Phase Equilibria of Ester + Alcohol Systems and Their Description with the Cubic-Plus-Association Equation of State

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The knowledge and the capability to describe the phase equilibria of binary systems formed by a fatty acid ester and an alcohol are of great interest in biodiesel production, where these mixtures can be found after the transesterification unit and where they must be separated to purify the biodiesel stream and to recover the unreacted alcohol. Despite this interest, little information is available on the vapor−liquid equilibria (VLE) of fatty acid ester + alcohol systems. To overcome this lack of data, new VLE measurements of six ester + methanol/ethanol systems were carried at atmospheric pressure. This new experimental data was successfully modeled with the Cubic-Plus-Association equation of state (CPA EoS), with global average deviations of 0.5% for the bubble-point temperatures. In all cases small and temperature independent parameters were enough to adequately describe the measured data. Furthermore a constant value for the cross-association energy parameter was proposed for each alcohol system, as well as a linear correlation for the binary interaction parameter with the ester chain length, making the CPA EoS a powerful predictive model for these systems.

Introduction

Thermodynamic models with a good predictive ability are essential while using process engineering simulation tools to evaluate the design and optimize conditions at production facilities.

Ester + alcohol systems are of great interest from an industrial point of view, for example, for the production of copolymer products for applications in coatings and adhesives[1] and particularly for the emerging biodiesel manufacturing processes. With the growing interest in biodiesels there is an increased need to correctly understand their production processes.[2] Since one of the biodiesel drawbacks is its production costs, improvement of the process design and the increase of the plant efficiency without further environmental impacts are required to have competitive biodiesel production units.[3]

A considerable volume of research and review works covers the reasons for replacing conventional fuels by biodiesel, noting its characteristics and advantages.[4−6] The most used process to produce biodiesel is catalyzed transesterification, that is a reaction between an oil and an alcohol, producing fatty acid alkyl esters (biodiesel) and glycerol.[7] Conventionally, alkaline-catalyzed reactions occurring with an excess of alcohol are used.[6]

Methanol is the most commonly used alcohol with this process, among other reasons because it is in general cheaper than other alcohols.[6] Still, ethanol can prevail in regions where it is less expensive than methanol, because of its production and accessibility.[8]

In an effort to ensure that only high-quality biodiesel is accessible to marketplaces, the majority of countries imposed biodiesel quality standards, the alcohol content being one of them. The maximum amount of methanol in biodiesel is regulated by the European biodiesel standards EN-14214[9] (test method EN-14110), the limit being 0.2% in mass. A higher alcohol content in biodiesel can cause engine problems such as accelerated deterioration of natural rubber seals and corrosion of Al and Zn pieces and influences the fuel properties causing lower density and viscosity values, lower flash points, and transport and storage problems.[10]

The recovery of excess alcohol to minimize operating costs and environmental impact[6] and to control the alcohol content in biodiesel is achieved through alcohol recovery sections in biodiesel production plants. Excess alcohol removal from the fatty acid ester stream leaving the transesterification reactor can be performed by flash evaporation or distillation.[6,11] Distillation is the most used method and the recovered alcohol is reused in the transesterification process.[6,11]

The knowledge about the vapor−liquid equilibrium (VLE) conditions of these systems is essential for a correct sizing of the operation units involved in methanol recovery. However, vapor−liquid equilibrium data at atmospheric pressure are not available in the literature for binary systems with methanol (or ethanol) and long chain fatty acid esters. For that reason, in this work, new VLE measurements at atmospheric pressure were performed for binary systems of alcohol (methanol or ethanol) with methyl laurate, methyl myristate, and methyl oleate, some of the major components of biodiesel.

Despite their importance, it is a quite demanding task to describe the phase equilibria of these systems, owing to their large deviation from ideality,[12] and in fact only a few of the available thermodynamic models can successfully represent such systems without a significant amount of data to regress the model parameters.

Resa et al.[13,14] reported isobaric vapor−liquid equilibria data for methanol binary mixtures containing ethyl butyrate and ethyl propionate and correlated it with the Margules, van Laar, UNIQUAC, NRTL, and Wilson equations and the ASOG method. The same approach was followed by Tu et al.,[15] which presented isobaric vapor−liquid equilibria data for the binary mixtures of methanol with methyl acetate and methyl acrylate and satisfactorily described them with the Margules, Wilson, NRTL, and UNIQUAC models. The isobaric vapor−liquid equilibria of methyl butanoate, propyl butanoate, and ethanol

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binary systems and their modeling with the UNIFAC and ASOG models can also be found in the literature.[16,17] Another approach used by Soto et al.[18] that reported isobaric vapor−liquid equilibrium data for the binary system composed of ethanol and ethyl methanoate was to model it with two different versions of the UNIFAC model.[18]

In spite of all these works using activity coefficient models, to adequately describe the phase equilibria in broader temperature and pressure conditions, equations of state have been found to be more appropriate, considering the balance between accuracy, predictivity, and simplicity.[19,20] Not many studies on ester + alcohol systems with equations of state can be found in the literature. Among these, Ferreira et al.[21] applied the group contribution with association equation of state (GCA-EoS) to model binary systems of small esters and alcohols, and later Andreatta et al.[22] applied the new GCA-EoS parameters estimated by Ferreira et al. to predict the LLE of the ternary mixture methyl oleate + glycerol + methanol.

To extend the applicability of the widespread used cubic equations of state with classical mixing rules to systems of polar compounds that are able to form hydrogen bonds, the Cubic-Plus-Association (CPA) equation of state was proposed by Kontogeorgis et al.,[23,24] combining the Soave−Redlich−Kwong (SRK) cubic term for describing the physical interactions with the Wertheim's first-order perturbation theory, which can be applied to different types of hydrogen-bonding compounds. Within our thorough research program of proposing a thermodynamic model able to correctly describe the phase equilibria of relevance for the biodiesel industry, the CPA EoS had already been successfully applied to describe the water solubility in fatty acid esters and biodiesels,[25] the mutual solubilities of water and fatty acid binary mixtures,[26] and the vapor−liquid equilibrium of several glycerol + alcohol[27] and water + glycerol systems.[27] The purpose of this study is to extend this good applicability of the CPA EoS to binary mixtures consisting of an ester and an alcohol, not yet covered by our earlier studies.

It will be shown that the CPA EoS is able to accurately take into account the increased solvation due to the interaction between the ester and the hydroxyl group, through a solvation scheme for the cross association energy and volume, and in addition, that the k_{ij} values are shown to follow a linear trend with the ester carbon number, enhancing the model predictivity.

Experimental Section

Chemicals. Methanol (Lab-Scan, ≥ 99,9%), ethanol (Riedel-de Haën, ≥ 99,8%), methyl laurate (Aldrich, ≥ 98%), methyl myristate (SAFC, ≥ 98%), and methyl oleate (Aldrich, ≥ 70%, methyl ester) were used in this work. GC-FID (Varian-3800 series) was employed to determine the accurate composition of the methyl oleate sample. The column used was a DB1-ht with 15 m × 0.32 mm i.d., coated with a 0.1 μm film of dimethylpolysiloxane. The GC conditions were as follows: oven temperature from 80 to 200 at 5 °C/min followed by a 1 min isotherm, injector temperature of 250 °C, injection volume of 0.5 μL, split ratio of 20:1, total carrier gas (helium) flow rate of 2 mL/min, and detector temperature of 220 °C. The obtained wt % compositions were the following: methyl myristate (1.8%), methyl palmitate (4.7%), methyl palmitoleate (4.7%), methyl stearate (1.9%), methyl oleate (71.1%), methyl linoleate (9.9%), and others (5.9%).

Apparatus and Procedures. Isobaric VLE data (T, x) at 1 atm were measured using an ebuliometer previously used for measuring the VLE at atmospheric pressure for several glycerol + n-alcohol systems (from methanol to n-butanol) and for the glycerol + water system. Pressure was kept constant through a vacuum line with a calibrated Baratron heated capacitance manometer 728A MKS, with an accuracy of 0.50%. A detailed description of the experimental set up can be found elsewhere.[27]

A liquid solution rich in fatty ester was introduced into the ebuliometer and heated up to its boiling point. The temperature was evaluated using a calibrated Pt100 sensor (±0.05 K), and the liquid phase was sampled and its composition was determined. Subsequently, fixed amounts of alcohol were introduced into the ebuliometer to change the mixture composition, and the procedure was repeated. The composition of the binary liquid mixtures in the boiling still were obtained from refractive index measurements, using an Abbe type refractometer with an uncertainty of 0.006.

Table 1. VLE Experimental Results at 1 atm for Several Methanol + Ester Systems

methyl laurate + methanol		methyl myristate + methanol		methyl oleate + methanol	
x_{ester}	T_b (K)	x_{ester}	T_b (K)	x_{ester}	T_b (K)
0.9096	392.58	0.9085	398.42	0.8822	387.11
0.8855	375.67	0.8578	373.70	0.7851	359.94
0.8402	365.15	0.8342	362.81	0.7049	350.63
0.7419	354.12	0.7307	351.34	0.6375	346.91
0.6757	349.55	0.6465	346.78	0.5546	344.13
0.6051	347.00	0.5767	344.58	0.5085	342.85
0.5679	345.05	0.5289	343.31	0.4877	342.18
0.5234	343.86	0.4771	342.49	0.4589	341.62
0.4745	343.01	0.4408	341.87	0.4327	341.18
0.4399	342.51	0.4084	341.35	0.4086	340.77
0.3608	341.36	0.2731	340.51	0.3473	339.94
0.2991	340.83	0.2731	340.08	0.2797	339.61
0.2621	340.43	0.2321	339.82	0.2430	339.34
0.2302	340.15	0.2043	339.61	0.2092	339.15
0.2024	339.96	0.1801	339.49	0.1835	339.02

Results and Discussion

There is a practical difficulty in obtaining high purity methyl oleate. As a result, a commercial ester with a methyl oleate purity of about 71% was used owing to its higher availability. As mentioned in the Chemicals section, the GC-FID analysis of this sample led to the conclusion that the major components are within the C17−C19 chain length range. Methyl stearate and methyl linolenate constitute the main contaminants of the used commercial ester. For these reasons, experimentally as well as for modeling, this multicomponent system will be hereafter referred as "methyl oleate". For modeling purposes it will also be considered as a pseudocomponent identical to pure methyl oleate.

Experimental Results. Experimental isobaric VLE results for binary systems ester (methyl laurate, methyl myristate, methyl oleate) + alcohol (methanol, ethanol) at atmospheric pressure are reported in Tables 1 and 2. The adequacy of the experimental set up used for measuring VLE data was previously shown, when performing measurements of VLE of glycerol + alcohol and of the glycerol + water systems,[27] as already stated in the experimental section.

For mixtures poor in ester, the boiling temperature does not change significantly, and since our intention was to study ester-rich systems, important to characterize fatty acid ester purification processes, no measurements were performed for mixtures with a mole fraction of ester lower than 0.2.

Analyzing the reported data, it appears that any change in the mixture composition for ester mole fractions above 0.7 causes a sudden increase in the mixture boiling temperature. The temperature tends to stabilize quickly for ester molar

Table 2. VLE Experimental Results at 1 atm for Several Ethanol + Ester Systems

methyl laurate + ethanol		methyl myristate + ethanol		methyl oleate + ethanol	
x_{ester}	T_b (K)	x_{ester}	T_b (K)	x_{ester}	T_b (K)
0.9224	413.01	0.9333	420.08	0.9100	427.35
0.8710	389.38	0.8543	389.10	0.8334	388.47
0.8015	376.59	0.7851	376.41	0.7463	374.01
0.7398	369.08	0.7240	369.67	0.6900	367.79
0.6845	365.40	0.6695	365.74	0.6246	363.63
0.6349	362.87	0.6057	362.61	0.5814	361.49
0.5899	361.70	0.5632	360.79	0.5305	359.91
0.5623	360.40	0.5247	359.56	0.4964	358.78
0.5363	359.81	0.4897	358.74	0.4653	358.37
0.5001	359.03	0.4786	357.90	0.4279	357.24
0.4776	358.36	0.4475	357.45	0.4025	356.70
0.4362	357.94	0.4188	356.82	0.3791	356.28
0.3990	357.26	0.3839	356.40	0.3184	356.72
0.3497	356.64	0.3758	356.19	0.2793	354.89
0.3205	356.16	0.3525	355.83	0.2369	354.46
0.2874	355.78			0.2125	354.19
0.2691	355.47				

fractions below 0.5. The saturation liquid lines are very similar for each alcohol system, which is related to the similar deviations in the liquid phase nonideality of the various systems here considered.

Correlation of the CPA Pure-Compound Parameters. CPA is a three-parameter EoS for nonassociating fluids (a_0, c_1, and b) and a five-parameter EoS for associating fluids (a_0, c_1, b, ε, and β). Detailed information about the CPA EoS can be found in Appendix A.

The compounds of the ester family studied in this work are all non-self-associating. In a previous work,[25] their CPA pure component parameters were determined for esters from 2 up to 19 carbons atoms, covering different kinds of esters such as methyl, ethyl, propyl, and butyl esters and also different acetates and formates. An excellent description of vapor pressures and liquid densities was achieved, with global average deviations of 2.3% and of 1.4%, respectively. In the same work it was possible to establish quadratic and linear correlations for these parameters. Parameters for some selected esters are reported in Table 3. These include all the ester compounds determined experimentally in this work, as well as some shorter-chain esters, whose mixtures with alcohols were also considered for evaluation purposes and to check the effect of the ester chain length in the k_{ij} values, as will be presented later.

The two alcohols studied here, methanol and ethanol, were considered as having two association sites, the 2B association scheme, described in Appendix A. Their set of CPA pure compound parameters were also determined in an earlier work from our research group,[28] and are presented in Table 3.

Correlation of the Vapor−Liquid Equilibria. Having the pure compound parameters, it was possible to describe the new experimental vapor−liquid equilibria data of binary systems with methanol/ethanol and a methyl ester with the CPA EoS.

As discussed at Appendix A, the cross-association between the ester group and the hydroxyl group was considered, as previously done for aromatic hydrocarbons + water systems[29,30] and for ester + water systems,[25] using the solvation scheme involving combining rules for the cross association energy and leaving the cross association volume as an adjustable parameter.

For the methanol mixtures, in addition to the experimental VLE data measured in this work, VLE data for other ester + methanol systems with different ester chain lengths were available in the literature, namely for methyl acetate,[15] ethyl propionate,[14] ethyl butanoate,[13] and hexyl acetate.[31] In a first attempt, both the binary interaction k_{ij} and the cross association β_{ij} parameters were fitted to the experimental VLE data. As expected, since the cross-association between methanol and the ester will always occur between the hydroxyl and the ester group, the regressed values for β_{ij} were close to 0.13. Therefore, this parameter was fixed to that value and the k_{ij} values were then refitted to the experimental data. A generalized linear correlation for the binary interaction parameter, k_{ij}, was found with the carbon number of the ester, C_n, described by eq 1. One should also notice that this linear dependency had previously been observed when applying the CPA EoS to model the phase equilibria of water + ester,[25] water + fatty acid,[26] and alkanes + water systems.[30]

$$k_{ij} = -0.004C_n + 0.019 \tag{1}$$

With a temperature independent k_{ij} and a constant value for β_{ij} for all binaries it was possible to describe the experimental VLE data of methanol systems with global average absolute deviations inferior to 0.6%. Binary interaction parameters and average deviations are presented in Table 4, and the VLE for the methanol systems with methyl laurate, methyl myristate, methyl oleate, and hexyl acetate are presented as examples in Figures 1 −4.

Because of the good results obtained for methanol mixtures, the same methodology was adopted in the following calculations for ethanol systems. Again, additional VLE data for several ethanol + ester systems available in the literature were also considered while modeling these mixtures with the CPA EoS. VLE data for ethanol binaries with ethyl methanoate,[18] methyl butanoate,[16] and hexyl acetate[31] were used. The regressed values for β_{ij} were close to 0.10. Fixing this parameter, the k_{ij} values were recalculated, and their values were also found to correlate linearly with the ester carbon number, as described by eq 2.

$$k_{ij} = -0.003C_n + 0.034 \tag{2}$$

With a single value of k_{ij} for each system, together with a constant value for the cross-association energy for all systems,

Table 3. CPA Pure Compound Parameters and Modeling Results

compound	a_0 ($J \cdot m^3 \cdot mol^{-2}$)	c_1	$b \times 10^5$ ($m^3 \cdot mol^{-1}$)	ε ($J \cdot mol^{-1}$)	β	AAD % P^σ	AAD % ρ
ethyl methanoate	1.46	0.84	6.65			0.37	0.59
methyl acetate	1.46	0.89	6.68			0.82	1.87
methyl butanoate	2.35	0.98	9.83			1.65	1.02
ethyl propionate	2.35	0.99	9.82			0.64	0.66
hexyl acetate	4.08	1.13	15.17			0.38	1.35
methyl laurate	7.46	1.37	24.04			0.80	1.31
methyl myristate	8.84	1.51	27.95			3.66	
methyl oleate	10.70	1.86	33.39			4.81	1.74
methanol	0.43	0.75	3.22	20859	0.034	0.29	0.14
ethanol	0.68	0.94	4.75	21336	0.019	0.35	0.51

Table 4. CPA Binary Interaction Parameters and Modeling Results for Methanol + Ester Systems (β_{ij} = 0.13)

	k_{ij}	AAD%
ethyl propionate	−0.0019	0.15
methyl acetate	0.0072	0.03
hexyl acetate	−0.0137	0.41
ethyl butanoate	−0.0058	0.54
methyl laurate	−0.0326	0.27
methyl myristate	−0.0432	0.39
methyl oleate	−0.0589	0.41

Table 5. CPA Binary Interaction Parameters and Modeling Results for Ethanol + Ester Systems (β_{ij} = 0.10)

	k_{ij}	AAD %
ethyl methanoate	0.0254	0.17
methyl butanoate	0.0190	0.15
hexyl acetate	0.0129	0.53
methyl laurate	−0.0002	0.33
methyl myristate	−0.0046	0.11
methyl oleate	−0.0197	0.34

it was possible to describe the VLE data of ethanol systems with very good agreement with the experimental results. Values for the binary interaction parameters and average deviations are presented in Table 5. VLE for the systems with methyl laurate, methyl myristate, methyl oleate, and hexyl acetate are depicted in Figures 1−4.

Methanol has a higher acid Kamlet−Taft solvatochromic parameter than ethanol,[32] which suggests a stronger solvation between methanol and the basic esters. The CPA EoS considers these methanol stronger solvation interactions with esters through a higher value for the β_{ij}. In the same way, since water has even greater acid Kamlet−Taft solvatochromic parameters than alcohols, stronger solvating interactions occur between esters and water than between esters and alcohols, the correlated cross-association volume parameter (β_{ij}) of 0.13 for methanol systems being physically reasonable when compared with the value previously observed for water + ester mixtures, β_{ij} = 0.20.[25]

Considering the modeling results it is possible to see that the alcohol mole fractions in the vapor phase are very close to unity for low temperatures, and that the vapor−liquid two phase region is higher for methanol systems.

The overall prediction of the VLE phase diagrams of ester + alcohol systems provided by the CPA EoS is almost excellent, using only small, temperature independent and linearly correlated k_{ij} values and constant values for β_{ij} depending on the alcohol, showing the adequacy of the CPA EoS to take into account the solvation phenomena encountered in ester + alcohol mixtures. The results obtained, considering the predictive character observed in this work, supports the use of this model for the description of this type of systems, following also successful previous applications to the description of other systems relevant to biodiesel production and purification.

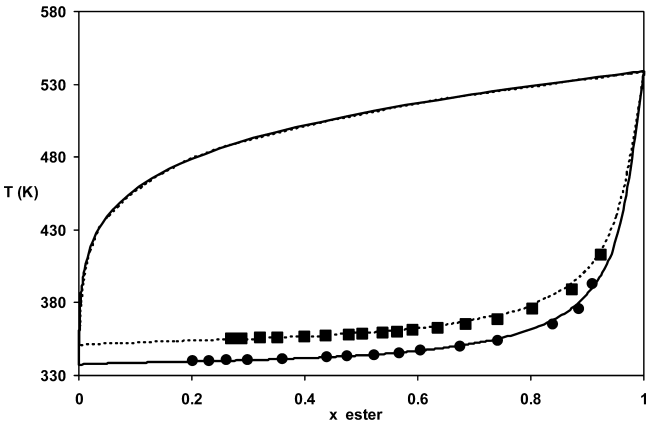

Figure 1. Experimental VLE for methanol + methyl laurate (●) and ethanol + methyl laurate (■) systems. CPA results for the methanol system (—) and for the ethanol system (---).

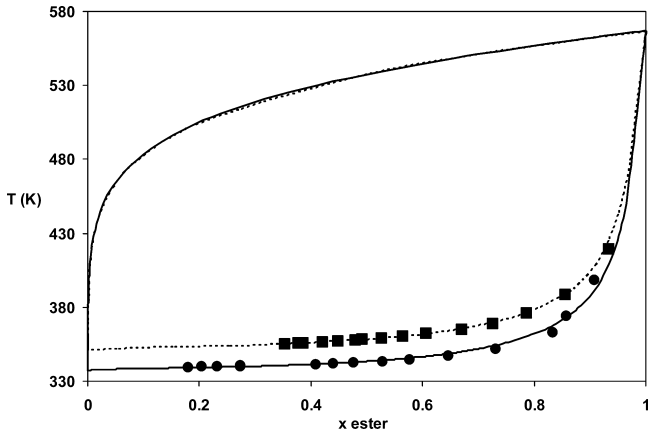

Figure 2. Experimental VLE for methanol + methyl myristate (●) and ethanol + methyl myristate (■) systems. CPA results for the methanol system (—) and for the ethanol system (---).

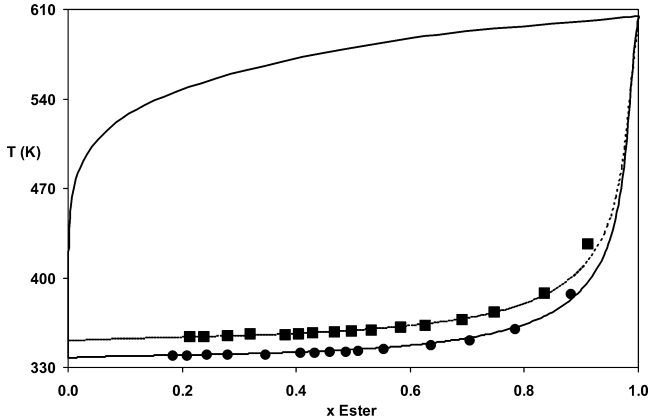

Figure 3. Experimental VLE for methanol + methyl oleate (●) and ethanol + methyl oleate (■) systems. CPA results for the methanol system (—) and for the ethanol system (---).

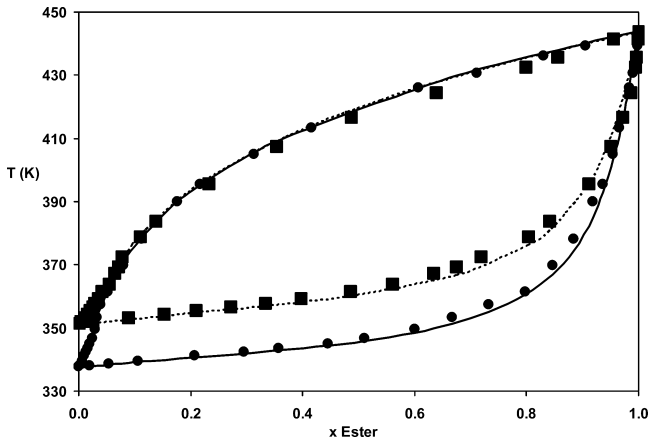

Figure 4. Experimental VLE for methanol + hexyl acetate[31] (●) and ethanol + hexyl acetate[31] (■) systems. CPA results for the methanol system (—) and for the ethanol system (---).

Conclusions

New experimental measurements of isobaric vapor−liquid equilibria of six ester + alcohol (methanol or ethanol) systems are presented, which are of great interest for the design and development of biodiesel purification processes.

The Cubic-Plus-Association equation of state was extended here to the modeling of that novel experimental data. It was demonstrated that the CPA EoS can take into account the strong polar interactions between esters and alcohols, describing the VLE of ester + alcohol systems with global average deviations inferior to 0.5%.

A single, small, and temperature-independent binary interaction parameter was sufficient and a constant value for the cross association volume was adopted for each of the alcohol binaries. The binary interaction parameter was found to be linearly correlated with the ester carbon number, allowing the CPA EoS to predict the phase equilibria of ester + alcohol systems for which small or no experimental data are available.

The results obtained from the CPA equation of state, in very good agreement with the experimental data, prove once more the good capability of this model to describe systems of importance for biodiesel production and purification.

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Appendix A

Kontogeorgis and co-workers[23,24,33] proposed an association equation of state that combines a physical contribution from a cubic equation of state, such as the Soave−Redlich−Kwong (SRK), with an association term accounting for intermolecular hydrogen bonding and solvation effects,[34−36] originally proposed by Wertheim and already used in other associating equations of state such as SAFT.[37]

This Cubic-Plus-Association (CPA) equation of state, can be expressed in terms of the compressibility factor as

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{A\,i}) \quad \text{(A1)}$$

where a is the energy parameter, b the co-volume parameter, ρ is the density, g is a simplified radial distribution function,[38] X_{Ai} is 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

$$a(T) = a_0[1 + c_1(1 - \sqrt{T_r})]^2 \quad \text{(A2)}$$

where a_0 and c_1 are regressed (simultaneously with b) from pure component vapor pressure and liquid density data. When the CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional mixing and combining rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad \text{(A3)}$$

and

$$b = \sum_i x_i b_i \quad \text{(A4)}$$

X_{Ai} is related to the association strength Δ^{AiBj} among two sites in two different molecules and is obtained by simultaneously solving the following set of equations:

$$X_{Ai} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{Bj}\Delta^{A_iB_j}} \quad \text{(A5)}$$

with

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right]b_{ij}\beta^{A_iB_j} \quad \text{(A6)}$$

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

The simplified hard-sphere radial distribution function, $g(\rho)$ is represented by[38]

$$g(\rho) = \frac{1}{1 - 1.9\eta} \qquad \text{where} \qquad \eta = \frac{1}{4}b\rho \quad \text{(A7)}$$

CPA has three pure component parameters (a_0, c_1, and b) for non-associating components, such as esters, while for associating components, like alcohols, it has five (a_0, c_1, b, ε, β). In both cases, these are optimized simultaneously from vapor pressure and liquid density data.

For mixtures containing a self-associating and a non-associating compound, no combining rules are required for the association term and thus, the k_{ij} binary interaction parameter in the physical term is the only adjustable parameter.

For the estimation of this k_{ij} parameter using the VLE data presented in this work, the objective function used was

$$\text{OF} = \sum_i^{NP}\left(\frac{T_b^{\text{calc}} - T_b^{\text{exp}}}{T_b^{\text{exp}}}\right)^2 \quad \text{(A8)}$$

On the other hand, when CPA is employed to mixtures containing cross-associating molecules, combining rules for the association energy and volume parameters are required. A particular case of this situation is found when systems are constituted by a self-associating compound and an inert compound that can solvate with the associating component. For that kind of systems, a different procedure, other than the commonly used combining rules, is required to obtain the cross-associating energy and volume. As proposed by Folas et al.,[29] the cross-association energy between the ester and the alcohol is considered to be half the alcohol association energy, and the cross association volume is left as an adjustable parameter, to be fitted from equilibrium data. The referred approach was already successfully applied to model the water solubility in fatty acid esters and biodiesels.[25]

The association term depends on the type and number of association sites. For alcohols, either the two-site (2B) or the three-site (3B) association schemes may be used. The results from Huang et al.[39] and from Kontogeorgis et al.[24] suggested the use of the 2B scheme for alcohols. The 2B association scheme had already provided very good results while modeling the vapor−liquid equilibria of several glycerol + alcohol systems.[27]

For the ester compounds, as shown before for modeling the water solubility in fatty acid esters,[25] a single association site is considered that can cross-associate with the alcohol.

Nomenclature

a = energy parameter in the physical term
a_0, c_1 = parameters for calculating a
A_i = site A in molecule i
b = covolume
g = simplified hard-sphere radial distribution function
k_{ij} = binary interaction parameter
P = vapor pressure
R = gas constant
T = temperature
x = mole fraction
X_{Ai} = 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 indexes
r = reduced
Superscripts
assoc = association
phys = physical
List of Abbreviations
AAD = average absolute deviation

$$\%\mathrm{AAD} = \frac{1}{NP}\sum_{i=1}^{NP}\mathrm{ABS}\left[\frac{\mathrm{exptl}_i - \mathrm{calcd}_i}{\mathrm{exptl}_i}\right]100$$

CPA = Cubic-Plus-Association
EoS = equation of state
VLE = vapor−liquid equilibria
SRK = Soave−Redlich−Kwong
UNIQUAC = universal quasi-chemical activity coefficient model
NRTL = nonrandom two liquid
ASOG = analytic solution of groups

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