with up to two unsaturated bonds. Using a molecular weight linear dependent binary interaction parameter, the soft-SAFT EoS was able to provide an excellent description of the water solubility in fatty acid esters.

For the alcohol systems, twelve binary systems were considered, in a broad range of temperature and pressure conditions, including near/supercritical temperatures, covering a large variety

of chain lengths and different esters families, allowing a stringent test of the soft-SAFT predictive capability. Using a very limited amount of mixture data, it was possible to predict the VLE for all the methanol and ethanol systems using only one temperature independent and constant binary interaction parameter.

The soft-SAFT model was also able to correctly predict the water solubility in four methylic biodiesels produced from different oil sources, using an entirely predictive scheme for computing the required biodiesel molecular and binary interaction parameters, for which only the biodiesel fatty acid ester composition is required to be known. This approach can be extended to predict the water solubility in any biodiesel produced whatever it is its raw material.

The results of this work clearly show the advantages of using a refined association equation of state, based on a sound statistical mechanics background (yet keeping it simple with a small number of parameters), appropriately considering molecular shape and interactions among the molecules. By applying the soft-SAFT EoS to the description of several thermodynamic properties of fatty acid esters and biodiesels, and showing its excellent predictive ability to accurately describe the phase equilibria of the highly non-ideal systems here considered, this model proves to be a useful tool for the biodiesel industry in the development, scale-up and optimization of biodiesel production and purification processing units, namely those devoted to the water and alcohol removal.

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