Re-evaluating the CPA EoS for improving critical points and derivative properties description

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ABSTRACT

Although the CPA EoS was initially developed 20 years ago to meet industrial solicitations, namely the need to describe mixtures of hydrocarbons and water, including the formation and dissociation of hydrates, it has only recently received a widespread use in mid-stream and downstream oil and gas processing, or in the petrochemical and chemical industries. One of the reasons for such limited use of the model in the industry is the necessity to parameterize every associating component from saturation data. This involves access to pure component databases and some advanced knowledge in thermodynamics and numerical methods, which are often behind the scope of process design engineers.

This work revisits the CPA model, evaluating its strengths and weaknesses and attempting at identifying some opportunities for improvement. Using n-alkanols from C1 to C10 and their mixtures with other n-alkanols and n-alkanes, it investigates the description of the pure component critical points, saturated liquid densities as a function of temperature and some second-order derivative properties. It also explores new methodologies to regress the CPA parameters in a more systematic way, making it easier to generate parameters with less intervention from the user.

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1. Introduction

Design and optimization of processes using multifunctional molecules is of great importance to the chemical, petrochemical, pharmaceutical, cosmetics, food and energy industries. There is a need for simple, yet accurate, models able to cope with the requirements of the industry. Before the mid of the 1990's there were few reliable equation of state based approaches for the description of mixtures including strongly polar and associative molecules in broad ranges of temperature and pressure. The development of excess Gibbs energy mixing rules for equations of state provided some opportunities for modelling mixtures with polar compounds, but at the expense of having to use more parameters and in some cases having to re-estimate them. A good review on the use of excess Gibbs energy models in equations of state has been reported by Kontogeorgis and Coutsikos [1].

Based on Wertheim's ideas on association [2–5] the Statistical Associating Fluid Theory (SAFT) [6,7] EoS was developed and on its trail the CPA [8] model appeared as an alternative to model

associating mixtures while keeping all the advantages, simplicity, and well known behaviour of cubic equations of state. The CPA can thus be seen as a special case of a cubic equation of state where associating components are involved. The CPA relevance as a simple, yet accurate, model for associative compounds has been growing since then, both in the academia and in the industry, although its use in the industry is still essentially limited to upstream oil and gas applications, where mixtures of water and hydrocarbons during production and the formation of hydrates in transportation are the most well-known applications of the model [9,10].

Although CPA would be the right option to replace cubic equations of state in process simulators, up to until recently, not many commercial simulators implemented the model. This model can be found for example, in the physical properties package Multiflash™ and in the SPECS software from CERE at the Technical University of Denmark. So its use in process simulation was until recently limited to what could be achieved by using the CAPE-OPEN interface with these two packages. Nowadays, CPA is a well-established model in the literature and has been expanded to other fields of applications, as is the case of biodiesel [11–14]. It is also gaining ground in the field of industrial simulators, being now available in the Petro-

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SIM™ and Hysys simulators, as well as in many in house simulators.

The n-alkanols are a well-studied family with CPA. Various studies have been reported on their mixtures with other alkanols [15,16], water [17,18], amines [19] and hydrocarbons [16–18,20–23], as well as on other relevant properties of the pure compounds such as surface tension using a combined EoS/gradient theory approach [24]. Villiers et al. [25] have also studied the description of derivative properties for both n-alkanes and n-alcohols. Other CPA applications include the description of glycols with water and hydrocarbons [26–30], mixtures with organic acids [31], description of fluorocarbons [32] and the extension to some multifunctional compounds, as alkanolamines [33] and phenolic compounds [34,35].

As for other association equations of state, the CPA model needs to be parameterized for every new associating component that has not previously been studied. The right balance between the attractive and repulsive terms in the equation of state can only be achieved if all parameters are regressed simultaneously from equilibrium data, usually from vapour pressure and saturated liquid densities. Although one can now find in the open literature sets of CPA parameters for the most common compounds, their number and variety is still quite limited. There is also not much reflexion on how to systematically parameterize molecules with multiple associating groups such as alkanolamines or oxygenated compounds relevant for biorefinery applications such as polyols, and phenolics, many of them solid at room temperature or for which no saturation pressures and densities are available, or even measurable. These are some of the actual model drawbacks hampering its success and more widespread use in commercial simulators, since the common end user of a process simulator is understandably reluctant in regressing the CPA parameters for all new associating components present on his process.

A project is currently being developed aiming at generating accurate CPA parameters with little or no user intervention. Ideally this should be done using a small set of data already available from the simulator pure component database and fitting as few parameters as possible, so that the model parameters are transferable or predictive. For that purpose, it is necessary to understand the balance between the cubic and associative terms and evaluate all known weaknesses of the current CPA model.

This work started from the standard version of the CPA model [17] and investigated its known weaknesses: 1) not meeting the defined critical temperature, 2) missing the temperature dependence of pure component saturated liquid densities, 3) using an α function in the cubic term that can provide unreliable results for a few properties in some extreme conditions (as discussed by Le Guennec et al. [36]), and 4) having an incorrect description of the molar volume pressure dependence, which lead to a poor description second derivative properties. For this analysis the n-alkanols will be used as case study, as this family should also allow us to look into the associative parameters for the −OH group, trying to establish some "rules" or tendencies for their change with chain length.

The focus of this work will then be an evaluation of the advantages and disadvantages of a modified CPA model that will try to overcome the identified limitations of the model. The properties in study are the vapour pressure, liquid density, liquid isobaric heat capacity and heat of vaporization. In our analysis we have also found that an excessive focus in pure component properties other than vapour pressure and liquid density can sometimes provide erroneous results for mixtures. So, the VLE of binary systems containing n-alkanols with alkanes or two n-alkanols will also be studied to insure that the new sets of parameters are transferrable for mixtures. LLE equilibria is also studied for mixtures of alcohols and alkanes.

2. s-CPA model

Below we will refer to the published simplified CPA model as s-CPA [17]. 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 [37]. Equation (1) presents the s-CPA in terms of the compressibility factor.

$$
\begin{aligned}
Z &= Z^{phys} + Z^{assoc} \\
&= \frac{1}{1 - B\rho} - \frac{A(T)\rho}{RT(1 + B\rho)} - \frac{1}{2}\left(1 + \rho\frac{\delta \ln g}{\delta \rho}\right)\sum_i n_i \sum_{A_i}(1 - X_{A_i})
\end{aligned}
\tag{1}
$$

Where A represents the energy parameter ($A(T) = n^2 a(T)$), B the covolume parameter ($B = nb$), ρ is the density, g is a simplified hard-sphere radial distribution function [17], X_{A_i} is the mole fraction of component i not bonded to site A and n_i is the mole number of component i.

As proposed by Michelsen et al. [38], it is preferable to use a single sum over sites to improve computational efficiency, thus equation (1) can be rewritten as:

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

Where m_i is the mole number of sites of type i. The mixture a and b parameters are obtained from the following mixing rules:

$$
a = \sum_i \sum_j x_i x_j a_{ij}
\tag{3}
$$

$$
b = \sum_i x_i b_i
\tag{4}
$$

where:

$$
a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})
\tag{5}
$$

and k_{ij} are binary interaction parameters.

The alpha function most used with s-CPA is the Soave function [37] which has a quasi-linear dependency with temperature.

$$
a(T) = a_0\left(1 + c_1\left(1 - \sqrt{T_r}\right)\right)^2
\tag{6}
$$

An alternative alpha function that provides a more flexible temperature dependence is the Mathias-Copeman function [39] which is also one of the most widely applied alpha functions for cubic EoS. This function presents a cubic dependence with temperature:

$$
a(T) = a_0\left(1 + c_1\left(1 - \sqrt{T_r}\right) + c_2\left(1 - \sqrt{T_r}\right)^2 + c_3\left(1 - \sqrt{T_r}\right)^3\right)^2
\tag{7}
$$

Equation (8) relates X_i to the association strength.

$$
X_i = \frac{1}{1 + \rho\sum_j x_j \sum_j X_j \Delta^{ij}}
\tag{8}
$$

where:

$$\Delta^{ij} = gb^{ij}\beta^{ij}\left(e^{\frac{\varepsilon^{ij}}{RT}} - 1\right) \qquad (9)$$

where, ε and β are the association energy and volume for interactions between sites i and j.

The use of a simplified radial distribution function is the difference between the s-CPA and the original version of CPA [8]. This function is given by equation (10) [17,40].

$$g(\rho) = \frac{1}{1 - 0.475b\rho} \qquad (10)$$

In this work, as suggested by Oliveira et al. [41] for SAFT, we also looked at adding more pure component properties in the fitting of the CPA parameters that is usually based on the simultaneous fitting of vapour pressures and saturated liquid densities. Cp data was also added, but a weighted procedure was used that remains more heavily weighted towards vapour pressures and liquid densities. We started using values from the literature as first estimates, and used as objective function.

$$OF = wt^P \sum_i^{np} \left(\frac{P_i^{exp.} - P_i^{calc.}}{P_i^{exp.}}\right)^2 + wt^\rho \sum_i^{np} \left(\frac{\rho_i^{exp.} - \rho_i^{calc.}}{\rho_i^{exp.}}\right)^2$$
$$+ wt^{Cp} \sum_i^{np} \left(\frac{Cp_{res.i}^{exp.} - Cp_{res.i}^{calc.}}{Cp_{res.i}^{exp.}}\right)^2 \qquad (11)$$

where wt is the weight given to a specific property during the optimization process. The weights used had the value of 1 for density and vapour pressure and varied between 0.05 and 0.1 for Cp.

For binary mixtures equations (12)–(14) were considered to optimize the values of k_{ij}. (12 and 13 for VLE and 14 for LLE):

$$OF = \sum_i^{np} \left(\frac{T_{bub}^{exp.} - T_{bub}^{calc.}}{T_{bub}^{exp.}}\right)^2 \qquad (12)$$

$$OF = \sum_i^{np} \left(\frac{P_{bub}^{exp.} - P_{bub}^{calc.}}{P_{bub}^{exp.}}\right)^2 \qquad (13)$$

$$OF = \sum_k^{npo} \sum_i^{np} \left(\frac{x_{i,k}^{exp.} - x_{i,k}^{calc.}}{x_{i,k}^{exp.}}\right)^2 \qquad (14)$$

where npo is the number of phases to optimize.

For systems containing two or more associative compounds a combining rule for the cross-associative parameters is required. In this work we used CR-2 [16], presented as CR-1 in some papers [42]. As proposed by Kontogeorgis et al. [15] this combining rule is adequate for systems containing only alcohols.

$$\beta^{ij} = \sqrt{\beta^i \beta^j} \qquad (15)$$

$$\varepsilon^{ij} = \frac{(\varepsilon^i + \varepsilon^j)}{2} \qquad (16)$$

The associative scheme chosen for alcohols was the 2B [6] scheme. As analysed by Kontogeorgis et al. [42], fitting binary phase equilibria for the studied compounds with the more accurate (and complex) 3B [6] scheme does not improve the results when comparing to the 2B scheme. It is also important to note that for the

prediction of pure component properties, the same authors and de Villiers et al. [25] showed that each scheme is usually better at describing different sets of properties.

The data correlations from Multiflash™ [43] and DIPPR [44] were used for the liquid volume and heat of vaporization. For vapour pressure the curves were regressed from the experimental data present on both the DIPPR [44] and TRC [45] databases. As for liquid heat capacities both the latter databases were used but also some other literature data was taken into account [46–48]. For the vapour density data, the data from the TRC database [45], Polikhronidi et al. [49] and Bazaev et al. [50] were considered, elsewhere estimates where generated from the ideal gas law.

3. Results and discussion

3.1. Adjusting the critical point

The use of CPA usually involves the regression of cubic and associative parameters to saturated liquid density and vapour pressure data away from the critical point. Due to this procedure, both the critical temperature and critical pressure tend to be overestimated. This can be observed for methanol in Fig. 1, calculated using the parameters from Oliveira et al. [24].

This creates an inconsistency in the model, where the critical temperature set to be used in the calculation of the a parameter is not obeyed by the model. It was then investigated how the CPA model and the parameters regression could be improved, to eliminate this inconsistency.

For that purpose the definition of the critical point for a pure component, detailed in equations (17–19) is used in the parameters regression forcing a_0 and b to obey the conditions of equations (17–19). This is expected to enhance the predictive capacity of the model, as part of the parameters are now anchored to the critical point. Analysis and modifications with similar objectives were proposed by Polishuk for SAFT + cubic [51] and PC-SAFT [52]. With CPA, Vinhal et al. [53] have presented a work with a similar objective, but a different approach.

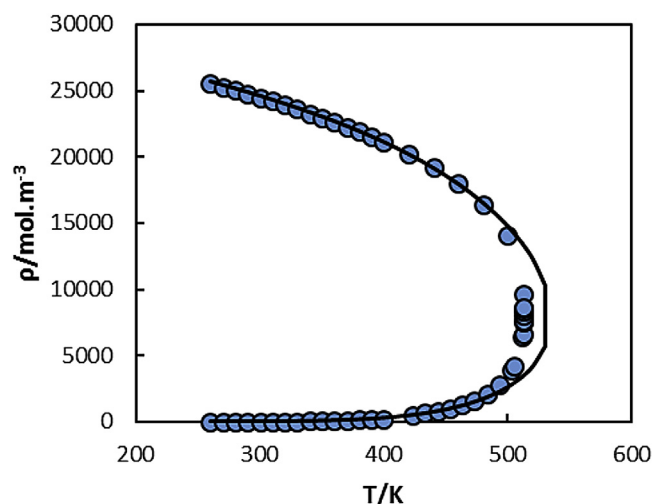$$P_{CPA}\left(Tc^{exp}, Vc^{calc}\right) = Pc^{exp} \qquad (17)$$

Fig. 1. Methanol saturated densities with s-CPA.

$$\frac{\partial P_{CPA(Tc^{exp})}}{\partial V} = 0 \qquad (18)$$

$$\frac{\partial^2 P_{CPA(Tc^{exp})}}{\partial V^2} = 0 \qquad (19)$$

This approach was first tested on the methanol data. To obtain the first estimates for the association term it was taken into account the relations presented by Kontogeorgis et al. [10] where the association parameters are related to the enthalpies and entropies of hydrogen bonding:

$$\varepsilon \propto -\Delta H \qquad (20)$$

$$\beta \propto e^{\frac{\Delta S}{R}} \qquad (21)$$

The same authors shown similarities between the results of the CPA associative parameters and the association contribution to the heat of vaporization (H_a). Based on this idea two sets were tested, the first used the value of $|H_a|$ presented by Nath et al. [54] as the energy parameter, while for β we used a value close to that proposed by Kontogeorgis et al. [17] The second set, used a similar approach for ε, but instead recalculated H_a with data from the DIPPR database [44] while for β the value obtained was $RT_{boil}e^{\frac{\Delta S^v}{R}}$. After adjusting the a_0 and b values, the Soave alpha function was adjusted to vapour pressure data. The parameters and deviations for the vapour pressure and of liquid densities are presented in Table 1. As can be observed from Table 1 and Fig. 2, while set 1 provides better estimates of vapour pressures, liquid densities and liquid heat capacities for methanol, the results are much worse than those obtained using the best parameter set from the literature [24].

The first estimates were the results of simple assumptions and, as expected, present large deviations. Using theoretical estimates for the association parameters and with values of a_0 and b being fitted to the critical point, the only parameter left to be optimized is c_1. However, there are other interesting remarks before further improvements. Results for other properties present qualitatively correct descriptions despite the deviations, as shown in Fig. 2 for the isobaric liquid heat capacity. A possible way to improve these results is to replace the simple Soave-type alpha function with a 3-parameter Mathias-Copeman function. Indeed, if the Mathias-Copeman function is used instead of the Soave function, by fitting only the vapour pressure data, the results become quite accurate for vapour pressure, heat of vaporization and liquid Cp, as reported in Table 2.

Still, the estimates of liquid densities are not yet as accurate as required. The use of a temperature independent volume shift in cubic equations of state, as well as a linear combining rule have been studied by Jaubert and co-workers [55,56]. It was shown, that with this approach it is possible to improve the description of the liquid volume without decreasing the accuracy of phase equilibria and without affecting most other properties, such as Cp or heat of vaporization. The volume shift (c_{vs}) applied is as follows:
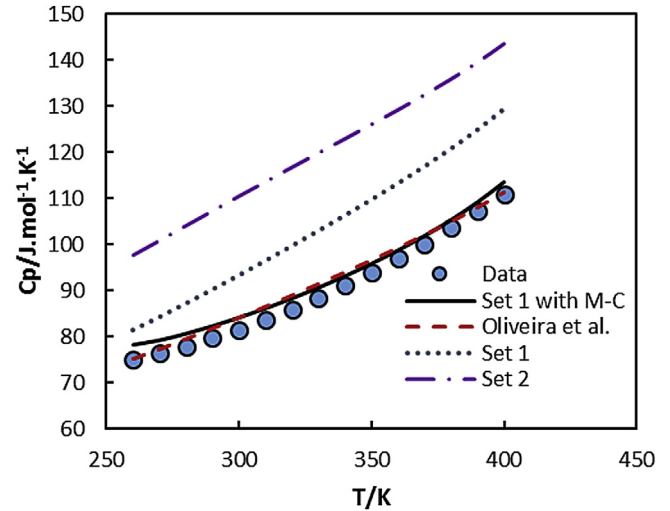
$$v_t = v_0 - c_{vs} \qquad (22)$$

Fig. 2. Results for the liquid Cp of methanol using sets 1 using both alpha functions [37,39], set 2 and the results from Oliveira et al. [24].

To improve the volume description, a Peneloux type volume shift [57] was introduced in CPA. This volume shift is constant and is obtained by matching the liquid density at a reduced temperature of 0.7 Tc. The results are shown in Table 2 for the first set of associative parameters. The description of liquid density obtained, Fig. 3, is less accurate than what was observed with the parameters by Oliveira et al. [24] This is probably due to the higher value of the co-volume parameter, which will affect the general behaviour of the density curve, despite the volume shift. The results for vapour pressure are improved. Without adjusting the range of temperatures between 400 K and the critical point, the present value of % AAD for vapour pressure is below 0.8%. The results for liquid Cp, Fig. 2, and heat of vaporization present similar accuracy to those from the literature. It should be noted that these are preliminary results, using an approximate approach for the associative parameters. The capacities of this approach to improve the presented derivative properties will be further explored below in the next section.

Given the results with the Mathias-Copeman alpha function it was interesting to investigate if the description of liquid density near the critical point could still be improved. For that purpose a more flexible alpha function, based on the Mathias-Copeman function [39] but with up to 5 parameters was used:

$$a(T) = a_0$$
$$\times \left(1 + STR \times c_1 + STR^2 \times c_2 + STR^3 \times c_3 + STR^4 \times c_4 + STR^5 \times c_5\right)^2 \qquad (23)$$

where STR is $(1 - \sqrt{T_r})$

It was found that by increasing the values for the associative strength (Δ) the value of the co-volume will be reduced. With this approach it was possible to greatly improve the liquid density results in both methanol and ethanol. However, for these smaller

Table 1
Parameters and %AAD between 0.5 and 0.78 T_r, for the first tests with methanol.

Set	a_0 (Pa.m^6.mol^{-2})	b (10^5.m^3.mol^{-1})	c_1	$\beta.10^2$	ε (J.mol^{-1})	% AAD P^{sat}	ρ_{liq}
1	0.59	4.34	0.780	1.46	21866	4.63	25.7
2	0.77	4.78	0.847	1.03	19816	8.40	33.3
Oliveira et al. [24]	0.43	3.22	0.747	3.41	20859	0.45	0.34

Table 2
Mathias-Copeman parameters using the first set of associative parameters (Table 1), with a constant volume shift, and respective %AAD between 0.5 and 0.78 T_r.

Set					%AAD			
	$c1$	$c2$	$c3$	Vshift/dm^3.mol^{-1}	p^{sat}	Cp	ΔH^{vap}	ρ_{liq}
Set 1 using the M-C alfa function	1.05	−1.61	2.01	0.0226	0.30	2.56	1.12	2.26
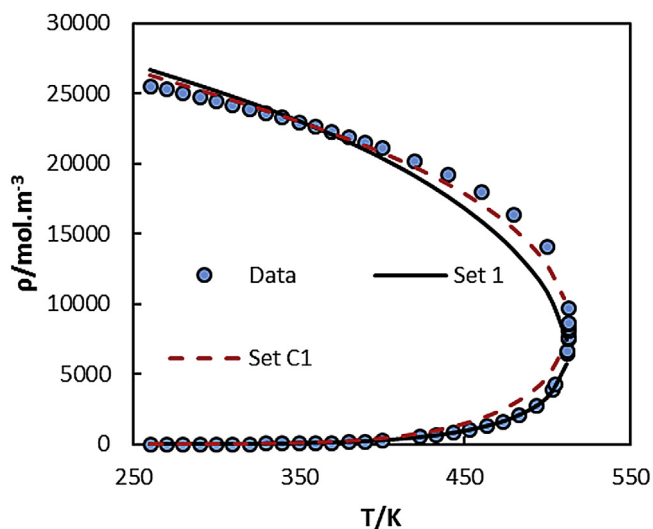
Fig. 3. Density results for methanol with a 3 parameter Mathias-Copeman function [39] (set 1, Table 2) and with a 5-parameter alpha function after optimization of the association parameters (Table 3).

compounds, there is an important degradation of the description of the vapour phase density at higher temperatures, as well as of the Cp (with average absolute deviations larger than 13% between 260 and 400 K) and the heat of vaporization (with an average absolute deviation close to 30% in the same temperature range). Vapour pressure accuracy is slightly decreased for the analysed compounds, especially in the case of butanol. Fig. 3 presents the results for the saturated densities of methanol. The results for all the alcohols analysed are presented in Table 3. The experimental critical point data of the first ten n-alkanols is presented in Table 4.

For heavier alcohols, from heptanol to nonanol, it is possible to compromise and decrease only slightly the accuracy of the density description while also predicting the results for Cp. The description of heat of vaporization is also improved, presenting a %AAD of 3.06%

between 285 and 445 K in the case of 1-heptanol.

Results for the liquid densities from ethanol to 1-pentanol are presented in Fig. 4a and from 1-heptanol to 1-nonanol are presented in Fig. 4b. Fig. 5 presents results for Cp for the studied compounds. For 1-heptanol it was possible to achieve a better compromise between liquid density and second derivative properties than for the other alcohols. This has to do with using higher values for the association parameters, which increases the accuracy of the density description near the critical point, but if not high enough, tend to decrease the accuracy for the temperatures below 0.7 Tc, as is presented in Fig. 6. The fact that a higher association strength works well for 1-heptanol but less so for higher alkanols might be explained by the change in liquid density curvature above 1-heptanol. As can be seen in Fig. 6, using the 1-heptanol association parameters for 1-octanol and 1-nonanol, the curvatures obtained are far more accentuated, this is also more severe for 1-nonanol than for 1-octanol.

This kind of compromise was not achieved for 1-propanol up to 1-pentanol, and the results present similarities to those of methanol and ethanol. In a first approach, the values of the association energy parameter were set as constant to test the predictive capacities of the model. Nevertheless, despite the high variability of the β parameter, no relevant improvements were observed by varying the two parameters simultaneously.

The values obtained for the critical volume present an average deviation below 5% for methanol, ethanol, 1-butanol and 1-pentanol. For 1-propanol and the heavier alcohols these deviations are higher, with a value of 18.86% for 1-octanol being the highest deviation. It is important to note that from 1-heptanol to 1-nonanol a compromise between the description of liquid density and of the derivative properties was tested, and thus, the critical volume is expected to be less well estimated. For these compounds, if volumes at 0.9 Tc are considered only for 1-nonanol an error above 5% is observed.

The description of Cp presents an inaccurate behaviour for some of the lighter alkanols. This can be linked to the higher values of the associative volume, but also to some extent to the alpha function, which, being highly flexible, if not restricted may provide some

Table 3
Parameters and results for the alcohol optimization (set C-1).

Alcohol carbon N$^\circ$	1	2	3	4	5	7	8	9
a_0 (Pa.m^6.mol^{-2})	0.20	0.27	0.35	0.52	0.90	2.31	4.35	5.14
b (10^5.m^3.mol^{-1})	2.29	3.08	3.80	5.17	7.59	13.90	17.60	19.66
c_1	0.35	0.72	0.32	0.45	0.98	0.89	1.64	1.56
c_2	−0.04	−3.38	2.05	1.44	−6.91	−4.29	−8.95	−5.77
c_3	1.85	23.48	2.12	3.78	49.21	36.54	42.40	23.87
c_4	0.00	−39.98	0.00	0	−93.35	−79.95	−83.21	−40.93
c_5	0.00	21.75	0.00	0	53.49	56.82	60.25	24.97
$\beta.10^2$	3.76	3.63	4.85	4.94	5.04	1.56	0.15	0.11
ε (J.mol^{-1})	26913	26913	26913	26913	26913	26913	26913	26913
Vshift/dm^3.mol^{-1}	−0.007	−0.015	−0.023	−0.024	−0.024	0.019	0.037	0.043
%AAD ρ_{liq}	2.90	2.02	2.10	2.74	3.72	2.90	3.42	4.81
%AAD p^{sat}	2.96	2.85	1.39	3.49	0.11	0.03	0.57	0.74
T range (K)	260–512.64	260–513.92	260–536.78	280–563.10	310–588.1	320–632.30	330–652.30	330–670.90
Tc calc. (K)	512.6	513.9	536.8	563.1	588.1	632.3	652.3	670.9
Pc calc. (MPa)	8.09	6.13	5.17	4.42	3.90	3.09	2.78	2.53
%Dev. Vc calc.	−3.31	−4.28	−7.23	−3.027	−2.42	14.07	18.86	16.76

Table 4
Literature critical points for the first 10 n-alkanols [43,44].

Alcohol carbon N°	1	2	3	4	5	6	7	8	9	10
$Tc^{exp.}$ (K)	512.6	513.9	536.8	563.1	588.1	610.3	632.3	652.3	670.9	688.0
$Pc^{exp.}$ (MPa)	8.09	6.14	5.17	4.42	3.90	3.42	3.09	2.78	2.53	2.31
$Vc^{exp.}$ (dm^3.mol^{-1})	0.118	0.167	0.219	0.275	0.326	0.387	0.444	0.509	0.576	0.645
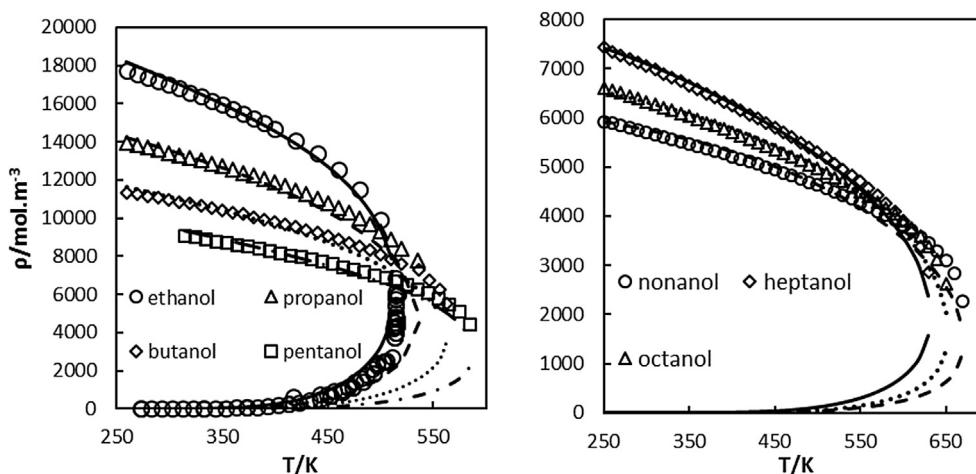
Fig. 4. a and b – Liquid density results from ethanol to 1-pentanol and from 1-heptanol to 1-nonanol, respectively, with a 5-parameter alpha function and optimized association parameters.
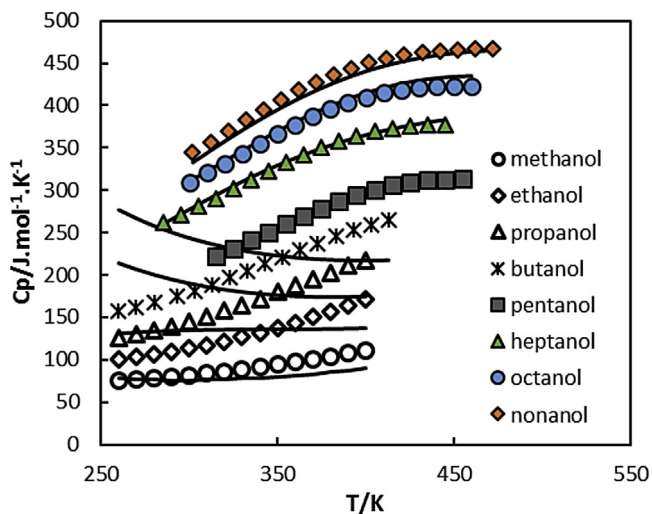
Fig. 5. Cp results for the studied compounds with optimized association parameters (results are from the sets of Table 3).

incorrect behaviour for derivative properties. In this case, the most relevant contribution should be the former. The temperature range used in the vapour pressure optimization was larger than the presented range in Fig. 5, which should decrease the influence of the alpha function flexibility.

This analysis shows that by fitting the critical point, it is possible to obtain a correct description of liquid density on a larger range of temperatures with CPA, without using a cross-over method [58,59] or an approach based on the renormalization group theory [60,61]. However, by using this approach, the accuracy of the results for the vapour phase is decreased. This analysis will be continued when discussing results for binary mixtures.

The final parameter set obtained in this section will be hereafter referred as Critical-1 (C1).

3.2. Improving derivative properties

After the analysis of the performance of a modified CPA model to reproduce the liquid density curve while providing an accurate description of the critical point, it is important to look into its predictive behaviour. In this study we will be looking simultaneously at the liquid density, heat of vaporization, liquid Cp and vapour pressure from methanol to 1-decanol. As before, the values for the association energy parameter were considered constant and only the volume parameter was optimized. The alpha function used in this analysis is the modified Mathias-Copeman function with up to 5 parameters (equation (23)).

These results are compared with those for the simplified CPA, without any modifications, after an optimization considering vapour pressure, liquid density and heat capacity with the weights for each property being 1, 1 and 0.1 respectively. This re-parameterization is required to compare the two versions of the model, with both optimized against the same datasets.

For the n-alcohols between propanol and 1-decanol it was observed that the modified version could describe the target properties using a constant value for the association volume, while keeping the constant value for the association energy. A similar approach was tested in s-CPA, however, the results presented much higher deviations and were thus not considered. Tables 5 and 6 present the parameters obtained for CPA before and after modifications, respectively, and the deviations obtained for each set.

Although the values for the energy and co-volume parameters from the cubic term are being directly calculated from the critical point, it is still important to look at their tendencies, as they are affected by the parameters from the associative term. In Fig. 7a and b it is possible to compare these tendencies before and after the modifications to CPA.
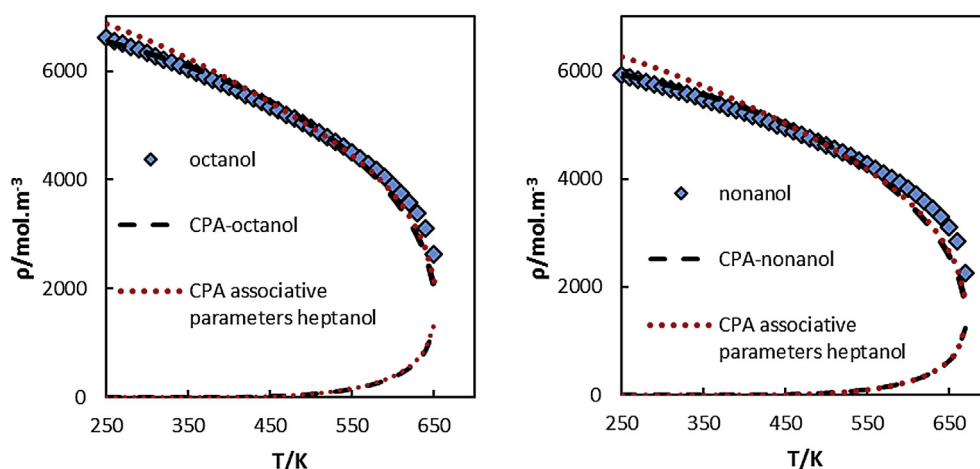
Fig. 6. a and b — Comparison between the liquid density results for 1-octanol and 1-nonanol, using the cubic term parameters presented in Table 3 and using 1-heptanol associative parameters.

Table 5
Parameter sets and results for the optimization of the s-CPA version (with no modifications).

Alcohol carbon N°	1	2	3	4	5	6	7	8	9	10
a_0 (Pa.m^6.mol^{-2})	0.42	0.78	1.15	1.68	2.31	2.83	3.46	4.09	4.66	5.46
b (10^5.m^3.mol^{-1})	3.21	4.8	6.38	8.03	9.73	11.3	12.98	14.69	16.34	18.12
c_1	0.72	0.62	0.88	0.85	0.81	0.93	0.88	0.97	1.06	1.07
$\beta.10^2$	3.3	0.6	0.77	0.34	0.15	0.14	0.06	0.05	0.04	0.02
ε (J.mol^{-1})	21294	24335	21913	23162	24582	23848	27151	27413	27532	28415
%AAD P^{sat}	0.28	0.46	0.62	0.36	0.27	0.54	0.88	0.33	0.95	0.77
%AAD $\rho_{liq.}$	0.18	0.43	0.43	0.59	0.59	0.81	1.16	1.22	0.94	1.25
%AAD Cp $_{liq.}$	1.13	2.00	5.31	3.95	2.93	3.31	0.66	1.22	1.81	1.03
%AAD H^{vap}	0.69	1.15	0.35	1.29	0.81	0.27	1.68	0.28	1.75	0.58
%AAD Cp $_{res.}$	2.38	4.37	12.6	9.46	7.04	8.65	1.79	3.36	5.18	3.03
T$_{range}$ (K)	260–400	260–400	260–400	260–410	315–455	275–455	285–445	300–460	300–470	330–490
Tc$^{calc.}$ (K)	529.47	532.02	550.83	576.50	605.65	626.70	653.00	672.10	697.05	711.95
Pc$^{calc.}$ (MPa)	9.75	7.83	6.53	5.47	4.61	4.11	3.66	3.30	3.05	2.80
%Dev. Vc calc.	−16.80	−14.56	1.03	3.12	−3.03	5.76	−3.83	−4.85	−6.64	−8.57

Table 6
Parameter sets for the optimization of the modified CPA (set C2).

alcohol carbon N°	1	2	3	4	5	6	7	8	9	10
a_0 (Pa.m^6.mol^{-2})	0.68	1.13	1.60	2.07	2.58	3.18	3.78	4.48	5.21	6.01
B (10^5.m^3.mol^{-1})	4.61	6.40	7.75	9.45	11.14	13.13	15.01	17.17	19.37	21.75
c_1	0.90	0.99	1.12	1.13	1.31	1.49	1.06	1.63	1.59	1.69
c_2	−2.47	−0.93	−0.89	−1.38	−3.72	−5.73	0.66	−6.76	−4.88	−6.10
c_3	3.26	−2.64	1.49	8.04	20.54	29.81	−0.76	35.77	22.93	30.13
c_4	0	6.22	−13.85	−31.50	−56.54	−70.72	−4.99	−81.78	−46.11	−63.28
c_5	0	0	22.67	37.84	55.71	60.07	7.32	67.68	32.33	48.54
$\beta.10^2$	0.46	0.16	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
ε (J.mol^{-1})	24913	24913	24913	24913	24913	24913	24913	24913	24913	24913
%AAD P^{sat}	0.34	0.32	0.12	0.27	0.44	0.21	0.26	0.05	0.79	0.27
%AAD $\rho_{liq.}$	1.94	0.93	0.48	0.64	0.59	0.68	0.47	0.39	0.69	0.34
%AAD Cp $_{liq.}$	0.91	2.20	2.25	1.38	1.37	1.77	1.25	1.14	1.57	0.83
%AAD H^{vap}	1.57	0.50	0.71	1.40	0.42	0.85	1.89	0.48	1.91	0.77
%AAD Cp $_{res.}$	1.79	4.93	5.52	3.50	3.32	4.60	3.36	3.18	4.43	2.77
T$_{range}$ (K)	260–400	260–400	260–400	260–410	315–455	275–455	285–445	300–460	300–470	330–490
Vshift (dm^3.kmol^{-1})	18.6	19.1	15.5	17.1	17.5	21.7	23.7	29.0	37.2	42.2
Tc$^{calc.}$ (K)	512.6	513.9	536.8	563.1	588.1	610.3	632.3	652.3	670.9	688.1
Pc$^{calc.}$ (MPa)	8.09	6.14	5.17	4.42	3.90	3.42	3.09	2.78	2.53	2.31
%Dev. Vc calc.	29.81	27.99	24.42	22.18	22.75	21.84	22.13	21.40	21.01	21.22

It is also important to look at the tendencies for the volume shift, to verify if these still follow a seemingly quadratic trend with the carbon number of the n-alcohols. This is shown in Fig. 8.

Due to the use of a highly flexible α function with multiple adjustable parameters, the results for heat capacity and heat of vaporization presented anomalous tendencies at the lower temperatures. By extending the lower temperature range, used for vapour pressure optimization, between 50 and 100 K the description of both properties, in the original temperature range, is improved. This is not, however, a consistent method, being highly
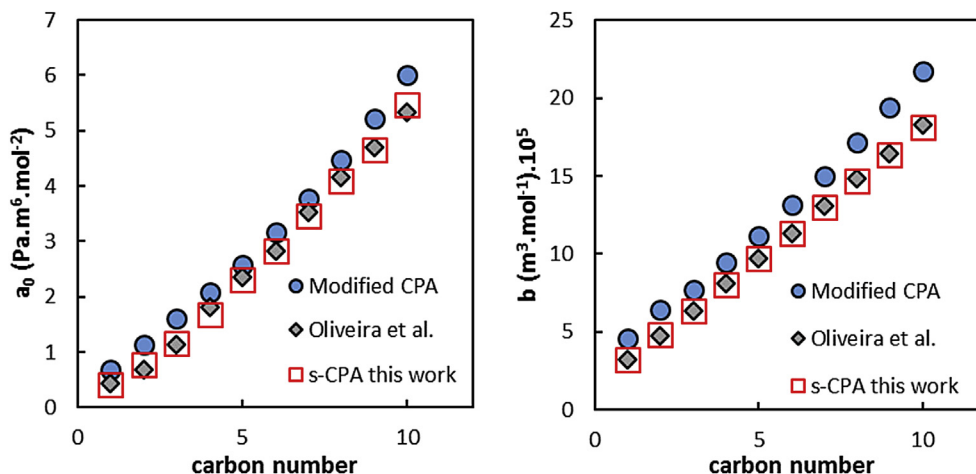
Fig. 7. a and b - tendencies of the energy and co-volume parameters of the cubic term for primary alkanols, respectively (parameters from Tables 5 and 6 and Oliveira et al. [24]).
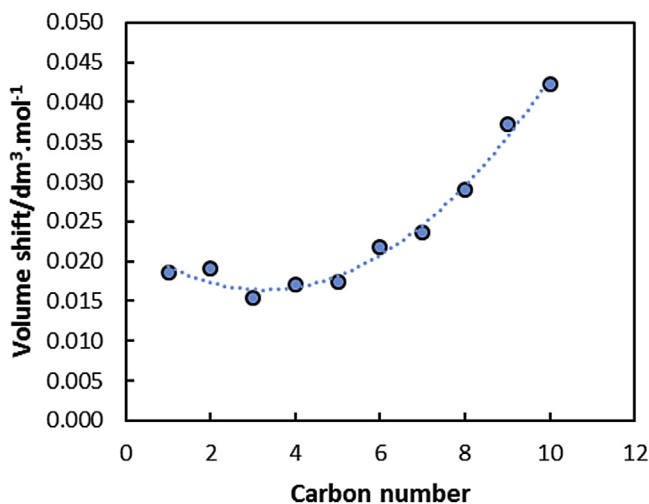

Fig. 8. Volume shift values for the studied alcohols (from Table 6).

affected by the quality of the vapour pressure data, and should be improved by using a better and more restricted alpha function as proposed by Jaubert and co-workers [36].

The obtained volume shifts show a different trend for the first two alcohols. As for the trend from propanol to 1-decanol, these results might be changed by using a group contribution method instead of a constant value for the β parameter, nevertheless despite some outliers, tendencies can be observed.

Due to the new optimization procedure here proposed, and the use of a more flexible alpha function, the modified version presents a higher accuracy for the vapour pressure in most cases. It is also able to describe well the liquid densities in the studied temperature ranges, and the results are, in most cases, similar to those of s-CPA if not better. As for the description of liquid Cp, in both cases it is possible to describe the property for heavier alcohols within Tr ranges between 0.5 and 0.7, nevertheless after the modifications (set C-2) the results seem to be more consistent for this property in the whole range of compounds studied. Heat of vaporization despite not being fitted in neither of the tests is well described in both cases. In general, the results from the modified version compare well with those from the calculated s-CPA set. Figs. 9 and 10 present the results for heat capacity and liquid density for these compounds.

After the study of saturation properties, it is important to look at the description of some single phase properties, the results for this section are presented in Fig. 11 and in our supplementary material file. Looking at single phase densities it is possible to obtain a fair description between pressure and liquid density, however, due to the wrong temperature dependency of the saturation liquid density these results are not very accurate. Usually with SRK a temperature dependent volume shift is used in order to describe these properties. Baleed et al. [62] made a very relevant study on this, showing diverse volume shifts and their description of single phase properties. In a similar way, we tried using the following equation for the volume shift with CPA, optimized at two different temperatures:

$$v_t = v_0 - c_{vs}^0 - c_{vs}^1 T \qquad (24)$$

Using a temperature-dependent volume shift it is possible to obtain a very reasonable estimation of the single phase liquid density up to 60 MPa, from 1-propanol to 1-decanol, in normal operation temperatures. The use of a lower association volume enables this, as for ethanol and methanol the results are only able to describe high pressure densities up to 20 and 10 MPa respectively. With this approach it is also possible to obtain an accurate description for the isochoric heat capacity at atmospheric pressure, however as can be seen in the results (in Supporting Information), this comes from a compensation of the errors on the isobaric expansivity and isothermal compressibility. These incorrect descriptions also lead to an incorrect prediction of the speed of sound. This incorrect description of the volume dependency with pressure in CPA was already mentioned by de Villiers et al. [25] in their study of derivative properties in alkanes and alcohols. For heavier alcohols the modified version seems to present a more accurate description of the change of density with pressure. This is in accordance with what was suggested by Polishuk [63], as by increasing the values of the co-volume an improvement of the pressure dependency was verified. Still, for lighter alcohols s-CPA presents better results for these properties, than the modified version with a constant volume shift.

3.3. Phase equilibria for binary mixtures

To model binary VLE systems of alcohols with alkanes, the C2 set succeeds in their description with values for the interaction parameters only slightly higher than those obtained before the modifications. The C1 set presents some difficulties in achieving a
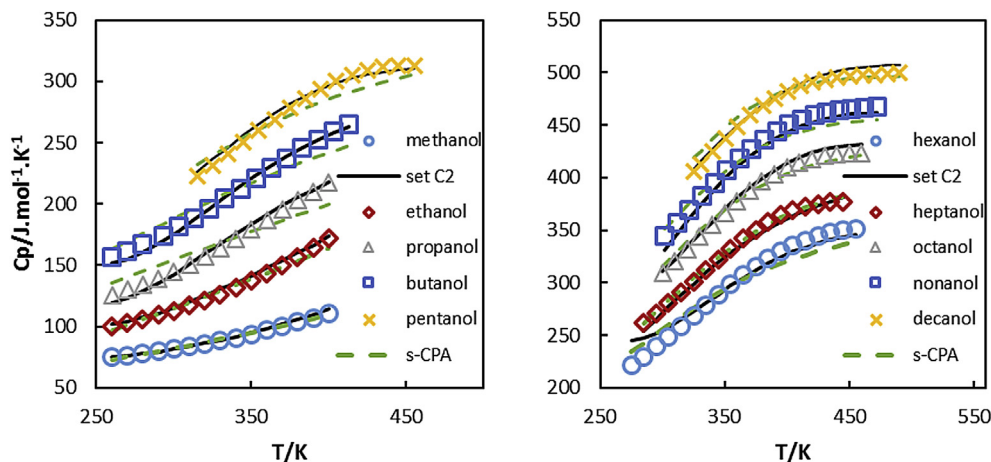
Fig. 9. a and b — Liquid heat capacity description with the modified CPA for the analysed alkanols.
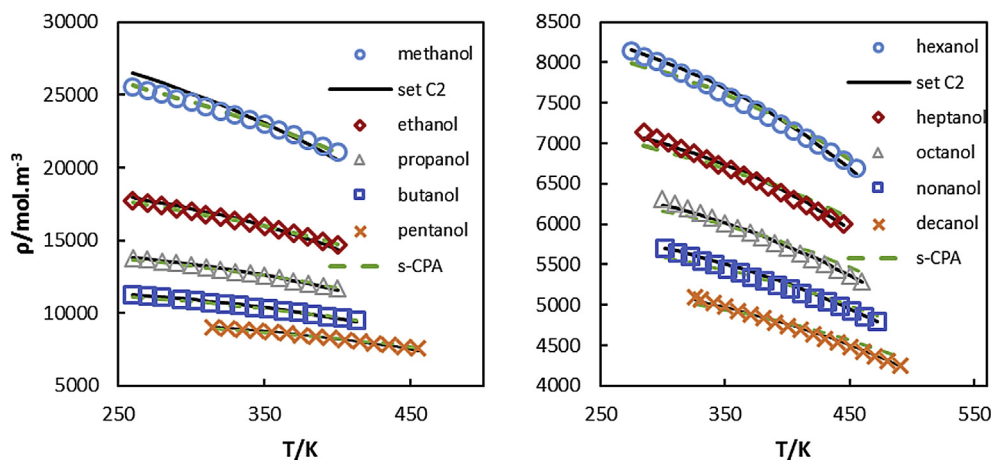

Fig. 10. a and b — Liquid density description with the modified CPA for the analysed alkanols.
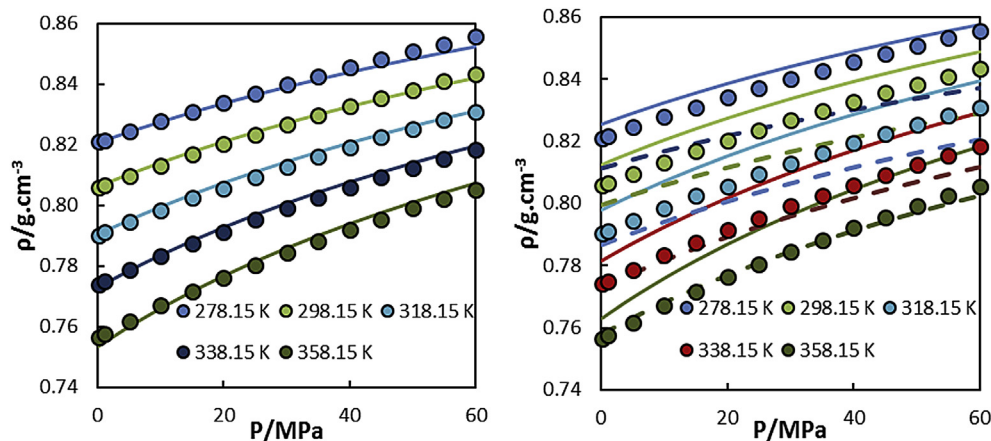

Fig. 11. a and b — High pressure density descriptions with CPA for 1-butanol at 5 different temperatures. Modified CPA with a temperature dependent volume-shift (left), s-CPA (right, dashed lines), Modified CPA (right, full lines). Experimental data is from Dávila et al. [64].

good description and despite presenting good results for the liquid phase it displays some problems with the quality of the vapour phase description. These results are presented in Table 7 and Fig. 12. The alkane parameters used with the non-modified version (s-CPA) are from Oliveira et al. [24].

Similar results were obtained for the prediction of alcohol — alcohol systems (no kij). While set C1 produces high deviations, set C2 achieves very reasonable predictions. Table 8 presents a comparison between the predictions of set C2 and the results with s-CPA.

Table 7
Results for the optimization of three binary systems with n-hexane.

System	Alcohol Set	kij	%AAD Tbub
1-propanol + n-hexane [45]	s-CPA	0.024	0.30
	Set C1	−0.049	0.57
	Set C2	0.041	0.21
1-butanol + n-hexane [45]	s-CPA	0.012	0.22
	Set C1	−0.066	0.17
	Set C2	0.027	0.35
1-pentanol + n-hexane [45]	s-CPA	0.022	0.17
	Set C1	−0.026	0.22
	Set C2	0.031	0.21
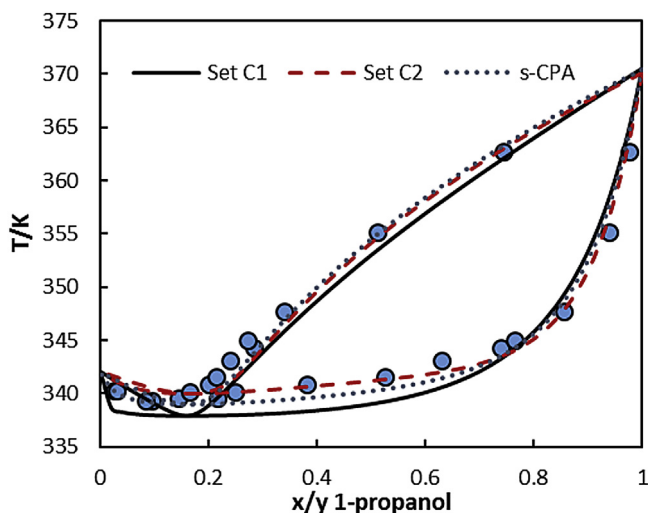
Fig. 12. Description of the system 1-propanol + hexane, with the three sets in analysis.

Table 8
Predictions for the alcohol − alcohol binary systems.

System	Alcohol Set	%AAD Tbub
1-propanol + methanol [65]	s-CPA	0.77
	Set C1	2.06
	Set C2	0.38
1-butanol + metanol [65]	s-CPA	1.52
	Set C1	4.51
	Set C2	1.12
1-butanol + ethanol [66]	s-CPA	0.37
	Set C1	1.86
	Set C2	0.36
1-pentanol + metanol [65]	s-CPA	3.09
	Set C1	7.11
	Set C2	2.91
1-pentanol + ethanol [66]	s-CPA	1.07
	Set C1	3.47
	Set C2	1.12
1-octanol + methanol [67]	s-CPA	1.20
	Set C1	3.06
	Set C2	1.24

Table 9
Binary interaction parameters for the presented LLE binary systems.

Set	Kij	
	MeOH − Hexane [68]	EtOH − Hexadecane [69]
C1	−0.02	−0.100
C2	0.036	−0.026
Kontogeorgis et al. [17,18]	0.007	−0.035
Oliveira et al. [24]	−0.007	−0.027

Liquid-liquid modelling presents higher difficulties, however, despite the need for higher k_{ij} values in most situations, the C2 set is able to achieve very good results for this type of equilibria. For C1 these results present high deviations due to the expected excess of the associative contribution. Figs 13 and 14 present the results for the systems, methanol + hexane and ethanol + hexadecane.

As can be observed, the set C2 is able to adjust adequately the data despite of a slight overestimation of the critical point. The results for this set can be compared with those from the alcohol sets from Kontogeorgis and co-workers [17] [18], which presented the best results for both systems. Table 9 presents the binary interaction parameters used for these 2 systems.

The description of the VLE equilibria for the systems above is in high agreement with the results of s-CPA. Using the binary interaction parameter from the LLE optimization in both cases, yields very similar results. A higher kij (0.052) is needed if an accurate description of the VLE is wanted with set C2. The results from set C1 are rather accurate for the liquid phase with the presented kij, nevertheless present some relevant deviations in the vapour phase. This results are presented in Fig. 15.

4. Conclusions

In this study some of CPA's weaknesses were reanalysed and efforts were made to improve them. In a first step it was shown how the critical point can be introduced in the parameterization. Using this approach, and a more flexible alpha function along with a constant volume shift to improve liquid densities, it was possible to describe the liquid density curve in a larger range of temperatures than before, including the region near the critical point. However, by doing so, the quality of the vapour density description is lost, and thus the properties dependent on the quality of volumetric properties are not correctly predicted, as is the case of the heat of vaporization. This also tends to affect negatively the description of both VLE and LLE systems.

A second approach was then adopted, retaining the description of the critical pressure and temperature, but relaxing the description of the liquid density curve for higher temperatures. Using this approach, it was possible to consider the association energy a constant between the n-alkanols with 1 and 10 carbons and from propanol to decanol it was also possible to consider the association volume constant. With this constraints, and considering a temperature range used in most applications, this version of CPA was
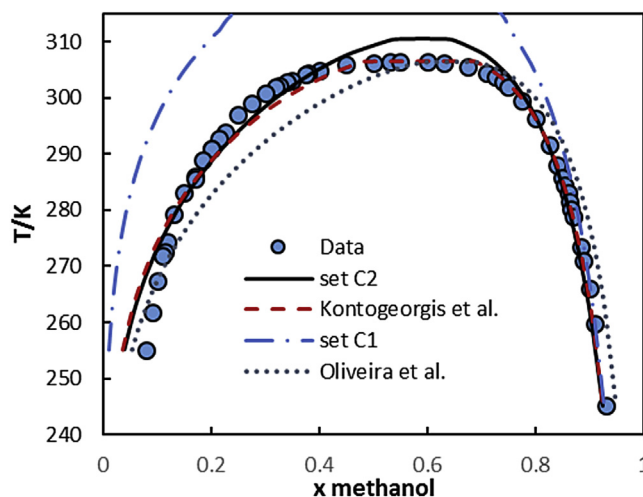

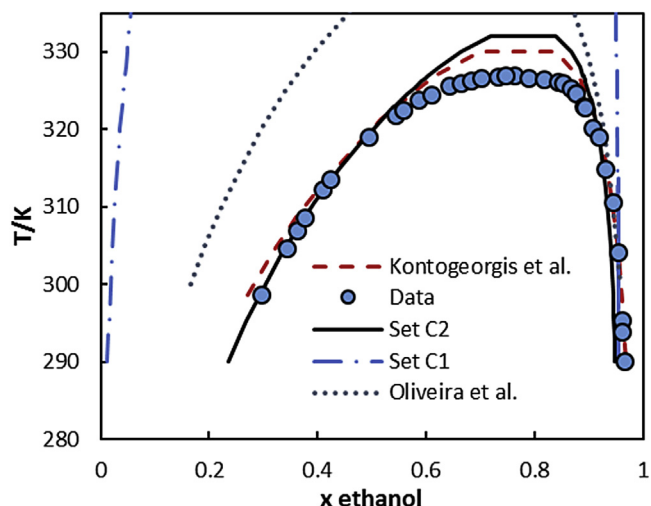**Fig. 13.** Results for the LLE equilibria of methanol + hexane (kij values are presented in Table 9).

Fig. 14. Results for the LLE equilibria of ethanol with hexadecane (kij values are presented in Table 9).

able to predict Cp and heat of vaporization, while providing an accurate description of the vapour pressure and of the liquid density after introducing the volume-shift. These results compare well with those from s-CPA with a fitting in the parameterization to density, vapour pressure and liquid Cp.

Considering the binary phase equilibria description, the results of this second test are in good agreement with those from the literature, despite requiring binary interaction parameters with a somewhat higher positive values.

Using only pure component vapour pressure data on the optimization routine is a relevant drawback, as the parameterization becomes largely dependent on the quality of the available data for this property. Also for some compounds this property is very difficult or even impossible to measure due to decomposition of the compounds, thus future studies must address the use of a different optimization property, or more than one property simultaneously. One alternative is to analyse if the alpha parameters should be optimized simultaneously with the associative term.

Other relevant issue is the alpha function used. Due to the high number of parameters, the optimization of the vapour pressure had to be extended to larger ranges of temperature so that relevant derivative properties presented a correct behaviour. To address this issue it is intended to follow the work of Jaubert and co-workers [36] in future developments of the CPA parameterization.

To summarise, a first set of modifications was evaluated and is able to describe the critical point and the density curve in a large range of temperatures, nevertheless leading to high inaccuracies in the description of derivative properties. The second set of modifications provides a CPA parameterization with a high predictive potential, which can be more consistent in the description of isobaric heat capacity than the original s-CPA.

Funding and acknowledgments

Nomenclature

|	
A, a	energy parameter of CPA
a_0	value of the energy parameter at the critical point
A_i	site A in molecule i
B, b	co-volume
$c_1 - c_5$	alpha function parameters
Cp	Isobaric heat capacity
c_{vs}	volume shift
g	radial distribution function
k_{ij}	binary interaction parameter for the cubic term energy
m_i	the mole number of sites of type i
n_i	mole number of component i
P	vapour 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
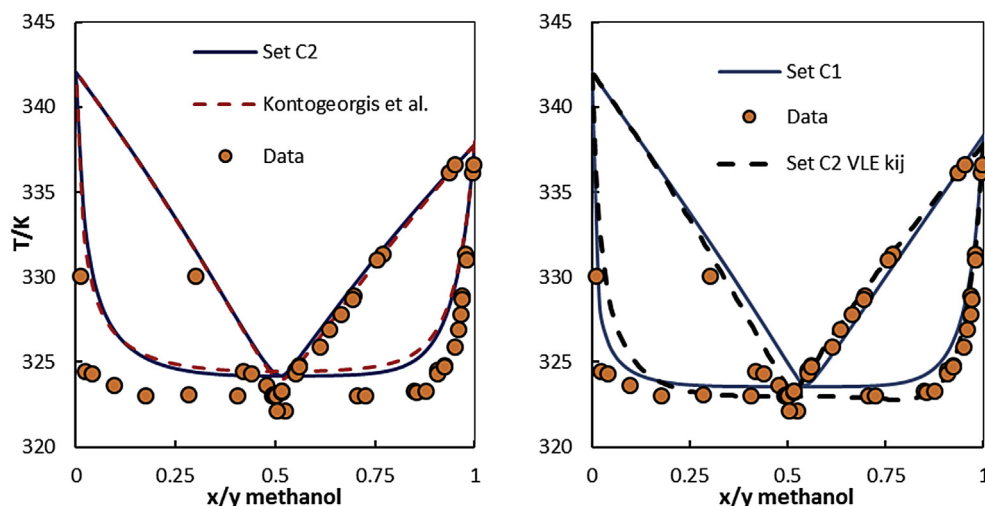
Fig. 15. a and b − VLE results for the system methanol + hexane, using some of the kij presented in Table 9 and an optimized value (0.052) for VLE with set C2.

Z	compressibility factor

Greek symbols

β	association volume
ε	association energy
ρ	molar density
Δ	association strength

Sub and superscripts

assoc, phys	association and physical terms
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
%Dev	percentage of deviation
CPA	cubic plus association
EoS	equation of state
s-CPA	simplified cubic plus association
SRK	Soave-Redlich-Kwong

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2017.01.002.

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