

# Modeling of the Mixture Critical Locus with a Modified Cubic Plus Association (CPA) EoS: Aromatics, Ketones, Ethers, Diethyl Carbonate, and THF

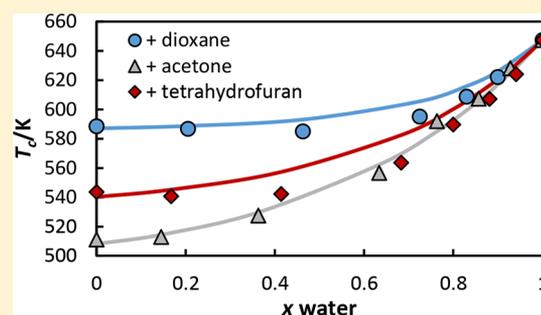
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## Supporting Information

**ABSTRACT:** The description of the critical data of a mixture is of importance for various applications such as supercritical processes, reactions close to the critical temperature, or safety design in piping. In a previous work, we have shown that a modified cubic-plus-association (CPA) equation of state is able to provide an accurate representation of critical points for mixtures of associating compounds or for mixtures of associating compounds with hydrocarbons. In the present work, this study is extended to mixtures containing associating and solvating compounds. Binary and ternary mixtures of alkanols, diethylamine or water with ketones, aromatics, ethers, tetrahydrofuran, or diethyl carbonate are studied. Binary interaction parameters are fitted from subcritical LLE or VLE data. For the binary mixtures, when analyzing the curves of  $T_c$  and  $P_c$  versus composition, the average deviation on  $P_c$  is below 2.4%, while the average  $\Delta T_c$  is below 2.5 K. Three ternary mixtures are also investigated. For these, deviations are below 4.0% and 4.3 K, respectively.



## 1. INTRODUCTION

The behavior of supercritical fluids presents intermediate characteristics between liquids and gases. These properties make these fluids highly versatile, creating interesting opportunities for diverse applications.<sup>1</sup> However, the proper knowledge of the critical locus for mixtures is not only relevant for supercritical applications but also for the correct optimization of near critical applications and prevention of potential operational hazards.

Cubic equations of state are well-known tools to determine mixture critical pressures and temperatures for nonassociating compounds, although they fail to accurately represent all properties at the critical point (such as the critical density).<sup>2</sup> When considering mixtures with associating compounds, the cubic equations of state are in many cases still able to describe critical temperatures and pressures. However, the description of subcritical properties is often incorrect, and so having a model that is able to represent the subcritical, critical, and supercritical conditions is an advantage.

In a previous work,<sup>3</sup> the modified cubic-plus-association equation of state (CPA EoS), which also forces the correct description of pure component critical pressure and temperature, was applied to some mixtures containing associating compounds. This model allies the simplicity and robustness of a cubic term with the improved dealing of associating mixtures offered by an association term. Such an approach improves the description of subcritical properties of mixtures containing associating compounds while in most cases keeping an accurate

description of the critical points.<sup>3</sup> The results obtained by this approach were in line with those obtained by the recent reparametrizations of the simplified CPA<sup>4</sup> and PC-SAFT.<sup>5</sup>

In the case of mixtures containing one solvating compound, Polishuk et al.<sup>6</sup> analyzed the description of critical points for mixtures containing water and aromatics, using the CP-PC-SAFT EoS.<sup>7</sup> Qian et al.<sup>8</sup> have also analyzed mixture critical points including some solvating compounds, alkenes, and aromatics, using the PPR78 EoS.<sup>9</sup> In their recent studies of critical points of mixtures containing MTBE and diethyl carbonate, Han et al.<sup>10</sup> and He et al.<sup>11</sup> applied diverse non-EoS methods to describe binary and ternary mixtures.

In this study, we consider mixtures containing at least one associating and one solvating compound. To describe the interaction between solvating and associating compounds, we applied the approach proposed by Folas et al.<sup>12</sup> This approach was already used with this version of CPA to model the LLE of water and aromatics with good results.<sup>13</sup>

The binary mixtures analyzed in this study contain aromatics, ketones, ethers, tetrahydrofuran (THF) or diethyl carbonate, using binary interaction parameters fitted either to LLE or to VLE data, in most cases, at near atmospheric conditions. Three

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ternary mixtures are also analyzed for methyl-*tert*-butyl-ether (MTBE) with alkanols and alkanes and for diethyl carbonate with ethanol and heptane.

The determination of multicomponent mixture critical points was made following the algorithms from Heidemann and Khalil,<sup>14</sup> Michelsen,<sup>15</sup> and Hoteit et al.,<sup>16</sup> or otherwise by calculating bubble and dew point curves and finding their ending points.

## 2. MODEL

The modified CPA model uses in its base the same equations as the simplified CPA EoS.<sup>4</sup>

$$Z = Z^{\text{phys}} + Z^{\text{assoc}}$$

$$= \frac{1}{1 - B\rho} - \frac{A(T)\rho}{RT(1 + B\rho)} - \frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i m_i (1 - X_i) \quad (1)$$

In eq 1,  $A$  is the energy parameter ( $A(T) = n^2 a(T)$ ), whereas  $B$  is the covolume parameter ( $B = nb$ ). The density is represented by  $\rho$ , a simplified hard-sphere radial distribution function is introduced as  $g$ ,<sup>4</sup>  $X_i$  is the fraction of nonbonded sites of type  $i$ , and finally,  $m_i$  is the mole number of sites of type  $i$ . Equations 2 and 3 present the mixing rules for  $a$  and  $b$ .

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (2)$$

$$b = \sum_i x_i b_i \quad (3)$$

where:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (4)$$

and  $k_{ij}$  is a binary interaction parameter.

The differences between the simplified CPA model<sup>4</sup> and the modified version applied in this work are the alpha function, the use of a temperature-independent volume shift, the fitting of the pure component critical point and the parametrization procedure.<sup>5,13,17,18</sup> In terms of alpha function, this CPA model uses a modified Mathias–Copeman<sup>19</sup> function, which can use up to five parameters:

$$a(T) = a_c (1 + T'c_1 + T'^2c_2 + T'^3c_3 + T'^4c_4 + T'^5c_5)^2 \quad (5)$$

with  $T' = (1 - \sqrt{T_r})$ ;  $T_r = \frac{T}{T_c}$

When extrapolating above the critical point, the use of high-order polynomial functions may cause inconsistencies.<sup>20</sup> To avoid these problems, it should be ensured that, above the critical point, the alpha function decreases monotonically with temperature.<sup>21</sup> Following these guidelines, this EoS uses an extrapolation based on the API Soave alpha function by Graboski and Daubert,<sup>22</sup> which conforms to the following restrictions:

$$\left\{ \begin{array}{l} T < T_c; \alpha = \text{eq 5} \\ T = T_c; \alpha = 1 \\ 1 < T_r < 1.1; \alpha = \{\text{continuous interpolation function}\} \\ T_r > 1.1; \alpha = \alpha_{\text{API}} = (1 + S_1(1 - \sqrt{T_r}))^2 \end{array} \right. \quad (6)$$

$\alpha_{\text{API}}$  is the Soave type alpha function proposed by Graboski and Daubert.<sup>22</sup> and  $S_1$  is the parameter from the API alpha function.

The parametrization procedure in this version of CPA starts from given association parameters and then forces the correct description of  $T_c$  and  $P_c$  by employing the following restrictions:

$$P_{\text{CPA}}(T_c^{\text{exp}}, V_c^{\text{calcd}}) = P_c^{\text{exp}} \quad (7)$$

$$\left( \frac{\partial P}{\partial v} \right)_T \Big|_{T=T_c, v=v_{\text{calcd}}} = 0 \quad (8)$$

$$\left( \frac{\partial^2 P}{\partial v^2} \right)_T \Big|_{T=T_c, v=v_{\text{calcd}}} = 0 \quad (9)$$

The main parametrization routine fits the alpha function parameters to the saturation pressure, whereas the liquid density is obtained through a temperature independent Péneloux type volume shift:<sup>23</sup>

$$v_l = v_0 - c_{\text{vs}} \quad (10)$$

The association term parameters are adjusted in an external cycle and can be fitted using other pure component properties, as well as binary phase equilibrium data. A group-contribution approach, or transferability approach, for such association parameters can also be employed.<sup>13,17</sup>

To obtain the binary interaction parameters that were not previously reported,<sup>13,17,18</sup> we fitted the CPA results to VLE data using one of the two following objective functions (for isobaric and isothermal VLE, respectively):

$$\text{OF} = \sum_i^{np} \left( \frac{T_{\text{bub}}^{\text{exp}} - T_{\text{bub}}^{\text{calcd}}}{T_{\text{bub}}^{\text{exp}}} \right)^2 \quad (11)$$

$$\text{OF} = \sum_i^{np} \left( \frac{P_{\text{bub}}^{\text{exp}} - P_{\text{bub}}^{\text{calcd}}}{P_{\text{bub}}^{\text{exp}}} \right)^2 \quad (12)$$

The CR-2<sup>24</sup> combining rules were applied for the cross-associative parameters:

$$\beta^{ij} = \sqrt{\beta^i \beta^j} + \beta_0^{ij} \quad (13)$$

$$e^{ij} = \frac{(\varepsilon^i + \varepsilon^j)}{2} \quad (14)$$

Where  $\beta_0^{ij}$  is a cross-association binary interaction parameter fitted from equilibrium data and used to consider induced cross-association. In what follows, the association scheme for the hydroxyl group is the 2B scheme, as discussed in a previous work.<sup>17</sup> The same scheme was applied for diethylamine. For water, the selected scheme was 4C.

On a previous article,<sup>18</sup> we discussed the application of the method proposed by Folas et al.<sup>12</sup> to describe solvation using the modified CPA model. This approach considers both eqs 13 and 14, and thus the energy of association is half that of the associating compound, whereas the volume of association is fitted through  $\beta_0^{ij}$ . In the present work, this is expanded to the study of mixture critical points containing at least one solvating and one associative components.

## 3. RESULTS AND DISCUSSION

As in a previous article,<sup>3</sup> most of the binary interaction parameters were obtained by fitting the VLE of the systems at

Table 1. Binary Interaction Parameters Applied in This Work

compd 1	compd 2	data	$k_{ij}$	$\beta_0^i$
water	benzene	LLE <sup>25</sup>	0.170	0.010
water	Toluene	LLE <sup>25</sup>	0.145	0.009
water	<i>p</i> -xylene	LLE <sup>25</sup>	0.111	0.007
water	<i>o</i> -xylene	LLE <sup>25</sup>	0.119	0.008
water	naphthalene	LLE <sup>26</sup>	0.120	0.005
water	1-methylnaphtalene	LLE <sup>27</sup>	0.103	0.007
methanol	benzene	VLE (1 bar) <sup>28</sup>	0.034	no $\beta_0^i$
ethanol	benzene	VLE (1 bar) <sup>29</sup>	0.042	no $\beta_0^i$
1-propanol	benzene	VLE (1 bar) <sup>30</sup>	0.039	no $\beta_0^i$
2-propanol	benzene	VLE (313 K) <sup>31</sup>	0.043	no $\beta_0^i$
1-butanol	benzene	VLE (1 bar) <sup>32</sup>	0.032	no $\beta_0^i$
diethylamine	benzene	VLE (308 K) <sup>33</sup>	-0.028	no $\beta_0^i$
water	acetone	VLE (473 K) <sup>34</sup>	-0.100	0.020
ethanol	acetone	VLE (1 bar) <sup>35</sup>	0.041	0.018
ethanol	2-butanone	VLE (1 bar) <sup>36</sup>	0.028	0.014
2-propanol	2-butanone	VLE (1 bar) <sup>37</sup>	0.022	0.005
water	THF	VLE (six press.) <sup>38,39</sup>	-0.018	0.028
1-butanol	diethyl ether	VLE (four Temp.) <sup>40</sup>	no $k_{ij}$	no $\beta_0^i$
methanol	MTBE	VLE (1 bar) <sup>41</sup>	0.013	0.018
ethanol	MTBE	VLE (1 bar) <sup>42</sup>	0.005	0.008
1-propanol	MTBE	VLE (1 bar) <sup>43</sup>	0.014	0.008
heptane	MTBE	VLE (1 bar) <sup>41</sup>	0.020	no $\beta_0^i$
diethyl carbonate	ethanol	VLE (1 bar) <sup>44</sup>	0.010	0.006
diethyl carbonate	heptane	VLE (1 bar) <sup>45</sup>	0.060	no $\beta_0^i$

near-atmospheric conditions (whenever this is not the case it is mentioned in the text). The binary interaction parameters are presented on Table 1. The VLE description using these binary interaction parameters is presented as Supporting Information. Table A1 in the Supporting Information presents the  $T_c$  and  $P_c$  values applied for each compound. The pure component parameters for the compounds in analysis can be found in the Supporting Information.

**3.1. Systems Containing Aromatics.** As a first step and having previously studied the LLE of water + aromatics,<sup>18</sup> it is of interest to verify if the same binary interaction parameters are able to describe mixture critical points. Figure 1 presents the results for water + benzene.

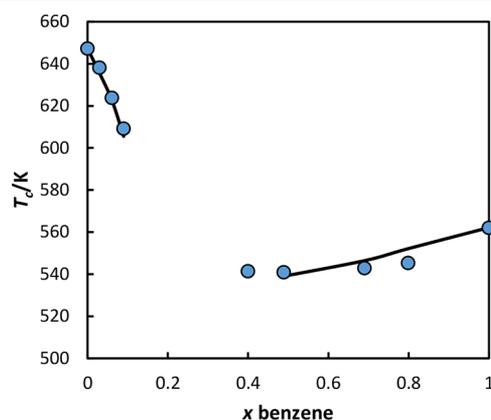


Figure 1. Results for the VLE mixture critical temperatures of water + benzene. Full lines, results using the modified CPA. Data from Hicks and Young.<sup>46</sup>

The results show that the solvation approach was able to accurately capture the dependence on composition of the critical temperature. An average  $\Delta T$  of 2.5 K (a summary of the average

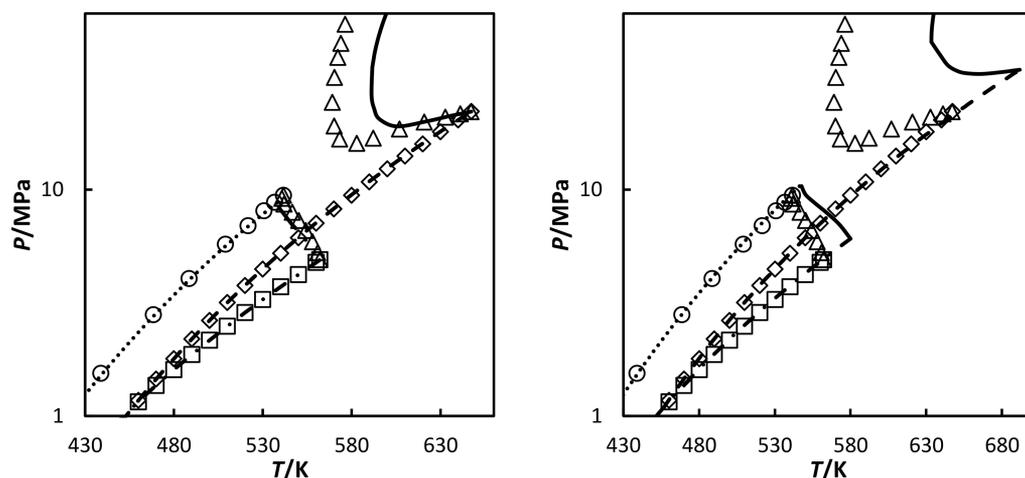
deviations is presented on Table 2) is obtained for the data of Hicks and Young.<sup>46</sup> Figures 2 and 3 analyze the description of critical data for water + aromatics, in terms of  $T$  vs  $P$ .

Table 2. Deviations on  $T_c$  and  $P_c$  for the Mixtures in Analysis<sup>a</sup>

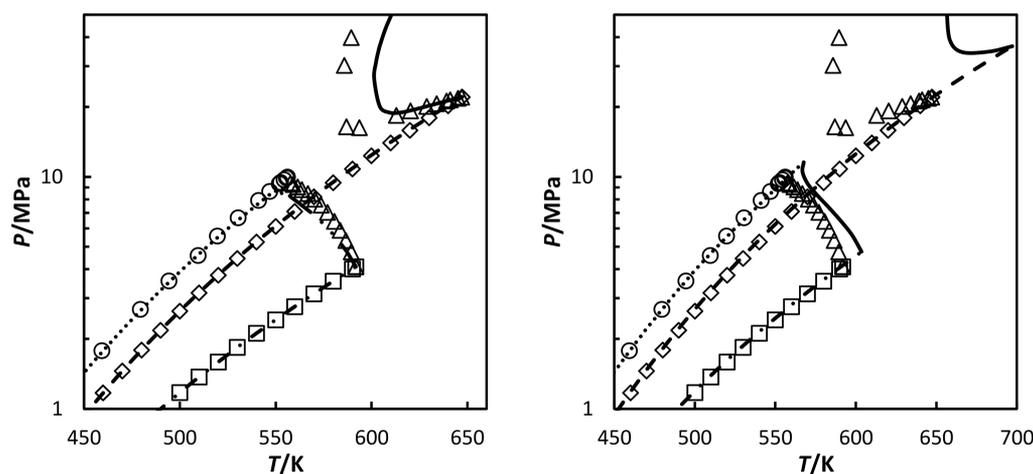
mixture	%AAD		$\Delta T$ (K)
	$T_c$	$P_c$	
water + benzene	0.44	6.21	2.51
methanol + benzene	0.31	5.15	1.61
ethanol + benzene	0.25	2.83	1.32
1-propanol + benzene	0.12	1.42	0.65
1-butanol + benzene	0.19	1.31	1.07
2-propanol + benzene	0.20		1.05
dimethylamine + benzene	0.99		5.20
water + acetone	0.53		3.00
ethanol + acetone	0.46		2.37
ethanol + 2-butanone	0.14		0.72
2-propanol + 2-butanone	0.16		0.83
1-butanol + diethyl ether	0.21	0.51	1.12
water + THF	1.49		8.52
methanol + MTBE	0.72	2.80	3.56
ethanol + MTBE	0.65	1.56	3.22
1-propanol + MTBE	0.71	0.35	3.65
ethanol + diethyl carbonate	0.28	1.24	1.49
methanol + 1-propanol + MTBE	0.83	3.12	4.22
ethanol + heptane + MTBE	0.71	3.97	3.57
ethanol + heptane + diethyl carbonate	0.46	3.74	2.45

<sup>a</sup>These deviations are for the data, where an experimental composition is available.

Figure 2 presents a comparison of the results for water + benzene, using the modified CPA and the recently proposed VS-PC-SAFT.<sup>48</sup> In Figure 3, a similar comparison is conducted for the results of water + toluene, using the modified CPA



**Figure 2.** Phase diagrams for water + benzene using the modified CPA (left) and with the volume shifted PC-SAFT (right).  $\diamond$ , pure water saturation pressures;<sup>47</sup>  $\square$ , pure hydrocarbon saturation pressures;<sup>47</sup>  $\Delta$ , VLE critical points;<sup>26</sup>  $\circ$ , liquid–liquid–gas line.<sup>26</sup>



**Figure 3.** Phase diagrams for water + toluene using the modified CPA (left) and with PC-SAFT (right).  $\diamond$ , pure water saturation pressures;<sup>47</sup>  $\square$ , pure hydrocarbon saturation pressures;<sup>47</sup>  $\Delta$ , VLE critical points;<sup>26</sup>  $\circ$ , liquid–liquid–gas line.<sup>26</sup>

and the original PC-SAFT using the parameters from Gross and Sadowski<sup>5,49</sup> and a  $k_{ij}$  of 0.09.

The results presented in Figures 2 and 3 show very similar trends for the subcritical lines, using the three approaches with all equations predicting a type IIIa phase diagram,<sup>50</sup> which is in agreement with the experimental data. However, the results concerning critical data are largely improved when applying the modified CPA. This is in a part due to the correct description of the pure component critical pressures and temperatures in this version of CPA. Nevertheless, it is important to note that recently Polishuk and co-workers<sup>6</sup> have applied the critical point (CP) PC-SAFT to describe the same mixtures with accurate results for the critical data. For the mixtures, water + *o*-xylene and water + *p*-xylene the results using the modified CPA are presented in the Supporting Information.

Figure 4 presents results for two more aromatic mixtures with water, naphthalene, and 1-methylnaphthalene. These binary mixtures are known to form type II phase diagrams.

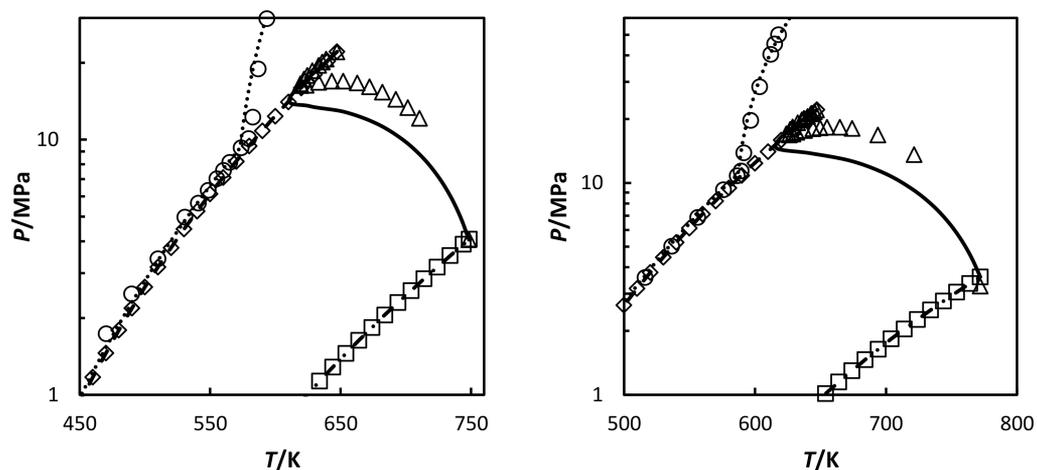
The results in Figure 4 are accurate for most lines, presenting, however, relevant deviations on the critical pressures for the VLE critical points. When comparing these results to those of Polishuk and co-workers,<sup>6</sup> it is interesting to note that although the VLE critical points are less accurate, the present approach is more accurate for the description of LLE critical points. This

should come from the fitting to LLE data applied in this work, whereas the work with CP-PC-SAFT applies no binary interaction parameters. Both the present method and CP-PC-SAFT tend to underestimate the liquid–liquid–gas line at lower temperatures.

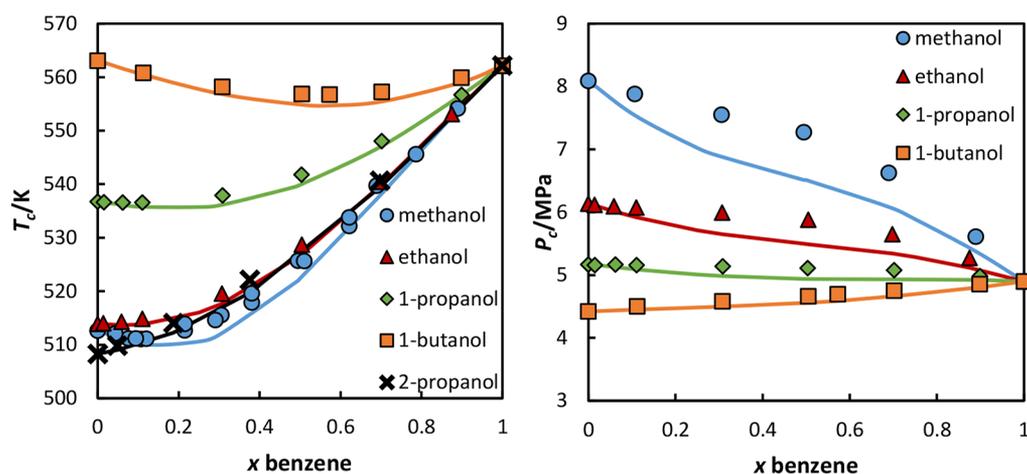
The LLE results for these two mixtures are presented in the Supporting Information.

Besides the study of water + aromatics, it is important to look at the description of aromatics + alkanols. The present model found type I diagrams for these mixtures. (The full diagrams where CPA predicts type I behavior are presented in the Supporting Information). For these systems, as reported with s-CPA,<sup>12</sup> it is possible to describe VLE accurately without the use of a  $\beta_{ij}^j$ . Small variations are observed between the two approaches. Figure 5 presents the results for binary systems of benzene with five different alkanols.

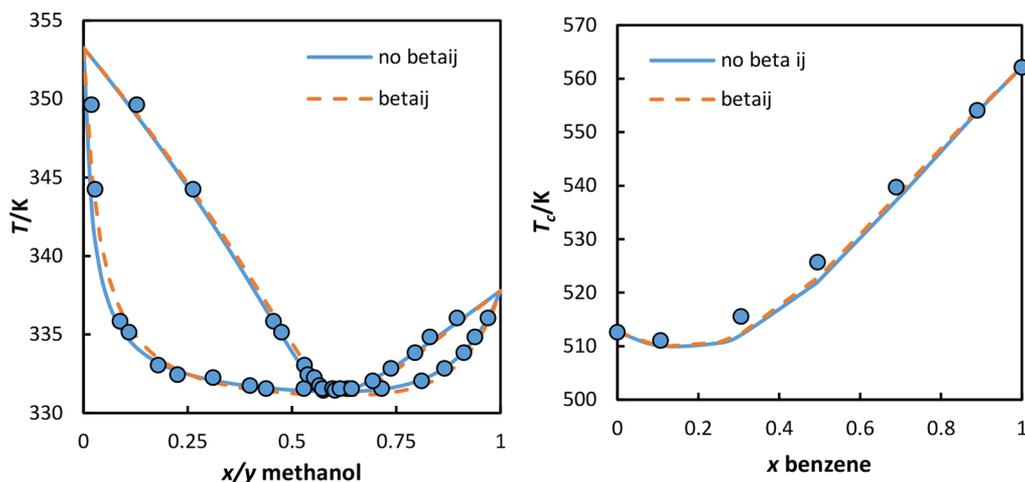
Without a  $\beta_{ij}^j$  value, it is still possible to obtain an accurate description for the critical temperatures, mostly within 2 K from the experimental data. However, for the critical pressures, the deviations are significant for the systems with smaller alkanols. Such a behavior was also previously observed for the mixtures of alkanols + alkanes.<sup>3</sup> It is also important to note that, for methanol + benzene, there is a relevant impact of the cross-association for the subcritical VLE at low methanol concentrations.<sup>12</sup> Figure 6 presents the differences between considering solvation or



**Figure 4.** Phase diagrams for water + naphthalene (left) and water + 1-methylnaphthalene (right) using the modified CPA.  $\diamond$ , pure water saturation pressures;<sup>47</sup>  $\square$ , pure hydrocarbon saturation pressures;<sup>47</sup>  $\Delta$ , VLE critical points;<sup>26</sup>  $\circ$ , liquid-liquid-gas line and LLE critical points.<sup>26</sup>



**Figure 5.** Results for the mixture critical points of alkanols + benzene. Full lines, results using the modified CPA. Data from Hicks and Young.<sup>46</sup>



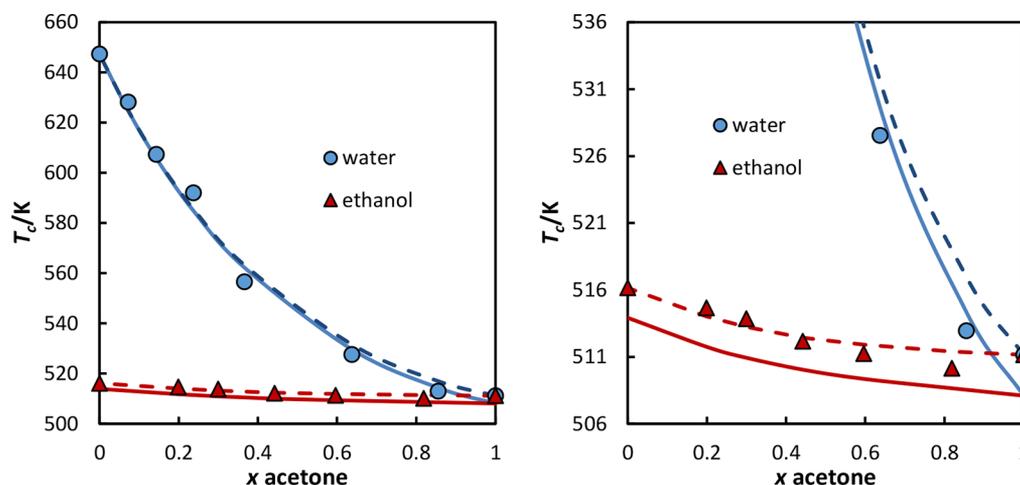
**Figure 6.** VLE at 1 bar (left) and mixture critical temperatures for methanol + benzene. The beta<sub>ij</sub> set uses ( $k_{ij} = 0.058$ ;  $\beta_{ij} = 0.005$ ). Data from Hicks and Young<sup>46</sup> and Nagata.<sup>28</sup>

considering benzene as an inert compound, for VLE at 1 bar and at critical temperatures. For the differences between the critical pressures, see the [Supporting Information](#).

Because of the decrease in the influence of the association term, for the heavier alkanols, the results for mixtures containing these compounds are less influenced by the introduction of a

binary interaction parameter for the volume of association. In the right part of [Figure 5](#), 2-propanol is not presented because of the lack of experimental  $P_c$  data.

**3.2. Systems Containing Ketones.** The modeling of ketones is not straightforward using CPA. For some applications they may be considered as solvating compounds, while for



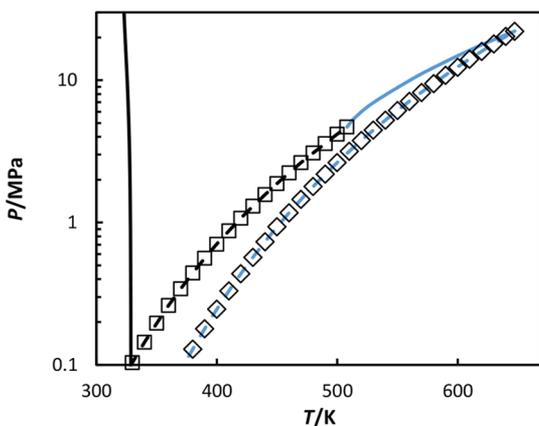
**Figure 7.** Critical temperature results for water + acetone and ethanol + acetone. The image on the right is a detail of the one on the left. Full lines, parameter sets considering Multiflash critical data;<sup>47</sup> dashed lines, parameter sets considering the critical temperatures from Marshall et al.<sup>52</sup> Experimental data from Marshall et al.<sup>52</sup>

others an associative scheme (usually 2B) is applied.<sup>51</sup> In this work, ketones are considered solvating compounds. Figure 7 presents the results for the mixtures acetone + water and acetone + ethanol. For all these mixtures, except water + acetone, phase diagrams of type I were found and are presented in the Supporting Information.

The pure component critical temperatures used in this work were taken from Multiflash,<sup>47</sup> and are slightly different than those from Marshall et al.<sup>52</sup> used as experimental data in Figure 7. The analysis of critical data from the DIPPR<sup>53</sup> and TRC databases<sup>33</sup> corroborates the use of the critical data from Multiflash.<sup>47</sup> When the critical data from Marshall et al.<sup>52</sup> are used, the model keeps a similar trend but is unable to describe the behavior suggested between 0.6 mole fraction of acetone and pure acetone. It is important to note that by using different  $T_c$  and  $P_c$  data, the cubic term parameters are changed, only the association parameters are kept with the same values.

In the case of water + acetone, the modified CPA overestimates the possibility of an immiscibility and predicts a phase diagram of type II, with LLE critical points at lower temperatures. This is presented on Figure 8.

For the mixture water + acetone the average  $\Delta T$  is below 3.2 K for both sets of pure component critical temperatures, but using



**Figure 8.** Phase diagram for water + acetone.  $\diamond$ , pure water saturation pressures;<sup>47</sup>  $\square$ , pure acetone saturation pressures.<sup>47</sup> Full lines are the critical predictions using the modified CPA. Dashed lines are calculated saturation curves for the pure compounds.

the critical temperatures in Multiflash this average is slightly smaller (3.0 K). For ethanol + acetone, there is an opposite behavior due to both components presenting a higher critical temperature in Marshall's data. Thus,  $\Delta T$  is 0.49 K for the case using Marshall's critical temperatures, whereas it is 2.37 K using the standard set.

A similar situation is observed for diethylamine + benzene, which is presented in the Supporting Information.

For 2-butanone, two mixtures are analyzed, with ethanol and with 2-propanol. These are presented on Figure 9.

The results of critical temperatures for the mixtures containing 2-butanone are accurate (in both cases the average  $\Delta T$  is below 0.85 K). Thus, it seems reasonable to consider ketones as solvating compounds for the estimation of critical points. Although the results for the critical data are very similar, when using either approach, the introduction of a  $\beta_i^j$  significantly improves the description of subcritical phase equilibria. In the case of 2-propanol mixed with 2-butanone, it appears that the best description is obtained considering 2-butanone as an inert compound. However, both results should be within the data experimental uncertainty, both in this case and in the case containing ethanol, thus it is not completely clear which approach is better for these mixtures.

**3.3. Systems Containing Ethers.** Critical data concerning the mixtures diethyl ether + 1-butanol and THF + water are also available. Figures 10 and 11 present these results.

The present approach is able to accurately predict the properties for 1-butanol + diethyl ether, without the need of any binary interaction parameter. The %AAD for pressure is below 0.52%, whereas the average  $\Delta T$  is of 1.12 K. One of the reasons for these accurate results, while considering no solvation, is due to the smaller relevance of the association term in 1-butanol, which reduces the need for explicitly accounting solvation in these mixtures. It is also important to note that 1-butanol and diethyl ether present very similar structures, with both molecules having the same chemical formula, which leads to a simpler description of their interactions, with a smaller overall need for binary interaction parameters.

For diethyl ether + 1-butanol the modified CPA predicted a type I phase diagram, whereas for THF + water, the equation of state predicted a type II diagram, similar to what was predicted for water + acetone. Figure 12 presents the type II phase diagram for water + THF.

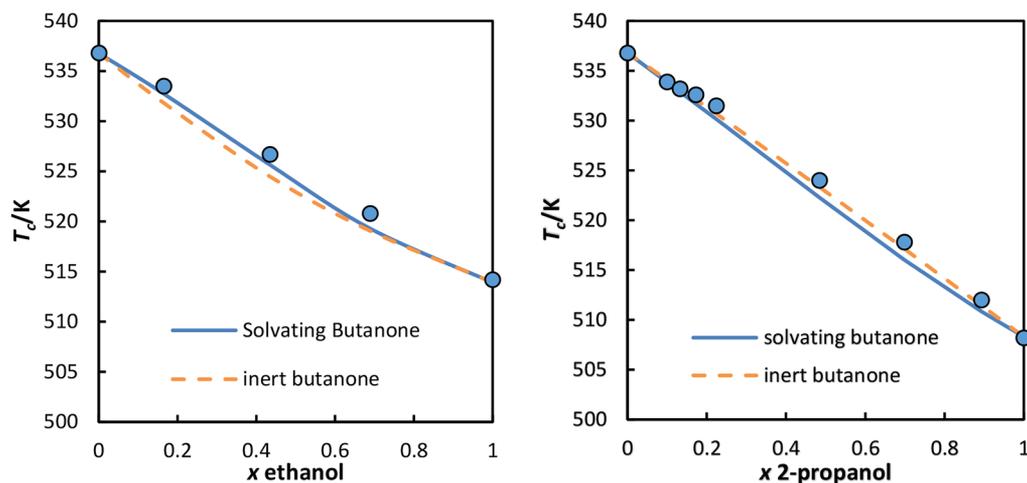


Figure 9. Critical temperature results for ethanol +2-butanone (left) and 2-propanol +2-butanone (right). Experimental data from Nazmutdinov et al.<sup>54</sup>

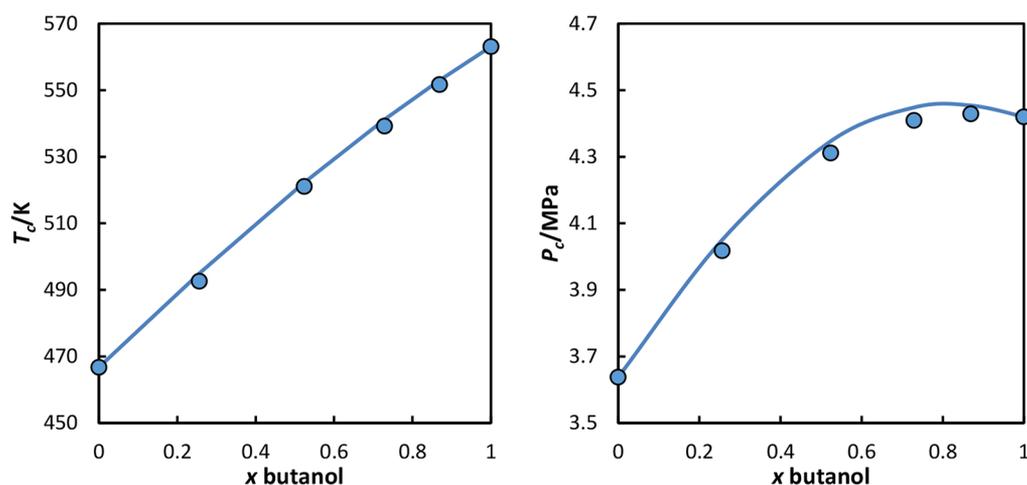


Figure 10. Critical data for 1-butanol + diethyl ether. Full lines, results using the modified CPA. Experimental data are from Kay and Donham.<sup>40</sup>

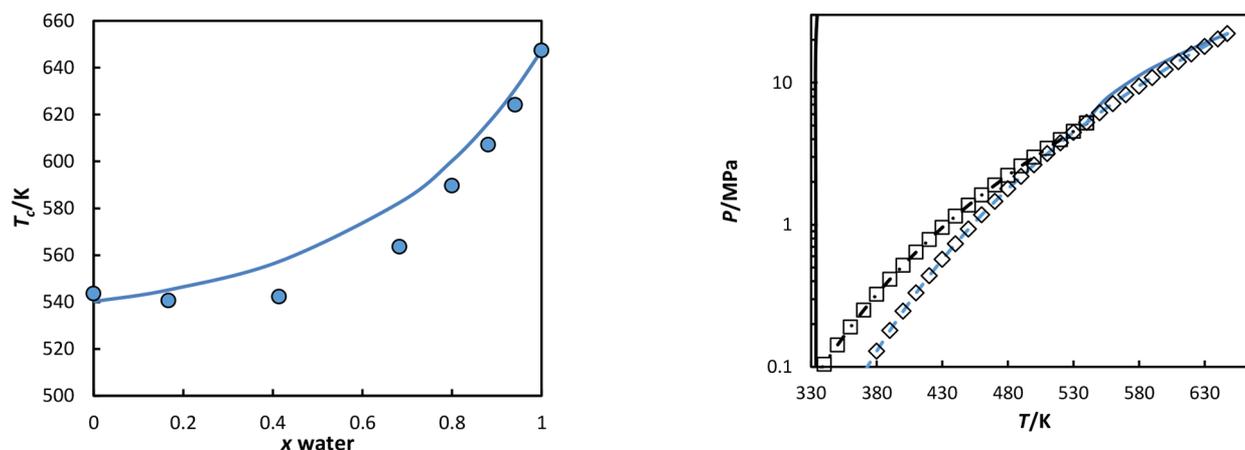
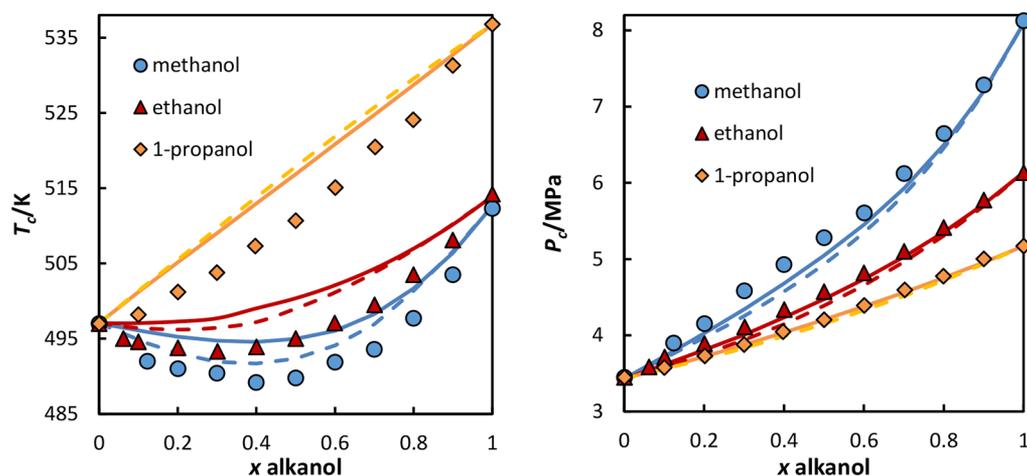


Figure 11. Critical temperature description for water + THF. Full lines, results using the modified CPA. Experimental data are from Marshall et al.<sup>52</sup>

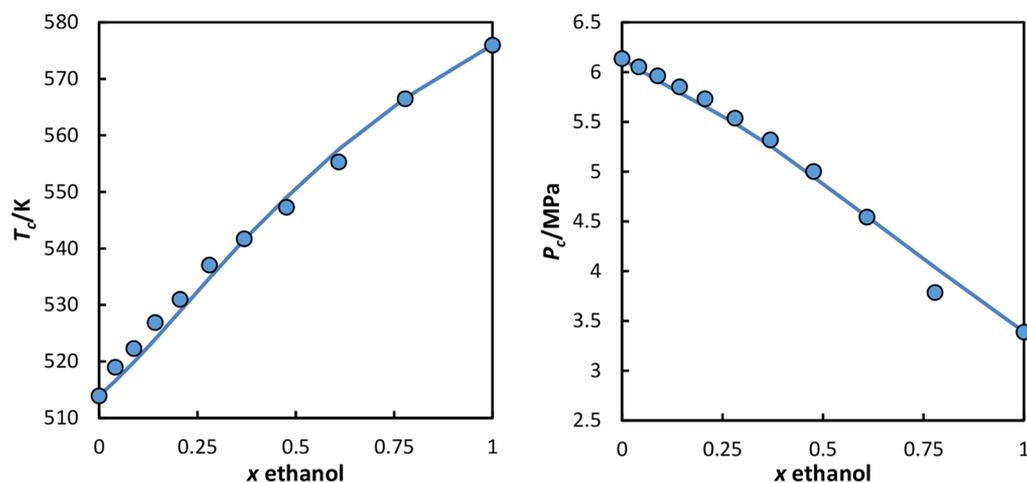
Figure 12. Phase diagram for water + THF.  $\diamond$ , pure water saturation pressures,<sup>47</sup>  $\square$ , pure THF saturation pressures.<sup>47</sup> Full lines are the critical predictions using the modified CPA. Dashed lines are calculated saturation curves for the pure compounds.

This behavior is not supported by the literature data and a diagram of type VI was instead expected for this mixture as suggested by Wallbruch and Schneider.<sup>55</sup> The results for water + THF, in terms of VLE critical points, present some relevant deviations for the critical temperature at intermediate compositions (average  $\Delta T$  of 8.52 K). No data were available for the critical pressures of this mixture. From the study of the systems where both  $T_c$  and  $P_c$

data were available, the introduction of solvation seemingly improves the description of some critical pressures, when considering a strongly associating molecule (like water or methanol). This is verified in the mixtures containing MTBE, as will be shown below, where critical temperature also presents relevant deviations, while critical pressure is well-described.



**Figure 13.** Critical data for MTBE + 1-alkanol. Full lines, results considering solvation; dashed lines, MTBE considered as an inert compound. Experimental data is from Han et al.<sup>10</sup>



**Figure 14.** Critical data for diethyl carbonate + ethanol. Full lines, results using the modified CPA. Experimental data is from He et al.<sup>11</sup>

The remaining mixtures in analysis presented phase diagrams of type I, which are presented in the [Supporting Information](#).

For methyl *tert*-butyl ether (MTBE) Han et al.<sup>10</sup> and Wang et al.<sup>56</sup> have studied mixture critical properties of binary and two ternary systems, containing at least one associative compound. The results for the binary systems are presented on [Figure 13](#).

The results, for mixtures containing MTBE, present mostly higher deviations in the critical temperature description than for the case of alkanes + alkanols. However, the deviations for the critical pressures are smaller. There is also a decrease in accuracy for  $T_c$  in methanol and ethanol, when considering solvation, while the critical pressures are improved for all mixtures. The %AAD for pressure in these mixtures is always below 3%, (below 0.35% in the case of 1-propanol). The average  $\Delta T$  is above 3.22 K for all these mixtures ([Table 2](#)). As previously stated, for the heavier alkanols (in this case 1-propanol), the results present small differences between using or not cross-association binary parameters. It is also interesting to note that for 1-propanol, the behavior obtained due to the introduction of a binary interaction parameter for the volume of association is opposite to that observed with methanol and ethanol. This should result from the decrease in relevance of the association term, from ethanol to 1-propanol. However, the behavior for the critical pressures is maintained. A similar change in behavior was observed for the mixtures containing 2-butanone. The improved behavior for

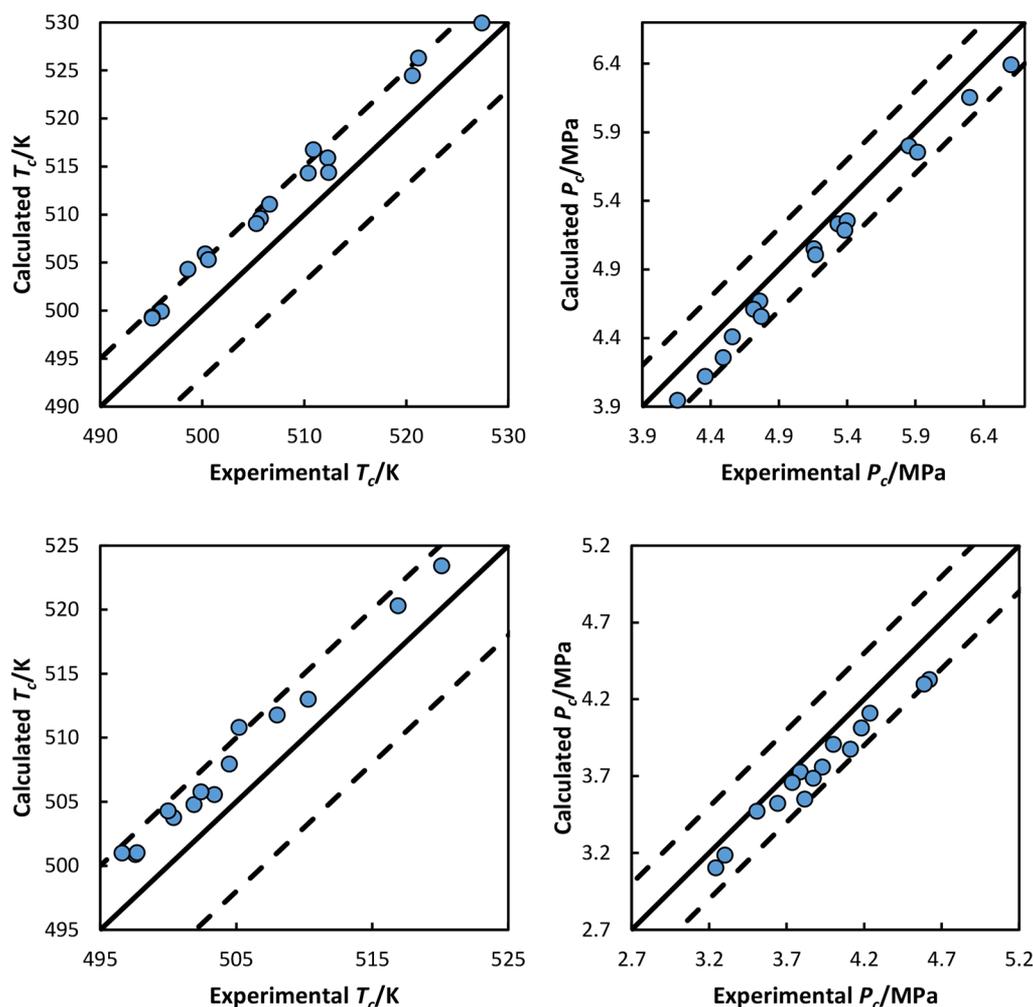
critical pressures and decrease in accuracy for critical temperatures when using a binary interaction parameter for the volume of association, may be linked to the higher steric hindrance of MTBE, when compared to the remaining compounds analyzed in this study. However, this is not clear, as this behavior was only observed for the mixtures containing MTBE.

**3.4. Diethyl Carbonate Containing Systems.** In [Figure 14](#), the results for the mixture diethyl carbonate + ethanol are presented.

As in the case of the mixtures containing MTBE, the description of the critical pressure of diethyl carbonate + water are accurate, except for a single data point at higher concentrations of ethanol (%AAD of 1.23% for the whole mixture). A good trend is also obtained for the results of the critical temperature (average  $\Delta T$  of 1.49 K).

**3.5. Ternary Mixtures.** As mentioned before, critical locus data are available for two ternary systems, MTBE + methanol + 1-propanol and MTBE + heptane + ethanol. The average percentage of absolute deviations obtained for the first of these systems are of 0.83 and 3.12% for  $T_c$  and  $P_c$ , respectively (average  $\Delta T$  of 4.2 K). For the second system these are 0.71% and 3.97% (average  $\Delta T$  of 3.6 K). The parity diagrams for these ternary systems are presented in [Figure 15](#).

These results present deviations similar to those of the binary systems and are in good agreement with the experimental data.



**Figure 15.** Parity diagrams for  $T_c$  and  $P_c$  of MTBE + ethanol + heptane (bottom) and for MTBE + methanol + 1-propanol (top). The dashed lines correspond to  $\pm 5$  K and  $\pm 0.3$  MPa. Experimental data is from Wang et al.<sup>56</sup>

A ternary mixture of diethyl carbonate + ethanol + heptane reported by He et al.<sup>11</sup> was also studied here. These results are presented in Figure 16.

For this mixture the %AAD are of 0.46% for  $T_c$  (average  $\Delta T$  of 2.45 K) and 3.74% for  $P_c$ . These values are similar to those obtained for the ternary mixtures with MTBE, presenting a slightly better description of critical temperatures. These deviations are also within the same order of magnitude as those obtained for the binary mixtures.

Table 2 presents the average deviations for the results obtained in this work.

#### 4. CONCLUSIONS

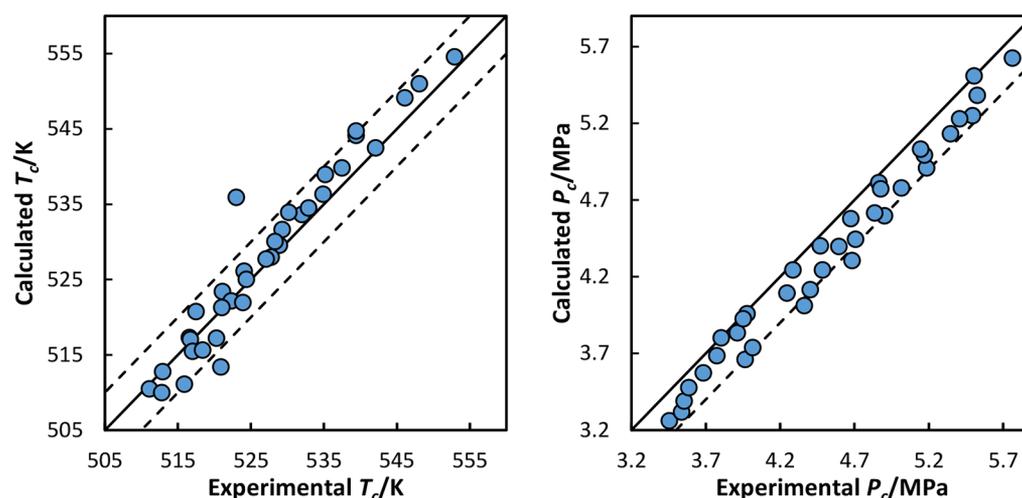
The estimation of mixture critical locus with the modified CPA was extended here to solvating compounds. An accurate representation was obtained for the critical temperatures for most of these mixtures, while for the critical pressures accurate results were obtained for all binary mixtures except for benzene + alkanols where deviations were slightly higher than for the other mixtures investigated. However, it is notorious that for the specific case of the MTBE mixtures, there is an improvement on the description of the critical pressure, and a corresponding decrease on the accuracy of the critical temperatures. Although this is only true for the case of mixtures containing MTBE, there are some cases where both an accurate description of the critical

temperatures and critical pressures were obtained, as is the case of 1-butanol + diethyl ether and diethyl carbonate + ethanol.

For mixtures of water + aromatics, the present results were compared with PC-SAFT, both the original and the volume-shifted version. The modified CPA presents better results for the critical temperatures and pressures for these mixtures while keeping an accurate description of the pure compound saturation pressures and liquid–liquid–gas lines. The results are also comparable with the CP-PC-SAFT and while the present approach presents higher deviations for VLE critical points in these mixtures, for the mixtures presenting a phase diagram of type II, the modified CPA presents an accurate description of the liquid–liquid critical points.

It is also important to note that for various of these compounds, there are reported pure component critical temperatures that deviate more than 4 K from other literature data. Although in many cases, the uncertainties are not stated, it should be considered that the expected deviations can be on this order of magnitude for the mixture critical temperatures.

There is a slight degradation on the accuracy of the model when going from binary to ternary mixtures. However, the higher value on the deviation for critical temperatures (an average  $\Delta T$  of 4.3 K, whereas for binary mixtures, it is 2.5 K) is most likely due to the lower accuracy for the mixtures with MTBE.



**Figure 16.** Parity diagrams for  $T_c$  and  $P_c$  of diethyl carbonate + ethanol + heptane. The dashed lines correspond to  $\pm 5$  K and  $-0.3$  MPa. Experimental data is from He et al.<sup>11</sup>

In these mixtures, the binary interaction parameters were either fitted to LLE data or to VLE, in most cases, at or near atmospheric conditions, which provides a more predictive capacity to this version of the model, when compared to cases where interaction parameters are regressed from near critical conditions.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.8b03657](https://doi.org/10.1021/acs.iecr.8b03657).

Subcritical VLE and LLE for the mixtures in analysis, analysis of critical points for three extra mixtures and  $T$  vs  $P$  descriptions of type I phase diagrams (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ NOMENCLATURE

$A$ ,  $a$  = energy parameter of CPA ( $\text{Pa m}^6 \text{ mol}^{-2}$ ).

$a_c$  = value of the energy parameter at the critical point ( $\text{Pa m}^6 \text{ mol}^{-2}$ ).

$B$ ,  $b$  = covolume ( $B = nb$ )

$c_1 - c_5$  ( $c_x$ ) = alpha function parameters

$c_{vs}$  = volume shift ( $\text{m}^3 \text{ mol}^{-1}$ )

$k_{ij}$  = binary interaction parameter for the cubic term

$m_i$  = mole number of sites of type  $i$

$n$  = mole number

$P$  = vapor pressure (Pa)

$R$  = universal gas constant

$S_1$  = API alpha function parameter

$T$  = temperature (K)

$T_c$ ,  $P_c$  = critical temperature, critical pressure (K and Pa, respectively)

$T_r$  = reduced temperature ( $T/T_c$ )

$T' = (1 - \sqrt{T_r})$

$v$  = molar volume ( $\text{m}^3 \text{ mol}^{-1}$ )

$v_0$ ,  $v_t$  = molar volume before and after translation, respectively ( $\text{m}^3 \cdot \text{mol}^{-1}$ )

$x$  = mole fraction

$X_i$  = mole fraction of sites of type  $i$  not bonded

$Z$  = compressibility factor

## Greek symbols

$\beta$  = association volume

$\beta_{ij}^0$  = binary interaction parameter for the association volume

$\Delta^{ij}$  = Association strength between site  $i$  and site  $j$

$\varepsilon$  = association energy ( $\text{J mol}^{-1}$ )

$\rho$  = molar density ( $\text{mol m}^{-3}$ )

## Sub and superscripts

bub = value of the property on the bubble point

$i$ ,  $j$  = pure component indexes

exp, calcd = experimental, calculated

phys, assoc = physical term, association term

## Abbreviations

%AAD = percentage of average absolute deviation:

$$\% \text{AAD} = \frac{|\Omega_i^{\text{exp}} - \Omega_i^{\text{calcd}}|}{\Omega_i^{\text{exp}}} 100\%$$

CPA = cubic plus association

EoS = equation of state

OF = Objective function

s-CPA = simplified cubic plus association

MTBE = methyl *tert*-butyl ether

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