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Modeling derivative properties and binary mixtures with CO₂ using the CPA and the quadrupolar CPA equations of state

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Abstract

The cubic plus association (CPA) equation of state (EoS) is extended to include quadrupolar interactions. The quadrupolar term is based on a modification of the perturbation terms by Larsen et al. (*Mol. Phys.* **1977**, *33*, 4, 987) for a hard sphere fluid with a symmetric point quadrupole moment. The new quadrupolar CPA (qCPA) can be used without introducing any additional pure compound parameters. Alternatively a single additional adjustable parameter can be employed.

To evaluate qCPA several pure compound properties are predicted. The model is furthermore evaluated for its ability to predict and correlate binary vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) of mixtures containing CO₂ and hydrocarbons, water, alcohols, or selected quadrupolar compounds.

The results indicate that most pure compound property predictions are satisfactory but similar to other CPA approaches. When binary mixtures are considered, qCPA appear to offer a systematic improvement as compared to the cases where quadrupolar interactions are ignored. This improvement is particularly pronounced when mixtures of CO₂ and hydrocarbons are considered, where the model is almost fully predictive. Using the same modeling approach

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qCPA can accurately correlate both the phase behaviour of CO_2 + hydrocarbon mixtures as well as mixtures of CO_2 + a self-associating compound.

Keywords: equation of state, CPA, quadrupole, CO_2 , acid gas, association

1. Introduction

In recent years CO_2 has received a significant amount of negative attention due to its status as a greenhouse gas and the fact that the amount of CO_2 in the atmosphere continues to rise. This is believed to be largely due to the combustion of fossil fuels. Technologies are thus needed, which can limit the emission of CO_2 to the atmosphere. One such potential technology is carbon capture and storage. During this process, transport of CO_2 rich mixtures is an important step which requires accurate knowledge of the phase behaviour, as well as other thermodynamic properties, of mixtures containing hydrocarbons, water and other fluids such as alcohols [1].

Accurate equilibrium predictions of CO_2 containing mixtures, however, are challenging with traditional equations of state. The reason for this may be that CO_2 has a large quadrupole moment. The large quadrupole moment of CO_2 , as well as size asymmetry, are for instance believed to be the reasons for the liquid liquid equilibrium (LLE) between CO_2 and heavy hydrocarbons, and the reason for the low temperature azeotrope formed between mixtures of CO_2 and lighter hydrocarbons. Cubic equations of state such as the Soave-Redlich-Kwong (SRK) equation of state (EoS), however, treat CO_2 as an inert compound. Even in a modern EoS such as the Statistical Association Fluid Theory (SAFT) only dispersive forces are usually considered for CO_2 . The continued use of these models may be attributed to the fact that several mixtures, such as CO_2 + hydrocarbons, are described quite well, when a single binary interaction parameter (k_{ij}), is used.

To deal with polar and quadrupolar interactions a number of multipolar terms have been suggested in the literature. These terms are mainly based on a third order perturbation theory developed from statistical mechanics by Stell

and co-workers [2–5]. The perturbation theory was originally developed for pure fluids using the Stockmayer potential or the conceptually simpler hard sphere model with a central point dipole or quadrupole. Using the former potential,
 30 Gubbins and Twu [6, 7] developed directly applicable expressions for polar and quadrupolar fluid mixtures.

During the last decade a number of quadrupolar terms have been included in the SAFT framework. Inspired by Stell and co-workers [2–5] Gross [8] developed a new quadrupolar expression using the two center Lennard-Jones pair poten-
 35 tial as the reference fluid. The resulting quadrupolar contribution was added to the Perturbed-Chain SAFT (PC-SAFT) to give the Perturbed-Chain Polar SAFT (PCP-SAFT). This EoS can be used without any additional adjustable parameters.

Karakatsani et al. [9, 10] and Karakatsani and Economou [11] introduced
 40 two quadrupolar terms to the PC-SAFT framework. Both terms are based on the perturbation terms from by Larsen et al. [5], which use the pure hard sphere fluid as the reference fluid. The authors suggest two quadrupolar terms; an expression which employs the full correlation integrals from Larsen et al. [5], this term does not use any additional adjustable parameters, and a simpler
 45 version where the correlation integrals are truncated at the zeroth order term.

Later, NguyenHuynh et al. [12] extended a group contribution SAFT EoS to quadrupolar (and polar) fluid mixtures. The quadrupolar term used by the authors is based on the theory of Gubbins and Twu [6, 7]. The term is extended to chain molecules using a procedure suggested by Jog et al. [13] and Jog and
 50 Chapman [14].

It seems that improved predictions and correlations (smaller k_{ij}) are typically obtained for binary vapor liquid equilibrium (VLE) when a quadrupolar term is coupled to SAFT or PC-SAFT. The quadrupolar models, however, have some limitations; The models are only applicable to molecules with a highly
 55 symmetric quadrupole moment, so that the quadrupole moment reduces to a single scalar value. It has furthermore been shown that false liquid-liquid splits may be predicted by the models [15]. Mixtures of several quadrupolar molecules

are challenging, and the results are often better if only one component is assumed to have a quadrupole moment [8].

60 Another more pragmatic approach to account for the quadrupole moment of CO_2 is to consider CO_2 to be a self-associating compound. Such procedures often work well resulting in improved predictions and correlations with small interaction parameters [16–19]. Unfortunately the improvement is obtained at the cost of additional pure component parameters and, in some cases, an extra
65 adjustable parameter for the binary mixtures.

In this work, inspired by the recent advances within the SAFT-family, and in an effort to obtain a physically more correct and predictive model, a quadrupolar term is proposed and combined with the well-known cubic plus association (CPA) EoS (Kontogeorgis et al. [20]). The term is based on the explicit ex-
70 pressions developed by Larsen et al. [5] for a hard sphere fluid with a point quadrupole. To simplify the expressions we truncate the correlation integrals at the zeroth order term, similar to the approach used in the truncated Perturbed-Chain Polar SAFT (tPC-PSAFT) [10, 11].

To evaluate the new quadrupolar CPA (qCPA) the pure fluid properties
75 of CO_2 are predicted both in the critical region and in the compressed liquid region. The model is furthermore applied for the prediction and correlation of binary mixtures with CO_2 and n-alkanes, water, alcohols and a few quadrupolar compounds. The model is compared with two other CPA approaches namely non-associating (n.a.) CPA, where CO_2 is assumed to be an inert compound,
80 and the case when CO_2 is assumed to be self-associating following the 4C association scheme (notation from Huang and Radosz [21]). Tsivintzelis et al. [18] have published similar results with the two CPA approaches for most of the binary mixtures investigated in this work.

2. Models

85 The CPA EoS (Kontogeorgis et al. [20]) is an engineering EoS which has been extensively studied in the literature (e.g. [22–24]). It combines the SRK

EoS with the association term from Wertheim’s theory, which is also employed in SAFT [25–27]. The SRK term accounts for the physical interactions between molecules, while the association term takes hydrogen bonding interactions into
90 account.

Polar and quadrupolar interactions are not explicitly taken into account in the original formulation. However, to obtain a physically more consistent model the effect of the quadrupole is explicitly included in this work by introducing a simplified quadrupolar term to CPA.

In the literature CPA is typically presented as a pressure explicit EoS, however, it is often much more convenient to express an EoS in terms of the residual Helmholtz energy, $(A^r(T, V, \mathbf{n}))$, since all other residual properties can be obtained as partial derivatives of the state variables T , V and $\mathbf{n}$. The reduced residual Helmholtz free energy for qCPA can be expressed as the addition of the physical SRK term, Wertheim’s association term and the quadrupolar term:

$$\frac{A_{CPA}^r(T, V, \mathbf{n})}{RT} = \frac{A_{SRK}^r(T, V, \mathbf{n})}{RT} + \frac{A_{Assoc}^r(T, V, \mathbf{n})}{RT} + \frac{A_{Quad}^r(T, V, \mathbf{n})}{RT} \quad (1)$$

95 where R is the ideal gas constant. In the absence of association or quadrupolar interactions equation (1) reduces to the SRK EoS.

2.1. The SRK contribution

Consider a mixture of total composition n , with total volume V and temperature T . The reduced residual Helmholtz energy of the SRK EoS for n moles of a mixture is expressed as [28]:

$$\frac{A_{SRK}^r(T, V, \mathbf{n})}{RT} = -n \ln \left(1 - \frac{B}{V} \right) - \frac{D(T)}{RTB} \ln \left(1 + \frac{B}{V} \right) \quad (2)$$

If the conventional van der Waals one-fluid mixing rules are employed then $D(T)$ and B are given by

$$D(T) = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (3a)$$

$$B = \sum_i n_i b_{ii} \quad (3b)$$

where b_{ii} is the pure compound co-volume parameter for component i , also denoted b_0 . The cross energetic parameter, a_{ij} , is calculated using the classical geometric mean rule

$$a_{ij} = \sqrt{a_{ii}(T)a_{jj}(T)}(1 - k_{ij}) \quad (4)$$

where k_{ij} is a binary interaction parameter, typically correlated to experimental data. The temperature dependent energetic parameter, $a_{ii}(T)$, is given as

$$a_{ii}(T) = a_0 \left(1 + c_1 \left(1 - \sqrt{T_r} \right) \right)^2 \quad (5)$$

where a_0 and c_1 are pure compound parameters and T_r is the reduced temperature ($= T/T_c$).

100 2.2. Association contribution

The contribution to the reduced residual Helmholtz free energy from the association term is given by [25–28]:

$$\frac{A_{Assoc}^r(T, V, \mathbf{n})}{RT} = \sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \quad (6)$$

where A_i indicates bonding sites on molecule i and X_{A_i} denotes the fraction of A-sites on molecule i *not* bonded to another association site. These fractions are found by solving the system of non-linear equations given by

$$X_{A_i} = \frac{1}{1 + \frac{1}{V} \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (7)$$

where the association strength, $\Delta^{A_i B_j}$, between site A on molecule i and site B on molecule j depends on both T , V and n according to

$$\Delta^{A_i B_j} = g(n, V) \left(\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right) b_{ij} \beta^{A_i B_j} \quad (8)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume between site A of molecule i and site B of molecule j respectively. b_{ij} is the cross-covolume calculated from the classical arithmetic mean rule

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2} \quad (9)$$

and g is the Radial distribution function (RDF). Originally the RDF was approximated with the expression from the Carnahan-Starling (CS) EoS. Use of the CS RDF in CPA is an approximation, however, since CPA uses the van der Waals repulsive term rather than the CS hard-sphere term employed in SAFT. Kontogeorgis et al. [29] proposed a simpler expression for g

$$g(n, V) = \frac{1}{1 - 1.9\eta} \quad (10)$$

Which essentially is the RDF of CPA. $\eta(= B/4V)$ is the reduced fluid density. No mixing rules are required in the association term, but combining rules are required for $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ if more than one associating compound is present. One of the most common combining rules is the so-called CR-1, given as;

$$\epsilon^{A_i B_j} = \frac{1}{2} (\epsilon^{A_i B_i} + \epsilon^{A_j B_j}) \quad (11a)$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \quad (11b)$$

The association term is dependent on the association scheme (see Eq. (7)), i.e. the number and type of association sites for the associating compound. To denote the different association schemes the notation of Huang and Radosz [21] is adopted.

105 2.3. Quadrupole contribution

The expression for the quadrupolar term is an adaptation of the third order perturbation theory developed by Stell and co-workers [2–5]. It uses the same base model as Karakatsani et al. [10, 11] employed in the development of their polar PC-SAFT equations of state. The reduced residual Helmholtz free energy for the expression is calculated from a Padé approximation as

$$\frac{A_{Quad}^r(T, V, \mathbf{n})}{RT} = \frac{A_{2,Quad}^r(T, V, \mathbf{n})/RT}{1 - A_{3,Quad}^r(T, V, \mathbf{n})/A_{2,Quad}^r(T, V, \mathbf{n})} \quad (12)$$

Where A_2^r and A_3^r indicate the second- and third-order perturbation terms respectively. The first-order term is effectively zero [5]. The third-order term is the sum of both a two-body and a three-body contribution, since it has been

shown that for multi-polar interactions three-body contributions cannot be ignored [4]. That is;

$$\frac{A_{3,Quad}^r(T, V, \mathbf{n})}{RT} = \frac{A_{3,2,Quad}^r(T, V, \mathbf{n})}{RT} + \frac{A_{3,3,Quad}^r(T, V, \mathbf{n})}{RT} \quad (13)$$

Larsen et al. [5] developed explicit expressions for pure symmetric hard spheres with a point quadrupole at their centre. In this work we extend these expressions to mixtures and relate them to the model parameters of CPA. The expressions are

$$\frac{A_{2,Quad}^r}{RT} = -\frac{7}{10} \frac{N_A}{V (k_b T)^2} \sum_i^{nc} n_i \sum_j^{nc} n_j \frac{Q_{ij}^4}{\sigma_{ij}^7} I_{10}^{HS} \quad (14)$$

$$\frac{A_{3,2,Quad}^r}{RT} = \frac{36}{245} \frac{N_A}{V k_b^2 T^3} \sum_i^{nc} n_i \sum_j^{nc} n_j \frac{Q_{ij}^6}{\sigma_{ij}^{12}} I_{15}^{HS} \quad (15)$$

$$\frac{A_{3,3,Quad}^r}{RT} = -\frac{1}{6400} \frac{N_A^2}{V^2 (k_b T)^3} \sum_i^{nc} n_i \sum_j^{nc} n_j \sum_k^{nc} n_k \frac{Q_{ijk}^6}{\sigma_{ij}^3 \sigma_{ik}^3 \sigma_{jk}^3} I_{TQ}^{HS} \quad (16)$$

where N_A is the Avogadro constant, k_b is Boltzmann's constant, Q is the quadrupolar moment, σ is the hard sphere diameter and I_n and I_{TQ} are correlation integrals with the hard sphere model as the reference fluid.

In the work of Larsen et al. [5] the correlation integrals in equations (14)-(16) were approximated by analytical density polynomials of fifth and third order respectively. To simplify the model, and in particular the volume derivatives, we assume that these correlation functions can be truncated already at the zeroth order term. The zeroth order coefficients are given analytically as [5]:

$$I_n^{HS} \approx J_{0,n} = \frac{4\pi}{n-3} \quad (17a)$$

$$I_{TQ}^{HS} \approx J_{0,TQ} = 54\pi^2 \quad (17b)$$

Thus, rather than being a function of the volume, the correlation functions are simply three constants. This approach has been employed with a measure of success in tPC-PSAFT [9–11], although an additional adjustable parameter was needed to retain a performance comparable to the non-truncated version.

No mixing rules are required in the quadrupolar term (Eq. (14)-(16)). Combining rules are, however, required if more than one quadrupolar compound

is present. If geometric-mean combining rules are employed the form of the quadrupolar term becomes similar to the quadrupolar expressions proposed by Gubbins and Twu [6, 7] as well as that suggested by Gross [8]. Thus the cross quadrupolar moment for two- and three-body contributions are calculated as

$$Q_{ij} = \sqrt{Q_{ii}Q_{jj}} \quad (18)$$

$$Q_{ijk} = \sqrt[3]{Q_{ii}Q_{jj}Q_{kk}} \quad (19)$$

Finally, it would be advantageous to relate the molecular diameter of the hard-sphere, to a co-volume parameter similar to that used in CPA. When de Villiers et al. [30] extended CPA with the dipolar theories of Gross [31] and Jog and Chapman [14] they assumed that the original definition of the co-volume in terms of the molecular hard-sphere diameter could be employed ($b = (2/3) N_A \pi \sigma^3$). The quadrupolar term, however, is based on a hard sphere reference fluid, whereas CPA is based on the van der Waals repulsive term. Wong and Prausnitz [32] showed that the difference between the CS EoS and the van der Waals repulsive term can be reduced if $b^{eff} = b_0^Q \approx b/2$. Thus, using the effective co-volume we get

$$b_0^Q = (1/3) N_A \pi \sigma^3 \quad (20)$$

where b_0^Q is the co-volume parameter in the quadrupolar term. When Eq. (20) is employed the value of b_0^Q should, ideally, be similar to that of b_0 .

115 In this work two variants of the qCPA are evaluated; In the first version it is assumed that the co-volume from CPA can be set equal to the quadrupolar hard sphere co-volume i.e. $b_0 = b_0^Q$. Equation (20) is then used to calculate σ , which is used in eq. (14)-(16). In this way no additional adjustable parameters are introduced by the quadrupolar term. In the second version b_0^Q is employed
120 as an additional adjustable parameter. The experimental quadrupolar moment of CO₂ (-4.3 DÅ) is employed in both cases.

The terms described in this section are, in many aspects, similar to those employed by Karakatsani et al. [10, 11] in tPC-PSAFT. The main differences between the two equations of state are that the combining rules suggested in this

work (Eq. (18)-(19)) are in closer agreement with those employed by Gubbins and Twu [6, 7] and Gross [8] and that the base EoS is CPA rather than PC-SAFT.

3. Results and Discussion

3.1. Parameter Estimation

CPA has three adjustable parameters for non-associating compounds (a_0, b_0, c_1), and two additional parameters for associating compounds ($\beta^{A_i B_i}, \epsilon^{A_i B_i}$). The suggested qCPA can have either the same number of parameters or an additional parameter (b_0^Q). For non quadrupolar compounds qCPA reduces to CPA.

The pure compound parameters in CPA are typically fitted to experimental pressures and liquid densities at saturation using a weighted least squares objective function of the type

$$\min \phi = \sum_{i=1}^N \left[\left(\frac{\rho_{exp,i}^{liq} - \rho_{calc,i}^{liq}}{\rho_{exp,i}^{liq}} \right)^2 + \left(\frac{P_{exp,i}^{sat} - P_{calc,i}^{sat}}{P_{exp,i}^{sat}} \right)^2 \right] \quad (21)$$

where N is the number of experiments, P^{sat} the saturated pressure and ρ^{liq} the liquid density. Subscripts indicate experimental and calculated values respectively. The CPA parameters from literature, which are employed in this work, have been estimated using this objective function. The parameters are shown in Appendix A

Often, the 'experimental data' employed for parameter estimation originate from pure compound correlations such as those used by the Design Institute for Physical Properties (DIPPR) [33] or the National Institute of Standards and Technology (NIST) [34]. As the equations of state correlate the pseudo-experimental data with increasing accuracy, however, the risk of fitting parameters to any systematic bias in the correlations increases. Moreover, a common issue with modern equations of state appear to be, that as the number of adjustable parameters increases several parameter sets exist, which represent the pure compound properties within experimental error [12, 13, 20, 35].

We have recently investigated the uncertainty of the pure compound parameters for CO₂ using several different modeling approaches including the new qCPA [36]. To estimate the uncertainty of the model parameters real experimental data are employed, rather than a correlation, and a slightly different objective function is employed, which uses the variance as the weighting factor, rather than the experimental value.

$$\min \phi = \sum_{i=1}^N \left(\frac{y_i^{exp} - y_i^{calc}}{s_i^{exp}} \right)^2 \quad (22)$$

Where s^{exp} is the standard deviation and y_i^{exp} is the experimental value of the i th saturated liquid density or saturated pressure. We demonstrate in Bjørner et al. [36] that the parameter uncertainty is substantial when qCPA is employed with four adjustable parameters. To evaluate the model it was thus decided to select two parameter sets, which are within the uncertainty; one which reproduces well the VLE of CO₂ + propane at a single temperature and one which represents well the LLE of CO₂ + n-dodecane. We stress, however, that we have not directly used any VLE or LLE data in the parameter fitting. Table 1 shows the CO₂ parameters and associated %AADs for the approaches which we employ in this work. Very good agreement is obtained with all approaches. It is noteworthy, however, that the deviations for CO₂ with qCPA are lower than CPA without association (CPA n.a.) even when the same number of adjustable parameters are employed.

Besides CO₂ we employ a few other quadrupolar compounds, namely water, ethane, benzene and acetylene. We assume, however, that the quadrupolar moment of water is negligible compared to the directional forces of the association term, moreover the quadrupole moment of water is a tensor and it is thus difficult to treat with current models. It is also assumed that the small quadrupolar moment of ethane can be ignored. For benzene and acetylene, however, the quadrupole moment cannot be ignored and their parameters have been re-estimated. Table 2 shows these parameters, for the three parameter version of qCPA, as well as CPA parameters for 1-nonanol and acetylene.

The value of the quadrupolar moment of CO₂ is relatively well-defined, rang-

Table 1: CPA and qCPA pure compound parameters for CO₂ together with %AADs between experimental [37–39] and calculated saturated liquid densities and saturated pressures. The quadrupolar moment of CO₂ is fixed at the experimental value of -4.3 DÅ^a when qCPA is employed. Details on the parameter estimation can be found in [36].

Modeling approach	b_0 mL/mol	$\Gamma(a_0/(Rb_0))$ K	c_1 -	$\beta \cdot 1000$ -	ε/R K	b_0^Q mL/mol	P^{sat}	%AAD ^b ρ^{liq}
CPA, n.a. ^c	27.28	1550	0.77	-	-	-	0.18	0.95
CPA, 4C	28.41	1329	0.66	25.7	513	-	0.07	0.10
qCPA, 3 par	27.93	1284	0.68	-	-	= b_0	0.13	0.46
qCPA, 4 par set 1 ^d	28.2	1172	0.64	-	-	23.6	0.49	0.24
qCPA, 4 par, set 2 ^d	28.1	1230	0.64	-	-	25.4	0.42	0.29

^a 1DÅ = 1Buckingham = 10⁻²⁶esu = 3.3356 · 10⁻⁴⁰Cm².

^b%AAD = $\frac{100}{N^{exp}} \sum_i^{N^{exp}} \left| \frac{x_i^{calc} - x_i^{exp}}{x_i^{exp}} \right|$ where x stands for P^{sat} or ρ^{liq} and N^{exp} is the number of experimental data.

^c Not associating.

^d Parameters based on uncertainties and (indirectly) VLE or LLE data.

ing from -4.1 DÅ to -4.6 DÅ with a typical value of -4.3 DÅ [40–46]. Experimental values of the quadrupolar moment of benzene and acetylene, however, may vary considerably depending on the reference. The experimental quadrupolar moment of benzene range from -9.98 DÅ [40] to -3.6 DÅ [44], although
175 most of the experimental data is between -9.98 DÅ and -8.5 DÅ [40]. The situation is similar for acetylene which has a large positive quadrupole moment between 3.0 DÅ and 8.4 DÅ [40]. In this work we assume a fixed quadrupolar moment of -9 DÅ for benzene and 4 DÅ for acetylene.

3.2. Pure CO₂

180 3.2.1. Second virial coefficients

A limiting low-density test for a thermodynamic model is to evaluate its capabilities in predicting the second virial coefficient, B . It may be calculated from the expression

$$\lim_{\rho \rightarrow 0} \left(\frac{\partial Z}{\partial \rho} \right)_T = B \quad (23)$$

Table 2: Correlated CPA and qCPA pure compound parameters and %AAD in saturated liquid densities and saturated pressures. Experimental data from raw DIPPR data [33]. The experimental quadrupole moments of benzene (≈ -9 DÅ) and acetylene (≈ 4 DÅ) are employed in qCPA.

Compound	Model	Association scheme	T_r	b_0	$\Gamma(a_0/(Rb_0))$	c_1	$\beta \cdot 1000$	ε/R	%AAD	
			($= T/T_c$)	mL/mol	K	-	-	K	P^{sat}	ρ^{liq}
Benzene	qCPA	n.a.	0.5-0.9	75.57	2763.73	0.73	-	-	0.46 (0.68) ^a	0.71 (0.84)
Acetylene	qCPA	n.a.	0.6-0.9	33.54	1469.45	0.65	-	-	0.41 (0.43)	0.52 (0.68)
Acetylene	CPA	n.a.	0.6-0.9	33.28	1576.91	0.7	-	-	0.43	0.68
1-Nonanol	CPA	2B	0.45-0.9	163.79	3508	0.956	0.254	3570.1	0.40	0.79

^a Numbers in parenthesis are the %AAD with CPA.

where Z is the compressibility factor and ρ is the density. The contribution to the second virial coefficient from the SRK term is

$$B^{SRK} = b - \frac{a(T)}{RT} \quad (24)$$

The contribution from the association term can be expressed as

$$B^{assoc} = -S \left[\exp \left(\frac{\varepsilon^{AB}}{RT} \right) - 1 \right] b\beta^{AB} \quad (25)$$

where the constant S depend on the association scheme. Its value for several different schemes is shown in table 3.

Table 3: Value of S in equation (25) for 8 different association schemes. Detailed calculations for scheme 1A, 2B, and 4C can be found in [47]. Nomenclature follows Huang and Radosz [21].

Scheme	1A	2A	2B	3A	3B	4A	4B	4C
S	0.5	2	1	4.5	2	8	3	4

It is straight-forward to show, that the contribution to the second virial coefficient, from the quadrupole term may be expressed as:

$$B^{quad} = \frac{F'_2 - F'_{3,2}}{\rho(1 - F'_{3,2}/F'_2)^2} \quad (26)$$

Figure 1: Model predictions against experimental data for the second virial coefficient of CO_2 using CPA, n.a., CPA 4C, and the qCPA. Experimental data from [48–54].

where F' is the Helmholtz energy pr. mole. This expression is similar to that presented by Karakatsani and Economou [11].

185 The second virial coefficient of CO_2 was predicted with CPA and qCPA using the parameters and schemes presented in table 1. The results are visualized at relatively low temperatures in figure 1 and the %AADs are shown in table 4. All model predictions are in reasonable agreement with the experimental data, although deviations increase for all models at low temperatures, where
 190 the sharp decrease in the virial coefficient is not fully captured. It is clear from both figure 1 and table 4 that the least convincing result is obtained when CO_2 is assumed to be self-associating. This may be due to the fact, that CO_2 is not self-associating and this theoretically unfounded approach may become poor in the low density limit. On the other hand, when qCPA is employed the
 195 predictions are also slightly worse, than when non associating CPA is employed for CO_2 . The differences, however, are quite small.

Table 4: Percentage average absolute deviations between experimental and calculated second virial coefficients with the different models.

Model	CPA, n.a.	CPA, 4C	qCPA, 3par	qCPA, 4par, set 1	qCPA, 4par, set 2
%AAD	5.5	13.3	7.3	7.9	7.1

3.2.2. Critical Points

Models such as CPA and SAFT, whose parameters are fitted to the saturated liquid density and saturated pressure typically overestimate the critical point. As there are several applications of CO₂ near the critical region, it may be of interest to calculate its critical temperature and pressure, with the different models.

In table 5 the experimental critical temperature and pressure are compared with the calculated critical points for the different CPA modeling approaches. Unfortunately the addition of a quadrupolar term does not improve the prediction of critical points. Both CPA with the 4C scheme and the three versions of qCPA overestimate the critical pressure by approximately 12 bar and the critical temperature by roughly 9 K. The overall best model is CPA n.a., which is essentially equivalent to the SRK with fitted parameters. Comparable critical points were obtained for CO₂ by Diamantonis and Economou [1] using SAFT (309.5 K and 79.2 bar) and PC-SAFT (315.5 K and 90.9 bar) respectively. In both cases CO₂ was treated as a non-associating species.

Table 5: Experimental [55] and predicted critical pressure and temperature of CO₂ using CPA n.a., CPA 4C and qCPA with three different parameter sets.

Model	Exp	CPA n.a.	CPA 4C	qCPA 3par	qCPA 4par, set 1	qCPA 4par, set 2
T_C [K]	304.13	309.7	312.9	312.2	313.5	313.4
P_C [bar]	73.8	81.	86.4	84.9	86.3	85.7

3.2.3. Derivative Properties

Despite the industrial need for simultaneous descriptions of phase equilibria
215 and derivative properties over a wide range of temperatures and pressures, equations of state are rarely evaluated for their performance for derivative properties [30, 56]. To the best of our knowledge only relatively few systematic evaluations of the performance of CPA or SAFT for derivative properties have been published. Lafitte et al. [57, 58] evaluated the performance of various SAFT
220 variants, with emphasis on SAFT-VR Mie, for predicting derivative properties of alkanes and alcohols and recently, de Villiers et al. [30] predicted derivative properties for similar compounds using both CPA, PC-SAFT and SAFT.

Table 6 shows the %AAD values for the density and various derivative properties of CO₂ at two temperatures in the compressed liquid region and one in
225 the critical region. It is gratifying to see that in most cases the deviations for each modeling approach are quite similar at the three temperatures. See the supporting material for results at saturation.

Compressed liquid region. It can be seen from table 6 that in the compressed liquid region the predictions with CPA 4C and qCPA are typically similar and
230 better than CPA n.a. A pronounced exception is the prediction of C_V^{res} where both CPA 4C and qCPA gives poor results and CPA n.a. performs better, at least in terms of %AAD. A similar observation was made by de Villiers et al. [30] for n-alkanes where the original SAFT performed better than CPA and PC-SAFT for the prediction of C_V but worse for other properties. Using SAFT
235 and PC-SAFT Diamantonis and Economou [1] calculated derivative properties for several small molecules including non-associating CO₂ over an extensive temperature range. Both models performed well far from the critical region with PC-SAFT being somewhat more accurate. Considering the different models and temperature/pressure intervals their results are surprisingly similar to the
240 results for non-associating CPA. The speed of sound predictions, however, are significantly better with the SAFT-type models compared to the CPA-based models. This is unsurprising, as it is by now well established that SAFT can

predict the trend of the speed of sound much better than CPA-based models [1, 59].

Table 6: %AAD values of ρ^{liq} , u , C_P^{res} , C_V^{res} , and μ_{JT} for CO₂ at three reduced temperatures using CPA n.a., CPA 4C and qCPA with three different parameter sets. Pseudo-experimental data from NIST [34].

Models	T_r	P range [bar]	% AAD				
			ρ^{liq}	u	C_P^{res}	C_V^{res}	μ_{JT}
CPA, n.a.	0.8	100-1000	2.6	12.2	15.2	6.5	17.0
CPA, 4C			1.1	9.8	6.2	42.5	20.1
qCPA, 3par			1.6	10.2	6.3	30.0	12.0
qCPA, 4par, set 1			1.2	9.2	4.6	35.7	13.3
qCPA, 4par, set 2			1.3	9.7	7.1	30.6	14.5
CPA, n.a.	0.9	100-1000	2.7	13.0	8.1	15.9	15.2
CPA, 4C			1.8	10.4	4.7	41.8	12.9
qCPA, 3par			2.0	11.2	3.8	33.9	4.7
qCPA, 4par, set 1			1.7	10.3	2.9	38.7	1.8
qCPA, 4par, set 2			1.7	10.7	4.6	33.8	1.7
CPA, n.a.	1.1	0-250	3.2	4.9	3.9	32.5	7.3
CPA, 4C			1.6	3.8	6.3	31.4	4.8
qCPA, 3par			2.0	4.2	5.4	32.2	5.1
qCPA, 4par, set 1			1.4	4.0	5.9	32.2	4.3
qCPA, 4par, set 2			1.1	4.1	4.7	32.2	4.2

245 Figure 2 shows C_V^{res}/R (a) and C_P^{res}/R (b) predictions for CO₂ at $T_r = 0.8$ and 0.9. Predictions with CPA 4C and the different qCPA parameter sets are very similar, with qCPA being slightly better. More importantly both model approaches predict quite accurately the intersecting isobaric heat capacities at

Figure 2: Normalized isochoric (a) and isobaric (b) heat capacity predictions of CO_2 with CPA and qCPA in the compressed liquid region and at $T_r = 0.8$ and 0.9. Pseudo-experimental data from NIST [34].

approximately 300bar (see figure 2b), whereas CPA n.a. predict this point
 250 around 800bar. The C_V^{res} predictions in figure 2a illustrate clearly that most of
 the models have difficulties with C_V^{res} predictions.

Notice that while CPA n.a. yields the best C_V^{res} predictions it is the poorest
 in terms of C_P^{res} . However, C_P^{res} depend on C_V^{res} as can be seen from equation
 (B.2) in Appendix B. This suggests that a large part of the improved C_P^{res}
 255 predictions with qCPA and CPA 4C is due to the over-prediction of C_V^{res} . In
 this way at least part of the improvement is in fact due to a cancellation of
 errors between the C_V^{res} and the ratio between $(\partial P/\partial T)_{V,n}^2$ and $(\partial P/\partial V)_{T,n}$.

Figure 3a compare the prediction of the liquid density of CO_2 at $T_r=0.8$
 and 0.9 against data from NIST. Figure 3b compares the predictions against
 260 the experimental data from Brewer et al. [60] in the more restricted pressure
 range of 200-400 bar and at $T_r = 0.9$ and $T_r = 0.93$. In general the performance
 is satisfactory for all model approaches, in particular at moderate pressures.
 The density predictions for CPA n.a. at elevated pressures appear to be worse

Figure 3: Density predictions of CO₂ with CPA and qCPA in the compressed liquid region. At $T_r = 0.8$ and 0.9 (a) compared to pseudo-experimental data from NIST [34] and at $T_r = 0.9$ and $T_r = 0.93$ (b) compared to experimental data from Brewer et al.[60].

than for CPA 4C and qCPA. Note from figure 3b, however, that between 200
 265 and 300 bar the density predictions of CPA n.a. are better than the predictions
 using CPA 4C. The predictions with qCPA are satisfactory in the whole pres-
 sure range. See the supporting material for the %AAD values between model
 predictions and the density values from Brewer et al. [60].

Critical region. The critical region is important due to the observed extrema
 270 and inflection points in the derivative properties, which serves as a valuable test
 for any EoS. Table 6 shows the %AAD values for the derivative properties of CO₂
 at $T_r = 1.1$ and in a pressure range of 0-250 bar. With the exception of C_V^{res} the
 predictions of all model approaches are quite good. Figure 4a clearly shows that
 the maximum in C_V^{res} is not predicted by any of the models. A similar result
 275 was obtained by de Villiers et al [30] for n-alkanes using CPA, SAFT and PC-
 SAFT. This suggests a fundamental problem with the temperature dependence
 of both the SRK term and the dispersion term in SAFT. As seen in figure 4b all

Figure 4: Normalized isochoric (a) and isobaric (b) heat capacity predictions of CO₂ with CPA and qCPA in the critical region ($T_r = 1.1$). Pseudo-experimental data from NIST [34].

the model variants evaluated in this work capture the maximum in C_P^{res} with good accuracy.

280 As the low %AAD in table 6 suggests all model approaches predict the inflection point in the density and the minimum in speed of sound. Especially the density predictions are surprisingly accurate. In both cases CPA n.a. perform slightly worse than the other models.

In summary we have seen that the qualitative difference between the various
 285 model variants is not particular large for the prediction of derivative properties, and all models typically predicts the same trends. With the clear exception of C_V^{res} all models generally perform satisfactory considering that the model parameters have not been correlated to any of the properties. While the model differences are smaller than expected, qCPA and CPA with the 4C scheme
 290 typically perform slightly better quantitatively than CPA n.a. This may suggest a small improvement in the volume predictions and/or the ratio between $(\partial P/\partial T)_{V,n}$ and $(\partial P/\partial V)_{T,n}$.

3.3. Binary Mixtures

The primary objective of an equation of state is typically the correlation and prediction of the VLE or LLE between mixtures of different compounds. In this section the new qCPA is employed for the prediction ($k_{ij} = 0$) and correlation of several different CO₂ containing binary mixtures. A single temperature independent interaction parameter is employed for the correlations.

3.3.1. CO₂ + n-alkanes

The VLE of several CO₂ + n-alkane mixtures have been predicted using the different modeling approaches. Characteristic results for these predictions are visualized in figures 5-7 and in supplementary materials. The results, in terms of %AAD, are presented in table 7 both for the predictions ($k_{ij} = 0$) as well as when an interaction parameter has been correlated to the VLE data. Moreover the LLE of CO₂ plus a number of heavy alkanes (C₁₂, C₁₄ and C₁₅) have been predicted and correlated to experimental data using the different modeling approaches. These results are presented in table 8 and 9.

As described in section 3.1, some of the CO₂+n-alkane mixtures have been utilized indirectly to obtain the two parameter sets for qCPA when b_0^Q is used as an additional adjustable. Parameter set 1 for qCPA has been selected partly based on the CO₂ + propane VLE at a single temperature, while parameter set 2 has been selected partly based on the CO₂ + n-dodecane LLE (see supplementary materials for the illustrations).

The CO₂ + ethane VLE is shown in figure 5 at four temperatures. The low temperature azeotrope, observed for this VLE, is predicted very well with qCPA at all temperatures. Particularly when parameter set 1 is employed. CPA n.a. fails to predict the phase behaviour, clearly indicating the need for an improved model for CO₂.

It should be mentioned that Gross [8] has presented equally good CO₂ + ethane VLE predictions using the PCP-SAFT, although their predictions were compared to simulation results rather than experimental data. Using a group contribution method with a quadrupole term for CO₂ NguyenHuynh et al. [71]

Table 7: Deviations for CPA and qCPA predictions ($k_{ij} = 0$) and correlations ($k_{ij} \neq 0$) of a number of CO_2 + n-alkane VLEs. Including the correlated k_{ij} . Experimental data from references [61–70].

System	T range [K]	Modeling approach	%AAD in P ^a	% AAD in y_1	%AAD in x_1	k_{ij}	% AAD in P ^a	% AAD in y_1	%AAD in x_1
$k_{ij} = 0$									
$\text{CO}_2(1)+\text{methane}(2)$	230-293	CPA, n.a.	16.4	11.5	10.2	0.089	1.0	4.6	0.4
		CPA, 4C	4.9	9.0	2.0	0.016	2.3	5.2	0.7
		qCPA, 3par	1.3	8.1	0.9	-0.007	1.2	4.7	0.4
		qCPA, 4par, set 1	12.2	7.4	5.6	-0.057	1.3	4.9	0.5
		qCPA, 4par, set2	6.0	7.6	3.8	-0.032	1.3	4.8	0.4
$\text{CO}_2(1)+\text{ethane}(2)$	213-270	CPA, n.a.	17.5	>100	>100	0.130	3.0	2.7	4.9
		CPA, 4C	9.3	29.7	71.0	0.067	0.3	2.1	1.9
		qCPA, 3par	6.2	18.4	45.0	0.022	0.6	2.5	4.4
		qCPA, 4par, set 1	0.7	2.8	4.4	0.000	0.7	2.8	4.4
		qCPA, 4par, set2	3.1	9.3	22.3	0.017	0.9	3.5	6.2
$\text{CO}_2(1)+\text{propane}(2)$	230-270	CPA, n.a.	29.1	6.4	104.1	0.129	5.0	1.6	11.6
		CPA, 4C	17.7	2.9	50.4	0.074	3.0	2.2	6.6
		qCPA, 3par	12.9	2.1	34.3	0.035	4.3	1.8	10.0
		qCPA, 4par, set 1	3.7	1.9	8.5	0.000	3.7	1.9	8.5
		qCPA, 4par, set2	8.2	1.8	20.0	0.021	4.0	1.9	9.1
$\text{CO}_2(1)+\text{butane}(2)$	250-418	CPA, n.a.	22.6	8.5	59.4	0.124	4.2	11.1	11.5
		CPA, 4C	14.1	6.9	32.7	0.071	2.8	5.3	9.3
		qCPA, 3par	10.3	6.4	24.0	0.045	3.0	5.4	9.8
		qCPA, 4par, set 1	3.3	5.4	10.3	0.000	3.3	5.4	10.3
		qCPA, 4par, set2	7.2	5.9	17.5	0.028	3.3	5.3	9.6
$\text{CO}_2(1)+\text{pentane}(2)$	294-423	CPA, n.a.	19.5	1.9	29.7	0.110	2.1	1.3	2.6
		CPA, 4C	11.8	1.5	16.0	0.065	2.2	1.3	2.7
		qCPA, 3par	7.3	1.4	9.6	0.038	2.1	1.3	2.6
		qCPA, 4par, set 1	2.3	1.3	2.8	0.000	2.3	1.3	2.8
		qCPA, 4par, set2	4.6	1.3	5.9	0.024	2.3	1.3	2.8
$\text{CO}_2(1)+\text{hexane}(2)$	273-303	CPA, n.a.	23.68	-	27.55	0.115	1.83	-	2.44
		CPA, 4C	14.32	-	18.68	0.067	1.02	-	1.4
		qCPA, 3par	8.71	-	11.58	0.037	1.45	-	1.98
		qCPA, 4par, set 1	1.38	-	2.04	0.000	1.38	-	2.04
		qCPA, 4par, set2	5.27	-	7.1	0.021	1.6	-	2.27
$\text{CO}_2(1)+\text{decane}(2)$	277-584	CPA, n.a.	25.82	0.28	34.65	0.103	5.73	0.26	5.87
		CPA, 4C	15.55	0.28	18.79	0.060	2.46	0.26	2.48
		qCPA, 3par	9.1	0.26	10.25	0.028	3.19	0.26	3.34
		qCPA, 4par, set 1	1.93	0.26	1.87	0.000	1.93	0.26	1.87
		qCPA, 4par, set2	5.34	0.27	5.69	0.011	2.96	0.26	3.06

^a Liquid phase deviation only.

Figure 5: VLE predictions ($k_{ij} = 0$) between CO_2 and ethane at four temperatures using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [62, 63].

also presented excellent results for the CO_2 + ethane and CO_2 + propane systems. These results, however, are not directly comparable to the results in this work, as the authors correlated the CO_2 parameters to the CO_2 + propane VLE in addition to the saturated liquid density and vapor pressure. Moreover a non-zero k_{ij} is employed; its value being obtained from another correlation. The predictions and correlations presented by Tsivintzelis et al. [18] for CO_2 + n-alkane mixtures with CPA are obviously similar to the CPA 4C and CPA n.a. results presented in this work.

Figures 5-7 illustrate that the series behaviour from C_2 - C_{10} is captured quite well with qCPA, and the predictions with qCPA continues to be excellent, especially for parameter set 1. Unfortunately all models overestimate the critical point (see figure 6). As already mentioned this is an unfortunate characteristic of such equations of state. Cross-over approaches exist which may deal with the problem, at the cost of more complex expressions and additional parameters. Figure 6 show the CO_2 + n-butane VLE prediction. Gross [8] also showed very

Figure 6: VLE predictions ($k_{ij} = 0$) between CO_2 and n-butane at three temperatures using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [64, 66].

good results for this system as well as for the CO_2 + n-pentane VLE using the PCP-SAFT. In these cases a k_{ij} of approximately 0.04 was needed to correlate both systems. Using qCPA with parameter set 1, however, the best k_{ij} is approximately zero. A more fair comparison, considering the number of adjustable parameters, may be to compare the optimum k_{ij} for the three parameter version of the qCPA (see table 7) with those found for PCP-SAFT. These k_{ij} 's are of a similar magnitude despite the different base models. Close to the critical point, however, PCP-SAFT seem to perform better.

Generally the qCPA approaches with four parameters appear to yield the best VLE predictions for CO_2 + n-alkanes, followed by the three parameter version of qCPA, then CPA 4C and finally by CPA n.a. An exception to this trend is the CO_2 + methane system which is shown in figure 8. Except in the vicinity of the critical point quite good predictions are obtained when CO_2 is considered an associating species and when qCPA with three adjustable parameters is employed. However, when qCPA is employed with an additional adjustable parameter rather poor predictions are obtained.

Figure 7: VLE predictions ($k_{ij} = 0$) between CO_2 and n-decane at three temperatures using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [65].

Figure 8: VLE predictions ($k_{ij} = 0$) between CO_2 and methane at two temperatures using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [62].

As the LLE between CO₂ and heavy hydrocarbons is believed to be, partly,
 355 due to the quadrupolar moment of CO₂ a successful quadrupolar term should
 improve the models ability to correlate these LLEs. A characteristic correla-
 tion of the CO₂ + n-pentadecane LLE is visualized in figure 9a. All model
 approaches can correlate the LLE of CO₂ and the heavy alkane. A much larger
 interaction parameter, however, is needed when CO₂ is modelled as an inert
 360 or self-associating compound, compared to when CO₂ is modelled with qCPA.
 The correlated interaction parameter and the results, in terms of %AAD, are
 shown in table 8. As is typically the case, the LLE results are very sensitive
 to the binary interaction parameter, and many models do not even predict the
 presence of a LLE without this parameter. As figure 9b illustrate, however, the
 365 four parameter version of qCPA can predict ($k_{ij} = 0$) the LLE of these mixtures
 fairly well. The %AAD of the predictions are shown in table 9.

Table 8: Correlated k_{ij} and calculated %AADs for the CO₂ + heavy n-alkane
 LLE systems using the CPA and qCPA. Experimental data from [72].

System	P range [bar]	Model	k_{ij}	%AAD in HC phase	%AAD in CO ₂ phase	Average %AAD in CO ₂
CO ₂ (1)+n-dodecane (2)	20-29	CPA n.a.	0.102	0.59	0.39	0.49
		CPA 4C	0.054	0.42	0.18	0.30
		qCPA 3par	0.019	0.47	0.3	0.39
		qCPA 4par, 1	-0.025	0.42	0.25	0.34
		qCPA 4par, 2	-0.003	0.44	0.28	0.36
CO ₂ (1) +n-tetradecane (2)	31-83	CPA n.a.	0.100	0.31	0.06	0.19
		CPA 4C	0.058	0.29	0.11	0.20
		qCPA 3par	0.023	0.24	0.08	0.16
		qCPA 4par, 1	-0.017	0.35	0.11	0.23
		qCPA 4par, 2	0.003	0.28	0.11	0.19
CO ₂ (1) +n-pentadecane (2)	32-80	CPA n.a.	0.105	0.25	0.04	0.14
		CPA 4C	0.059	0.15	0.12	0.13
		qCPA 3par	0.025	0.07	0.06	0.07
		qCPA 4par, 1	-0.017	0.11	0.11	0.11
		qCPA 4par, 2	0.004	0.09	0.09	0.09

3.3.2. CO₂ + self-associating compounds - Approach to induced association

When mixtures of CO₂ + self-associating compounds, such as alcohols and
 water, are considered it raises the important question of whether CO₂ should be
 370 modelled only as a quadrupolar molecule or as a quadrupolar *and* a solvating

Table 9: %AADs for the predicted LLEs of CO_2 + heavy n-alkane systems using the four parameter version of qCPA. Experimental data from [72].

System	P range [bar]	Model	%AAD in hydrocarbon phase	%AAD in CO_2 phase	Average % AAD in CO_2
$k_{ij} = 0$					
CO_2 (1)+n-dodecane (2)	20-29	qCPA set 1	2.49	0.53	1.51
		qCPA set 2	0.57	0.34	0.45
CO_2 (1) +n-tetradecane (2)	31-83	qCPA set 1	1.44	0.13	0.79
		qCPA set 2	0.28	0.11	0.16
CO_2 (1) +n-pentadecane (2)	32-80	qCPA set 1	1.37	0.07	0.72
		qCPA set 2	0.35	0.14	0.24

Figure 9: Correlation (a) and prediction (b) of the CO_2 +n-pentadecane LLE, where CO_2 is modelled with CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [72].

molecule (i.e. a molecule with electron donor *or* electron acceptor sites). Several studies indicate Lewis acid-Lewis base type interactions for CO₂ with polar, associating molecules such as water and alcohols [18, 73–76]. As an engineering approach the Lewis acid-Lewis base interaction can be viewed as an induced
375 cross-association (solvation). This kind of cross-association, where one component self-associates but the other only has electron donor or electron acceptor sites, is difficult to treat with current models since the association parameters, $\varepsilon^{A_i B_i}$ and $\beta^{A_i B_i}$, are available only for the self-associating compound. That is, while the compounds cross-associate with each other, the cross-association volume cannot be determined from the CR-1 combining rule (equation (11b)). As
380 a pragmatic solution the cross-association volume, $\beta^{A_i B_j}$, is often fitted to the experimental data (simultaneously with the binary interaction parameter, k_{ij}) while the association energy, $\varepsilon^{A_i B_i}$, of the solvating compound is set to zero. This approach typically works well, however, the improved correlations may, at
385 least partially, be attributed to an increased flexibility due to a higher number of adjustable parameters.

A simple alternative to correlating the cross-association volume, $\beta^{A_i B_j}$, for solvating mixtures was proposed by Kleiner and Sadowski [77]. The method assumes that the cross-association volume can be set equal to the association
390 volume of the self-associating compound. In this way equations (11a)-(11b) can be directly employed without the need for any adjustable parameters beyond a k_{ij} . Clearly improved correlations can be obtained if both the binary interaction parameter and the cross-association volume are fitted to the experimental data. The added model flexibility of such an approach would, however, make it difficult
395 to critically compare the models.

Another important question is how many solvation sites CO₂ has. Indeed in a recent work NguyenHuynh et al. [78], illustrated, using the GC-PPC-SAFT, that very good results could be obtained for mixtures of CO₂ and alcohols if CO₂ was assumed to have two cross sites. Similarly Figure 10 illustrate the
400 predictions ($k_{ij} = 0$) with qCPA for the CO₂ + ethanol mixture and the vapor liquid liquid equilibrium (VLLE) of the CO₂-rich phase of the CO₂ + water

Figure 10: Predicted ($k_{ij} = 0$) VLEs of the CO₂ + ethanol system (a) and the CO₂-rich vapor phase of the CO₂ + water system (b) with qCPA with three parameters and assuming zero, one or two solvation sites. It is assumed for both systems that $\beta_{crs} = \beta_{assoc}$. Experimental data from [79–85].

mixture using zero, one or two cross association sites. The cross association
 parameters were determined using the approach by Kleiner and Sadowski [77].
 When cross association is not taken into account, or only one cross association
 site is considered, the equilibrium pressure in figure 10a is overestimated and
 a false liquid-liquid phase split is predicted. Similarly the minimum in the
 water solubility in the CO₂-rich phase is captured quite accurately when two
 cross-association sites are assumed, but not when CO₂ has one or zero sites
 (see figure 10b). That is, when qCPA is employed CO₂ is assumed to have
 two solvation sites, and the cross-association parameters are found using the
 approach of Kleiner and Sadowski [77].

In the case where we consider CO₂ to be a self-associating compound the
 cross-association between CO₂ and the associating compound is handled by
 directly applying the CR-1 mixing rule (see eq. (11a)-(11b)).

415 *CO₂ + alcohols.* In general qCPA performs quite well for many of the alcohol systems, even with a zero k_{ij} , but a non-zero temperature independent interaction parameter is used to better represent the phase equilibria. The results are summarized in terms of %AADs in table 10. Characteristic VLE results are shown for CO₂ + methanol in figure 11 at three temperatures. Despite
420 a very large binary interaction parameter the highest deviations are obtained when CO₂ is considered a self-associating molecule following the 4C association scheme. The model which captures the trend of the VLEs most accurately is clearly qCPA. The correlations with the different qCPA parameter sets for CO₂ are similar, although a smaller interaction parameter (in absolute terms) is
425 needed when qCPA with three adjustable parameters is employed. In all cases a small negative interaction parameter is necessary, whereas a positive interaction parameter is needed when CO₂ is considered either self-associating or inert. Surprisingly good correlations, with a low interaction parameter, are obtained when CO₂ is considered an inert. The model, however, does not capture the
430 trend of the experimental data quite as well as qCPA, especially at higher temperatures where the pressure is overestimated and a false liquid-liquid split may occur.

Figure 12 illustrate that the phase behaviour description of the simultaneous VLE and LLE of the CO₂ + nonanol system is satisfactory with all models
435 using a temperature independent interaction parameter. The same is the case for the CO₂ + octanol system. Notice that when qCPA with three parameters is employed for the CO₂ + octanol system the optimum k_{ij} is found to be zero, i.e. the model is predictive for this system. It is noteworthy, that as the chain length of the alcohols increases the binary interaction parameter tend to decrease or
440 increase when CO₂ is treated as either a self-associating or an inert compound respectively. When CO₂ is treated as a quadrupolar molecule, however, the small interaction parameter seem to be almost constant for the various systems.

CO₂ + water. The capabilities of association theories for modeling the important CO₂ + water mixture has been extensively studied in recent literature using

Figure 11: Correlation of the CO_2 + methanol VLE using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [80, 81, 86–88].

Figure 12: Correlation of the CO_2 + nonanol VLE and LLE using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [81, 90].

Table 10: CPA and qCPA deviations and k_{ij} for CO₂ + alcohol VLE and LLE mixtures. Experimental data from references [79–81, 86–89].

System	T range (K)	Modeling approach	k_{ij}	% AAD in P	% AAD in y_1	%AAD in x_1
CO ₂ (1)+methanol(2)	230-313.2	CPA, n.a.	0.027	7.9	0.4	10.5
		CPA, 4C	0.180	18.7	0.5	48.6
		qCPA, 3par	-0.010	4.7	0.2	8.9
		qCPA, 4par, set 1	-0.050	5.6	0.2	9.7
		qCPA, 4par, set2	-0.050	5.6	0.2	10.1
CO ₂ (1)+ethanol(2)	291.15-313.2	CPA, n.a.	0.050	9.4	0.4	10.1
		CPA, 4C	0.200	6.1	0.2	7.2
		qCPA, 3par	-0.019	3.9	0.4	8.3
		qCPA, 4par, set 1	-0.057	2.7	0.3	6.5
		qCPA, 4par, set2	-0.030	2.9	0.3	6.5
CO ₂ (1)+propanol(2)	313.4	CPA, n.a.	0.058	10.7	0.2	7.4
		CPA, 4C	0.180	6.7	0.1	11.0
		qCPA, 3par	-0.020	4.1	0.2	5.1
		qCPA, 4par, set 1	-0.050	3.4	0.2	3.2
		qCPA, 4par, set2	-0.030	3.0	0.2	3.1
CO ₂ (1)+octanol(2) ^a	308.2-328.2	CPA, n.a.	0.070	12.9	0.4	10.8
		CPA, 4C	0.160	14.8	0.3	10.3
		qCPA, 3par	0.000	11.0	0.3	7.4
		qCPA, 4par, set 1	-0.040	10.4	0.3	6.6
		qCPA, 4par, set2	-0.020	10.8	0.3	7.7
CO ₂ (1)+nonanol(2) ^a	308.1-328.2	CPA, n.a.	0.070	19.6	0.8	9.1
		CPA, 4C	0.140	23.5	0.5	13.7
		qCPA, 3par	0.000	18.5	0.8	6.4
		qCPA, 4par, set 1	-0.045	17.1	0.7	6.4
		qCPA, 4par, set2	-0.025	18.1	0.7	7.6

^a Deviations based on both VLE and LLE data.

both CPA [16, 18, 91, 92] and SAFT-based models [16, 91, 93–95]. The mixture has also been studied, with mixed success, using some of the multipolar SAFT-based equations of state [96–98]. It is clear from most investigations, however, that the best results for CO₂ + water are almost always obtained when CO₂ is considered to be a solvating molecule.

As stated previously we assume that CO₂ cross-associates with two solvation sites and that $\beta^{A_i B_j} = \beta_{crs} = \beta_{water}$. Figure 13 illustrates the correlation of the CO₂-rich vapor phase and the water-rich liquid phase at 323.15K. All models correlate the solubility of CO₂ in the water-rich phase quite well (figure 13a), although a large interaction parameter is needed when CO₂ is assumed to be a self-associating compound. However, as also demonstrated by Tsivintzelis et al. [18], CPA cannot capture the minimum in the solubility of water in the vapor phase when CO₂ is modelled as an inert compound, nor is the trend of the experimental data captured if CO₂ is modeled as a self-associating compound (see figure 13b). When CO₂ is treated as a quadrupolar compound which cross-associates with water the minimum in solubility in the CO₂ phase is, at least qualitatively, captured.

Instead of treating CO₂ as a purely inert compound a more fair model comparison may be to also assume CO₂ to cross-associate, using the same assumptions as we did for qCPA. Figure 14 compares the model correlations in the CO₂-rich vapor phase using either CPA or qCPA with three adjustable parameters where CO₂ is assumed to solvate with water in both cases. It can be seen from the figure that if CO₂ is assumed to be solvating, then the minimum in the water solubility is captured equally well in CPA and qCPA. This suggests that taking cross-association between CO₂ and water into account is in fact the dominant contribution to modeling the CO₂ + water system. We note that to model both phases simultaneously a relatively high k_{ij} is needed, when the quadrupolar nature of CO₂ is not explicitly taken into account. Table 11 summarizes the results in terms of %AAD both with and without an interaction parameter.

Figure 13: Correlation of the CO₂ solubility in the water rich liquid phase (a) and the water solubility in the CO₂ rich vapor phase (b) for the CO₂ + water system. CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters is employed. Experimental data from [82–85, 99].

Table 11: Deviations for CPA and qCPA predictions ($k_{ij} = 0$) and correlations ($k_{ij} \neq 0$) for the CO₂(1) + water(2) mixture at 323.15 K (both VLE and LLE data). Including the correlated k_{ij} . Experimental data from references [82–85, 99]

Modeling approach	% AAD in y_2	%AAD in x_1	k_{ij}	% AAD in y_2	%AAD in x_1
$k_{ij}=0$					
CPA, n.a.	62.5	4.6	0.005	62.9	3.6
CPA with solvation	10.3	>100	0.128	21.5	4.2
CPA, 4C	>100	>100	0.255	>100	4.5
qCPA, 3par	13.7	25.9	0.033	17.1	3.7
qCPA, 4par, set 1	17.0	11.5	-0.015	15.5	3.6
qCPA, 4par, set2	14.7	7.5	0.010	15.8	3.5

Figure 14: Correlation of the water solubility in the CO_2 rich vapor phase for the CO_2 + water system. Comparing the performance of CPA with solvation, and qCPA with solvation. Experimental data from [82–85].

475 *Mixtures with two quadrupolar compounds.* CO_2 has so far been the only quadrupolar compound explicitly considered in this work, although both water and ethane have a quadrupole moment, which we have ignored. It is important, however, to evaluate the capabilities of the new model for mixtures of two or more quadrupolar compounds. More specifically such an evaluation may provide an indication
 480 as to the adequacy of the proposed mixing rules and cross-quadrupolar interactions. Here we investigate mixtures of CO_2 and either benzene or acetylene.

A fixed experimental quadrupole moment of $-9 \text{ D}\text{\AA}$ is employed for benzene. See table 2 for the re-estimated qCPA pure compound parameters. The predicted VLE of benzene and CO_2 is compared to experimental values in figure
 485 15. All model approaches, except when both CO_2 and benzene are treated as inert compounds, perform very well and quite predictively. Interestingly CPA performs very well when CO_2 is assumed to be associating, despite the fact that both CO_2 and benzene are solvating molecules rather than associating ones.

Figure 15: Prediction of the CO_2 + benzene VLE at two temperatures (upper: 347.25 K and lower: 315.45 K) using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [86, 100].

The results in terms of %AAD are presented in table 12. Gross [8] modelled this system using the PCP-SAFT and regular PC-SAFT, however, the results with the former model were worse than with PC-SAFT. To improve the results Gross had to set the cross-quadrupolar interactions to zero.

Acetylene is modelled with a fixed quadrupolar moment of $4 \text{ D}\text{\AA}$ the re-estimated pure compound parameters can be found in table 2. The VLE between CO_2 + acetylene results in an uncommon negative azeotrope, which is believed to be caused by the opposite sign of the quadrupole moments for the two components [102]. Ideally a quadrupolar term would be able to model this effect. Figure 16 shows, however, that a positive azeotrope is predicted by both qCPA and CPA 4C. All models are capable of correlating the azeotrope. The reason that this quadrupole-quadrupole pair is so poorly represented by the quadrupolar model is believed to be due to the fact that all quadrupolar moments are raised to even powers (see Eq. (14)-(16)). The sign of the quadrupole moment

Table 12: Deviations for CPA and qCPA predictions ($k_{ij} = 0$) and correlations ($k_{ij} \neq 0$) for the $\text{CO}_2 + \text{benzene}$ mixture. Including the correlated k_{ij} . Experimental data from [86, 100].

T range (K)	Modeling approach	% AAD in P	%AAD in x_1	k_{ij}	% AAD in P	%AAD in x_1
$k_{ij}=0$						
298.2-347.3	CPA, n.a.	26.8	23.9	0.068	14.3	6.2
	CPA, 4C	15.8	9.5	0.020	12	3.9
	qCPA, 3par	17.8	13.3	0.008	10.5	3.4
	qCPA, 4par, set 1	11.9	5.7	-0.038	12.0	3.8
	qCPA, 4par, set2	15.8	10.9	-0.014	12.0	3.8

Figure 16: Prediction of the $\text{CO}_2 + \text{acetylene}$ VLE at 233 K using CPA n.a., CPA 4C, or qCPA with three or four adjustable parameters. Experimental data from [101].

thus becomes inconsequential and $\text{CO}_2 + \text{acetylene}$ is effectively modeled as two quadrupoles of the same sign. The preferred molecular orientation for two quadrupoles of opposite sign, however, is end to end whereas it is perpendicular if they are of the same sign.

4. Conclusion

In an effort to improve the predictive capabilities of classic thermodynamic models, primarily for mixtures containing CO_2 , a quadrupolar equation of state contribution, developed from statistical mechanics [5], have been modified and combined with CPA. The resulting qCPA can be used without introducing any other adjustable pure compound parameters or, alternatively, an additional adjustable parameter can be used. The model results were compared with CPA n.a. and CPA 4C.

When the same number of adjustable parameters are used for CPA n.a. and qCPA, a systematic improvement in the correlation of the saturated liquid density and vapor pressure is observed. This is particularly true for the strongly quadrupolar CO_2 molecule, but applies to benzene and acetylene as well.

The models were employed to predict various pure compound properties for CO_2 including the second virial coefficient, the critical properties and various derivative properties. qCPA and CPA 4C seem to perform slightly better than CPA n.a. in regards to the derivative properties. On the other hand CPA n.a. is slightly more accurate in representing the second virial coefficient and the critical point. The differences between the modelling approaches, however, are generally small. The main reason for deviations in the derivative properties seem to be caused by a deficiency in the second order derivatives.

It was found that qCPA (all approaches) significantly improves the prediction of binary VLE and the correlation of LLE between $\text{CO}_2 + \text{n-alkane}$ mixtures. A significantly smaller interaction parameter is needed to correlate the experimental data with qCPA compared to the CPA approaches. When it comes to $\text{CO}_2 + \text{associating mixtures}$ very good correlations were obtained with qCPA

when solvation was taken into account using the approach suggested by Kleiner and Sadowski [77] and a single small binary interaction parameter. The model was finally applied to two quadrupolar-quadrupolar mixtures, which illustrated
535 that the model seem to have difficulties for quadrupolar mixtures of opposite sign such as CO_2 + acetylene. Overall explicitly accounting for the quadrupolar forces appears to offer significantly improved predictions, and better (smaller k_{ij}) correlations, for CO_2 containing mixtures compared to the two other CPA approaches.

540 The performance of the qCPA approaches is similar with regards to the derivative properties of CO_2 and for mixtures of CO_2 + self-associating compounds. For CO_2 + n-alkanes the four-parameter versions of qCPA both perform somewhat better than the three-parameter version. Nevertheless this modest improvement may not justify the increased model flexibility and uncertainty
545 in the parameter estimation. Unless the primary focus is binary CO_2 + n-alkane mixtures the most promising approach is thus considered to be qCPA with three adjustable parameters.

Appendix A. Employed pure compound parameters

The pure compound parameters from literature which has been used in this
550 work are shown in table A.13.

Table A.13: CPA pure compound parameters from literature employed in this work.

Compound	Association scheme	b_0 mL/mol	$\Gamma(a_0/(Rb_0))$ K	c_1 -	$\beta \cdot 1000$ -	ε/R K	Reference
Methane	n.a.	29.10	959.03	0.45	-	-	[103]
Ethane	n.a.	42.90	1544.55	0.58	-	-	[103]
Propane	n.a.	57.83	1896.45	0.63	-	-	[104]
n-Butane	n.a.	72.08	2193.08	0.71	-	-	[104]
n-Pentane	n.a.	91.01	2405.11	0.80	-	-	[104]
n-Hexane	n.a.	107.89	2640.03	0.83	-	-	[104]
n-Decane	n.a.	178.65	3190.54	1.13	-	-	[104]
n-dodecane	n.a.	216.24	3471.04	1.20	-	-	[105]
n-tetradecane	n.a.	250.53	3678.42	1.29	-	-	[105]
n-pentadecane	n.a.	274.53	3751.99	1.34	-	-	[105]
Benzene	n.a.	74.99	2867.19	0.76	-	-	[104]
Water	4C	14.52	1017.34	0.67	69.20	2003.25	[29]
Methanol	2B	30.98	1573.71	0.43	16.10	2957.78	[29]
Ethanol	2B	49.11	2123.83	0.74	8.00	2589.85	[106]
1-Propanol	2B	64.11	2234.52	0.92	8.10	2525.86	[106]
1-Octanol	2B	148.80	3367.99	1.15	0.14	3218.55	[106]

Appendix B. Equations for the derivative properties

This appendix list expressions for the derivative properties evaluated in this work, namely the residual isochoric- and isobaric heat capacities, the residual enthalpy, the Joule-Thomson coefficient and the speed of sound. The properties
555 are given in terms of the reduced residual Helmholtz energy.

Residual isochoric heat capacity.

$$C_V^{res}(T, V, \mathbf{n}) = -RT^2 \left(\frac{\partial^2 F}{\partial T^2} \right)_{V, \mathbf{n}} - 2RT \left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{n}} \quad (\text{B.1})$$

Residual isobaric heat capacity.

$$C_P^{res}(T, V, \mathbf{n}) = C_V^{res} - T \frac{\left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}}^2}{\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}}} - nR \quad (\text{B.2})$$

Residual enthalpy.

$$\frac{H^{res}(T, V, \mathbf{n})}{nRT} = Z - \frac{T}{N} \left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{n}} - 1 \quad (\text{B.3})$$

The Joule-Thomson coefficient.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_{H, \mathbf{n}} = -\frac{1}{C_P} \left[V + T \left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}} / \left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}} \right] \quad (\text{B.4})$$

The speed of sound.

$$u = \sqrt{-V^2 \frac{C_P}{C_V} \frac{\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}}}{M_W}} \quad (\text{B.5})$$

where

$$\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial V^2} \right)_{T, \mathbf{n}} - \frac{nRT}{V^2} \quad (\text{B.6})$$

$$\left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial V \partial T} \right)_{\mathbf{n}} - \frac{P}{T} \quad (\text{B.7})$$

and M_W is the molecular weight. It is seen that the second order derivatives $(\partial^2 F / \partial V^2)_{\mathbf{n}, T}$, $(\partial^2 F / \partial V \partial T)_{\mathbf{n}}$ and $(\partial^2 F / \partial T^2)_{\mathbf{n}, V}$ are crucial in order to obtain accurate derivative property predictions.

The enthalpy and the heat capacities are expressed as a sum of two contributions; an ideal, temperature dependent, contribution (ig) and a residual contribution (res) obtained from an EoS. In this work the C_P^{ig} is calculated from the DIPPR correlation [33]. The ideal isochoric heat capacity and enthalpy is calculated through their relation to C_P^{ig} .

Abbreviations

CPA cubic plus association.

CS Carnahan-Starling.

DIPPR Design Institute for Physical Properties.

EoS equation of state.

LLE liquid liquid equilibrium.

NIST National Institute of Standards and Technology.

PC-SAFT Perturbed-Chain SAFT.

PCP-SAFT Perturbed-Chain Polar SAFT.

qCPA quadrupolar CPA.

RDF Radial distribution function.

SAFT Statistical Association Fluid Theory.

SRK Soave-Redlich-Kwong.

tPC-PSAFT truncated Perturbed-Chain Polar SAFT.

VLE vapor liquid equilibrium.

VLLE vapor liquid liquid equilibrium.

580 **Nomenclature**

$A^r(T, V, \mathbf{n})$ Residual Helmholtz energy.

A_2^r Second order term in the perturbation expansion for quadrupolar interactions.

585 A_3^r Third order term in the perturbation expansion for quadrupolar interactions.

A_i bonding sites on molecule i .

B Second virial coefficient or expression for co-volume mixing term..

C_P^{res} The residual isobaric heat capacity.

C_V^{res} The residual isochoric heat capacity.

590 D Mixing rule for the energetic part of SRK.

I_{TQ} Three-body correlation integral.

I_n Two-body correlation integral.

N_A Avogadro's constant.

P_C Critical pressure.

595 P Pressure.

Q Quadrupole moment.

R The gas constant.

S Constant in expression for the second virial coefficient of the association term..

600 T_C Critical temperature.

T_r Reduced temperature $T_r = T/T_C$.

T Temperature in Kelvin.

	V	Volume.
	X_{A_i}	Fraction of sites A on molecule i which do <i>not</i> form bonds with other sites
605		(site monomer fraction).
	Z	compressibility factor.
	$\Delta^{A_i B_j}$	Association strength between site A on molecule i and site B on molecule
		j .
	$\beta^{A_i B_j}$	cross-association volume.
610	η	Reduced density.
	$\mathbf{n}$	Vector of molar composition.
	μ_{JT}	The Joule-Thomson coefficient.
	ρ	Density.
	σ	Hard-sphere diameter.
615	$\varepsilon^{A_i B_j}$	cross-association energy.
	a_0	Pure compound energetic parameter in the SRK term.
	a_{ij}	Cross energetic parameter in the SRK term.
	b_0^Q	co-volume parameter in the quadrupolar term.
	b_0	Pure compound co-volume.
620	b_{ii}	Pure compound co-volume for component i .
	b_{ij}	cross-covolume.
	c_1	Pure compound parameter in the SRK term.
	g	Radial distribution function.
	k_b	Boltzmann's constant.

625 k_{ij} Binary interaction parameter.

n Total composition.

s^{exp} standard deviation.

u The speed of sound.

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