

Modeling of the Mixture Critical Locus with a Modified Cubic Plus Association Equation of State: Water, Alkanols, Amines, and Alkanes

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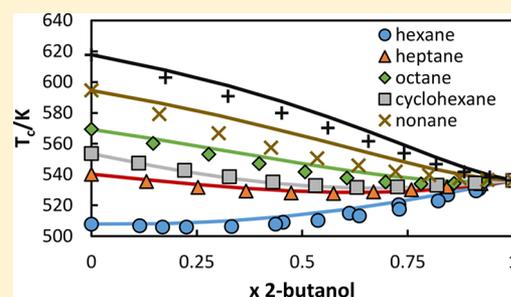
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S Supporting Information

ABSTRACT: In a phase envelope, an adequate description of the critical point is of high importance. It identifies the conditions where the bubble and dew curves meet, and where the nature of the single phase region outside the phase envelope changes. The knowledge of the mixture critical point is relevant to preventing production and transport problems, as well as to optimizing near-critical and supercritical processes. A modified cubic plus association (CPA) model was recently shown to accurately describe the vapor–liquid equilibrium (VLE) critical temperatures and pressures of pure compounds. The model is usually fitted to pure component data between $0.45T_c$ and $0.85T_c$, while forcing the correct description of both T_c and P_c . Here, the performance of the model is evaluated for mixtures.

Interaction parameters are regressed from VLE/liquid–liquid equilibrium (LLE) data at lower temperatures. Accurate results, for binary and ternary mixtures, were obtained. These results concern mainly mixtures containing, water, alkanes, alkanols, and amines. The results obtained are compared to those from perturbed-chain statistical associating fluid theory (PC-SAFT), simplified CPA (s-CPA), and Soave–Redlich–Kwong. Results for liquid–liquid critical temperatures are also analyzed for mixtures of methanol/ethanol with alkanes. The average absolute deviations with this approach, when considering VLE fitted binary interaction parameters, are 0.58 for T_c and 5.18 for P_c , for the VL critical point (CP) data in analysis. For LL CP, the model can describe the results for compounds, with similar critical properties, as is the case of methanol and hexane.



1. INTRODUCTION

The use of supercritical fluids has long been an interesting option for diverse industrial processes. The use of supercritical CO₂ for the extraction of caffeine (decaffeination of coffee) is the oldest and better known process, and a large range of applications has since been proposed with supercritical fluids.¹ The knowledge of mixture critical points is also important for the adequate optimization of recovery processes of near-critical fluids and secondary/tertiary crude.² For these applications, it is important to have a correct knowledge of the critical properties of a mixture, for an adequate design and optimization of the process and to prevent operational issues. The unique properties of supercritical fluids, being neither fully liquidlike nor gaslike, are the main reason for their versatility and usefulness.

Equations of state are important tools in process simulation due to their ease of implementation and versatility. Cubic equations of state, the most successful of these models are, however, unable to completely describe the critical point of a compound or mixture,^{3,4} especially in terms of volumetric properties, without the use of specific treatments, e.g., crossover methods.^{5–7} These volumetric problems are not limited to the near-critical region, as the values for the covolumes of these equations of state are small, which leads to an overprediction of $-\left(\frac{\partial P}{\partial V}\right)_T$.^{8,9} Their limitations are even

more evident for systems where hydrogen bonding is important.

Apart from equations of state, there are other methods to predict critical properties of binary mixtures. In the case of ternary mixtures, methods such as those by Hicks and Young,¹⁰ Redlich and Kister,¹¹ Li,¹² Teja et al.,¹³ or Chueh and Prausnitz and variants^{14,15} can be applied. However, these are far more complex than equations of state and/or they overly rely on the correlation of experimental data, having little or no predictive capacity. Also, to predict critical pressures, some of these methods still rely on equations of state.

The most widely used methods for multicomponent mixtures rely on the use of cubic equations of state and are those of Heidemann and Khalil,¹⁶ Michelsen,¹⁷ and Hoteit et al.¹⁸

Although the full description of the pure component critical point is not achievable with classical approaches in cubic equations of state, these models could be modified to allow a good description of the pure component critical temperature and pressure, as both are used in the EoS parametrization. If

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the pure component critical temperatures and pressures are well described, it would be reasonable to assume that the mixture critical points could also be well estimated. Equations of state including an association term (including s-CPA,¹⁹ SAFT,²⁰ PC-SAFT,²¹ CP-PC-SAFT,²² and s-PC-SAFT²³) have been applied for the description of critical properties of binary mixtures including an associative compound + hydrocarbon or a gas,^{24–28} with very good results for both the critical temperature and critical pressure. However, the correct description of the critical points, even for pure compounds, using this type of EoS involves the need for specialized parametrization methods.²⁴ Recent studies on this subject, with EoS approaches, not explicitly considering association, include those of Wei et al.,²⁹ Neichel and Franck,³⁰ Bidart et al.,³¹ and Qian et al.³²

The version of CPA used in this work has been parametrized using an approach where the energy and covolume parameters of the physical term are obtained directly from the pure compound critical data, similarly to what is done in a cubic EoS, but with defined association parameters. It is thus able to adequately describe the pure compounds' critical properties, as shown in previous works.^{33–35} In this work, the ability to describe the critical locus of a large range of binary and ternary mixtures is studied. These include alkanols + water, alkanols + alkanols, and alkanols + alkanes. To highlight the capacities and limitations of the model, some specific systems are analyzed in detail, such as the phase equilibria of water + *n*-hexane. The binary interaction parameters applied here were not specifically fitted to the critical data, but instead fitted to the VLE/LLE at low temperatures or to gas solubility data; thus for most cases the binary interaction parameters can be/were obtained from subcritical phase equilibria. A comparison of the results obtained by Vinhal et al.²⁴ with the s-CPA and Gil et al.²⁵ with PC-SAFT is presented for the systems of methanol with alkanes and alkanols with *n*-hexane, respectively. LLE critical temperatures are also analyzed for methanol/ethanol with alkanes. For these mixtures the binary interaction parameters were tested considering the fitting of the critical point at specific pressures or the fitting of the overall LLE at 0.1 MPa.

2. MODEL

The main equation of CPA can be written as presented below:

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} = \frac{1}{1 - B\rho} - \frac{A(T)\rho}{RT(1 + B\rho)} - \frac{1}{2} \left(1 + \rho \frac{\delta \ln g}{\delta \rho} \right) \sum_i m_i (1 - X_i) \quad (1)$$

A is the energy parameter ($A(T) = n^2 a(T)$), B is the covolume parameter ($B = nb$), ρ is the molar density, g is a simplified hard-sphere radial distribution function,¹⁹ X_i is the mole fraction of nonbonded sites of type i , and m_i is the mole number of sites of type i . The mixing rules for a and b are presented in eqs 2 and 3:

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

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

with

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

and k_{ij} are binary interaction parameters.

Using the simplified CPA¹⁹ as a starting point, the version of CPA used in this work is obtained by introducing some relevant modifications. First, a modified Mathias–Copeman function,³⁶ which can use up to five parameters, is applied:

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

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

The use of a high order polynomial can potentially introduce inconsistencies when extrapolating the results above the critical point, some of which are pointed out by Segura et al.³⁷ Thus, it is necessary to introduce a correction. Mathias³⁸ shows that by ensuring that the alpha function decreases monotonically with temperature, most of these issues are avoided. This version of CPA uses an extrapolation based on the API Soave alpha function by Graboski and Daubert.³⁹ The following conditions are used for this extrapolation:

$$\begin{aligned} T < T_c & \quad \alpha = \text{eq 1} \\ T = T_c & \quad \alpha = 0 \\ 1 < T_r < 1.1 & \quad \alpha = \{\text{continuous interpolation function}\} \\ T_r > 1.1 & \quad \alpha = \alpha_{\text{API}} = 1 + S_1 (1 - \sqrt{T_r}) \end{aligned} \quad (6)$$

where α_{API} is the Soave-type alpha function proposed by Graboski and Daubert;³⁹ S_1 is the parameter from the API alpha function.

To ensure the correct descriptions of T_c and P_c , some restrictions are introduced in the pure component parametrization process, with a_c , $v_{c,\text{calc}}$ and b being forced to fulfill these properties.

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

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

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

Similar modifications have been proposed by Polishuk for SAFT + cubic^{9,40} and PC-SAFT.⁴¹

The molar volume is not used in the main parametrization routine of CPA, being obtained through a Péneloux-type volume shift:⁴²

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

The volume shift c_{vs} is temperature independent, and thus, as shown by Jaubert et al.,⁴³ this volume shift does not influence the results for vapor pressure, heat of vaporization, and heat capacities. By introducing this term, the descriptions of saturation pressures, T_c and P_c , as well as some derivatives of pressure, are improved, without a large degradation of the description of liquid densities.

To describe association, X_i is calculated from

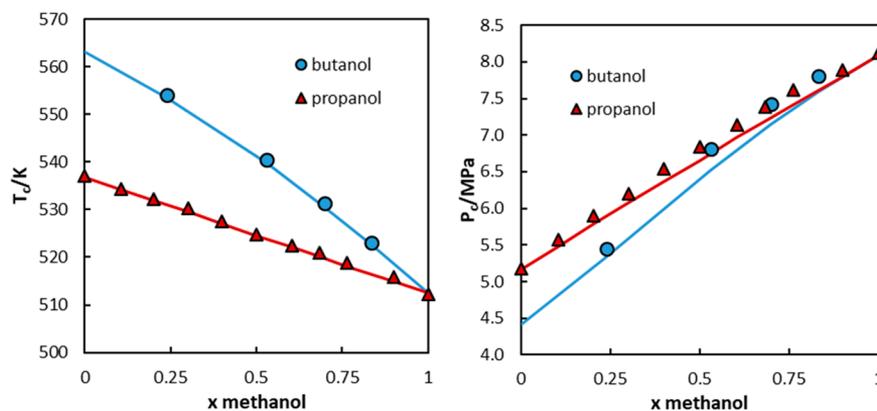


Figure 1. Predictions of T_c (left) and P_c (right) for the whole range of compositions for methanol + 1-propanol and methanol + 1-butanol. Lines are results using the modified CPA. Experimental data from Nazmutdinov et al.⁴⁶ and Wang et al.⁴⁷

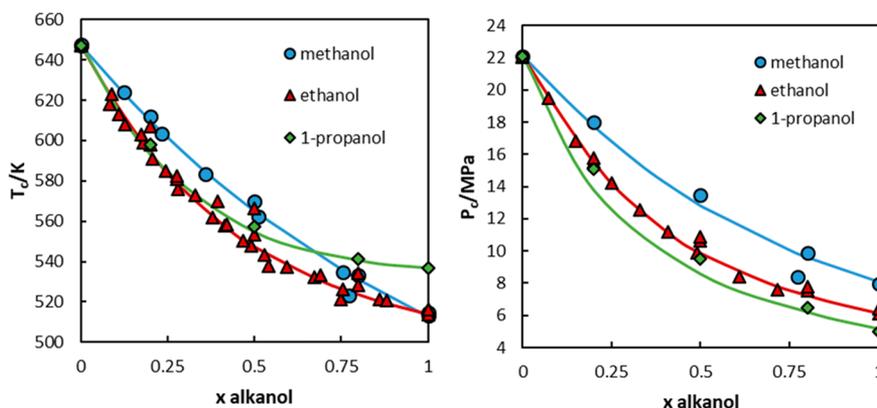


Figure 2. Results for T_c (left) and P_c (right) for water + methanol, water + ethanol, and water + 1-propanol mixtures. Lines are results using the modified CPA. For k_{ij} see Table A-2 in the Supporting Information. Experimental data from Hicks and Young,⁴⁸ Marshall and Jones,⁴⁹ and Bazaev et al.⁵⁰

$$X_i = \frac{1}{1 + g\rho \sum_j m_j X_j \Delta^{ij}} \quad (11)$$

where the association strength (Δ^{ij}) is given by

$$\Delta^{ij} = b^{ij} \beta^{ij} (e^{\varepsilon^{ij}/RT} - 1) \quad (12)$$

ε^{ij} and β^{ij} are, respectively, the association energy and volume, for interactions between sites i and j .

The simplified radial distribution function, applied with CPA, is given by eq 8.^{19,44}

$$g(\rho) = \frac{1}{1 - 0.475b\rho} \quad (13)$$

The alpha function parameters are fitted to the vapor pressure curve, with the association term being adjusted in a parallel cycle.

In this work, VLE systems were correlated and to obtain the respective k_{ij} values two different equations were applied, depending on the equilibrium conditions (eq 14 was applied when the VLE data was obtained at constant pressure, while eq 15 was applied for constant temperature conditions):

$$\text{OF} = \sum_i^{\text{np}} \left(\frac{T_{\text{bub}}^{\text{exp}} - T_{\text{bub}}^{\text{calc}}}{T_{\text{bub}}^{\text{exp}}} \right)^2 \quad (14)$$

$$\text{OF} = \sum_i^{\text{np}} \left(\frac{P_{\text{bub}}^{\text{exp}} - P_{\text{bub}}^{\text{calc}}}{P_{\text{bub}}^{\text{exp}}} \right)^2 \quad (15)$$

The fits to critical data use a sum of these equations (with equal weights and the fit being applied to T_c/P_c), except for the results presented in Figures 10 and 11, where only eq 14 was applied.

The cross-associating parameters for the mixtures studied in this work were obtained using the CR-2⁴⁵ combining rule.

$$\beta^{ij} = \sqrt{\beta^i \beta^j} \quad (16)$$

$$\varepsilon^{ij} = \frac{\varepsilon^i + \varepsilon^j}{2} \quad (17)$$

The association scheme applied for the hydroxyl group was the 2B scheme as used in a previous work.³⁴ The same scheme was applied for diethylamine and dipropylamine. For the water molecule, the selected scheme was 4C.

The general method applied for the calculation of mixture critical points is that of Hoteit, Santiso, and Firoozabadi.¹⁸ When no convergence is found through this method, the convergence of the bubble and dew curves is instead applied.

3. RESULTS AND DISCUSSION

Two compounds that have not been previously studied with this version of CPA are used in this work: diethylamine and

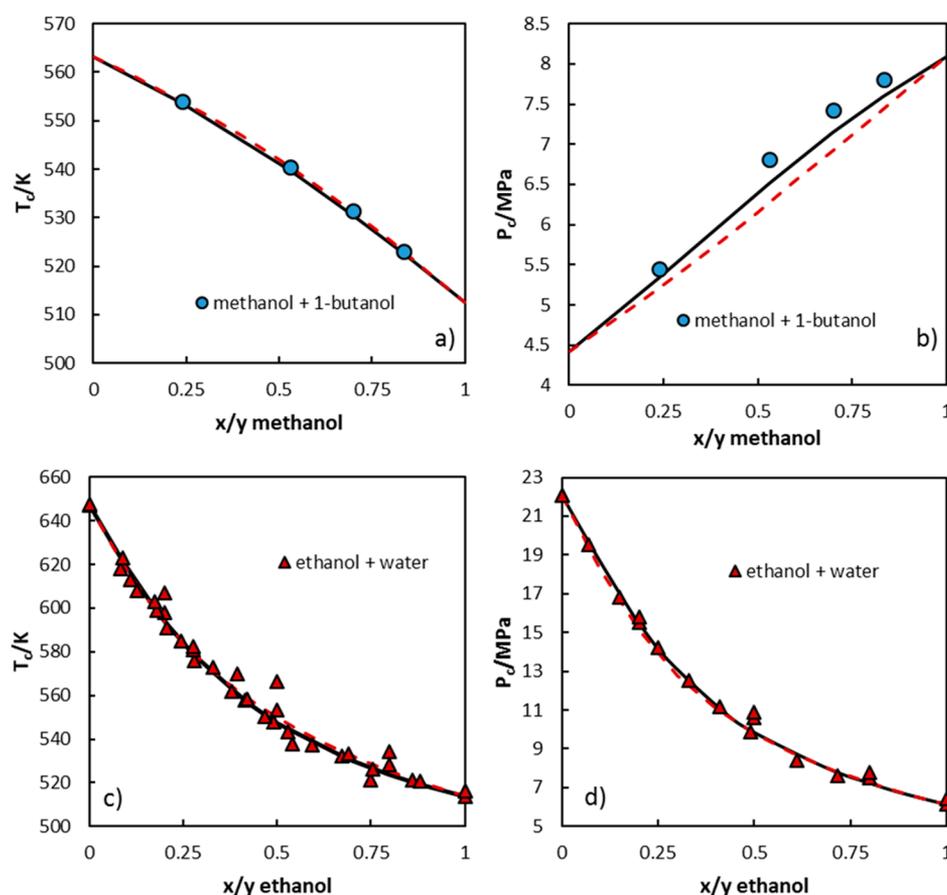


Figure 3. Results for T_c and P_c for methanol + 1-butanol (a, b) and ethanol + water (c, d). Full lines, modified CPA; dashed lines, SRK. For k_{ij} see Tables A-2 and A-9. Experimental data from Hicks and Young,⁴⁸ Marshall and Jones,⁴⁹ Bazaev et al.,⁵⁰ and Nazmutdinov et al.⁴⁶

dipropylamine. Their pure compound parameters as well as the deviations for their binary systems with hexane are presented in the [Supporting Information](#). Most of the binary interaction parameters for the systems presented here have been obtained in previous works.^{33–35} Tables containing the binary interaction parameters of each section are presented also in the [Supporting Information](#). In sections 3.1–3.4, the performance of the model is studied for the description of the critical points for a series of binary and ternary mixtures. Comparisons between the results of CPA and SRK for some of the mixtures studied are also presented.

3.1. Critical Points for Binary Mixtures of Two Associative Compounds. The predictions for the systems methanol + 1-alkanol are shown in [Figure 1](#). The descriptions of the binary equilibria containing these compounds, due to their similarities, are usually predictive, and thus, no binary interaction parameter is required. [Figure 1](#) presents the results for the systems methanol + 1-propanol and methanol + 1-butanol.

For these mixtures an accurate description of the critical temperatures was obtained. Critical pressures present somewhat higher deviations, in part due to the alpha function used in this modified version, but also due to the lower weight of the association parameters. The volumes of association used with this version are lower than those of s-CPA. Thus, even with higher energies of association, close to the critical point the association term will be less relevant than in s-CPA, and thus the behavior of the predicted P_c will be closer to those of SRK.

Other mixtures, as well as representations of P_c vs T_c , are presented in the [Supporting Information](#).

In [Figure 2](#), the predictions for the critical loci for a series of systems of water + alkanols are presented. Given the quality of the descriptions achieved for these strongly associative systems, it is important to stress that these are results obtained using the binary interaction parameters for these compounds from VLE for a large range of temperatures. The binary interaction parameters for these mixtures were obtained in a previous work³⁵ and are presented in the [Supporting Information](#).

Using the binary interaction parameters fitted to VLE in a large range of subcritical conditions, the model is able to predict accurately the critical temperatures and pressures of binary mixtures of associative compounds.

While CPA is a more accurate model for the description of subcritical phase equilibria of associating mixtures (when considering the same mixing rules for both models), cubic EoS are also able to describe the critical locus using the binary interaction parameters used to fit subcritical data. Thus, in [Figure 3](#) a comparison of the results of SRK and CPA for methanol + 1-butanol and ethanol + water is presented.

The critical temperatures/pressures obtained with both models are similar. However, some improvements in the description of the critical pressure for the first mixture are observed. The subcritical phase equilibrium is, however, far superior with CPA, when considering the mixing rule here applied. An analysis of the influence of k_{ij} for methanol + 1-butanol is presented in the [Supporting Information](#) ([Figure A-23](#)).

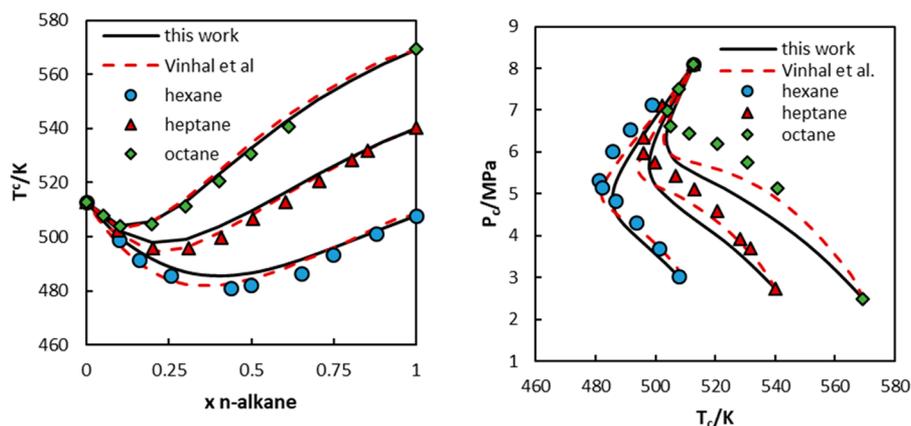


Figure 4. Results for T_c and P_c as a function of composition for methanol + hexane, methanol + heptane, and methanol + octane. Full lines, modified CPA; dashed lines, s-CPA. For modified CPA k_{ij} see Table A-3. Experimental data by de Loos et al.⁵¹

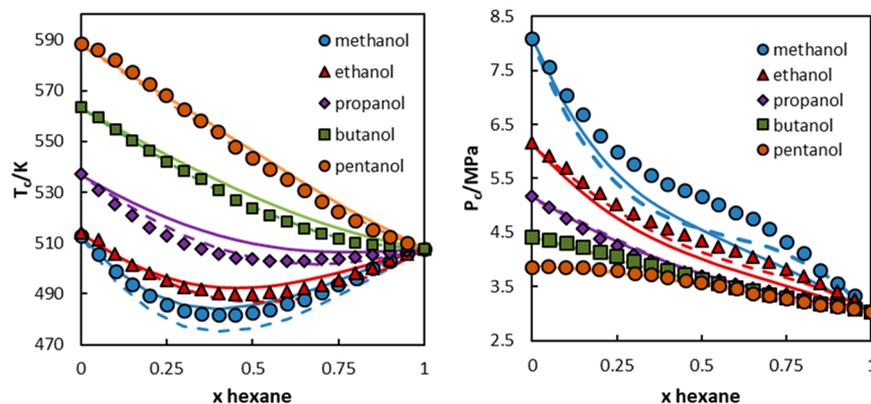


Figure 5. Critical points for hexane + alkanol. Full lines, modified CPA; dashed lines, SAFT results.³⁴ For CPA k_{ij} see Table A-3.

3.2. Critical Points for Binary Mixtures Containing an Associative Compound and an Alkane. Having investigated systems where both compounds are associative, it is now important to evaluate if this version of the CPA EoS is also able to provide accurate predictions for systems where only one component is associative. Vinhal et al.²⁴ have recently studied the description of these properties for methanol + n -alkanes using s-CPA with reparametrized sets (both the pure compounds and binary interaction parameters). Thus, it is important to compare here the results using the two methodologies.

The same authors have also studied how the new sets described LLE. Despite the decrease in accuracy, their results are still able to describe the results for methanol + hexane and methanol + octane, with some accuracy. As a first test, with the modified version the sets of binary interaction parameters obtained for the LLE of methanol + n -alkanes were applied and the results can be observed in Figure 4.

The higher deviations on T_c for the first two alkanes in analysis are mainly due to the use of the LLE k_{ij} instead of fitting these parameters from equilibria closer to the critical point (the results for methanol hexane are presented in Figure 5 and the %AAD using the two k_{ij} sets is presented in the Supporting Information). In the case of the critical pressure deviations, this is expected, as the use of a complex alpha function introduces problems near the critical point, as discussed above after Figure 1. The description of phase equilibria near the critical point using this modified CPA model was reported in a previous work.³⁴ In this manner,

despite enforcing the correct description of the critical pressure of the pure compounds, for mixtures of compounds of different families it is expected that the critical pressures will have a behavior closer to that of SRK, especially if the critical pressures of the two pure compounds are not similar. It is also important to note that, while in the present version the energy and covolume parameters, for the nonassociative compounds, can be obtained in the same way as in a cubic EoS, these need to be reparametrized when using the s-CPA method.

An evaluation of the model performance for systems of different alkanols with n -hexane was conducted considering a temperature dependent k_{ij} . However, as observed with SAFT,²⁵ for methanol and ethanol mixtures, those temperature dependent k_{ij} 's underestimate T_c 's for mixtures with the smaller alkanols. In the case of 1-propanol, this is not the case and there is a large overestimation of T_c for some compositions. For 1-butanol + hexane, a constant k_{ij} was able to correctly describe the VLE of the system in a range of temperatures between 283 and 393 K and thus no temperature dependency was used. A different approach, also evaluated here, is to consider the k_{ij} 's calculated for systems at a single condition (chosen from the usual measuring conditions). This approach presents a more accurate description of critical temperatures than the previous one possibly because of the higher quality of the available data for these conditions. The results for this latter approach are presented in Figure 5, while for the former the results are presented as Supporting Information. In Figure 5, a comparison is also presented between the results of this work and those of Gil et al.²⁵ using

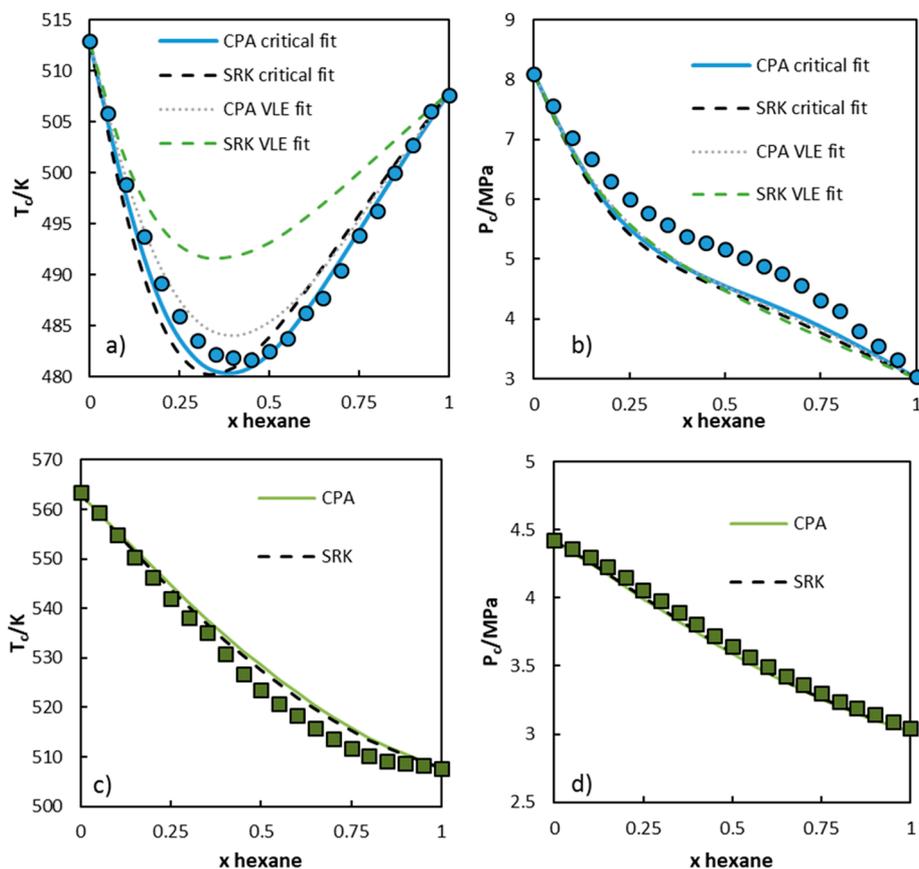


Figure 6. Description of *n*-hexane + methanol (a, b) and *n*-hexane + 1-butanol (c, d) with both SRK and CPA. For k_{ij} see Tables A-3, A-4, and A-9.

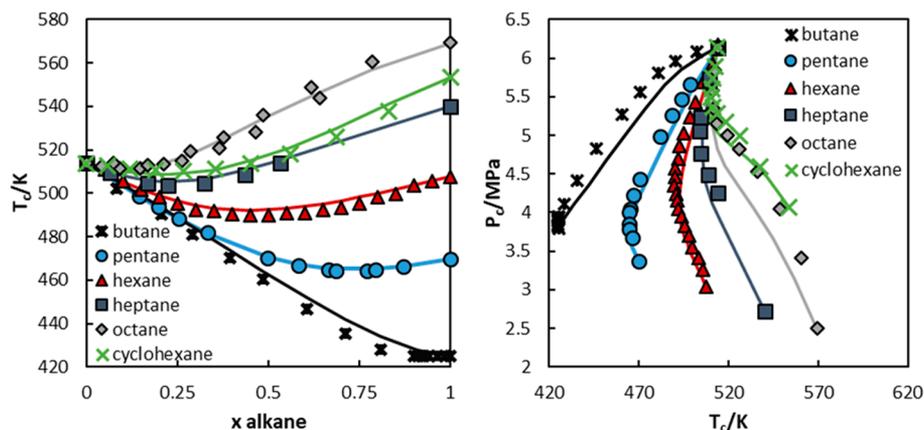


Figure 7. Results for systems containing ethanol + alkane. Lines are modified CPA results. For k_{ij} see Tables A-4 and A-5. Data from He et al.⁵³ and Soo et al.⁵⁴

PC-SAFT. The experimental data used for these compounds is from Gil et al.²⁵ and LagaLázaro.⁵²

The results for these systems are remarkable for an approach using constant association parameters. As with the results of Figure 4, following the approach of Gil et al.,²⁵ the association contribution in PC-SAFT should be stronger than that of the modified CPA. It is also important to note that the more accurate physical term of PC-SAFT is also contributing to a better description of the critical properties.

Figure 6 presents the comparison between CPA and SRK for the mixtures methanol + hexane and 1-butanol + hexane. For the first of these mixtures both a fit to subcritical VLE data and

a fit to the critical data were considered for the binary interaction parameters.

In the case of methanol + hexane, CPA presents very significant improvements in the description of the critical temperature, with both fitting approaches. Critical pressure results for this mixture are similar for all four approaches used. The results for the remaining mixture are similar using both equations.

It is also important to look at the description of ethanol and 1-propanol with different alkanes or cycloalkanes. The results for ethanol + alkanes are presented in Figure 7.

The results obtained are quite good for these mixtures. It is also important to look at mixtures containing secondary

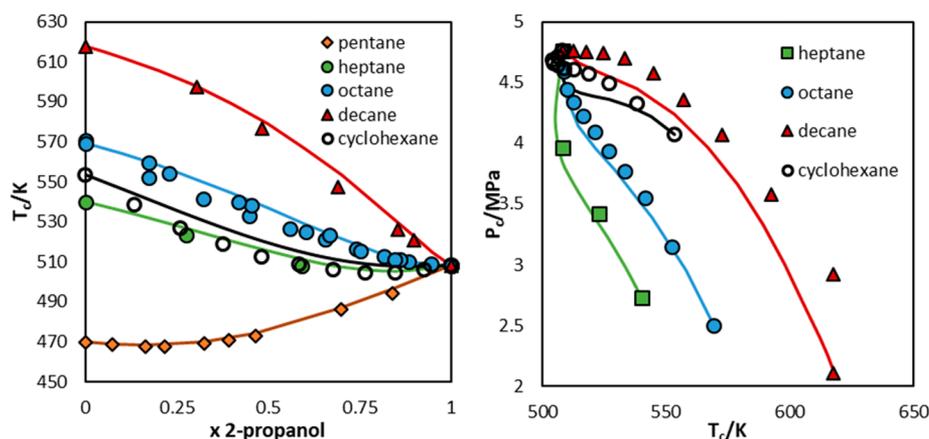


Figure 8. Results for mixtures of 2-propanol + alkane. Lines are modified CPA results. For k_{ij} see Table A-6. Data from He et al.,⁵³ Morton et al.,⁵⁵ and Nazmudtinov et al.⁴⁶

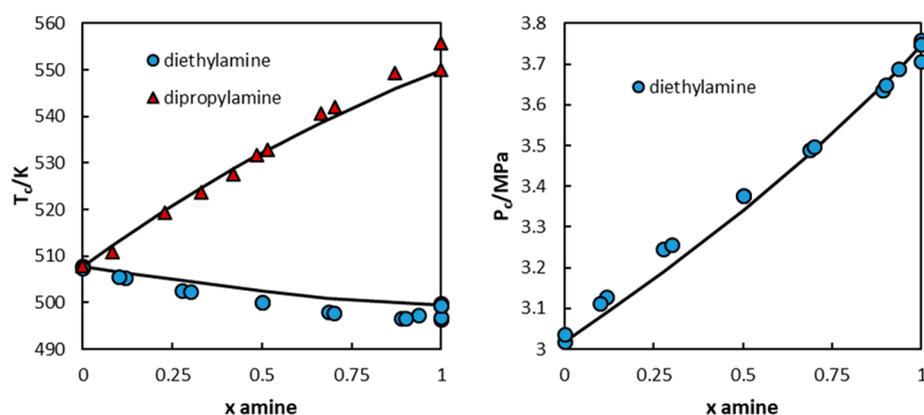


Figure 9. T_c and P_c results for diethylamine + hexane and T_c results for dipropylamine + hexane. Lines are modified CPA results. For k_{ij} see Table A-7. Experimental data from Mandlekar et al.,⁵⁶ Toczylnik and Young,⁵⁷ Kreglewski et al.,⁵⁸ and the TRC database.⁵⁹

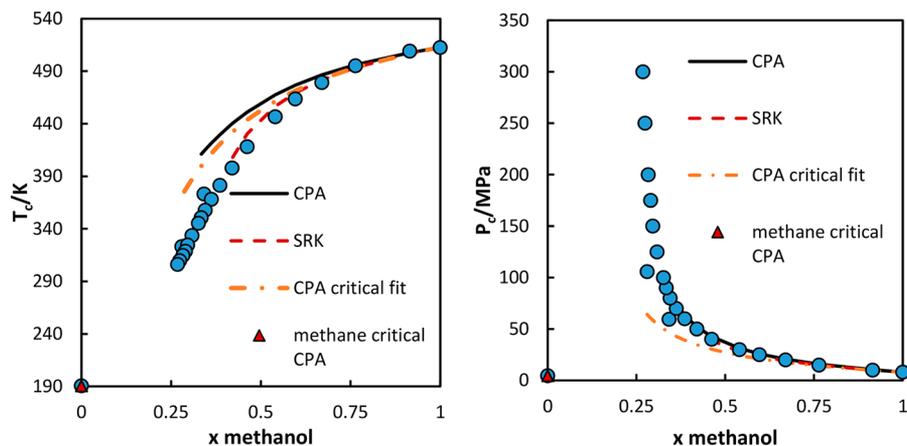


Figure 10. Results for T_c and P_c of methanol + methane. For k_{ij} see Tables A-8 and A-9. Experimental data from Brunner et al.⁶⁰ and Francesconi et al.⁶¹

alcohols. Thus, results for mixtures of 2-propanol with some alkanes are presented in Figure 8. Other binary mixtures of alkanols + alkanes are presented in the Supporting Information.

Two systems were analyzed for amines mixed with alkanes: diethylamine + hexane and dipropylamine + hexane. The results for these mixtures are presented in Figure 9. The results for the first system are predictive as this approach was applied for VLE systems between 293.15 and 353.15 K with accurate

results, showing only a slight deviation on the pure amine vapor pressure for some temperatures.

A good description of critical pressures is obtained for the system containing diethylamine. This is in part due to the small gap between the critical temperatures and pressures of both components. However, there is a noticeable difference in the description of critical temperatures for the mixture with the minima, reported by Mandlekar et al.,⁵⁶ close to 90% amine not being predicted by the model. It is important to note that a

large range of pure component critical temperatures is available for diethylamine and, thus, this might be due to the relevant degree of uncertainty for the critical data. As presented in Figure 9, some of these pure T_c data values are close to the temperature of the minima, presenting a relevant uncertainty in terms of this behavior.

For dipropylamine, some discrepancies are also verified for the pure component data, with some critical temperature data seemingly out of the behavior expected from the curve with the mixture data.

Figures 10–12 present the results for the mixtures methanol + methane and water + hexane. It is important to note that in these mixtures there are compositions for which there is no VLE critical point. For the first mixture, the k_{ij} ($0.074 + (2.18 \times 10^{-4})T$) obtained in a previous work,³⁵ from gas solubility data, was applied, as well as a new set, where the k_{ij} [$((0.194 - 4.67) \times 10^{-4})T$] was fitted so that the range of concentrations where a critical point is observed was similar to the experimental one. In Figures 10 and 11 a comparison with the SRK EoS is presented.

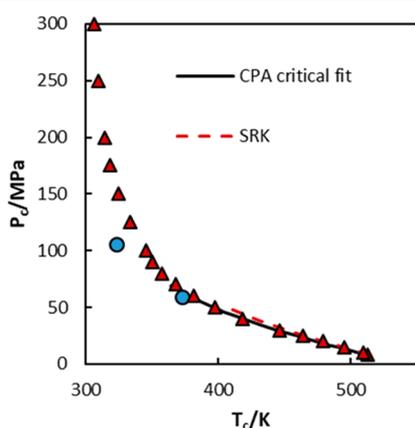


Figure 11. Results for P_c of methanol + methane represented as a function of T_c obtained for the same set. For k_{ij} see Tables A-8 and A-9. Experimental data from Brunner et al.⁶⁰ and Francesconi et al.⁶¹

Using the first approach described above, the results obtained overestimate the range of composition for which it is not possible to obtain critical data. The T_c is largely overestimated for higher methane concentrations, but becomes

more accurate as the fraction of methanol increases, while P_c is reasonably described for a large range of composition (%AAD is 4.63 between 0.334 and 0.915 x of methanol), although considerably high deviations are obtained for methane-rich mixtures. Fitting a k_{ij} so that the whole experimental composition range presents critical points (while for a concentration 5% below that of the experimental data, no critical point is verified) results in the second set. Both sets present a reasonable estimation of critical pressures, within experimental uncertainties, while this second set improves slightly the description of critical temperatures. SRK is capable of a better description of critical temperatures than both these sets; however, it underpredicts greatly the range of concentrations where a mixture critical point is available. This is visible in Figure 11, where critical pressures are represented as a function of the critical temperatures.

The introduction of the association term decreases the accuracy of the critical temperature, obtained for this specific mixture. On the other hand, it enables the x_c interval to be closer to the experimental data and a better description of P_c in relation to T_c .

Results for water + hexane are presented in Figure 12. Two sets of binary interaction parameters were used. The first was obtained from the LLE analyzed in a previous work,³⁵ while the second was fitted to the critical temperatures for fractions of water between 0.95 and 1. Using the LLE fitted binary interaction parameter, the model predicts critical points for most of the composition range. However, their values present high deviations. Fitting the k_{ij} to the critical data, while improving the accuracy for the lower water compositions, leads to the model only predicting critical points down to a water mole fraction of approximately 0.93.

3.3. Critical Points for Ternary Mixtures Containing One or More Associative Compounds. After analyzing these binary systems, it is important to look at the description of ternary systems containing alkanols and hydrocarbons. Figure 13 presents the parity diagram of the deviations for the mixture ethanol + pentane + hexane. The binary interaction parameters are those used before.

Deviations for this and other ternary mixtures are presented in Table 1. For the mixture containing ethanol + pentane + hexane, a comparison is made between the results of this modified version, PC-SAFT and the s-CPA. The parameters used for s-CPA are from Oliveira et al.; a comparison for this

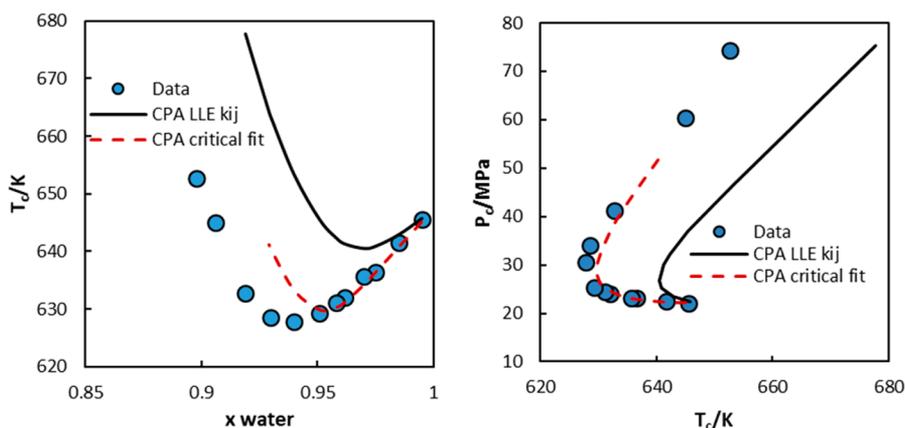


Figure 12. Details of results for T_c and P_c of water + hexane for high water compositions. Lines are modified CPA results. For k_{ij} see Table A-8. Experimental data are from Tsionopoulos and Wilson.⁶²

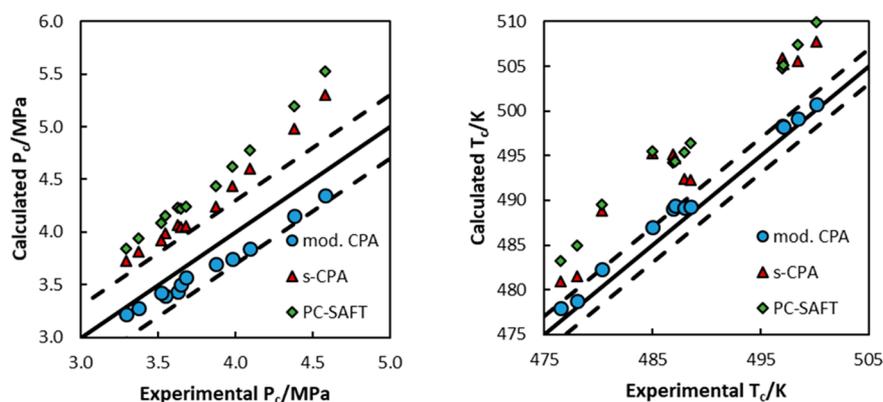


Figure 13. Parity diagrams for the results of the system ethanol + pentane + hexane. Dashed lines are for ± 0.3 MPa and ± 2 K, respectively. Experimental data from Soo et al.⁵⁴

Table 1. Average Absolute Percent Deviations for P_c and T_c of Ternary Systems Containing Alkanes and Alkanols with the Modified CPA Model

mixture no.	compd 1	compd 2	compd 3	%AAD		av $ T_c^{\text{exp}} - T_c^{\text{calc}} $ (K)
				P_c	T_c	
mix 1	ethanol	pentane	hexane	4.17	0.28	1.36
mix 1 ^a	ethanol	pentane	hexane	4.20	0.28	1.35
mix 2	methanol	1-propanol	heptane	7.58	0.38	1.94
mix 3	2-propanol	octane	decane	5.57	1.98	10.91
mix 4	1-propanol	octane	decane	6.55	1.05	5.88
mix 5	1-propanol	heptane	cyclohexane	3.14	0.11	0.61
mix 6	2-butanol	hexane	heptane	3.04	0.47	2.44
mix 7	2-butanol	octane	decane	3.46	0.70	3.98

^aThese results were obtained using SRK.

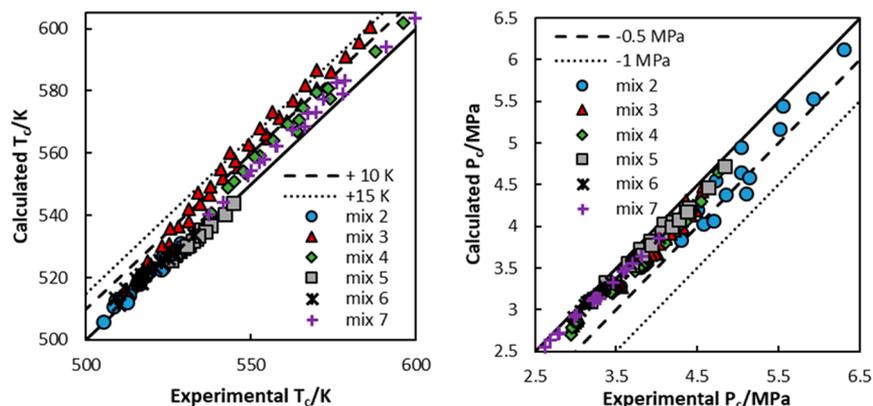


Figure 14. Parity diagrams for the results of mixes 2–7 (as presented in Table 1).

mixture, using SRK, is also presented in Table 1.⁶³ For PC-SAFT the parameter sets from the first works on this equation are here applied.^{21,64} The binary interaction parameters were calculated in the same way as those for the modified CPA and are respectively 0.056 and 0.036 for ethanol + hexane for s-CPA and SAFT, while for the mixture with pentane the values are 0.048 and 0.037. As expected, without refitting the parameter sets, both SAFT and s-CPA present far higher deviations than the modified CPA, which fits the pure component critical points. In Table 1, the deviations for six other ternary mixtures are presented. A similar table is presented, in the Supporting Information, for some of the binary mixtures. Figure 14 presents the parity diagram for the six new mixtures introduced in Table 1. The experimental data

for these mixtures are from Wang et al.,⁴⁷ He et al.,⁵³ and Xin et al.⁶⁵

The ternary systems present low deviations, similar to those previously obtained for the binary systems; thus it can be considered that the predictions of the ternary systems are very successful. As in the case of the binaries, the critical temperatures are well described with most mixtures presenting %AAD below 1%. It is apparent that, for both the binary and ternary mixtures, in most cases the approach here proposed tends to overestimate the critical temperatures and underestimate the critical pressures.

3.4. LLE Critical Points for Alkanols + Alkanes. LLE critical points are in most cases badly described by equations of state. However, to conclude this study it is important to look at

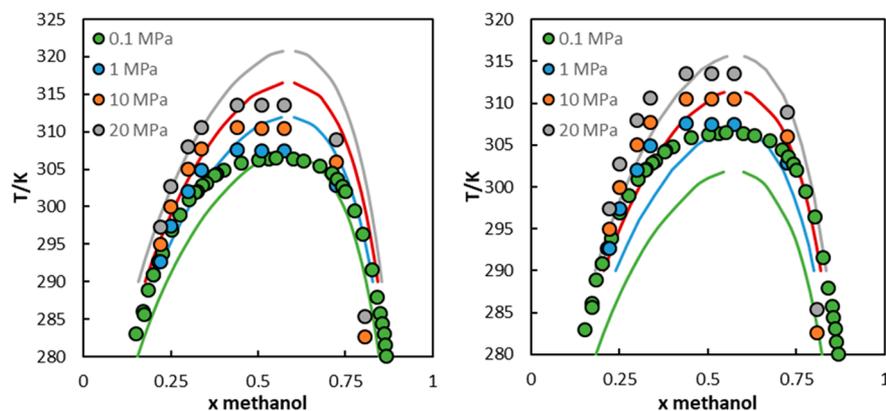


Figure 15. Results for LLE critical point description of methanol + hexane, using two different binary interaction parameters, fitted to the LLECP at 0.1 (left) and 1 MPa (right). k_{ij} presented in Table A-10. Data from Hölscher et al.⁶⁶ and Hradetzky and Lempe.⁶⁷

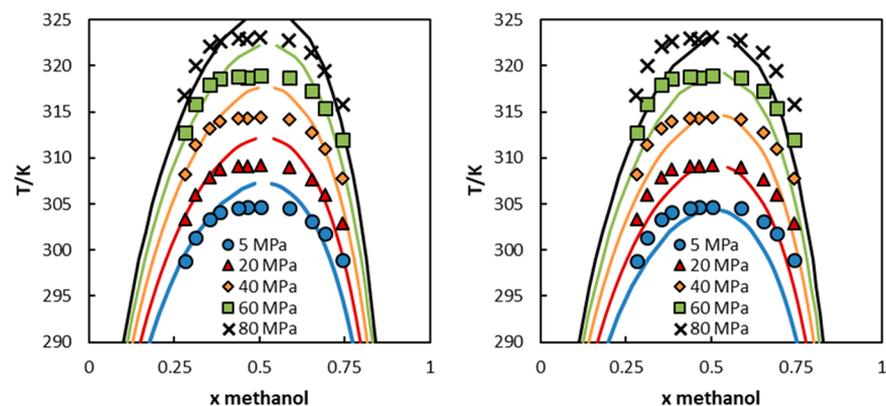


Figure 16. Results for LLE critical point description of methanol + methylcyclopentane, using two different binary interaction parameters, fitted to the LLE data (left) and the LLECP (right), both at 5 MPa. k_{ij} presented in Table A-10. Data from Becker and Deiters.⁶⁸

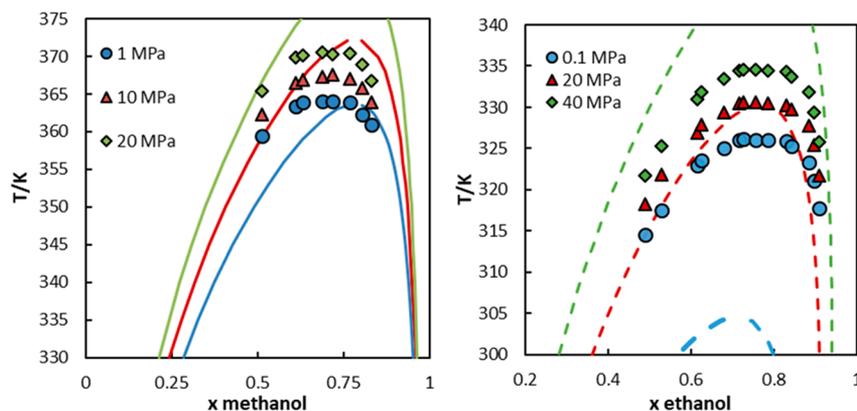


Figure 17. Results for LLE critical point description of methanol + decane (fitted at 1 MPa, left) and for ethanol + hexadecane (fitted at 20 MPa, right). k_{ij} presented in Table A-10. Data from Dahlmann and Schneider⁶⁹ and Hölscher et al.⁶⁶

the descriptions of these data when using the CPA model applied in this work. Four different mixtures are analyzed in this study: methanol + hexane, methanol + methylcyclopentane, methanol + decane, and ethanol + hexadecane. The binary results for the mixtures here presented were fitted to the LLE critical temperature at a specific pressure.

Figures 15 and 16 present the results for methanol + hexane and methanol + methylcyclopentane, respectively. Two sets of binary interaction parameters are used for both mixtures. In Figure 15, these were fitted to the critical temperature at two different pressures, while in Figure 16 the first set was fitted to

the general LLE data and the second was fitted to the LLECP, both at 5 MPa.

For these mixtures, a good description of critical temperatures was achieved for a large range of pressures, when the binary interaction parameters were fitted at pressures of 1 MPa or above.

Figure 17 presents the results for the mixtures methanol + decane and ethanol + hexadecane.

The results for these two mixtures are not very well described even when the binary interaction parameter is fitted to a higher pressure. This difference in accuracy seems to be

related to the large difference in both critical and boiling temperatures of the compounds in these mixtures, while in the mixtures of Figures 15 and 16, the compounds had very close values for these properties.

4. CONCLUSIONS

A modified version of CPA was evaluated for the description of critical data of mixtures. In these cases, the binary interaction parameters that are able to describe the VLE in a large range of conditions were used. The predictions of the critical locus, obtained in this way, are very accurate when both mixture compounds are associative as is the case of mixtures containing two alkanols or water + alkanol.

In the case of mixtures with just one associative compound, the T_c predictions are very good. The prediction of P_c is however slightly inferior to that of s-CPA, due to the heavier weight of the cubic term in the present version. The association term of this version, near the critical temperature, tends to be weaker than that of s-CPA. The predicted behavior of a mixture of an associating compound + nonassociating compound is thus closer to that of SRK, with the version of CPA here proposed, while in s-CPA the association contribution is able to improve the description of P_c . For the other systems of alkane + alkanol, using a linearly temperature dependent k_{ij} results in an underprediction of T_c and it seems better to use a binary interaction parameter fitted from VLE at near-atmospheric conditions. While this approach does not, in all cases, enable a good description of VLE in the whole range of temperatures, it is seemingly an accurate enough approach to describe the critical locus. For the mixture water + hexane, the approach used in the other systems for the estimation of k_{ij} would lead to high deviations in the properties, and thus, it was interesting to fit the critical data close to pure water, enabling a much more reasonable description of T_c and P_c at least for lower water concentrations.

In most mixtures, this version of CPA presents a critical description very similar to that of SRK, while greatly improving the description of phase equilibria containing associative compounds. This largely comes from the parametrization process. This parametrization applies a fit to critical data, similar to that of cubic EoS, fitting a_c and b to T_c and P_c . It improves the description of saturation pressure and some of its derivatives, without forcing the description of liquid densities in the main parametrization routine, by introducing a volume shift and focusing the main parametrization on nonvolumetric properties. Thus, the model ends up with sets of parameters, which are able to describe correctly VLE, both subcritical and at critical conditions. LLE results can also be obtained. Nevertheless, a second set of binary interaction parameters is needed for their correct description. This, however, comes at the cost of diminishing the relevance of the association parameters, at least near the critical boundary, which ends up reducing the accuracy of the description of critical pressures for some mixtures, when compared to results with the reparametrized s-CPA and PC-SAFT.

Good descriptions are also obtained for ternary systems containing one alkanol and two hydrocarbons. The predictions for the mixture containing ethanol + pentane + hexane were compared to those of other equations of state, where the critical point of the pure compound is not fitted. As expected, these models present higher deviations for these properties if their parameters are not readjusted taking into account critical data.

The description of the mixture water + hexane is good in a wide range of concentrations, while for methanol + methane the critical composition range and trend of P_c as a function of T_c are well described. This set is however unable to accurately describe the trend of T_c with the critical composition. These mixtures are more complex, as there are certain compositions where no critical point is observed. Using the previously applied binary interaction parameters for these mixtures, the range of compositions where critical points were observed was smaller than that of the experimental data. This was improved by changing the binary interaction parameter in the mixture of methanol + methane.

In most of the systems analyzed the binary interaction parameters were fitted either to LLE data or to VLE at ambient conditions, which provides a considerable predictive character to these modeling results.

In terms of LLE critical points, the results for methanol/ethanol with some alkanes were analyzed. For mixtures where the critical/boiling temperatures of the two compounds were similar, good results were obtained, when considering a fitting to the LLECP at a pressure equal to or above 1 MPa. However, for mixtures of two compounds where these properties were very different, the obtained results are not accurate.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b01960.

Binary interaction parameters, pure compound parameters for amines, as well as subcritical VLE descriptions and some more critical results for the mixtures in analysis (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

A , a = energy parameter of CPA ($A(T) = n^2a(T)$)

a_c = value of the energy parameter at the critical point

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

c_1 – c_5 (c_x) = alpha function parameters

C_p = isobaric heat capacity

c_{vs} = volume shift
 g = radial distribution function
 k_{ij} = binary interaction parameter for the cubic term energy parameter
 LLECP = liquid–liquid equilibria critical point
 m_i = mole number of sites of type i
 n = mole number
 P = vapor pressure
 R = universal gas constant
 S_1 = API alpha function parameter
 T = temperature
 T_c, P_c = critical temperature, critical pressure
 T_r = reduced temperature (T/T_c)
 $T' = (1 - \sqrt{T_r})$
 v = molar volume
 v_0, v_t = molar volume before and after translation, respectively
 x = mole fraction
 X_i = mole fraction of sites of type i not bonded
 Z = compressibility factor

Greek Symbols

β = association volume
 Δ^j = association strength between site i and site j
 ε = association energy
 ρ = molar density

Sub- and Superscripts

bub = value of the property on the bubble point
 i, j = pure component indices
 exp, calc = experimental, calculated
 phys, assoc = physical term, association term

Abbreviations

%AAD = percentage of average absolute deviation, %AAD = $\frac{|\Omega_i^{\text{exp}} - \Omega_i^{\text{calc}}|}{\Omega_i^{\text{exp}}} \times 100\%$
 API = American Petroleum Institute
 CP = critical point
 CPA = cubic plus association
 EoS = equation of state
 LLE = liquid–liquid equilibrium
 OF = objective function
 PC-SAFT = perturbed-chain statistical associating fluid theory
 s-CPA = simplified cubic plus association
 SRK = Soave–Redlich–Kwong
 VLE = vapor–liquid equilibrium

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