Improved Prediction of Water Properties and Phase Equilibria with a Modified Cubic Plus Association Equation of State

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Supporting Information

ABSTRACT: One of the major challenges of an equation of state lies in the description of water and aqueous systems. Its abundance and unique properties turn water into one of the most important molecules in the industry. However, because of these peculiar characteristics, its modeling is far more complex than for any other common solvent. In this work, a modified cubic plus association (CPA) model, which includes the correct description of the pure component critical temperature and critical pressure, is expanded to water and its systems. A brief analysis of the predicted water purity properties is conducted, comparing those to a previous version of the model. Results for a group of binary systems, including liquid−liquid equilibrium with alkanes and alcohols, highlighting their minima in aqueous solubility, and gas solubility in water/water solubility in gas, are also presented. Finally, ternary and multicomponent systems of water + hydrocarbons and water + polar compound + hydrocarbons are also modeled and discussed.

1. INTRODUCTION

The importance of water both in the industry and in the daily lives of the world population is undeniable, and its unique properties are an asset used in diverse ways in almost every process.

The correct description of pure water and its mixtures using an equation of state is both a necessity and a challenge. During the last decades, the development of association models brought a significant improvement to the accuracy of these systems. Some of the most well-known association models are based on perturbation theory, in most cases on Wertheim’s first-order thermodynamic perturbation theory (TPT1) for associating fluids.1 Cubic plus association (CPA)2 is one such models and combines the simplicity of a cubic equation of state with the theoretical background and accuracy expected from an association model.

This equation of state (EoS) is able to describe accurately binary vapor−liquid equilibrium (VLE), liquid−liquid equilibrium (LLE), and solid−liquid equilibrium (SLE) for mixtures of water, alkanols, and alkanes with very reasonable results also for the vapor−liquid−liquid equilibrium (VLLE) of ternary systems containing water an alkanol and an alkane.1 CPA has been shown, in many cases, to outperform more complex models in the description of these type of systems. Recently, Kontogeorgis and co-workers3−10 presented various works showing the capacities of CPA in describing water + hydrate inhibitor + petroleum fluid with very satisfactory results.

The above-mentioned hydrate formation/inhibition is one of the better known CPA applications, and these systems have been one of the main driving forces for the widespread of CPA, promoting its use on commercial and in-house software.

The ease of integration in process software and the simplicity of CPA are two of the main advantages of this model. The version studied here uses a mechanism to force the correct description of the pure component critical temperatures and pressures while keeping the other features intact.10,11

In this work, a modified CPA model10,11 was applied to the description of binary and multicomponent systems containing water while still preserving the accuracy of the pure water properties. For the latter, this study analyses the description of not only vapor pressure and liquid density, the most used properties in the parametrization of CPA, but also the estimation of derivative properties such as liquid Cp and heat of vaporization. A diverse group of mixtures is then analyzed with a focus on the description of water + alkanes and water + alcohols/hydrate inhibitors (MEG and methanol) while also studying petroleum related fluids and their equilibria with water and these polar compounds.

As will be demonstrated, this new version of the model can reasonably describe, for the first time for CPA, the minimum in the water solubility of hydrocarbons while also matching the pure components critical temperature and pressure and better representing second derivative properties such as liquid heat capacity and enthalpy of vaporization.

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2. MODEL
The modified version of CPA used here is based on the original (simplified) CPA model,\textsuperscript{12} to which a different $\alpha$ function and optimization process were introduced.

The $\alpha$ function is a modified Mathias–Copeman function,\textsuperscript{13} which can use up to five parameters:

$$a(T) = a_0(1 + T' x + T^2 x_2 + T^3 x_3 + T^4 x_4 + T^5 x_5)^2$$

with $T' = (1 - \sqrt{T}/T_c)$ and $T_c = T/T_c$.

This version of CPA uses some restrictions in the pure component parameterization process. The $a_0$ and co-volume ($b$) are forced to describe the critical temperature and critical pressure. In this manner, these two parameters are obtained from the critical data, increasing the predictive capacity of the model:

$$P_{\text{CPA}}(T_{\text{exp}}^{\text{calc}}, V_{\text{calc}}^{\text{calc}}) = P_{\text{exp}}^{\text{calc}}$$

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c}^{v=v_c^{\text{calc}}} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c}^{v=v_c^{\text{calc}}} = 0$$

It is also important to note that the molar volume is not optimized directly, being instead obtained from a single density point by a Peneloux type volume shift:\textsuperscript{14}

$$v_1 = v_0 - c_{v_1}$$

where $c_{v_1}$ is a temperature independent volume shift. Jaubert et al.\textsuperscript{15} have shown that using this type of volume shift does not influence the results for vapor pressure, heat of vaporization, and heat capacities.

During the parametrization, the $\alpha$ function parameters are generated directly by fitting to the vapor pressure curve. Introducing a change on the associative parameters leads to an automatic recalculation of the cubic term parameters. The associative parameters were fitted to the liquid heat capacity and vapor pressure data. As said above, the liquid density was not used in the main parameterization.

To optimize the binary interaction parameter ($k_i$) values, three different equations were applied depending on the type of equilibria and experimental data:

$$\text{OF} = \sum_{i}^{\text{all}} \left( \frac{T_{\text{exp}}^{\text{bub}} - T_{\text{calc}}^{\text{bub}}}{T_{\text{calc}}^{\text{bub}}} \right)^2$$

$$\text{OF} = \sum_{i}^{\text{all}} \left( \frac{P_{\text{exp}}^{\text{bub}} - P_{\text{calc}}^{\text{bub}}}{P_{\text{calc}}^{\text{bub}}} \right)^2$$

$$\text{OF} = \sum_{k}^{\text{all}} \sum_{i}^{\text{all}} \left( \frac{x_{i,k}^{\text{exp}} - x_{i,k}^{\text{calc}}}{x_{i,k}^{\text{calc}}} \right)^2$$

where $n_p$ is the number of phases to optimize.

For mixtures with more than one associative compound, combining rules are applied to calculate the cross-associative parameters. The CR-2 combining rules\textsuperscript{16} were applied whenever necessary:

$$\beta_i = \sqrt{\beta_i^b \beta_i^f}$$

$$e_i = \frac{(e_i^b + e_i^f)}{2}$$

This version of CPA uses a heteronuclear approach for association, thus association schemes are introduced for each group instead of a general scheme for the entire molecule. The association scheme applied here for the hydroxyl group is the 2B scheme as discussed in our previous works,\textsuperscript{10,11} while for water the selected scheme was 4C. This scheme is considered better than the 3B scheme for application on equations of state and is also suggested as the preferential scheme by a group of molecular simulation results.\textsuperscript{17}

3. RESULTS AND DISCUSSION

3.1. Pure Water Results.
Our experience with the version of the CPA model\textsuperscript{11} described above has shown that the selection of the associative parameters needs to be carried with care, especially for smaller and stronger associative compounds such as water and methanol. For methanol, we found that higher values for the associative parameters could be employed, improving the description of saturated pressures but decreasing the quality of LLE and derivative properties. The same holds true for water. Thus, the set presented here takes into account not only the description of pure water properties but also the need to correctly describe mixtures.

It is important to note that for nonassociative compounds, the model is simply SRK with the fitting of vapor pressure to a different $\alpha$ function and a constant volume shift fitted to a single density point. For associative compounds, from the experience of this and previous works, the fitting of associative parameters should be addressed by looking (or including in the parameterization) some derivative properties or binary data. For the set presented in this work, the association parameters were fitted to $C_p$. Even then, more than one set was able to describe the pure properties accurately. Thus, as between VLE and LLE, the latter is harder to model, the set of parameters presenting the best description of the LLE for n-hexane + water were selected.

The description of the remaining water properties is rather accurate. A comparison between the results for this set and those using s-CPA with the set from Kontogeorgis et al.\textsuperscript{12} is presented in Table 1 and Figures 1 and 2. A summary of the

<table>
<thead>
<tr>
<th>Set Obtained in This Work and the One from Kontogeorgis et al.\textsuperscript{12}</th>
<th>$T_{\text{range}}$ [260–450 K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kontogeorgis et al.\textsuperscript{12}</td>
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<tr>
<td>Parameter value</td>
<td>Parameter value</td>
</tr>
<tr>
<td>$a_i$ [Pa m$^3$ mol$^{-1}$]</td>
<td>0.123</td>
</tr>
<tr>
<td>$b_i$ [10$^{-1}$ Pa m$^3$ mol$^{-1}$]</td>
<td>1.452</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.674</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$c_3$</td>
<td>0</td>
</tr>
<tr>
<td>$a_i$ [Pa m$^3$ mol$^{-1}$]</td>
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<td>$c_1$</td>
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<td></td>
<td>-2.540</td>
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<tr>
<td>$c_3$</td>
<td>-2.012</td>
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</table>
calculated and experimental critical properties is reported in Table 2. Water critical constants ($T_c$, $P_c$, $V_c$) and temperature-dependent correlations for vapor pressure, liquid density, $C_p$ and ideal gas heat capacities were obtained from the Infodata database in the commercial software MultiFlash.\(^{18}\) The vapor pressure curve applied was:

$$
\ln P = \ln P_0 + \left[ (1 - T/T_c) + 1.540(1 - T/T_c)^{3/2} - 2.896(1 - T/T_c)^3 - 1.038(1 - T/T_c)^6 \right]/T_c
$$

As can be observed in Table 1, the water association energy ($\varepsilon$) used in the new set is higher than that used for the s-CPA. This will have a very relevant impact in the description of systems containing water as discussed below. The remaining pure associative compound parameters applied in this work are presented in our previous works.\(^{10,11}\) The parameters for the nonassociating compounds are presented as Supporting Information.

In Figure 1, it can be seen that changing the usual reference reduced temperature for the volume shift has a significant impact on the density results, particularly at lower temperatures. This change leads to a correct description of the heat of vaporization close to the critical point and an overall better trend with temperature for this property.

As discussed in some previous works, the use of an unconstrained, highly flexible $\alpha$ function can introduce some inconsistencies. However, for some specific compounds, like water, where the simple nature of CPA and similar EoSs are unable to capture the trends of many of its unique properties, the introduction of constrictions might lead to an even worse thermophysical description. In Figure 3, the $\alpha$ function used in this work for water is plotted between reduced temperatures of 0.4 and 1.

### Table 2. Experimental Critical Data and Results with the Two Parameter Sets

<table>
<thead>
<tr>
<th></th>
<th>data</th>
<th>this work</th>
<th>s-CPA(^{12})</th>
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</thead>
<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>647.3</td>
<td>647.3</td>
<td>656.6</td>
</tr>
<tr>
<td>$P_c$ (MPa)</td>
<td>22.12</td>
<td>22.12</td>
<td>23.73</td>
</tr>
<tr>
<td>$V_c$ (m$^3$·kmol$^{-1}$)</td>
<td>0.056</td>
<td>0.069</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Figure 1. Results for the description of water saturated liquid density and heat of vaporization using the two sets of parameters and different temperatures to fit the volume shift.

Figure 2. Results for the description of water heat capacity using the two parameter sets. $C_v$ data values are from Abdulagatov et al.,\(^{19}\) while the values for $C_p$ were taken from the Infodata database in MultiFlash.\(^{18}\)

Figure 3. Alpha functions analyzed in this work between $T_r$ 0.4 and 1.
As can be seen, this $\alpha$ function does not decrease in the whole range of temperatures, continuously increasing in the fitted temperature range. It is important to note that the $C_p$ was used in the parametrization of this set and that $C_v$ presents a seemingly correct physical behavior for the range of temperatures in analysis, as observed in Figure 2.

One important topic to address at this point is that from the experimental data available for liquid $C_p$ and $C_v$, the value of these properties seems to almost cross each other between 273.15 and 300 K, as can be observed in the work of Chen.\(^{20}\)

Knowing that

$$C_p - C_v = -T \frac{\partial (\partial P/\partial T)}{\partial V}$$

\[ (11) \]
For \( C_p \) to have the exact same value of \( C_v \) above 0 K, either the first derivative of pressure in relation to volume at constant temperature is finite or else the first derivative of pressure with relation to temperature at constant volume is zero. The second hypothesis is the one of interest. It is thus important to know how this happens with CPA:

\[
\left( \frac{\partial P}{\partial T} \right)_V^{\text{cubic}} = \frac{R}{V - b} - \frac{1}{V(V + b)} \frac{\partial \alpha}{\partial T}
\]  

(12)

In this term (cubic contribution to the derivative), the first term is always positive, while the second is positive only if the \( \alpha \) function monotonically decreases with temperature.

The contribution for pressure from the association term is

\[
P_{\text{association}} = RT h
\]

(13)

where:

\[
\tau = \frac{1}{2V} \left( V \frac{\partial \ln g}{\partial V} - 1 \right)
\]

(14)

\[
h = \sum_i m_i (1 - X_i)
\]

(15)

with \( m_i \) being the mole number of sites of type \( i \).

The derivative for this term is then:

\[
\left( \frac{\partial P}{\partial T} \right)_{V, \text{association}} = R h - R \tau T \sum_i m_i \frac{\partial X_i}{\partial T}
\]

(16)

\( h \) is always positive, as well as \( \sum_i m_i \frac{\partial X_i}{\partial T} \). The \( \ln g \) decreases with increasing volume, in this way its derivative is negative above 278 K, when considering saturation or atmospheric conditions. Taking this into account, the first term of the derivative (concerning association) is negative while the second term is positive above this temperature, the opposite being true below. In the case of the Soave \( \alpha \) function, one association term needs to compensate both the remaining association term and
the cubic terms for the total derivative to be zero. With the $\alpha$ function and water parameter set proposed in this work, between 273 and 300 K the second term of the cubic contribution is negative and liquid densities are not used directly in the parametrization. Thus, allowing $\frac{\partial P}{\partial T}$ to be close to zero while retaining a correct description of vapor pressures and its derivatives.

Considering $\frac{\partial P}{\partial T}$ able to be zero, or close, leads to an over reliance on $\frac{\partial P}{\partial V}$ for the description of saturation pressures, and thus, despite presenting a better physical behavior, the values of the volume are far from correct when using a volume shift anchored to a temperature far from this region. Through this compensation of errors, it is possible to increase the accuracy of predictions for pure properties of water and some LLE while keeping a correct description of VLE.

It will also be important to analyze the Pitfalls of Soave type $\alpha$ functions presented by Segura et al.\textsuperscript{21} and the guidelines by Deiters\textsuperscript{22} when looking at properties and phase equilibria where the associative compounds are near or at the critical point.

### 3.2. Modeling Mixtures Containing Water

#### 3.2.1. Binary Mixtures with Alkanes ($C_4$ to $C_{10}$)

As was referred before, the value of the association energy is higher with the proposed set of parameters, which in turn introduces a heavier weight into the temperature dependence of the associative contribution. This change, as well as the $\alpha$ function and the volume shift, depending on the kind of system and conditions, introduce important improvements on the results, leading however to less accuracy for a few other systems. A noteworthy example of this is the description of water + $n$-alkane and water + $n$-alkanol systems, where the increase in the association energy of water enables a better estimation of the minima in the solubility of $n$-alkanes in water and a better description of the solubility trend for the alkanols. The better trend for these systems is associated, in some cases, with higher deviations at low temperatures. Figures 4 and 5 present the results for water + alkane between $C_4$ and $C_{10}$. Experimental data for these systems was taken from Tsonopoulos et al.,\textsuperscript{23} Marche et al.,\textsuperscript{24} Heidman et al.,\textsuperscript{25} Jou et al.,\textsuperscript{26} Pereda et al.,\textsuperscript{27} Economou et al.,\textsuperscript{28} Schatzberg,\textsuperscript{29} Noda et al.,\textsuperscript{30} and Góral and co-workers\textsuperscript{31} and calculated with the expressions from Tsonopoulos.\textsuperscript{32}

As in the previous works with this version of CPA,\textsuperscript{11} the binary interaction parameters are larger than those of s-CPA. Figures 5 and 6 present the results for the remaining systems used in this analysis. It is important to note that the improvements in the description of the aqueous phase also introduce a change in the trend for the solubility in the hydrocarbon phase. Thus, if only the hydrocarbon phase was optimized, in some particular cases (mixture with decane) higher deviations would be observed for the aqueous phase than in s-CPA. However, it is important to note that a relevant variability in the experimental data is verified (noticeable when looking at the mixtures with hexane and octane). Two figures are presented in Supporting Information concerning this behavior, including the worst case, the mixture with decane.

Before addressing a different class of compounds, it is important to evaluate if there is any trend for the binary interaction parameters of water + $n$-alkanes, as previously observed with s-CPA by Oliveira et al.\textsuperscript{33} Using the results for the studied systems, it is possible to observe a good correlation...
for the binary interaction parameters, as can be observed from Figure 6.

Later in this paper, the results for some multicomponent systems will be analyzed, using water, methanol/MEG, and petroleum fractions. Thus, it is of importance to know how the binary interaction parameters of these two other compounds (MEG and methanol) behave for systems with alkanes. The results for methanol are presented in Supporting Information, while those for MEG are from a previous article.10 A trend is also obtained for these systems.

Equations 17–19 present the correlations used between the associative compounds (water, MEG,10 and methanol) and the hydrocarbon molecular weight. Figure 6 shows the description of the fitting of the $k_{ij}$'s through these equations.

$$k_{\text{MEG}} = -0.133 \ln(\text{MW}) + 0.701$$ (17)

$$k_{\text{H}_2\text{O}} = -0.195 \ln(\text{MW}) + 1.042$$ (18)

$$k_{\text{methanol}} = -2.89 \times 10^{-4} \text{MW} + 6.10 \times 10^{-2}$$ (19)

3.2.2. Binary Mixtures with Aromatic Hydrocarbons. Using the approach of Folas et al.34 for the description of aromatics ($\varepsilon_i = \frac{V_{assoc}}{2}$; $\rho_i^\theta = \text{fitted}$), it is possible to describe also the solubility of aromatics with this version of CPA. Figure 7 presents the results for water + benzene, water + toluene, water + ethylbenzene, and water + o/m/p-xylene. Experimental results for these systems were taken from Góral et al.,36 Miller and Hawthorne,37 Jou and Mather,38 Shen et al.,39 and Pryor and Jentoft.40

As in the case of alkanes, the version of CPA applied in this work presents a more accurate trend for the solubility of aromatics in the water phase. The results for this group of compounds are in general accurate.

3.2.3. Binary Mixtures with Alkanols. The improvement on the description of the solubility minima might be in part due to this version of CPA containing more accurate pure component information (more accurate $C_p$, corrected $T_c$, and $P_c$), however, the higher value for the association energy, and different $\alpha$ function, should be the main reason for this enhanced behavior. A similar effect is observed in systems containing water and n-alkanols. However, in this case, the improvement on the qualitative description of the systems does not ensure an increase in their overall accuracy, as the influence on the aqueous phase is less accurate in this case. Figure 8 presents the results for the systems water + 1-butanol and water + 1-octanol. Experimental data are from Góral et al.,41 Lohmann et al.,12 Hessel et al.,43 and Dallos and Liszi.44

For heavier alcohols, where the association contribution becomes smaller, this is less noteworthy. Also, the current version of the model is using the same association parameters for every OH$^-$ group in whatever alcohols,10,11 which might affect more the LLE results of smaller chain alcohols. The VLE of water with four light chain alcohols (methanol, ethanol, 1-propanol, and 2-propanol) were also analyzed. For the mixtures with methanol and ethanol, temperature independent binary interaction parameters ($k_{ij} = -0.045$ and $k_{ij} = -0.004$ respectively) were applied, while for the mixtures with 1-propanol and 2-propanol there was a need to apply a temperature dependency in these parameters (water + 1-
These results are very accurate and able to describe the VLE of these compounds in a wide range of conditions. Figure 10 presents the results for water + ethylene glycol (using a $2 \times 2B$ association scheme) at two different temperatures ($k_{ij} = -0.025$), as well as the prediction ($k_{ij} = 0$) of the VLE for water + 1,3-propanediol and the correlation ($k_{ij} = -0.030$) for the VLE of water + glycerol. Experimental data are from Kamihama et al.,49 Sanz et al.,50 Oliveira et al.,51 and Soujanya et al.47

The ternary system containing these compounds was also studied, yielding a 1.20% of absolute average deviation on the bubble temperatures and 4.15% on the dew temperatures when compared to the results of Sanz et al.50 A table with these results is also presented in the Supporting Information.

3.2.4. Solubility of Water in Gas/Gas in Water. Description of the solubility for binary systems containing lighter alkanes and water, despite being possible with a temperature independent binary interaction parameter, usually requires a temperature dependency for an accurate description of both phases. Figures 11 and 12 present the results for gas solubility of the three lighter alkanes with water. Experimental data values are from Kiepe et al.,52 Rigby and Prausnitz,53 Lekvam et al.,54 Mohammadi et al.,55 Coan and King,56 Chapoy et al.,57 and Kobayashi et al.58

The results for the system water + methane shows the model to be able to accurately describe the solubility of water in the gaseous phase while presenting good results in the liquid phase. For higher temperatures, the pressure dependencies start to present deviations. Similar results are obtained for the systems containing ethane and propane.

Aqueous mixtures containing nitrogen and carbon dioxide were also studied, while considering these compounds as nonassociative. For the former, the results are accurate in both phases, using a temperature dependent $k_{ij}$ ($k_{ij} = 3.30 \times 10^{-3}T -0.6$), while for the latter the solubility in water is well described ($k_{ij} = 7.20 \times 10^{-4}T -0.07$). These results are presented in Figure 13. Experimental data was obtained from Rigby and Prausnitz,53 King et al.,59 and Hou et al.60

3.3.1. Multicomponent Mixtures. Having established the ability of our new version of CPA to describe with accuracy binary systems with water and a range of different compounds, we turned our attention to the evaluation of its ability to describe more complex mixtures. For a start, two ternary systems were studied: MEG + water + methane and MEG + water + ethanol. The results for the VLLE of the first system are presented in Figure 14, while for the second the %AAD of the bubble temperature is 0.19 and for the dew temperatures is 0.71. The results for this second system when compared to the data of Kamihama et al.49 are presented as Supporting Information. More results at different conditions for the mixture presented in Figure 14 are presented in the Supporting Information.

As discussed in our previous work10 this version of CPA is able to describe multicomponent systems containing ethylene glycol. These mixtures have been analyzed by Kontogeorgis and co-workers,3–9 using s-CPA, with good results. Two of these systems have not been previously studied using this version of the model, and the results of these fluids when mixed with MEG are presented as Supporting Information.

It is important to note that the parameters used for the interactions between water/methanol and methane/ethane/ propane are those previously fitted in this work. For many of these systems, a temperature dependency was needed on the $k_{ij}$. 

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**Figure 10.** Results for water + ethylene glycol at two different temperatures (a), water + 1,3-propanediol at 30 kPa (b), and for water + glycerol at three different pressures (c).
to correctly describe the phase equilibria. The binary interaction parameters between associative compounds are those obtained for their binary VLE description.

Figures 15 and 16 present the results for some of the systems of water + MEG + oil-based fluid studied by Kontogeorgis and co-workers using the version of CPA proposed here. In the Supporting Information, a table is presented comparing the average deviations of the two CPA versions for these systems. The condensate description considered the real components up to five carbons. From six carbons up to nine carbons, four molecular lumps were considered (C6, C7, C8, C9), where all compounds in the mixture with that carbon number were considered. Heavier molecules with 10 or more carbons were considered in a single lump (C10+) with averaged properties.

Accurate results were also obtained for the polar compounds in the hydrocarbon phase in most systems, but a higher decrease on the accuracy was verified for the heaviest system (light oil) than with s-CPA.

Applying the same approach, the description of the gas condensate studied by Pedersen et al. was also tested. These results are presented in Figure 17 as well as those from Yan et al. using s-CPA. The results obtained for these system are, in general, comparable to those of s-CPA.

Concerning results with water + methanol + HC, the mixture presented by Pedersen et al. and a synthetic mixture from Rossihol were analyzed. These results were compared to those of Yan et al. in Tables A6 and A7 presented as Supporting Information. It is noteworthy that the results obtained with the two CPA versions diverge on the accuracy for
the methanol fraction in the hydrocarbon phase. The s-CPA presents significant deviations for this fraction in the synthetic mixture, while the version applied in this work provides a good description of the experimental data. The opposite is verified with the data from Pedersen et al., while the main component in the condensate being the same as in the quaternary mixture (methane, and in similar proportions). This should in part be due to the use of different combining rules, as the ratio water:methanol is rather different in these systems and the use of different approaches for the binary interaction parameters calculation between the two versions.

4. CONCLUSIONS

A new version of CPA was evaluated here for the description of water containing mixtures. While its description of density for small, highly associative compounds, with a volume shift applied at 0.7 \( T_c \), presents somewhat higher deviations, the trend with temperature is more accurate than that obtained with s-CPA. Moreover, if a lower \( T_r \) is used to fit the volume shift, it is possible to obtain reasonable results for density between 0.45 and 0.85 \( T_r \). The modifications applied in this version also lead to a better description of liquid \( C_p \) and correct values for \( T_c \) and \( P_c \). This also enables the correct trend for the description of the heat of vaporization as well as a better trend with temperature for \( C_p \). It is also important to note that for the compounds with hydroxyl groups studied in this work, it was possible to consider the association energy as constant. The parameters for water in this version also lead to a different behavior than previous versions on the solubility of alkanes/alkanols in water. The solubility of the second compound, in many of these systems, now presents a trend closer to what is experimentally observed.

Accurate results are obtained for the description of the vapor liquid equilibria with alkanols and the solubility of gases in water/water in gases. It is important to remember that a single combining rule for the association parameters was applied, while some of the results from s-CPA have used different combining rules.

In the case of multicomponent systems, seven petroleum fluids were studied, using correlations for the interaction parameters between water/MEG and the petroleum compounds/fractions. These results are in most cases accurate with a decrease in accuracy for heavier fluids, which is to be expected due to the large extrapolations used in these cases. The results for multicomponent systems are comparable to those of s-CPA while in general improving the results of binary LLE equilibria and pure properties.

This version of CPA is thus able to describe a relevant group of properties for a complex molecule like water while presenting very promising results for VLE and LLE and an accurate representation of multicomponent systems.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b03522. Pure component parameters as well as other VLE, LLE, and gas solubility results for systems containing water, hydrocarbons, and alcohols (including methanol and/or MEG); discussion on fitting interaction parameters using only hydrocarbon phase data (PDF)

Figure 15. Results for the system cond-1 + water + MEG at 323 K (a), cond-2 + water + MEG at 303 K (b), cond-3 + water + MEG at 323 K (c), and for the system light-oil-1 + water + MEG at 303 K (d). Data from Riaz et al.3,4,7 and Frost et al.6

Figure 16. Results for the system light-oil-2 + water + MEG at 323 K (left) and fluid-1 + water + MEG at 323 K (right). Data from Riaz et al.4 and Frost et al.9

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b03522.

Pure component parameters as well as other VLE, LLE, and gas solubility results for systems containing water, hydrocarbons, and alcohols (including methanol and/or MEG); discussion on fitting interaction parameters using only hydrocarbon phase data (PDF)

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Notes
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NOMENCLATURE

\( a \) = energy parameter of CPA
\( a_c \) = value of the energy parameter at the critical point
\( b \) = co-volume
\( c_1 - c_5 (c_x) \) = alpha function parameters
\( C_p \) = Isobaric heat capacity
\( c_v \) = volume shift
\( k_{ij} \) = binary interaction parameter for the cubic energy term
\( P \) = vapor pressure
\( T \) = temperature
\( v_0, v_t \) = volume before and after translation, respectively
\( x \) = mole fraction

Greek Symbols
\( \beta \) = association volume
\( \varepsilon \) = association energy
\( \rho \) = molar density

Sub and Superscripts
\( c_n \) = carbon number
\( \text{exp, calc} \) = experimental, calculated
\( i, j \) = pure component indexes
\( np \) = number of points
\( npo \) = number of phases to optimize

Abbreviations
\%AAD = percentage of average absolute deviation
CPA = cubic plus association
s-CPA = simplified CPA
EoS = equation of state
HC = hydrocarbon
MEG = monoethylene glycol
s-CPA = simplified cubic plus association

REFERENCES


Figure 17. Results for the water solubility in the hydrocarbon phase at 100 MPa (a) and 473.15 K (b) and for the methane solubility in the aqueous phase at 100 MPa (c) and 473.15 K (d) (left).


(60) Hou, S.-X.; Maitland, G. C.; Trusler, J. P. M. Measurement and modeling of the phase behavior of the (carbon dioxide+water) mixture at temperatures from 298.15K to 448.15K. J. Supercrit. Fluids 2013, 73, 87–96.


