

# Evaluating Cubic Plus Association Equation of State Predictive Capacities: A Study on the Transferability of the Hydroxyl Group Associative Parameters

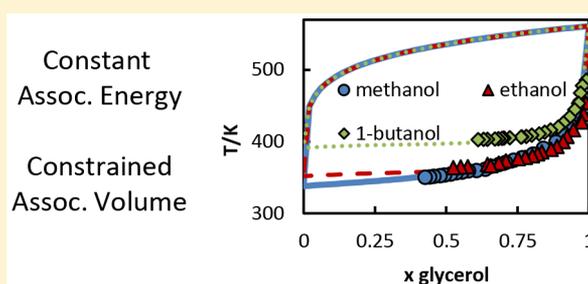
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**S** Supporting Information

**ABSTRACT:** To create a predictive method for an associative equation of state, the parameters of a specific associative group should be transferrable among molecules. The hydroxyl group, one of the most common associative groups, is a good starting point for this development. On the basis of a previous study where a modified version of the Cubic Plus Association (CPA) EoS was shown to present accurate results for alkanols with almost constant association parameters, this work addresses branched, secondary alcohols, 1, $\omega$ -alkanediols, and glycerol to evaluate how CPA can handle steric hindrances and the presence of more than one hydroxyl group. The pure component properties studied here are vapor pressure, saturated liquid density, saturated liquid isobaric heat capacity, and heat of vaporization. Some VLE, LLE, and GLE of binary systems are also analyzed, showing how the modifications affect the description of binary/multicomponent systems. Some systems containing petroleum fluids are also analyzed.



## 1. INTRODUCTION

Introduction of associative models was an important breakthrough for the description of polar and associative compounds and their mixtures. Combining an associative model based on perturbation theory with the simplicity of a cubic equation of state (EoS) in the physical term, the cubic plus association (CPA) EoS<sup>1</sup> is nowadays an important tool for process simulation, being applied in many in-house simulators as well as in the Petro-SIM and Hysys simulators.

Isomerism introduces relevant changes to the properties of the compounds and, due to the increase in steric hindrance, a hydroxyl group present in a branched alkanol is expected to behave differently from one in a primary alkanol with a similar carbon number. Besides their use as solvents, the alcohols studied in this work are applied in diverse industries: both 2-propanol and *tert*-butanol are used in the production of fuel additives, with the first being also used as a sanitization agent, and 2-butanol has applications in the perfume and food industries. These compounds are also applied as precursors for the production of diverse compounds of interest in the chemical industry.

The 1, $\omega$ -alkanediols are among the multifunctional compounds with the simplest structure, presenting two hydroxyl groups at the ends of a linear hydrocarbon chain. The properties and three-dimensional orientation of these molecules are mainly caused by the effect of hydrogen bonds, which makes these molecules interesting subjects to analyze as model molecules for hydrogen bonding, either in self-associating systems as well as to

describe solute–solvent interactions for dilute solutions. They present diverse fields of applications in the industry: monoethylene glycol (1,2-ethanediol) is one of the most important hydrate formation inhibitors, while various smaller diols can be used in refrigerating and thermostating systems as well as cryoprotectants. Diols are also used in the production of polymers such as polyurethanes and polyethers as well as drug additives in the pharmaceutical industry and for cosmetics formulations. Despite their importance, for most alkanediols, the experimental data on their thermophysical properties are scarce and often of questionable quality. Rowley et al.<sup>2</sup> recently carried a systematic study of the existing properties for six of these compounds. Their study created sets of recommended equations for vapor pressure and heat of vaporization while also providing some insight into the choice of experimental values for other properties, such as the isobaric heat capacity.

Due to their high associative nature, some diols present intramolecular association. This is the case of 1,3-propanediol and 1,4-butanediol, which bend to form a ring, resulting from the hydrogen bonding between the hydroxyl groups at their extremities.<sup>3</sup>

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Table 1. Parameters and Results for the Studied Diols and Glycerol

compound	MEG	1,3-Pr(OH) <sub>2</sub>	1,4-Bu(OH) <sub>2</sub>	1,5-Pe(OH) <sub>2</sub>	1,6-He(OH) <sub>2</sub>	glycerol
$a_c$ (Pa·m <sup>6</sup> ·mol <sup>-2</sup> )	1.72	2.25	2.72	3.22	3.82	2.59
$b$ 10 <sup>5</sup> (m <sup>3</sup> ·mol <sup>-1</sup> )	6.87	8.27	9.88	11.56	13.57	9.11
$c_1$	1.10	1.37	1.30	1.33	1.32	0.45
$c_2$	-3.64	-2.50	-1.23	-1.25	-0.52	4.16
$c_3$	12.16	6.27	3.32	4.04	2.26	-19.32
$c_4$	-37.1	-23.1	-18.0	-20.0	-16.1	19.9
$c_5$	42.5	28.4	24.4	25.2	22.2	0.0
$\epsilon$ (J mol <sup>-1</sup> )	24913	24913	24913	24913	24913	24913
$\beta$ 10 <sup>2</sup>	0.162	0.075	0.075	0.075	0.075	0.162
%AAD $P^{\text{sat}}$	0.50	0.63	0.71	0.77	0.94	0.53
%AAD $\rho_{\text{liq}}$	0.70	1.07	0.51	0.44	0.79	1.02
%AAD $H^{\text{vap}}$	0.34	1.84	3.00	0.67	0.22	0.51
$T_{\text{range}}$ (K)	330–490	293–533	293–533	293–533	318–438	330–530
$\nu$ shift (m <sup>3</sup> ·kmol <sup>-1</sup> )	0.020	0.019	0.017	0.019	0.022	0.025
$T_c$ (K)	719.0	718.2	723.8	730.0	737.0	850.0
$P_c$ (MPa)	8.20	6.55	5.52	4.75	4.08	7.50

Table 2. Parameters and Results for the Studied Alkanols

compound	2-PrOH	2-BuOH	2-PeOH	3-PeOH	tert-BuOH
$a_c$ (Pa·m <sup>6</sup> ·mol <sup>-2</sup> )	1.57	2.00	2.50	2.46	1.87
$b$ 10 <sup>5</sup> (m <sup>3</sup> ·mol <sup>-1</sup> )	7.90	9.44	11.18	11.05	9.42
$c_1$	1.20	1.15	1.02	0.95	1.12
$c_2$	-0.69	-2.01	0.54	-0.01	-0.95
$c_3$	1.20	13.82	-0.81	2.81	2.30
$c_4$	-21.5	-50.2	-9.6	-16.4	-13.0
$c_5$	40.2	58.0	17.5	21.3	25.0
$\epsilon$ (J mol <sup>-1</sup> )	24913	24913	24913	24913	24913
$\beta$ 10 <sup>2</sup>	0.034	0.034	0.034	0.034	0.030
%AAD $P^{\text{sat}}$	0.03	0.89	1.61	0.96	0.22
%AAD $\rho_{\text{liq}}$	1.68	0.16	0.46	0.50	0.74
%AAD $H^{\text{vap}}$	1.53	1.95	0.61	1.84	2.03
$T_{\text{range}}$ (K)	293–433	254–354	251–361	275–415	254–424
$\nu$ shift (m <sup>3</sup> ·kmol <sup>-1</sup> )	0.015	0.016	0.017	0.018	0.016
$T_c$ (K)	508.3	536.1	560.3	559.6	506.2
$P_c$ (MPa)	4.76	4.18	3.68	3.71	3.97

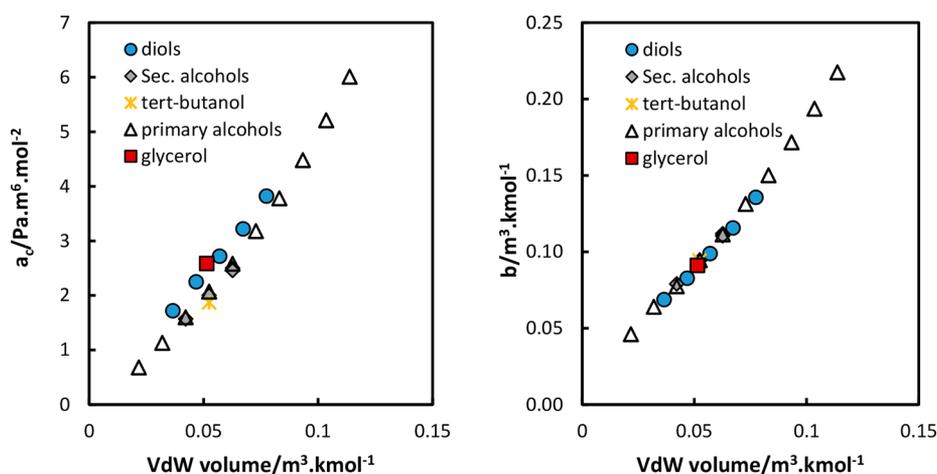


Figure 1. Energy and covolume parameters of the cubic term for compounds containing hydroxyl groups and their tendencies.

Glycerol, due to its nontoxic nature and chemical properties, is widely known in the food and pharmaceutical industries with diverse applications such as humectant, sweetener, lubricant, and solvent. Similarly to what was presented before for some diols, glycerol also presents important qualities as an

antifreezing agent for automotive applications. This molecule is also an intermediate for a large group of chemical reactions. Other applications of glycerol include uses for botanical extraction, as a component of liquids for electronic cigarettes, and use in ultrasonic testing.

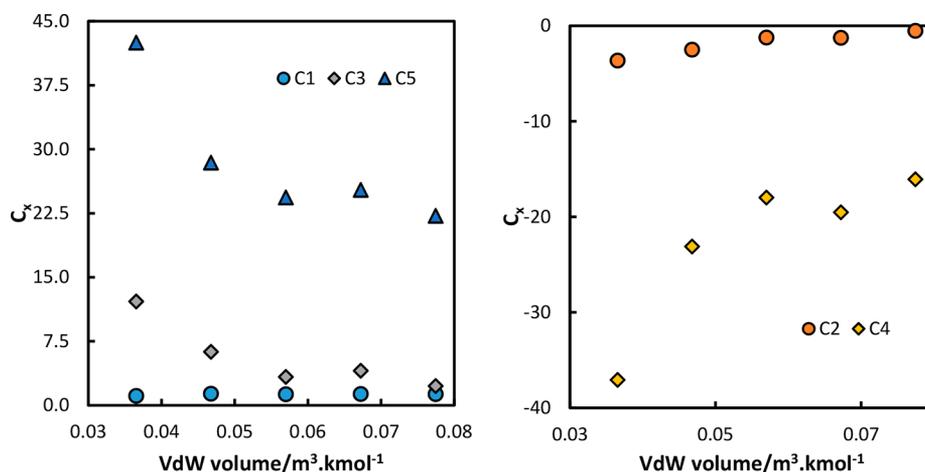


Figure 2. Alpha function (eq 5) parameters for the studied diols and their tendency with the van der Waals volume.

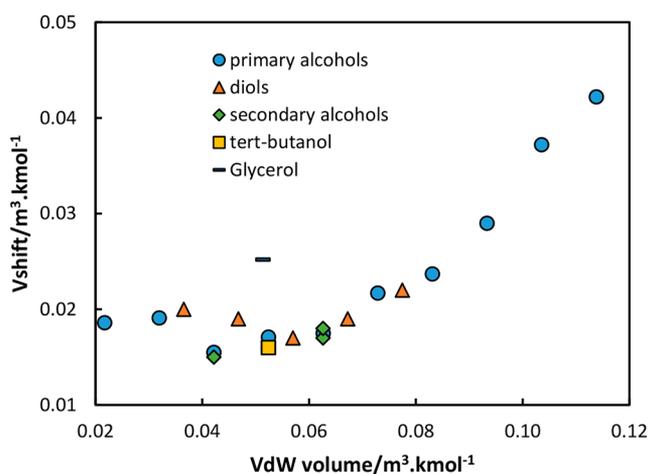


Figure 3. Volume shift parameters with relation to the van der Waals volume.

Alcohols have long been studied with the CPA EoS both for the description of their pure properties or in systems with water, hydrocarbons, or several other compounds.<sup>4–6</sup> Various sets of parameters have been proposed to describe the *n*-alcohols family, revealing important tendencies when considering only the optimization of vapor pressure and liquid density. There is, however, a dearth of studies concerning the influence of the position of the hydroxyl group in these molecules.

Models able to describe a variety of phase equilibria while providing a good description of both transport and thermodynamic properties are in great demand.<sup>7</sup> In the case of multifunctional molecules, the situation is even more dire as many of the properties are very difficult to measure or even impossible due to the thermal degradation of the compounds.<sup>8</sup> To improve the sets of parameters, increasing their accuracy for more properties, de Villiers et al.<sup>9</sup> proposed that the optimizations should be conducted using more properties and a larger range of pressure conditions. Oliveira et al.<sup>10</sup> studied the use of derivative properties in the parametrization of SAFT and showed relevant improvements with this approach.

In this study, parameter sets were obtained for a group of five secondary/branched alcohols (2-propanol, 2-butanol, 2-pentanol, 3-pentanol, and *tert*-butanol) and for five  $\alpha,\omega$ -alkanediols between MEG and 1,6-hexanediol using a modified CPA version that was previously proposed by us<sup>11</sup> which forces the accurate

description of both the pure component critical temperature and the critical pressure. The results for vapor pressure, liquid density, liquid heat capacity, and heat of vaporization were then analyzed in addition to some selected binary systems from the literature.

## 2. MODEL

To obtain the modified CPA here used, the starting point was the simplified CPA (*s*-CPA) as currently available from the literature.<sup>12</sup> CPA models account for physical interactions using a term based on a cubic EoS. In the case of *s*-CPA, this is the SRK EoS.<sup>13</sup> Using a single sum over sites, as proposed by Michelsen et al.,<sup>14</sup> CPA can be written in terms of compressibility factor, as

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

$$= \frac{1}{1 - B\rho} - \frac{A(T)\rho}{RT(1 + B\rho)}$$

$$- \frac{1}{2} \left( 1 + \rho \frac{\delta \ln g}{\delta \rho} \right) \sum_i m_i (1 - X_i) \quad (1)$$

where  $A$  represents the energy parameter ( $A(T) = n^2 a(T)$ ),  $B$  the covolume parameter ( $B = nb$ ),  $\rho$  is the density,  $g$  is a simplified hard-sphere radial distribution function,<sup>12</sup>  $X_{A_i}$  is the mole fraction of component  $i$  not bonded at site  $A$  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:

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

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

where:

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

and  $k_{ij}$  are binary interaction parameters.

Presently, the alpha function used with the modified CPA is a modified Mathias–Copeman function<sup>15</sup> that can use up to five parameters:

$$a(T) = a_c (1 + STR \times c_1 + STR^2 \times c_2 + STR^3 \times c_3 + STR^4 \times c_4 + STR^5 \times c_5)^2 \quad (5)$$

where  $STR$  is  $(1 - \sqrt{T_r})$  and  $C_1$  to  $C_5$  ( $C_x$ ) are the alpha function parameters.

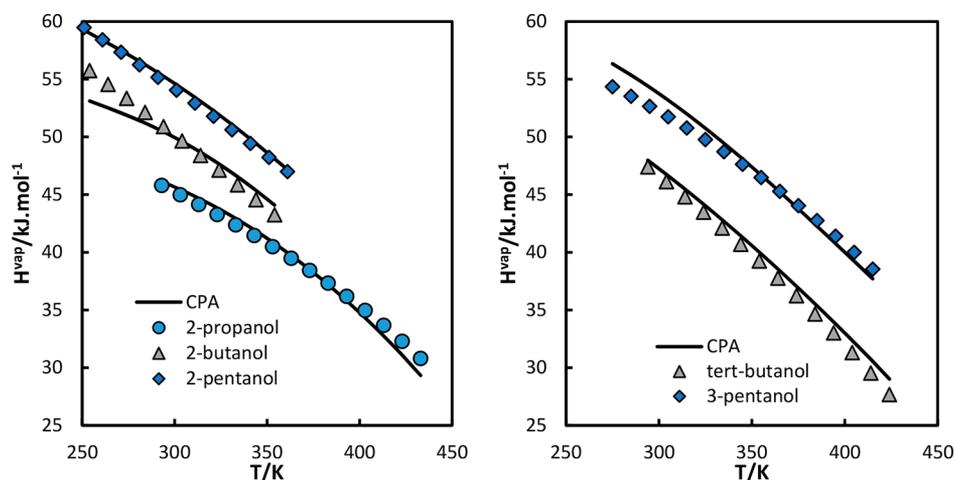


Figure 4. Results for the heat of vaporization of secondary/branched alkanols.

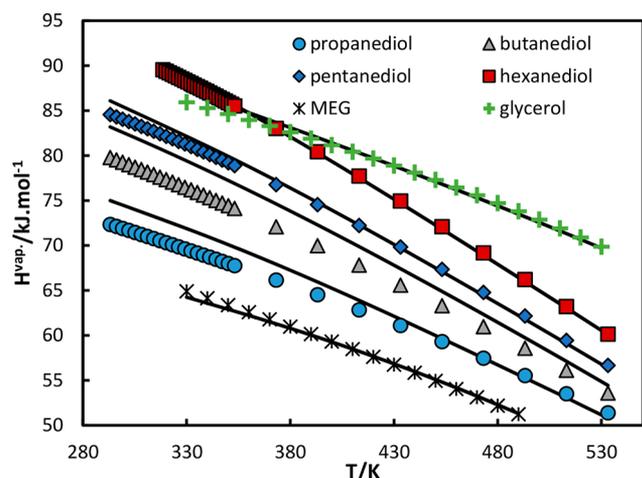


Figure 5. Results for the heat of vaporization of the analyzed alkanediols.

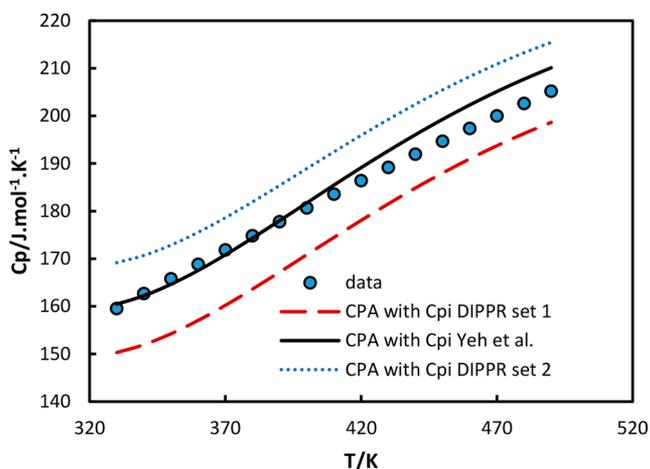


Figure 6. Results for the heat capacity of ethylene glycol using different sets of ideal gas heat capacity correlations.

Eq 6 introduces the calculation of  $X_i$ .

$$X_i = \frac{1}{1 + g\rho \sum_j m_j X_j \Delta^{ij}} \quad (6)$$

with the association strength ( $\Delta^{ij}$ ) given by

$$\Delta^{ij} = b^{ij} \beta^{ij} (e^{\varepsilon^{ij}/RT} - 1) \quad (7)$$

where  $\varepsilon^{ij}$  and  $\beta^{ij}$  are the association energy and volume for interactions between sites  $i$  and  $j$ .

The s-CPA uses a simplified radial distribution function, which is given by eq 8.<sup>12,16</sup>

$$g(\rho) = \frac{1}{1 - 0.475b\rho} \quad (8)$$

The difference of this new version of CPA lies in the restrictions used in the pure component parametrization process. This version forces  $a_c$  and  $b$  to obey the critical temperature and critical pressure. In this way, part of the parameters have a direct relation to the critical point, enhancing the predictive capacity of the model.

$$P_{\text{CPA}}(T_c^{\text{exp}}, V_c^{\text{calc}}) = P_c^{\text{exp}} \quad (9)$$

$$\left. \left( \frac{\partial P}{\partial v} \right) \right|_{T=T_c} = 0 \quad (10)$$

$$\left. \left( \frac{\partial^2 P}{\partial v^2} \right) \right|_{T=T_c} = 0 \quad (11)$$

The objective function used in the parametrization is also different from s-CPA. The molar volume is not optimized directly, being instead obtained through a Peneloux-type volume shift.<sup>17</sup>

$$v_t = v_0 - c_{vs} \quad (12)$$

where  $c_{vs}$  is the volume shift. Using this type of volume shift does not affect the calculations of vapor pressure, heat of vaporization, or heat capacities, as is discussed by Jaubert et al.<sup>18</sup>

Also relevant to this process is the separation of the optimization of associative and cubic terms. Given a starting point for the associative parameters, the cubic term is generated, with the alpha function being parametrized directly to the vapor pressure curve. The whole group of parameters can be then optimized by adjusting the associative parameters, as the cubic term is automatically generated from the critical data and vapor pressure curve.

The following equations were considered to optimize the values of  $k_{ij}$ .

$$OF = \sum_i^{np} \left( \frac{T_{\text{bub}}^{\text{exp}} - T_{\text{bub}}^{\text{calc}}}{T_{\text{bub}}^{\text{exp}}} \right)^2 \quad (13)$$

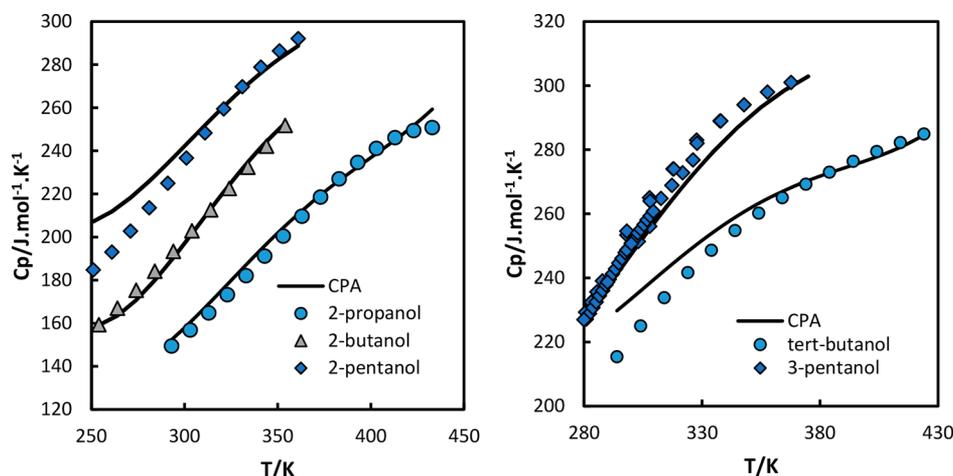


Figure 7. Results for the heat capacity of secondary/branched alkanols.

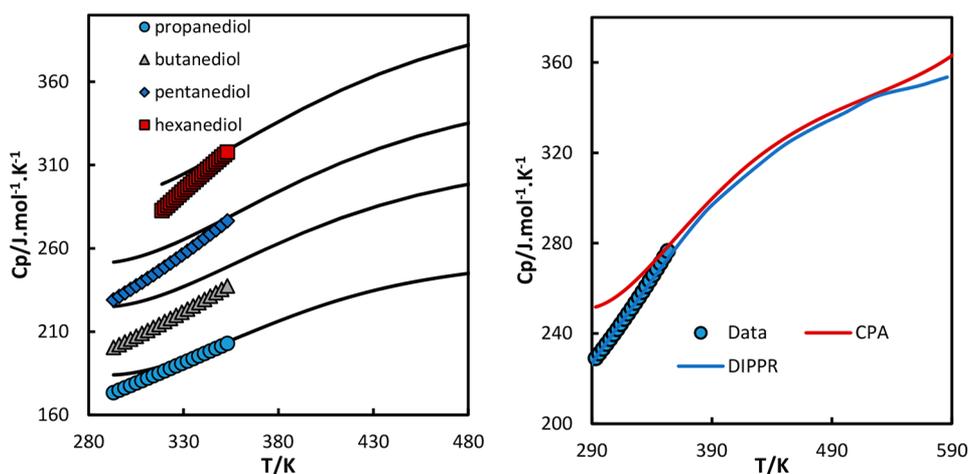


Figure 8. Results for the heat capacity of diols (left) and comparison with the predictions of DIPPR for the heat capacity of 1,5-pentanediol (right).

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

$$OF = \sum_k^{npo} \sum_i^{np} \left( \frac{x_{i,k}^{\text{exp}} - x_{i,k}^{\text{calc}}}{x_{i,k}^{\text{exp}}} \right)^2 \quad (15)$$

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

When two or more associative compounds are present in a mixture, CPA needs combining rules for the cross-associative parameters. CR-2<sup>19</sup> was here applied, as proposed by Kontogeorgis et al.<sup>5</sup>

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

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

Contrary to what is usually done with CPA, in this work, association schemes are linked to each group and not to each molecule. In this way, considering the 2B<sup>20</sup> scheme for the hydroxyl group: diols will have a  $2 \times 2B$  scheme. In this work this is not very relevant because the associative groups in  $1,\omega$ -alkanediols are rigorously the same, but for more complex molecules with varying types of groups, which can also be affected by steric hindrance, this will enable implementation of

group dependent parameters, which are expected to improve the predictive capacities of CPA.

Kontogeorgis et al.<sup>4</sup> compared the schemes for the hydroxyl group, fitting binary phase equilibria with both the 2B and the more accurate (and complex) 3B<sup>20</sup> scheme. Their results show that the 3B scheme does not improve the results when compared to those of the 2B scheme. Each of these schemes holds advantages in the description of specific properties as discussed by de Villiers et al.<sup>9</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Pure Component Analysis.** The description of some secondary/branched alkanols and  $\alpha,\omega$ -alkanediols is analyzed here using a modified CPA EoS<sup>11</sup> recently proposed. Being an extension of our previous studies on the hydroxyl group parametrization, the constant association energy parameter of  $24913 \text{ J}\cdot\text{mol}^{-1}$  was used, while the associative volume was considered constant within each family of compounds except for MEG, in which case the ethanol associative parameters proved more accurate. The parameters obtained with ethanol were also applied to glycerol. For monoalcohols (with a single OH group), the liquid heat capacity was used in the fitting of the associative volume parameter for secondary alcohols, while for diols and *tert*-butanol, this parameter was fitted only to vapor pressure data.

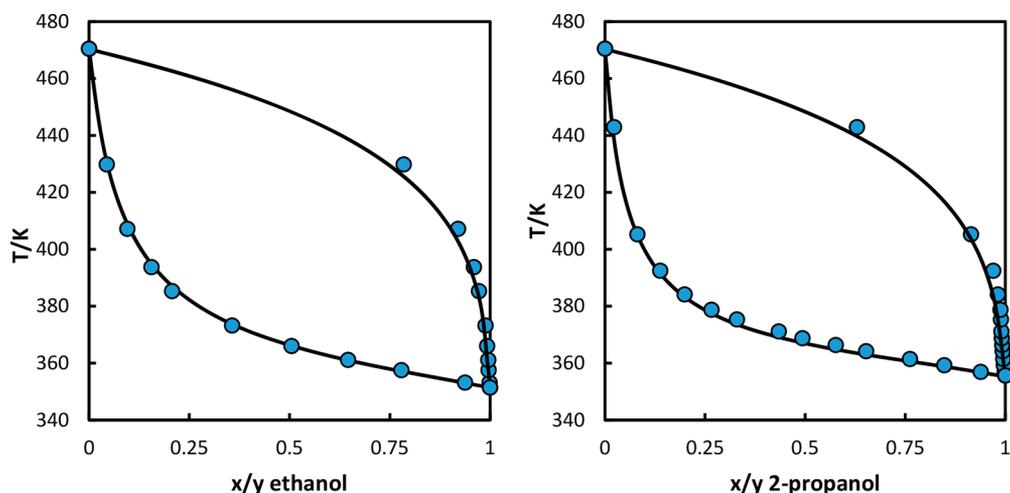


Figure 9. Predictions for the binary systems MEG + ethanol (left)<sup>29</sup> and MEG + 2-propanol (right) at 1 atm.<sup>30</sup>

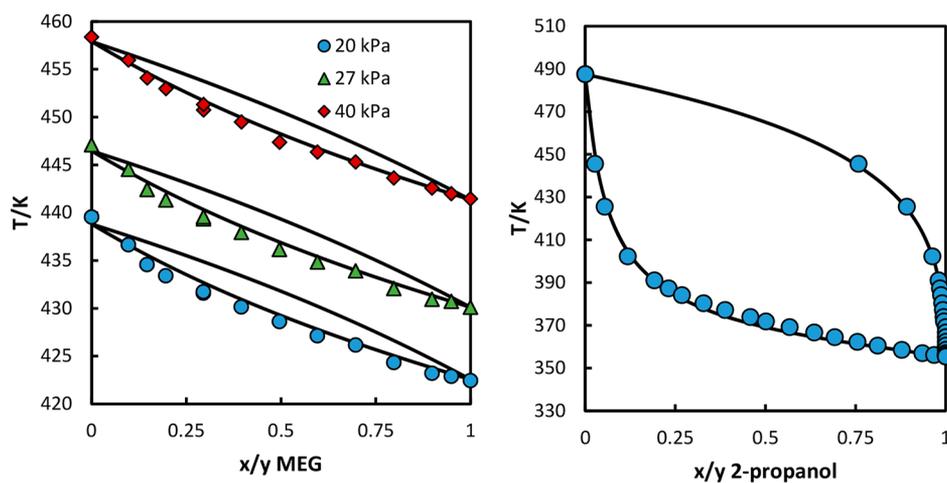


Figure 10. Predictions for the binary system MEG + 1,3-propanediol (left)<sup>31</sup> and results for the system 1,3-propanediol + 2-propanol (right)<sup>32</sup> at 1 atm with a  $k_{ij} = -0.015$ .

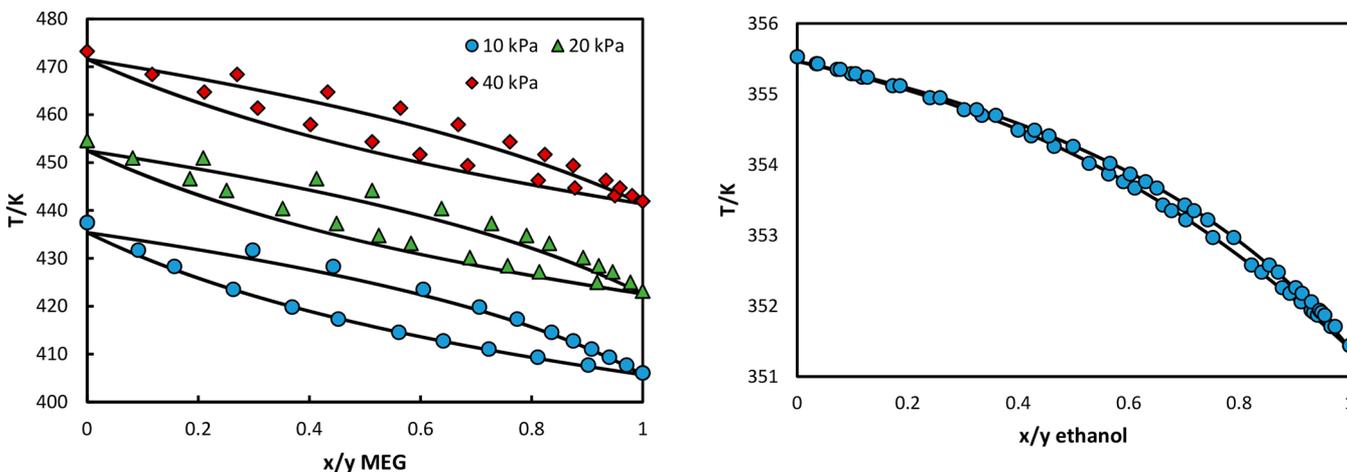


Figure 11. Predictions for the binary system MEG + 1,4-butanediol.<sup>33</sup>

The vapor pressure data used for the diols were obtained from Rowley et al.,<sup>2</sup> which enables the use of this version of CPA due to the large temperature range of vapor pressure data that can be estimated. For the remaining compounds, the vapor pressure curves were obtained from the DIPPR<sup>21</sup> and TRC<sup>22</sup> databases.

Figure 12. Results for the binary system *tert*-butanol + ethanol at 1 atm with a  $k_{ij} = -0.024$ .

For liquid density, the curves from Multiflash<sup>23</sup> and DIPPR<sup>21</sup> were applied except for 1,6-hexanediol, for which data by Bleazard et al.<sup>24</sup> were used. For the heat of vaporization, the data were taken from the DIPPR<sup>21</sup> and TRC<sup>22</sup> databases as well as from the Multiflash<sup>23</sup> correlations, while for heat capacity, most

data comes from Góralski and Tkaczyk.<sup>25</sup> Critical data were taken from Rowley et al.<sup>2</sup> and the TRC<sup>22</sup> and DIPPR<sup>21</sup> databases.

The parameter sets and results for liquid density, vapor pressure, and heat of vaporization as well as the critical data used in the parametrization are presented in Tables 1 and 2. Figure 1 presents the tendencies against the van der Waals volume for

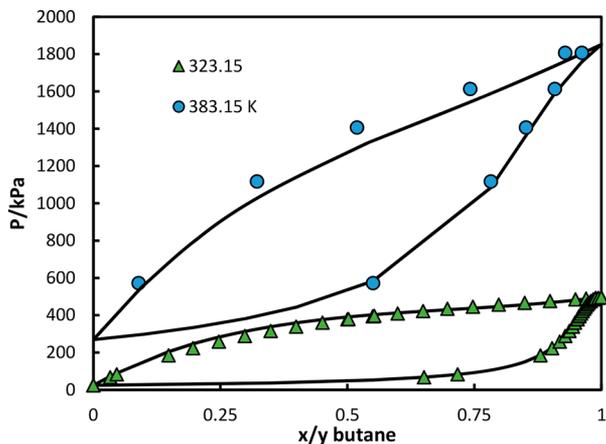


Figure 13. Results for the binary system *tert*-butanol + butane at 2 temperatures with a  $k_{ij} = 0.0551$ .

both the cubic term energy at the critical temperature ( $a_c$ ) and covolume parameters and a comparison to those for the primary alkanols.<sup>11</sup>

The critical data presented in Tables 1 and 2 correspond to both the experimental and calculated values because, within the presented tolerance, there are no differences between these two values.

As shown in Figure 1, both the covolume and energy parameters of the cubic term present dependencies on the van der Waals volume. It is also interesting to note that, in the case of diols, this is also true for the alpha function parameters despite the intercorrelation between these parameters. Nevertheless, an outlier is always observed, usually 1,4-butanediol or 1,5-pentanediol. This is also patent in Figure 2.

The values of the association volume seem to decrease for the higher steric hindrances. Dependencies similar to those previously observed for primary alcohols<sup>11</sup> are obtained when analyzing the volume shift. For diols, a minima similar to that found between methanol and 1-propanol is observed at 1,4-butanediol. Glycerol presents a higher value for the volume shift, which might have to do with the higher uncertainties for its critical data. These results are reported in Figure 3.

With this approach, liquid density, heat of vaporization, and vapor pressure were all well-described for MEG. For the

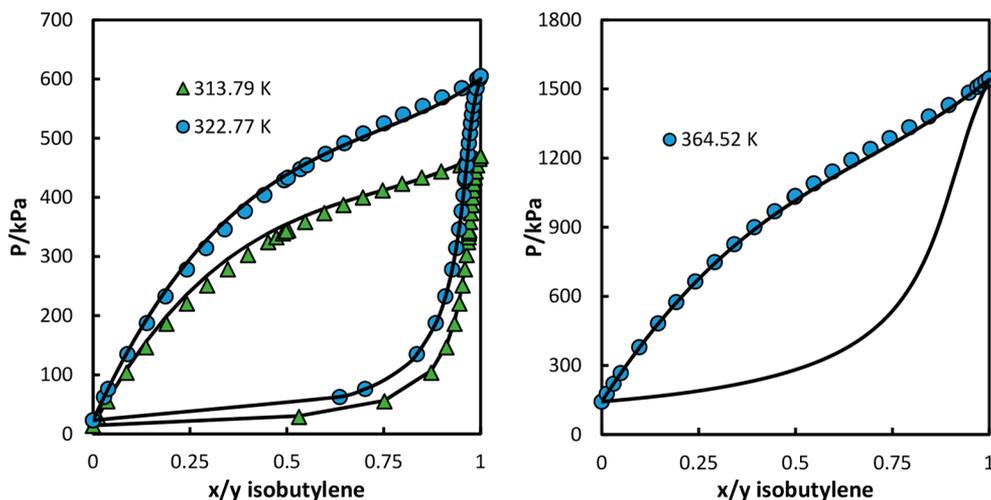


Figure 14. Results for the binary system *tert*-butanol + isobutylene at 3 temperatures with a  $k_{ij} = 0.0370$ .

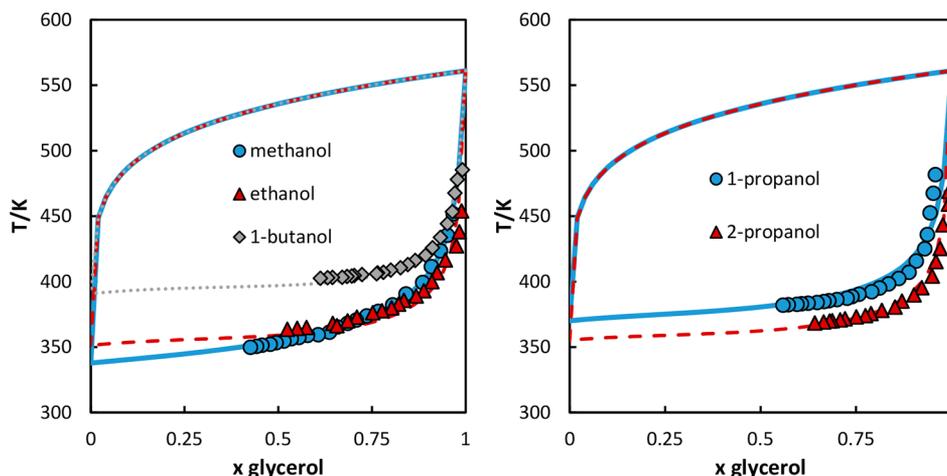


Figure 15. Results for the systems containing glycerol and an alcohol at 1 atm.<sup>34</sup>

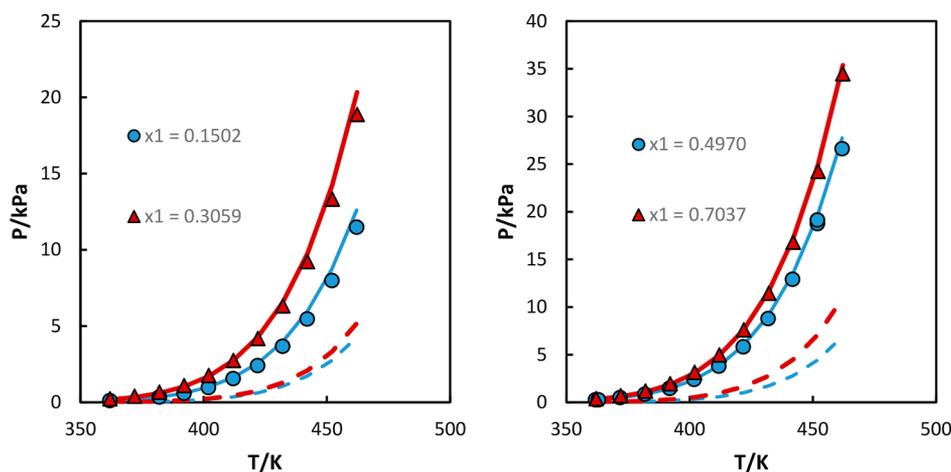


Figure 16. Results of the system 1,3-propanediol (1) + glycerol (2): full lines, Bubble points; dashed lines, dew points.<sup>35</sup>

Table 3. Binary Interaction Parameters for the Systems Containing Glycerol

second compound	$k_{ij}$
1,3-propanediol	0.015
methanol	0.008
ethanol	0.054
1-propanol	-0.009
2-propanol	0.000
1-butanol	0.018

remaining diols and glycerol, despite higher deviations, which are in part due to the higher uncertainties of the experimental data, the results are also accurate, with average deviations for each property inferior to 1% in most cases. For the other alcohols studied, the results are similar. The estimation for ethylene glycol proved to be able to describe LLE equilibria with alkanes, as will be shown in the next section. Predictions of heat of vaporization are reported in Figures 4 and 5.

The 1,4-butanediol is the diol which presents largest deviations. This is in part due to a high degree of uncertainty in its vapor pressure curve. This is very relevant when considering the heat of vaporization, liquid  $C_p$ , and also results for binary systems and will be further discussed below.

The  $C_p$  estimates show a large dependence on the ideal gas heat capacity, as shown on Figure 6 using various approaches for  $C_p^{\text{ideal}}$ . Because the equation of state provides only the residual contribution to the heat capacity, an accurate ideal gas heat capacity correlation is required. Three sets of correlations for ideal gas heat capacities were analyzed in the case of MEG. The first two are available from the data on the DIPPR database,<sup>21</sup> while the third is based on the studies of Yeh et al.<sup>26</sup> on the conformation of ethylene glycol.

It is important to note that some of these sets are based on group contribution methods, and similar variations are obtained by using different methods of the same type.<sup>27,28</sup>

The results for the liquid phase  $C_p$  of secondary/branched alcohols are presented in Figure 7.

The results present somewhat higher deviation for  $C_p$  at lower temperatures, where the data have more uncertainties and the EoS presents a lower accuracy due to the unconstrained alpha function, which having 5 available parameters is too flexible to fit to only a few properties without any constraints.

Despite the problem with the ideal gas heat capacity and the inaccuracies at lower temperatures, the  $C_p$  results for the

remaining diols follow the expected tendencies with an exception for 1,4-butanediol, for which the vapor pressure curve seems to present some inaccuracies, as will be discussed below when modeling binary systems. In Figure 8, the results for  $C_p$  are compared with the experimental data from Góralski and Tkaczyk,<sup>25</sup> and the results for 1,5-pentanediol are compared with the predictions of Rowley et al.<sup>2</sup>

For glycerol, the average deviations in  $C_p$  are higher than 10%.

In the presented results, it is of note that the increase in the number of parameters and the parametrization process have an important influence on the predictions. As presented above, two of the parameters are obtained from the fitting of the pure compound critical temperatures and pressures, enabling the correct description of these properties. The association parameters used here are in most part constant, and thus, when comparing this version to s-CPA, for most associating compounds, it has one more adjustable parameter (fitting the 5 parameters of s-CPA or fitting the 5 parameters of the modified Mathias–Copeman function plus the volume shift). It is important to note that some compounds (methanol, ethanol, and MEG) present accurate results without using the whole alpha function and, in future work, the use of different alpha functions with less parameters should be conducted.

The accuracy of these results is in line with those obtained for the primary alkanols; thus, it is now important to look at the impact of the parametrization used in the modeling of binary systems.

**3.2. Binary Systems Modeling.** The binary VLE systems analyzed for diols with other diols and alkanols present accurate descriptions of the experimental data, which are in most cases predictive. The systems analyzed were MEG + ethanol and MEG + 2-propanol, both of which are presented in Figure 9.

With 1,3-propanediol two systems were analyzed, 1,3-propanediol + MEG and 1,3-propanediol + 2-propanol. In the second case a binary interaction parameter with the value of -0.0153 was used, while for the first systems no interaction parameter was required. The results are presented in Figure 10.

As hinted before, some deviations were observed in the vapor pressure curve of 1,4-butanediol that now have an impact upon the description of the VLE data for binary systems. In Figure 11, the predictions for the system MEG + 1,4-butanediol are reported.

Differences higher than 2 K can be observed for the pure saturation temperature of 1,4-butanediol, showing a slight but

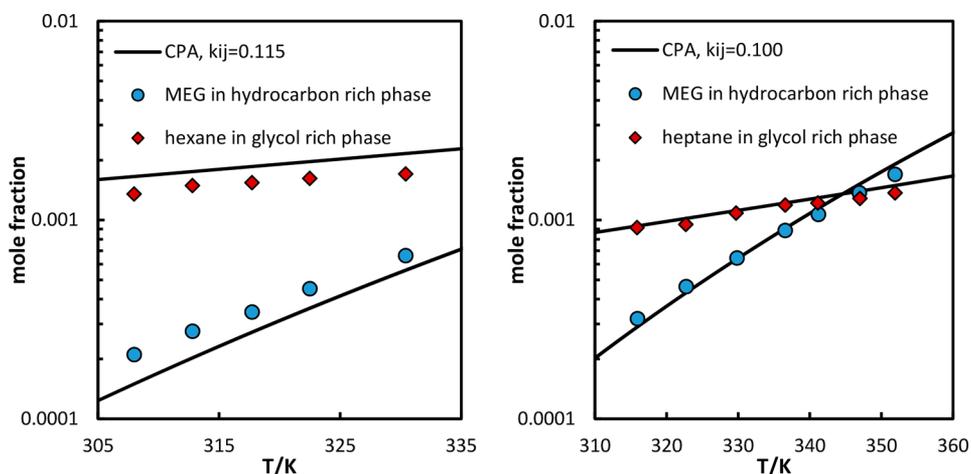


Figure 17. Mutual solubility results for the binary systems MEG + *n*-hexane (left) and MEG + *n*-heptane (right).

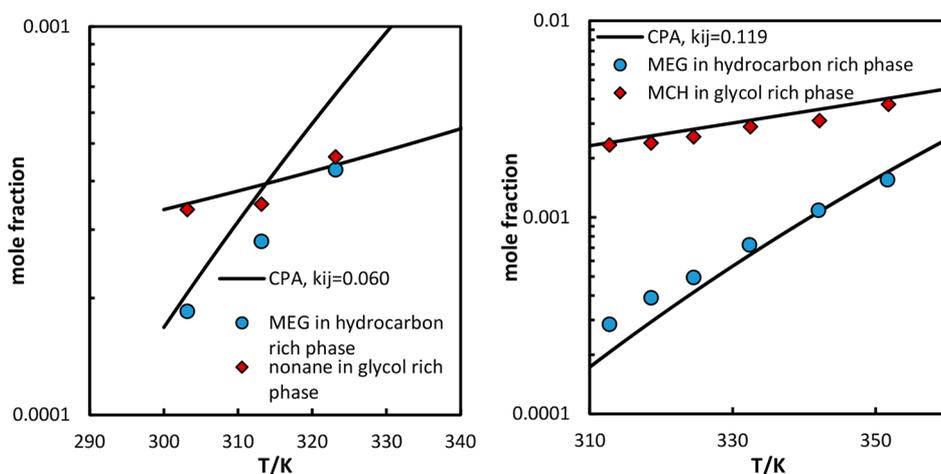


Figure 18. Mutual solubility results for the binary systems MEG + nonane (left) and MEG + methyl cyclohexane (right).

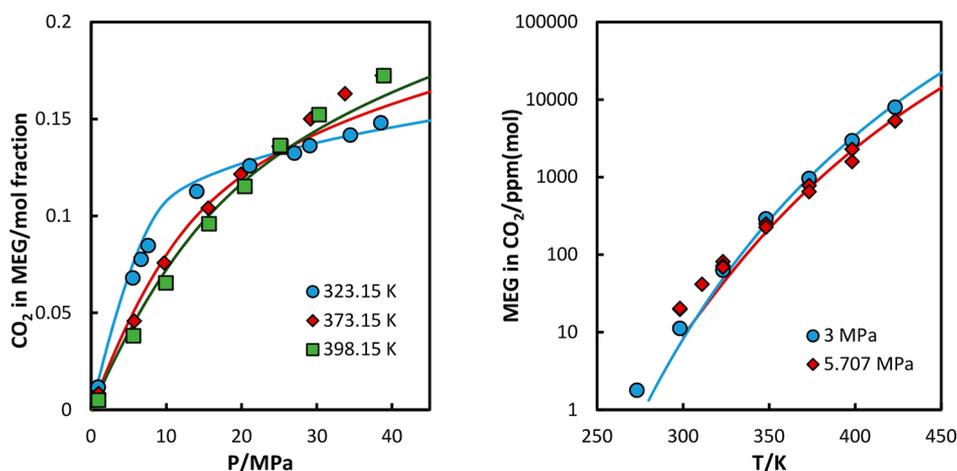


Figure 19. Solubility of CO<sub>2</sub> in MEG (left) and MEG in CO<sub>2</sub> (right);  $k_{ij} = 0.147$ .

relevant overestimation of the pure component vapor pressure. The deviations between CPA results for the pure 1,4-butanediol saturation pressure and the data of Yang et al.<sup>33</sup> are on average 7.9%, while the average for the applied vapor pressure curve was 7.2%, which is already a high uncertainty. These deviations are not very high in terms of absolute values of temperature but, as can be observed in Figure 11, are detrimental for the description

of the binary systems, especially at higher pressures. Combined with the higher uncertainty for the lower temperatures, it was thus expected that the derivative properties calculated would present higher deviations, as observed in the previous subsection.

The description of the VLE for binary systems of diols was mostly accurate, with only one of the systems requiring a binary interaction parameter. Results were also obtained for VLE

systems with *tert*-butanol. In this case, all systems required the use of a binary interaction parameter. The experimental data for these systems were taken from the TRC database.<sup>22</sup> Figure 12 presents the description of the system *tert*-butanol + ethanol using a binary interaction parameter of  $-0.024$ .

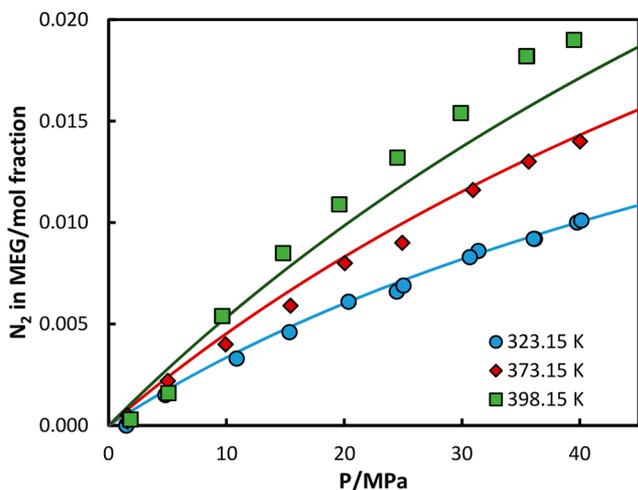


Figure 20. Solubility of  $N_2$  in MEG at 3 different temperatures;  $k_{ij} = 0.590$ .

The results for this system are highly accurate despite the narrow temperature difference between the boiling and dew temperatures. The results for *tert*-butanol + butane were also studied and are presented in Figure 13.

To finish the analysis of the VLE description of binary systems containing *tert*-butanol, the system with isobutylene was also studied, which is presented in Figure 14.

Binary systems with monoalcohols/1,3-propanediol were studied to verify the quality of the glycerol parameters. These systems are well described using small interaction parameters in most cases, as is presented in Figures 15 and 16. The binary interaction parameters for these systems are presented in Table 3.

It was previously shown that, using this version of CPA,<sup>11</sup> despite the higher values of the covolume (when compared to the original CPA model), it was possible to successfully describe LLE, albeit with slightly higher binary interaction parameters. Thus, the description of LLE systems containing MEG was analyzed, as well as the accuracy of the model to describe the solubility of gases in MEG. Comparing the results for MEG + alkanes with the data from Derawi et al.<sup>36</sup> and Riaz et al.,<sup>37</sup> presented in Figures 17 and 18, it is shown that the proposed parameters are able to describe these systems and, despite somewhat higher deviations in the system with hexane and the need of higher  $k_{ij}$  values, the results are comparable to those of s-CPA.<sup>38</sup>

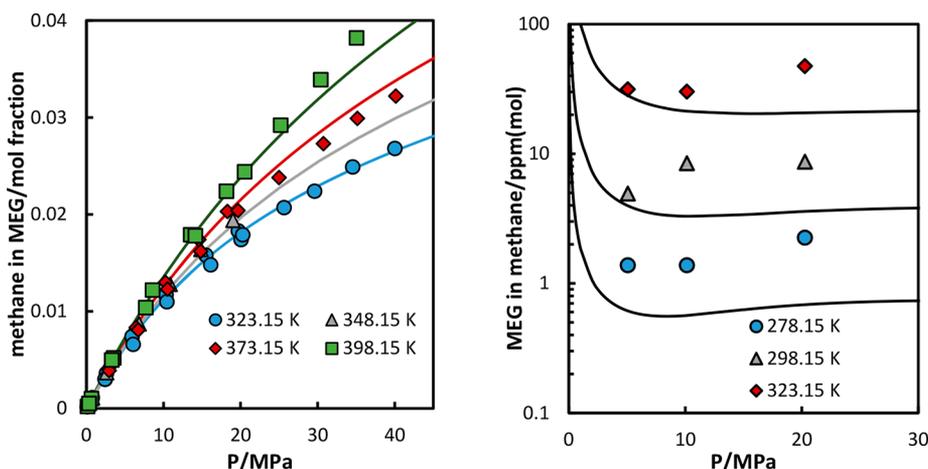


Figure 21. Solubility of methane in MEG (left) and solubility of MEG in methane (right);  $k_{ij} = 0.343$ .

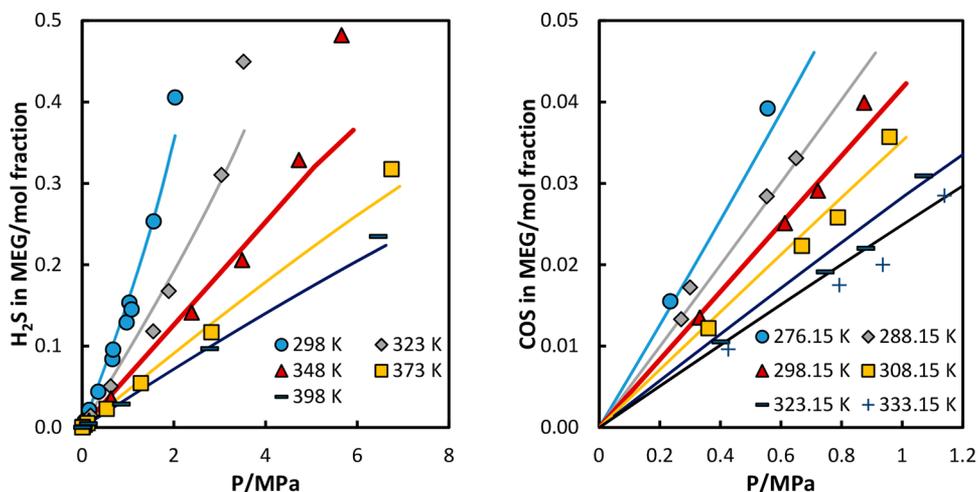
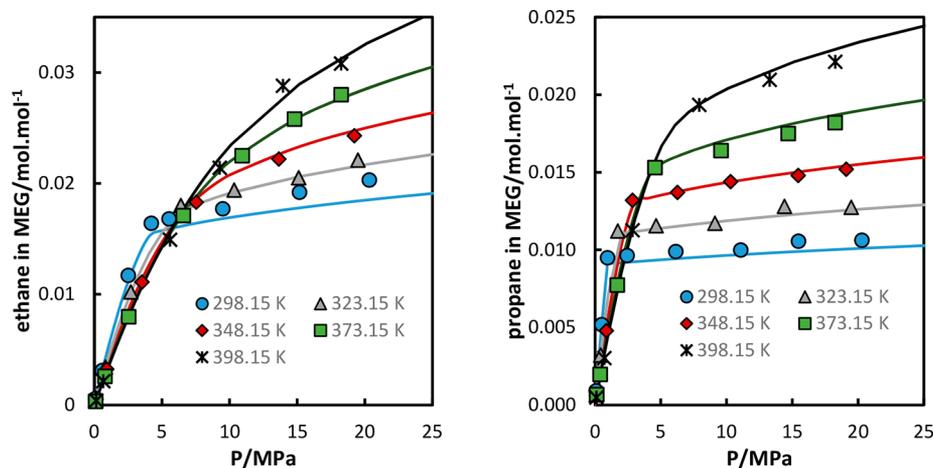
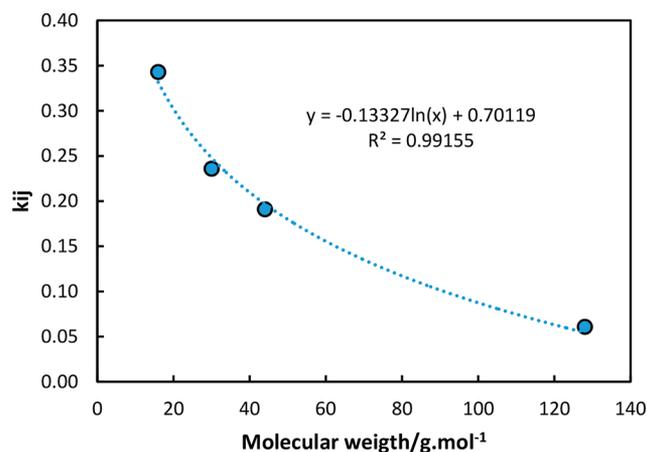


Figure 22. Results for the solubility of  $H_2S$  (left) and  $COS$  (right) in MEG with binary interaction parameters of 0.039 and 0.160 respectively.



**Figure 23.** Results for the solubility of ethane in MEG<sup>45</sup> (left) and propane in MEG<sup>46</sup> (right); the binary interaction parameters are 0.237 and 0.191, respectively.



**Figure 24.** Binary interaction parameters correlation for the studied systems of MEG with alkanes and their dependency with the alkane carbon number.

With these results, along with the results for the systems MEG + light alkanes, for which the modeling of the gas solubility is studied below, it is possible to correlate the binary interaction parameter values with the chain length of the alkane. The average absolute deviations for these systems are presented in the [Supporting Information](#).

To evaluate the ability of the model to describe the results for gas solubility in MEG ( $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{N}_2$ , and methane) and MEG solubility in gas (methane and  $\text{CO}_2$ ), modeling results were compared with those from the works by Jou et al.,<sup>39,40</sup> Zheng et al.,<sup>41</sup> Folas et al.,<sup>42</sup> and Afzal et al.<sup>43</sup> Larger binary interaction parameters were needed for all systems in study. Despite this fact, the descriptions are rather accurate and, in the case of the binary systems of MEG with methane,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{COS}$ , they compare well with the results from *s*-CPA.<sup>8,42,43</sup> The  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{COS}$  were considered to be inert in this study.

Figures 19–22 present the results for the five systems investigated.

Despite being considered as nonassociative compounds, the descriptions for the systems with  $\text{CO}_2$  and  $\text{N}_2$  present accurate results with CPA (Figure 19), being equivalent to those reported by Jou et al.<sup>40</sup> with Peng–Robinson.<sup>44</sup>

With methane, deviations are higher, as shown in Figure 21; nevertheless, the results are similar to those by Folas et al.<sup>42</sup>

with *s*-CPA and for the very low concentrations in study are satisfactorily accurate.

Similarly to  $\text{CO}_2$  and  $\text{N}_2$ , the systems with  $\text{H}_2\text{S}$  and  $\text{COS}$  are accurately described despite no association sites being considered in  $\text{H}_2\text{S}$  or  $\text{COS}$ .

To complete the study on the systems of MEG + *n*-alkanes (for which results with methane, hexane, heptane, and nonane were already analyzed), the solubility of ethane and propane in MEG are presented in Figure 23.

As discussed before, a dependency is observed for the binary interaction parameters of these systems with the alkane carbon number, as shown in Figure 24. The use of the correlation enables the description of the systems in study. The %AAD for each system with the original  $k_{ij}$  and the correlated value are presented in the [Supporting Information](#). To further test the quality of these parameters, an analysis was carried for five systems studied by Kontogeorgis and coworkers<sup>37,47–50</sup> using this binary interaction parameter correlation.

The  $k_{ij}$  values for linear and branched hydrocarbons were considered to be identical.

For most analyzed systems, this approach is able to describe with reasonable accuracy the fraction of MEG in the hydrocarbon-rich phase, or at least a correct temperature dependency is obtained. It is of note that despite the pure property description of ethylene glycol taking priority in this parametrization with two critical properties fitted, a reasonable  $C_p$  temperature dependency and very satisfactory deviations for both  $P_{\text{sat}}$  and  $\rho_{\text{liq}}$ , the essential description of these systems is still captured with light oil 1 being a particular case where the range of temperature for which the fraction of MEG in light oil is superior to that of light oil in MEG is closer to experimental data. The results for these systems as well as the comparison with the results of Kontogeorgis and coworkers<sup>37,47–50</sup> are presented in Figures 25–27. The deviations obtained for these systems are presented in the [Supporting Information](#).

This approach tends to overestimate the  $k_{ij}$  values for the C10+ fractions for lighter mixtures, leading to an underprediction of the fraction of hydrocarbons in MEG phase for some of these systems. However, this also enables improvements on heavier mixtures, as is the case of light oil 1, or in some instances improving the description of the hydrocarbon-rich phase.

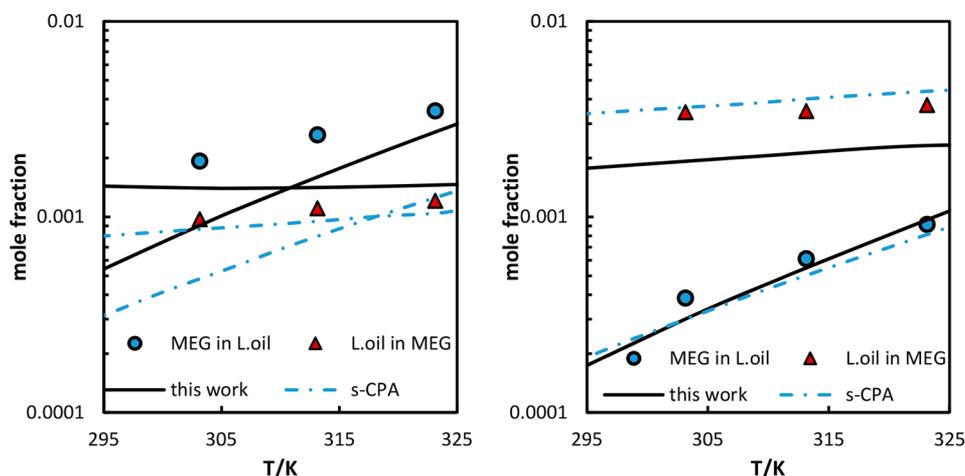


Figure 25. Results for the LLE descriptions of MEG with light oil 1 (left) and MEG with light oil 2 (right); experimental data is from Kontogeorgis and coworkers.<sup>49</sup>

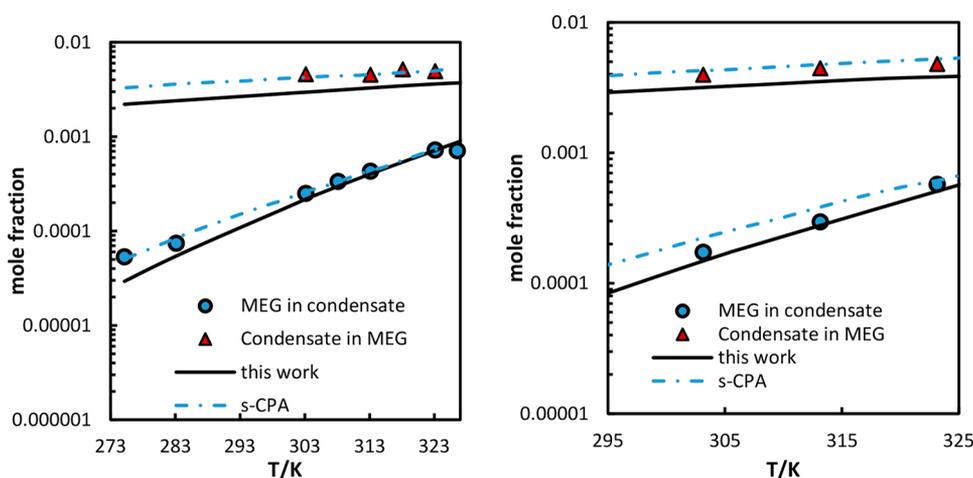


Figure 26. Results for the LLE descriptions of MEG with cond-1 (left) and MEG with cond-3 (right); experimental data is from Kontogeorgis and coworkers.<sup>47,50</sup>

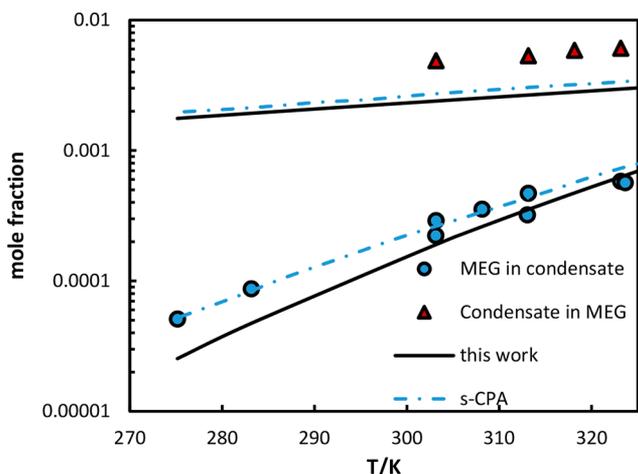


Figure 27. Results for the LLE descriptions of MEG with cond-2; experimental data is from Kontogeorgis and coworkers.<sup>47</sup>

#### 4. CONCLUSION

A modified CPA recently proposed was expanded to diols and some secondary/branched alcohols. The value of the associative energy was considered constant, while the associative volume

was adjusted to take into account different environments (including steric hindrance). The energy, covolume, and volume shift parameters show tendencies with the van der Waals volume. In the case of diols, the alpha function results also show tendencies for its parameters, showing promising results for the predictive capacities of this version.

Modeling results within the experimental uncertainty were obtained for most pure properties.  $C_p$  presents higher deviations; however, a part of these might be due to the uncertainties coming from the use of the ideal gas heat capacity correlations. However, the tendency for the property is in most cases correct, even when not using this property in the optimization, which usually is not observed with other versions of the equation. It is also of note that this version of CPA forces the correct description of both the critical pressure and critical temperature, providing a more reliable description of these properties but also of properties which depend on them, as is the case of heat of vaporization, for which, with this version, the results at the critical temperature will be 0 instead of presenting an overestimated application value while presenting mostly accurate results at normal application temperatures.

These improvements on the pure component description lead, in most cases, to the need for slightly higher binary interaction parameters. Despite this, the correlation results are of similar accuracy as those of s-CPA for most systems. Gas solubility in

ethylene glycol, as well as some cases of solubility of MEG in gases, were also analyzed with promising results. A final test was conducted to verify the quality of multicomponent description with this new version of CPA. The results show a very reasonable description of this system using a single correlation based on the studied systems of MEG with hydrocarbons.

To summarize, this modified version of CPA improves on the description of pure component properties with the description of the pure component critical pressure and temperature and an increase in accuracy for the predictions of heat of vaporization and liquid  $C_p$ . These results were obtained using a constant and transferable value for the association energy parameter for the hydroxyl group and a very simple approach for the association volume, improving on the predictive capacity of the model. The results obtained during the binary and multicomponent system calculations are accurate and in most cases present similar quality to those from s-CPA, despite the higher  $k_{ij}$  values.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b00760.

Deviations for calculated pure compound and VLE at constant pressure and temperature/composition, comparison of binary results, and deviation for remaining LLE and GLE (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ NOMENCLATURE

- $A$ ,  $a$  = energy parameter of CPA  
 $a_c$  = value of the energy parameter at the critical point  
 $A_i$  = site A in molecule  $i$   
 $B$ ,  $b$  = covolume  
 $c_1 = c_5$  ( $c_x$ ) = 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  
 $m_i$  = the mole number of sites of type  $i$   
 $n_i$  = mole number of component  $i$

- $P$  = vapor pressure  
 $R$  = gas constant  
 $T$  = temperature  
 $v_0, v_t$  = volume before and after translation, respectively  
 $x$  = mole fraction  
 $X_{A_i}$  = mole fraction of component  $i$  not bonded to site A  
 $Z$  = compressibility factor

## Greek Symbols

- $\beta$  = association volume  
 $\varepsilon$  = association energy  
 $\rho$  = molar density  
 $\Delta$  = association strength

## Sub- and Superscripts

- assoc, phys = association and physical terms  
 cn = carbon number  
 exp., calc = experimental, calculated  
 $i, j$  = pure component indexes  
 ig = ideal gas  
 np = number of points  
 npo = number of phases to optimize  
 res = residual

## Abbreviations

- %AAD = percentage of average absolute deviation  
 1,3-Pr(OH)<sub>2</sub> = 1,3-propanediol  
 1,4-Bu(OH)<sub>2</sub> = 1,4-buanediol  
 1,5-Pe(OH)<sub>2</sub> = 1,5-pentenediol  
 1,6-Hex(OH)<sub>2</sub> = 1,6-hexanediol  
 2-PrOH = 2-propanol  
 2-BuOH = 2-butanol  
 2-PeOH/3-PeOH = 2-pentanol/3-pentanol  
 CPA = cubic plus association  
 s-CPA = simplified CPA  
 EoS = equation of state  
 HC = hydrocarbon  
 MEG = monoethylene glycol  
 s-CPA = simplified cubic plus association  
 SRK = Soave–Redlich–Kwong  
 tert-BuOH = tert-butanol

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