Application of molecular modeling to the vapor-liquid equilibrium of alkyl esters (biodiesel) and alcohols systems

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Abstract

This work is focused on the thermodynamic modeling of systems related to biodiesel processing using the Perturbed Chain form of the Statistical Associating Fluid Theory (PC-SAFT). Different binary ester + ester and methanol or ethanol + ester systems were investigated. The PC-SAFT equation of state was able to predict the vapor-liquid equilibrium and solid-liquid equilibrium of different esters + esters binary systems. Furthermore, using a transferable cross-association parameters approach, the phase behavior of alcohols + alkyl esters of biodiesel was successfully predicted for a wide range of pressure and temperature conditions. Polar interactions seem to play a minor role in determining the phase behavior of mixtures considered in this work.

Keywords: PC-SAFT; biodiesel; alcohols; VLE; thermodynamic modeling.

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1. Introduction

Biodiesel has worldwide risen as a promising and an alternative biofuel. Its downstream process is mainly characterized as a complex mixture of long chain alkyl esters and short alcohols such as methanol, ethanol or glycerol. Mono, di, and triacylglycerols as well as fatty acids and water can also be present in minor quantities. These mixtures are normally found after the esterification or transesterification reaction units, where they must be separated to purify the biodiesel and to recover and recycle the unreacted alcohol [1].

The knowledge and the ability to predict the phase behavior of binary and multicomponent systems containing alkyl esters of fatty acids and alcohols is of a great interest to the biodiesel industry. A particular feature of ester + alcohol systems is the fact that the alcohols molecules are self-associating and both esters and alcohols are moderately polar in nature. Reliable thermodynamic models that can accurately predict the vapor-liquid equilibrium (VLE) of associating fluids are essential for an adequate process design and optimization. Despite their importance, it is quite challenging to predict the phase equilibrium of these systems, owing to their large deviation from ideality. Only few of the available models are able to capture the thermodynamics of such systems without requiring a significant amount of data to regress the model parameters [2, 3]. Experimental data on the VLE of binary and pseudo-binary systems related to the biodiesel production has recently been published in the literature [2, 4-10]. Even though those binary ester + ester and ester + alcohol systems have been correlated well using activity coefficient models, the ability of these models in accurately predicting the phase equilibria at conditions where experimental data lack is limited.

45   Ferreira et al. [11], using an equation of state approach, applied the group contribution

46   with association equation of state (GCA-EoS) to model binary systems of short esters and

47   alcohols. Later, Andreatta et al. [12] applied the new GCA-EoS parameters, estimated by

48   Ferreira et al. [11], to predict the liquid-liquid equilibrium (LLE) of the ternary mixture methyl

49   oleate + glycerol + methanol. Moreover, Oliveira et al. [2, 3] applied both the Cubic Plus

50   Association equation of state (CPA) [13] and the Soft version of Statistical Associating Fluid

51   Theory (soft-SAFT) [14, 15] to correlate the VLE of different binary systems involving esters +

52   short alcohols, at low to high pressures conditions.

53   The Perturbed Chain form of the Statistical Associating Fluid Theory (PC-SAFT),

54   proposed by Gross and Sadowski [16, 17], has been successfully applied to a wide range of

55   associating and non-associating systems. Moreover, Al-Saifi et al. [18] demonstrated that adding

56   the polar term, as developed by Jog and Chapman [19-21], to the perturbation theory results in a

57   significant improvement in the VLE predictions for alcohols + alkanes mixtures.

58   SAFT-based equations of state or its variances have been successfully applied to deal

59   with complex systems and it has becoming popular in engineering applications due its accurate

60   results. Such thermodynamics models have shown to be an important tool for phase behavior

61   description of complex systems when a prediction capability is required. In this context, we

62   attempt to investigate the performance of PC-SAFT and polar PC-SAFT (named PC-SAFT-JC)

63   approach to predict the phase behavior of systems concerning alkyl esters related to biodiesel and

64   alcohols, at low and high pressures-temperature conditions.

65

66   **2. Thermodynamics modeling and parameters estimation**

67   The SAFT equation of state is based on Wertheim's thermodynamic perturbation theory

68   of first-order [3, 16, 22-25]. This thermodynamic approach is normally expressed as a

69   summation of contributions to the residual Helmholtz free energy of the system. Such

70   contributions include: the hard sphere reference, the chain formation, the dispersion, the

71   association and the dipolar interactions. Different SAFT versions have been developed,

72   depending on the type of reference fluid and dispersion term adopted. Chapman et al. [22]

73   originally proposed the hard-chain reference term for the SAFT equation of state. Later, Gross

74   and Sadowski [16] used a more rigorous second and third order perturbation theory to model the

75   square well dispersion term in PC-SAFT. Other versions include: SAFT-VR which uses a

76   square-well with a variable range [26] as reference, soft-SAFT with a Lennard-Jones reference

77   fluid [14, 15], and GC-SAFT which uses a group contribution approach [27, 28].

78   The polar PC-SAFT EoS, as developed by Jog and Chapman [19-21], can be written as a

79   sum of contributions to the residual Helmholtz free energy, as follows:

80
$$a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{polar} \tag{1}$$

81   Where, hc represents the reference term of hard-chain ($a^{hc} = a^{hs} + a^{chain}$, sum of hard-spheres and

82   chain formation terms); $disp$ is the dispersion term, and $assoc$ and $polar$ are the terms

83   representing the association and dipolar contributions, respectively.

84   In the PC-SAFT framework, three pure component parameters, namely, the temperature-

85   independent segment diameter (σ), the dispersion energy between segments (ε) and the number

86   of segments per chain (m), must be fitted to saturated liquid density and vapor pressure data.

87   When mixtures are considered, the binary diameters and dispersion energies are calculated from

88   the conventional Berthelot-Lorentz combining rule [16]:

89
$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i - \sigma_j\right) \tag{2}$$

90
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right) \tag{3}$$

91 Where, one binary interaction parameter (k_{ij}) is used to correct the segment-segment dispersion

92 energy of unlike molecules.

93 The association term [23-25, 29] takes into account the inter-molecular interactions due

94 to hydrogen bonding. Two pure component parameters, the association energy (ε_{ii}^{HB}) and the

95 association volume (κ_{ii}^{HB}), determine the interaction between different association sites on a pure

96 component i. Additionally, for a mixture of associating compounds the combining rule as

97 proposed by Wolbach and Sandler [17, 30] has been used:

98
$$\varepsilon_{ij}^{HB} = \frac{1}{2}\left(\varepsilon_{ii}^{HB} + \varepsilon_{jj}^{HB}\right) \tag{4}$$

99
$$\kappa_{ij}^{HB} = \sqrt{\kappa_{ii}^{HB}\kappa_{jj}^{HB}}\left(\frac{\sqrt{\sigma_i \sigma_j}}{\frac{1}{2}\left(\sigma_i + \sigma_j\right)}\right)^3 \tag{5}$$

100 For binary mixtures of alcohols (self-associating compounds) and esters evaluated in this

101 work, the cross-association parameters ($\varepsilon_{jj}^{HB} = \varepsilon^{B_2}$ and $\kappa_{jj}^{HB} = \kappa^{B_2}$) were fitted using vapor-liquid

102 equilibrium data of ethyl acetate + alcohols and thereafter these parameters were transferred to

103 predict the phase behavior of longer alkyl esters with methanol or ethanol.

104 The dipolar term of Jog and Chapman (JC) has been proven to be successful in describing

105 associating systems [18, 31]. The contribution of the dipolar interactions to the change in free

106 energy has been taken by dissolving all of the bonds in a chain and forming a mixture of non-

107 bonded segments of both polar and non-polar segments. When adding the polar term in the PC-

108 SAFT framework one additional adjustable pure-component parameter is included (x_p), which

109 represent the polarizable fraction of the molecule. As demonstrated by Dominik et al. [31], $x_p m$ is

110 expected to be constant when working on a specific homologous series of compounds. On the

111 other hand, Al-Saifi [18] argued that better results are obtained by fitting x_p for methanol and

112 ethanol. They also evaluated three different dipolar terms for modeling and predicting the phase

113 behavior of alcohol containing systems. In general, the Jog and Chapman approach showed

114 superiority over other dipolar terms.

115   Systems considered in this work were modeled using PC-SAFT [31, 32], in which the

116 inclusion of dipole-dipole interactions, as proposed by Jog and Chapman[19, 20], was also

117 evaluated. Both models were fitted to pure saturated liquid densities and vapor pressure data.

118   The modified Nelder-Mead Simplex method [33] was used to fit the pure component

119 parameters by minimizing the objective function shown in Equation 6. Particle Swarm

120 Optimization (PSO) [34] algorithm was applied to obtain the initial guesses.

121
$$\min \ F_{obj} = \sum_{i=1}^{NPP} \left| \frac{p_i^{\exp} - p_i^{cal}}{p_i^{\exp}} \right| + \sum_{i=1}^{NPD} \left| \frac{\rho_i^{\exp} - \rho_i^{cal}}{\rho_i^{\exp}} \right| \qquad (6)$$

122   In Equation (6), $p_i^{\exp}$ and p_i^{cal} are respectively the experimental and calculated vapor

123 pressures of pure components at the "i" data. $\rho_i^{\exp}$ and ρ_i^{cal} are the experimental and calculated

124 density (saturated or subcooled liquid) of pure component, respectively. *NPP* and *NPD* are the

125 number of vapor pressure and density data used, respectively.

126   For the cross-association parameter estimations (Equations 4 and 5) the same optimization

127 strategy presented above was used, however through minimizing the function in Equation 8:

128
$$OF = \sum_{i=1}^{NOBS} (Y_i^{\exp} - Y_i^{cal})^2 \qquad (7)$$

129 Where, $Y_i^{\exp}$ and Y_i^{cal} are the pressure or the temperature of saturation of the liquid phase. In

130 order to calculate the pressure or temperature saturation (bubble or dew point) an algorithm

131 based on saturation point calculations [35] was used.

132   In this work, the statistical evaluation was performed throughout the absolute deviation

133   (*AD*), absolute average deviation (*AAD*) and/or root mean square deviation (*rmsd*) were used as

134   presented in Equation 8, 9 and 10, respectively.

$$AD = \frac{1}{NOBS} \sum_{i=1}^{NOBS} \left| X_i^{\exp} - X_i^{cal} \right| \tag{8}$$

$$AAD = \frac{100}{NOBS} \sum_{i=1}^{NOBS} \frac{\left| X_i^{\exp} - X_i^{cal} \right|}{X_i^{\exp}} \tag{9}$$

$$rsmd = \sqrt{\sum_{i=1}^{NOBS} \frac{\left(X_i^{\exp} - X_i^{cal} \right)^2}{NOBS}} \tag{10}$$

138   Where $X_i^{\exp}$ and X_i^{cal} are the respective experimental and calculated variables involved in

139   the calculations.

140

141   **3. Results and Discussion**

142   *3.1 Pure components fitting*

143   Table 1 presents the fitted parameters for methyl and ethyl esters using polar (PC-SAFT-

144   JC) and non-polar (PC-SAFT) models. Other esters considered in this work are also showed in

145   Table 1. Pure component parameters for short alcohols are reported in Table 2. The absolute

146   average deviation (*AAD%)* in fitting the vapor pressure and density is also shown in these tables.

147   As mentioned previously, the product of $x_p m$ is expected to be constant for components

148   within a homologous series. As presented in Table 1, the product $x_p m$ was fixed to a value of 1.5

149   (Set 1), while fitting x_p for the other two sets of parameters. It can be seen from Table 1 that Set

150   3 provided a lower error in terms of the vapor pressure with an acceptable error in the saturated

151   liquid density. Therefore, the $x_p m$ value of 0.6 was fixed for fitting the PC-SAFT-JC parameters

152   for all others alkyl esters.

153   Figures 1-3 show the vapor pressure and liquid density of different alkyl fatty acid esters

154   as a function of temperature. It can be seen that both versions of PC-SAFT were able to correlate

155   well the experimental data.

156   **Figures 1, 2 and 3**

157   Higher deviations from experimental data were observed regarding the vapor pressure

158   calculated by PC-SAFT for some of the ethyl esters. This drawback might be attributed to the

159   scattering observed in the experimental data measured for the corresponding pure esters [43].

160

161   *3.2 Ester + ester binary systems*

162   Processes under low pressures have gained importance in the chemical industry mainly

163   when fatty acids and its esters are involved. Such conditions can avoid the use of high

164   temperature that leads to the reduction of the energy consumption and degradation reactions [3,

165   51]. A molecular model that can deal with complex interactions in multicomponent systems and

166   accurately predict their phase behavior has a major importance in the fatty acid esters processing,

167   as well as in the biodiesel industry. Understanding the VLE of fatty acid ester containing systems

168   is significant for proper design and operation of units at low pressure conditions [52].

169   Consequently, we investigated how the models perform in predicting the phase behavior of

170   different ester + ester binary systems.

171   Vapor-liquid predictions using both PC-SAFT versions used in this work are presented in

172   Figures 4 to 6. In reference to Figure 4, it can be seen that PC-SAFT was able to predict the

173   vapor-liquid equilibrium of different ethyl ester systems, in which binary interaction parameters

174   were set to zero ($k_{ij} = 0$). As mentioned above, the small discrepancies observed for the binary

175   mixtures are related to the error observed in the measured vapor pressures of pure esters [53].

176   Still, PC-SAFT was able to capture the phase behavior of unsaturated mixtures (Figure 4(A)), as

177   well as saturated + unsaturated esters (Figure 4(C)). Regarding the former system, the

178   compositions of both phases are found to be very close to each other resulting in a narrower

179   vapor-liquid envelop, when compared to phase diagram involving saturated esters only.

180   **Figure 4**

181   In reference to Figure 5, PC-SAFT was also able to predict well the phase behavior of

182   binary methyl ester systems. The methyl palmitate + methyl stearate [40, 54] binary system

183   appears to present a larger deviation from ideality (Raoult's Law) in comparison to other similar

184   ethyl ester system (ethyl palmitate + ethyl stearate). As presented and discussed by Hou et al.

185   [40], the binary methyl palmitate + methyl stearate system tends to form an azeotrope at high

186   concentrations of methyl palmitate. For this system, both models with $k_{ij} = 0$ were not able to

187   predict correctly the experimental phase behavior observed for this binary mixture (Figure 6(A)).

188   However, setting the binary interaction parameter to $k_{ij} = 0.01$ proved to be adequate in getting

189   the correct vapor-liquid equilibrium for all isobars evaluated in this work, as it is shown in

190   Figure 6(B).

191   **Figure 5**

192   **Figure 6**

193   Predicting the melting point of different esters mixture is another important property for

194   biodiesel processing. In Figure 7, the melting point predictions for different ethyl esters using

195   PC-SAFT to correct the non-ideality in the liquid phase are presented. Following the approach

196   proposed by Corazza et al. [55], the solid-liquid equilibrium calculations were performed using

197   the phase change values reported in Table 3. In reference to Figure 7, it is observed that PC-

198 SAFT can be an important tool for the prediction of melting points for mixtures involving

199 saturated or unsaturated esters.

Figure 7 (SLE)

201   The non-polar version of PC-SAFT performed satisfactory well for most of the systems

202 composed by long-chain alkyl esters. This can be attributed to the small degree of non-ideal

203 behavior in such systems due to the similarity in molecular size and interactions. Consequently,

204 we concluded that the polar term is unnecessary to predict correctly the vapor-liquid equilibrium

205 of systems under consideration.

206

207   *3.3 Alcohol + ester mixtures*

208   The cross-association was considered in order to correctly predict the phase behavior of

209 alcohol + ester systems. VLE data for ethyl acetate with methanol, ethanol, 2-propanol and 1-

210 butanol [57] were used to fit the cross-association parameters. Again, binary interaction

211 parameters (k_{ij}) were all set to zero. Table 4 depicts the cross-association energy (ε^{HB}) and

212 volume (κ^{HB}) fitted between the positive site in the alcohol molecules and the negative sites in

213 the ester molecule. In this work, alcohols were modeled with two sites (a positive site on the

214 hydrogen and a negative site on one of the oxygen's lone pair of electrons). Esters were modeled

215 with two negative association sites, one on each of the oxygen atoms. Taking into account cross-

216 association, PC-SAFT was able to predict the phase diagram of alcohol + ester systems and from

217 (Supplementary Material) it can be seen the good performance of both PC-SAFT and polar PC-

218 SAFT in correlating ethyl acetate + alcohols binary systems considered in this work.

219   Considering the cross-association parameters to be transferable, the vapor-liquid

220 equilibrium of different alcohol + ester systems was predicted. Again, the binary interaction

221 parameters k_{ij} were all set to zero. Table 5 illustrates the computed deviations in bubble point and

222 vapor phase composition as predicted by the model in comparison to experimental data.

223 Deviations calculated for both models without considering the cross-association are presented in

224 parentheses (see Table 5). In general, it can be seen that the transferrable cross-association

225 energy and volume parameters were able to provide a good estimation of the saturation data. The

226 highest deviation of 3.45 K was observed for the system methanol + hexyl acetate, while the

227 lowest observed value was 2.02 K for the system ethanol + ethyl acetate. It is also shown that the

228 deviations related to the experimental and predicted values at high-pressure conditions both

229 models, PC-SAFT and polar PC-SAFT, presented similar results, in which smaller absolute

230 average deviation were found as the temperature is lower.

231   Figures 8 to 10 depict a comparison between the models predictions and experimental

232 data considering different binary systems presented in Table 5. All systems were predicted well

233 using the PC-SAFT equations of state where slightly lower deviations were observed for the

234 predictions using the non-polar version of PC-SAFT. It is visually observed that the correct

235 shape of the coexistent curves is obtained when the cross-association was included. Moreover,

236 predictions for alcohols + long chain alkyl esters (methyl or ethyl) were found to be in good

237 agreement with experimental data found in the literature up to high temperature and pressures

238 (Figure 10), in which the shape of phase envelopes was predicted in a satisfactory way.

239   Furthermore, regarding the systems at low pressure conditions (Figure 8 and 9), the

240 SAFT models were able to predict the sudden and sharp decrease in the bubble point temperature

241 as minor quantities of alcohol are added to the pure long chain esters. On the other hand, the

242 model tends to under-predict the saturation temperature when cross-association is not included.

243 In conclusion, adding the polar term seems to be unnecessary to describe well the phase behavior

244 of binary systems involving alkyl esters with short chain alcohols. Otherwise, including cross-

245 association was helpful in predicting the correct phase diagrams of ester + alcohol systems.

246   **Figure 8**

247   **Figure 9**

248   **Figure 10**

249 **4. Conclusions**

250   This works reports a thermodynamic modeling of systems involved in the biodiesel

251 processing, namely, fatty acid methyl and ethyl esters and alcohols. Vapor-liquid equilibrium for

252 binary systems comprising ester + ester and alcohol + ester were investigated using the PC-

253 SAFT equation of state, in which the Jog and Chapman polar term was also include and

254 compared. It was verified that both approaches were able to satisfactory predict the phase

255 behavior of esters + esters systems. Additionally, PC-SAFT accurately predicted the solid-liquid

256 equilibrium of ethyl ester binary systems. The VLE of ester + alcohol systems was predicted

257 using transferable cross-association parameters from methanol and ethanol with ethyl acetate

258 while setting the k_{ij} to be zero.

259   In general, the results presented in this work are helpful in understanding better the

260 interactions and the phase behavior of ester + short alcohol systems related to the biodiesel

261 downstream. PC-SAFT equation of state proved to be a promising and a reliable tool for

262 predicting the phase behavior of complex fluids.

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