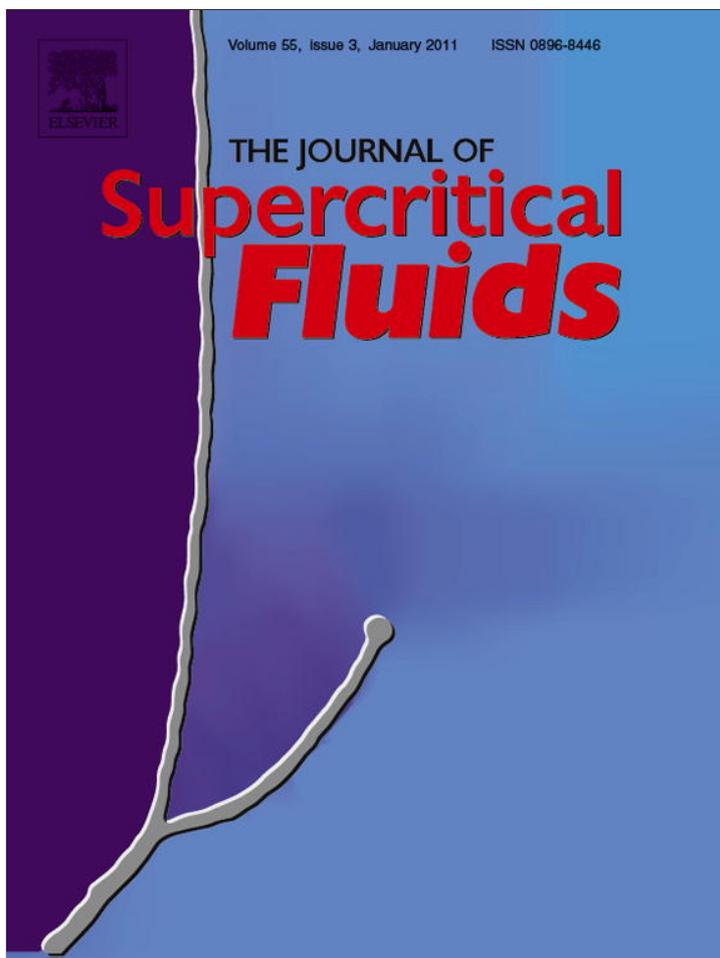


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## Evaluation of the CO<sub>2</sub> behavior in binary mixtures with alkanes, alcohols, acids and esters using the Cubic-Plus-Association Equation of State

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## ABSTRACT

Knowledge regarding the high pressure phase behavior of CO<sub>2</sub> mixtures is of primary importance for designing, operating and optimizing many industrial processes, such as supercritical fluid extraction for pharmaceutical, food and biodiesel industries and oil recovery enhancement through CO<sub>2</sub> flooding.

In the present work, it is investigated how the CPA EoS (Cubic-Plus-Association equation of state) can be used for an adequate description of the VLE of an extensive series of CO<sub>2</sub> binary systems containing *n*-alkanes, *n*-alcohols, esters and *n*-acids, in a broad range of temperatures and pressures. These families constitute a series of non-self associating, associating and cross-associating components whose potential associative interactions with CO<sub>2</sub> are evaluated here.

A detailed investigation regarding the differing behavior of CO<sub>2</sub> depending on the nature of the second component and how the CPA EoS can best describe them is presented here, namely explicitly considering the CO<sub>2</sub> association and also evaluating also its different association schemes.

It will be shown that it is important to consider CO<sub>2</sub> self- and cross-association to describe the VLE of *n*-alkane and small alcohol/CO<sub>2</sub> systems. However, it is not necessary to consider CO<sub>2</sub> association when dealing with systems of heavy alcohols, esters or acids.

The CPA EoS provides very good results for the extensive range of CO<sub>2</sub> binary systems considered here using, for most of them, single, small, temperature independent, positive and chain length dependent binary interaction parameters.

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### 1. Introduction

Binary systems consisting of CO<sub>2</sub> and alkanes, alcohols, acids and esters are of highly relevance for several technological applications. CO<sub>2</sub>, being easily available in high purity, cheap, non-toxic and non-flammable [1], is currently considered as an important solvent for supercritical separation processes. Supercritical extraction can replace commonly used separation processes, such as distillation and liquid–liquid extraction, with the advantages of lower extraction times, increased flexibility and no degradation of extracts [2]. CO<sub>2</sub>/hydrocarbons and CO<sub>2</sub>/alcohols systems have been a focus of great attention due to their importance as supercritical fluid/cosolvent pairs [3]. It is known that short alkanes and alcohols are the best co-solvents for the extraction of biomaterials and drugs of relevance for the cosmetic, pharmaceutical, surfactant, and food industries [4].

CO<sub>2</sub>/hydrocarbons and CO<sub>2</sub>/alcohols mixtures are also present in the oil and gas industries. Petroleum fuel has played a vital role in human life, and mankind is almost totally dependent on it for transportation as well as in other sectors of the economy. However, increased oil consumption in developing economies, along with the uncertainty concerning petroleum availability, increases the need to optimize oil recovery processes [5].

One of the enhanced oil recovery methods is CO<sub>2</sub> flooding. High pressure CO<sub>2</sub> is injected in to the oil reservoir forming a low viscosity and surface tension fluid that is easily displaced [6].

Being able to accurately describe the phase behaviour of CO<sub>2</sub>/hydrocarbons systems, in wide ranges of temperatures and pressures, is thus essential to understand an efficient oil displacement by CO<sub>2</sub> [7–8]. Additionally, CO<sub>2</sub>/hydrocarbons phase equilibria are also important for plants processing oil and gas produced by CO<sub>2</sub> flooding that have high CO<sub>2</sub> concentrations. Data for CO<sub>2</sub>/short alcohols is necessary for choosing the best alcohol to be injected in pipelines in order to prevent the formation of hydrates in oil and natural gas facilities [3].

Moreover, CO<sub>2</sub> and alcohol-containing systems are of relevance for methanol to hexanol synthesis through the syngas reaction, as

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**Nomenclature***Abbreviations*

AAD	$= \frac{1}{NP} \sum_{i=1}^{NP} \text{ABS}[(\text{exp}_i - \text{calc}_i)/\text{exp}_i] \times 100$
CO <sub>2</sub>	carbon dioxide
CPA	Cubic-Plus-Association
GC	group contribution
EoS	equation of state
$g^E$	excess molar Gibbs energy
LCVM	linear combination Vidal-Michelsen mixing rules
LPMR	low pressure mixing rule
MHV1	modified Huron-Vidal first order mixing rule
MHV2	modified Huron-Vidal second order mixing rule
NRF	non-random factor
NRTL	non-random two-liquid theory
PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
PCP-SAFT	Perturbed-Chain Polar Statistical Associating Fluid Theory
PR	Peng–Robinson
PRSV	Peng–Robinson EoS modified by Stryjeck and Vera
PSRK	Predictive Soave Redlich Kwong
RPM	Restrictive Permissive Model
SAFT	Statistical Associating Fluid Theory
SAFT-VR	Variable Range Statistical Associating Fluid Theory
SRK	Soave Redlich Kwong
UNIFAC	Universal Function Activity Coefficient
UNIQUAC	Universal Quasi-Chemical Theory
vdW1f	Van der Waals one fluid mixing rule
VLE	Vapor–Liquid Equilibria
WS MR	Wong–Sandler Mixing Rule

*List of symbols*

$a$	energy parameter in the physical term
$a_0, c_1$	parameters for calculating $a$
$A_i$	site $A$ in molecule $i$
$b$	co-volume
$g$	radial distribution function
$k_{ij}$	binary interaction parameter
$P$	vapor pressure
$R$	gas constant
$T$	temperature
$x$	mole fraction
$X_A$	fraction of molecule not bonded at site $A$
$Z$	compressibility factor

*Greek symbols*

$\beta$	association volume
$\varepsilon$	association energy
$\eta$	reduced fluid density
$\rho$	mole density
$\Delta$	association strength

*subscripts*

$i, j$	pure component indexes
liq.	liquid
r	reduced

*superscripts*

assoc.	association
phys.	physical

their subsequent separation from CO<sub>2</sub> requires the knowledge of their phase equilibria [9].

CO<sub>2</sub>/fatty acids systems have an important role in the industrial processing of vegetable oils, which have been receiving increased attention from the food, pharmaceutical and biodiesel industries. Supercritical CO<sub>2</sub> is an ideal solvent for removing harmful fatty acids from oils for human consumption, such as olive oil [10], and from waste cooking oils for biodiesel production [11].

CO<sub>2</sub>/fatty acid esters mixtures are also of relevance for the food and pharmaceutical industries due to the recently discovered benefits of some fatty acids for human health. The  $\omega$ -3 fatty acids, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), are known to be able to reduce the chances of arteriosclerosis, diabetes, eye, nervous system and cardiovascular diseases [12–13]. In order to remove a considerable amount of a specific fatty acid from a triglyceride feedstock, a transesterification is first carried out and the subsequent CO<sub>2</sub> fractioning is performed on fatty acid esters mixtures [14].

For a correct design and optimization of supercritical or near critical industrial processes it is essential to accurately describe the high pressure phase equilibria of the systems discussed. This is quite a difficult task due to the broad temperature and pressure conditions and the asymmetric nature of the mixtures considered. In addition, for alcohol, ester and acid containing systems, the presence of those polar compounds with strong associative interactions, increases the complexity of the phase equilibria description of these systems.

Recently, Carvalho and Coutinho [15] while studying the non-ideality of CO<sub>2</sub> solutions on low volatile compounds (heavy alcohols, alkanes, fatty acids and fatty acid esters) brought a new light upon the complexity of the interactions on these systems. The authors showed that the non ideality of these solutions and its impact on the CO<sub>2</sub> solubility is a result of a complex and delicate balance between the solute–solute, solute–solvent, and solvent–solvent interactions and cannot be inferred from the strength of solute–solvent interactions alone. The multiple interactions that are present in different binary CO<sub>2</sub> systems increase the difficulty that thermodynamic models have to deal with for correctly describing these systems.

Equations of state, such as the PR and the SRK EoS with simple or more complex mixing rules, are commonly used to describe the phase equilibria of systems containing supercritical compounds [16].

Due to the great importance of oil and gas as energy sources, experimental data for CO<sub>2</sub> systems containing alkanes and alcohols have been extensively published [17–20] and different models have been applied to describe these systems. Since there are so many studies addressing the modeling of these systems it is impossible to detail all the references in this work. Only the most relevant works, considering the amount of systems correlated, are here discussed.

Models applied for the description of CO<sub>2</sub>/alkane systems are presented in Table 1, along with their summarized description and results.

Regarding the recent works involving the description of the phase equilibria of CO<sub>2</sub>/ $n$ -alcohol systems, among the available cubic equations of state, the PR EoS was widely used. For instance, Chang et al. [40] applied the PR and the Patel–Teja equations of state, with the one-fluid van der Waals' mixing rules with two temperature dependent binary interaction parameters, and López et al. [41] the PR EoS coupled with the Wong–Sandler mixing rules, to successfully correlate VLE data of methanol to decanol/CO<sub>2</sub> containing systems. The SRK EoS with the Huron–Vidal mixing rule coupled with the UNIQUAC model was also used to describe the VLE of CO<sub>2</sub> binary systems containing 1-butanol [42] and 1-heptanol [43].

Considerably less work has been done concerning the description of systems of carboxylic acids and esters with CO<sub>2</sub>. Recent

**Table 1**  
Models applied to CO<sub>2</sub>/alkane systems, their description and results.

Author	EoS	Mixing Rule	Activity Coefficient Model	Results/ Comments
Kalospiros et al. [21]	PR	MHV2	UNIFAC	difficulties for highly asymmetric systems
Coutinho et al. [22]	PSRK SRK	MHV1 vdW1f		improvements for highly asymmetric systems using theoretically based combining rules for the cross energy and co-volume parameter highly temperature dependent binary interaction parameters improvement for highly asymmetric systems
Kontogeorgis and Vlamos [23]	PR	LCVM	UNIFAC	lack of theoretical basis
Polishuk et al. [24–25]	PR	LCVM	UNIFAC	difficulties for highly asymmetric systems that have not been considered for parameters evaluation
Chen et al. [26]	SRK	LPMR	UNIFAC	improvement for highly asymmetric systems
Haghtalab and Mahmoodi [27]	PR PSRK	LCVM MHV1	UNIFAC-NRF	improvement for highly asymmetric systems
Vitu et al. [28]	PR	vdW1f		correctly describing systems up to eicosane group contribution method for temperature dependent binary interaction parameters (PPR78)
López and Cardona [29]	PRSV	WS MR	NRTL	correctly describing systems up to decane temperature dependent binary interaction parameters
Passarello et al. [30]	original SAFT			two temperature independent binary interaction parameters
Garcia et al., Fu et al., Gross and Sadowski [31–33]	PC-SAFT			temperature independent binary interaction parameter
Galindo and Blas [34]	SAFT-VR			different pure compound molecular parameters for the subcritical and critical regions unique set of binary interaction parameters for both regions
Llovel and Vega [35]	crossover soft-SAFT			two temperature independent binary interaction parameters
Tang and Gross [36]	PCP-SAFT			enhanced the prediction provided by PC-SAFT
Thi et al. [37]	GC-PC-SAFT			group contribution method to estimate the pure compound parameters
Nguyen-Huynh et al. [38–39]	GC-PC-SAFT			method based on the London's theory to determine the binary interaction parameter

research on these binary mixtures has been driven by the growing interest from the biodiesel, food and pharmaceutical industries. Crampton et al. [44] and Chang et al. [45] used the modified PR and the modified SRK equations of state, with the van der Waals one-fluid mixing rules, to successfully correlate the VLE of binaries involving CO<sub>2</sub> and fatty acid esters.

Penedo et al. [46] used the PR EoS with the van der Waals mixing rules and two temperature independent binary interaction parameters, to describe CO<sub>2</sub>/acid systems phase equilibria. Polishuk et al. [47] used the same model but with no binary interaction parameters to predict the same series of systems.

The above described approaches are successful in describing the referred CO<sub>2</sub> systems but there is not an EoS and mixing rule able to describe all the CO<sub>2</sub> systems equally well and, it is usually required to use more than one and temperature dependent binary interaction parameters to accomplish a good description of the phase behavior of these systems.

To overcome the use of empirical corrections to cubic EoS or  $g^E$  mixing rules, the step forward in the modeling of polar and highly non ideal systems in large temperature and pressure ranges came with the development of association equations of state, that explicitly describe the specific interactions between like molecules (self-association) and unlike molecules (cross-association). One of these equations is the statistical associating fluid theory (SAFT). At Table 1 the different versions of the SAFT equation successfully applied to model CO<sub>2</sub>/*n*-alkane systems are presented and briefly discussed.

For *n*-alcohols containing systems, the original SAFT equation satisfactorily described the VLE of CO<sub>2</sub>/methanol and ethanol systems [48] at a single temperature, the PC-SAFT with a temperature dependent binary interaction parameter was used to model the VLE of CO<sub>2</sub>/alcohol systems up to nonanol [49], and the crossover soft-SAFT equation with two temperature independent binary

interaction parameters has been used to accurately describe binary CO<sub>2</sub> mixtures up to hexanol [35].

Another association EoS is the Cubic-Plus-Association EoS (CPA EoS), proposed by Kontogeorgis et al. [50]. The results reported so far for the phase equilibria of binary and multicomponent systems containing different inert and/or associating compounds, in a broad range of thermodynamic conditions show the CPA EoS quality, reliability and wide range of applicability [51–52]. Of particular interest for this paper are the previous applications of this model to successfully describe binary and multicomponent systems containing CO<sub>2</sub>, water and small alcohols. A description of these results will be presented in detail in Section 3.

Taking into account the works described above it is possible to see that up to now, an accurate general picture cannot be drawn about which mixing rules provide the best results for the asymmetric systems considered on this work. In spite of the results obtained by Coutinho et al. [22] and by Vitu et al. [28] some authors still do not believe that the van der Waals one-fluid (vdW1f) mixing rules can be used for this kind of systems and prefer to use more complex EoS- $g^E$  models that have nevertheless a number of limitations, as discussed above. It is also important to point out that while using EoS with complex  $g^E$  mixing rules it is often necessary to include temperature dependent binary interaction parameters that have to be correlated from experimental data due to the limited predictive capability of those approaches [16].

In addition, when using association equations of state such as the ones belonging to the SAFT family, the use of a temperature dependent binary interaction parameter is generally also necessary. To avoid that dependency one more binary interaction parameter has to be added.

In this work, a comprehensive study regarding the ability of the CPA EoS to model several CO<sub>2</sub>/*n*-alkane/*n*-alcohol/*n*-acid/ester binary systems in broad temperature and pressure ranges, which

has not yet been assessed, is performed. A discussion about the importance of considering self- and/or cross-association for CO<sub>2</sub> will also be presented.

## 2. Model

In this work, the Cubic-Plus-Association EoS is used. In terms of the compressibility factor the CPA EoS is expressed as:

$$Z = Z^{\text{phys.}} + Z^{\text{assoc.}} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

A Soave-type temperature dependency of the pure component energy parameter,  $a$  is used:

$$a(T) = a_0 [1 + c_1 (1 - \sqrt{T_r})]^2 \quad (2)$$

and  $b$  is the co-volume parameter,  $\rho$  is the density,  $g$  a simplified radial distribution function [53],  $X_{A_i}$  the mole fraction of component  $i$  not bonded at site A and finally  $x_i$  is the mole fraction of component  $i$ .

$X_{A_i}$  is calculated through the association strength,  $\Delta^{A_i B_j}$ , between two sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (3)$$

where

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp \left( \frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (4)$$

The following simplified hard-sphere radial distribution function is used [53]:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (5)$$

$$\eta = \frac{1}{4} b\rho \quad (6)$$

CPA requires the knowledge of three pure component parameters for the physical part,  $a_0$ ,  $c_1$  and  $b$ , and two more for the association term,  $\varepsilon$  and  $\beta$ . These last two are only present in associating compounds. These parameters are estimated through a simultaneous regression of liquid density and vapor pressure data, employing the following objective function:

$$OF = \sum_i^{NP} \left( \frac{p_i^{\text{exp.}} - p_i^{\text{calc.}}}{p_i^{\text{exp.}}} \right)^2 + \sum_i^{NP} \left( \frac{\rho_i^{\text{exp.}} - \rho_i^{\text{calc.}}}{\rho_i^{\text{exp.}}} \right)^2 \quad (7)$$

In order to determine the pure compound parameters it is necessary to assign an association scheme, that is, the number and type of association sites for the associating compound. The nomenclature proposed by Huang and Radosz [54] is adopted here.

For alcohols two association schemes can be applied, the 2B and the 3B. Kontogeorgis et al. [51] had shown that there is not much improvement in using the more rigorous 3B over the simpler 2B association scheme. The 2B association scheme has been commonly used to model the phase equilibria of several alcohol systems [55–56]. Therefore the most successfully applied association scheme for alcohols, the two-site (2B), is the association scheme applied in this work.

For acids the carboxylic group is treated as a single association site (1A). This association scheme had already been successfully applied to organic acid systems [57–59].

When dealing with mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules, and for mixtures composed of non-associating compounds the binary interaction parameter,  $k_{ij}$ , is the only adjustable parameter.

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (8)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (9)$$

$$b = \sum_i x_i b_i \quad (10)$$

For the estimation of the  $k_{ij}$  parameter the objective function employed was:

$$OF = \sum_i^{NP} \left( \frac{x_i^{\text{calc.}} - x_i^{\text{exp.}}}{x_i^{\text{exp.}}} \right)^2 \quad (11)$$

where  $x_i$  is the mole fraction of component  $i$  in the phases selected for the optimization.

Otherwise, when CPA is employed for mixtures containing cross-associating molecules, combining rules for the association energy and volume parameters are required. Several combining rules have been suggested and applied with different results for different phase equilibria and systems. One of the most successful ones is the Elliot combining rule [55], and this is the rule used here:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (12)$$

Within the cross-associating systems there is a special case that occurs when systems are constituted by a self-associating compound and a non-associating compound that can cross-associate with the associating compound, as can happen with ester containing systems. For the ester compound, a single association site able to cross-associate with the self-associating compound is considered [60]. For that type of systems a procedure proposed by Folas et al. [61] has been used to obtain the corresponding cross-association energy and volume. The cross-association energy between the ester and the self-associating compound is taken as half the self-associating compound association energy and the cross association volume is used as an adjustable parameter fitted to equilibrium data (modified CR-1 combining rule).

## 3. Results and discussion

### 3.1. CPA pure compound parameters for *n*-alkanes, *n*-alcohols, *n*-acids and esters

In order to apply the CPA EoS to calculate phase equilibria of binary systems constituted by CO<sub>2</sub> and alkanes, alcohols, esters and acids, the estimation of the CPA pure compound parameters has to be carried out through a simultaneous regression of vapor pressure and liquid density data.

The *n*-alkanes and esters are non-associating compounds and consequently it is only necessary to estimate the three parameters,  $a_0$ ,  $c_1$  and  $b$ , of the physical part represented by the SRK term.

Alcohols and acids are self-associating compounds being necessary to estimate five CPA pure compound parameters ( $a_0$ ,  $c_1$ ,  $b$ ,  $\varepsilon$  and  $\beta$ ). The 1A and the 2B association schemes are applied for acids and for alcohols, respectively.

A systematic study on the pure compound parameters for *n*-alkanes, *n*-alcohols, *n*-acids and esters was previously performed. The CPA parameters were calculated for the *n*-alkanes series from methane to *n*-hexatriacontane [62], for alcohols from methanol to *n*-eicosanol [62], for carboxylic acids from methanoic up to

**Table 2**  
CPA CO<sub>2</sub> pure compound parameters and modeling results ( $T_{\text{meit}} - 0.9T_c$ ).

	$a_0$ (J m <sup>3</sup> mol <sup>-2</sup> )	$c_1$	$b \times 10^5$ (m <sup>3</sup> mol <sup>-1</sup> )	$\varepsilon$ (J mol <sup>-1</sup> )	$\beta$	AAD %	
						$P$	$\rho$
<b>Non-associating</b>	0.35	0.76	2.72			0.22	0.83
<b>4C</b>	0.34	0.77	2.76	731.77	0.0642	0.15	0.31
<b>2B</b>	0.34	0.77	2.73	1237.14	0.1202	0.15	1.23

eicosanoic acid [59] and for esters from 2 up to 19 carbons atoms (covering 20 methyl esters, 2 ethyl esters, 2 propyl esters, 4 butyl esters and also for 14 acetates, 10 formates and 5 unsaturated methyl esters) [60]. An excellent description of the experimental vapor pressures and liquid densities was achieved with CPA for the selected families. Global average deviations for vapor pressures and for liquid densities were, respectively, of 1.76 and 2.07% for *n*-alkanes, of 0.73 and of 1.52% for *n*-alcohols, of 2.32 and 1.39% for esters and of 2.27 and 2.25% for *n*-acids.

These pure compound CPA parameters were shown to provide very good descriptions of the mutual solubilities of water and hydrocarbons [63], of the water solubility in fatty acid esters and biodiesel [60], of the mutual solubilities of fatty acids and water [59], of the LLE of ternary systems constituted by fatty esters, alcohols and glycerol [64], of the VLE of glycerol and *n*-alcohol systems [64] and of the VLE of fatty acid ester + alcohol systems at atmospheric pressure and at super and near critical conditions [65–66].

### 3.2. CPA pure compound parameters for CO<sub>2</sub>

Numerous studies concerning the CO<sub>2</sub>–CO<sub>2</sub> interactions have been carried during the last decade, using both experimental and theoretical approaches. Raman scattering [67] and *ab initio* calculations [68–70] were applied to study dimer and cluster formation of CO<sub>2</sub>. Today it is generally accepted that CO<sub>2</sub>, a linear simple molecule with a large quadrupole moment ( $-15 \times 10^{-40}$  C m<sup>2</sup> [71]) forms dimers with a slipped-parallel (offset face to face) geometry [67–68,70].

Considering CO<sub>2</sub> as a self-associative molecule, while applying association equations of state that explicitly take into account hydrogen bonding interactions, is a debatable issue. Folas et al. [72], using the CPA EoS with CO<sub>2</sub> considered as an inert compound, successfully modelled the VLE of the CO<sub>2</sub>/water system. Kontogeorgis et al. [52,73] with the SRK CPA EoS and Li and Firoozabadi [74] with the PR CPA EoS, showed the importance of considering the inert CO<sub>2</sub> solvation of water in order to obtain better results for the water solubility in liquid CO<sub>2</sub>. In the same work Kontogeorgis et al. [73] applied the solvation approach proposed by Folas et al. [61] for modeling the VLE of the CO<sub>2</sub> + methanol system.

Several other authors assumed that the quadrupolar interactions between CO<sub>2</sub> molecules could be represented by association interactions and considered CO<sub>2</sub> as a self-associating molecule. Perakis et al. [75], Voutsas et al. [76] and Pappa et al. [77], while modeling the VLE of water/ethanol/CO<sub>2</sub> system, CO<sub>2</sub>/ethanol, CO<sub>2</sub>/diethyl ether and CO<sub>2</sub>/water systems with the PR CPA EoS, showed that the best results are obtained when considering CO<sub>2</sub> with 4 associating sites.

With SAFT-like EoS, Button and Gubbins [78] modeled CO<sub>2</sub> as a four site molecule with the original SAFT EoS in the vapor–liquid equilibria of mixtures containing CO<sub>2</sub> and aqueous monoethanolamine or diethanolamine, and Ji et al. [79] as a three site molecule in the phase equilibria of CO<sub>2</sub>/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>O/NaCl systems with the SAFT1-RPM.

A different approach when modeling CO<sub>2</sub> systems with SAFT-family EoS is to extend the equations by the addition of a term that explicitly considers CO<sub>2</sub> quadrupolar interactions, involving two additional molecular parameters that are the quadrupolar

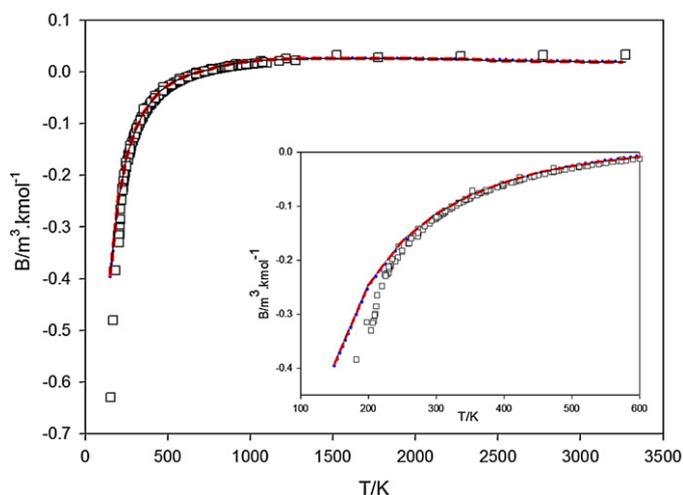
moment and the fraction of segments in the chain that contains the quadrupole. For instance, that supplementary term was added to the GC-PC-SAFT EoS to successfully predict the VLE of the homologous series CO<sub>2</sub>/*n*-alkane (up to tetratetracontane) [39], to the PCP-SAFT model to describe the surface tension of CO<sub>2</sub> [80] and to the soft-SAFT equation to predict the VLE of CO<sub>2</sub> and perfluoroalkane mixtures [81].

In this work, a detailed study about the importance of whether CO<sub>2</sub> should be considered as a self- and/or cross-associating molecule or not, while modeling the VLE of several CO<sub>2</sub> and *n*-alkanes, *n*-alcohols, *n*-acids and esters containing systems with the CPA EoS, is performed. CO<sub>2</sub> will be considered as inert (non-self- or cross-associating molecule), and as a self-associating molecule, both with the 2B and 4C association schemes. The CO<sub>2</sub> parameters for CPA were estimated using saturated liquid density and vapor pressure data from DIPPR correlations [82].

A very good description of CO<sub>2</sub> vapour pressure and liquid density is achieved, as seen in Table 2, considering CO<sub>2</sub> both as inert or as a self-associating molecule (2B and 4C).

It seems that the values for the three pure compound parameters of the physical part (SRK) are independent of considering association or not. If association is considered the results are also very similar when using both the 2B or 4C schemes. In addition, considering association or not is also irrelevant for the quality of the description of the CO<sub>2</sub> densities and vapor pressures. Consequently, the description of further properties was investigated aiming at selecting the best set of parameters and association scheme for CO<sub>2</sub>.

The prediction of second virial coefficient data can be used to screen among different sets of equivalent CPA parameters, as some sets that are capable of providing excellent correlations of vapor pressures and saturated liquid densities cannot correctly predict second virial coefficients at low temperatures, as stated by Kontogeorgis et al. [50]. However good and similar predictions for CO<sub>2</sub> second virial coefficients were obtained both considering CO<sub>2</sub> as an inert or as a self-associating molecule, described by the 2B and the 4C association schemes (Fig. 1). Considering association or not



**Fig. 1.** Prediction of CO<sub>2</sub> second virial coefficients with the parameter sets from Table 2 (□, DIPPR data; —, 4C set; ---, 2B set; ···, inert CO<sub>2</sub>).

**Table 3**  
CPA composition deviations for CO<sub>2</sub> + *n*-alkane VLE and  $k_{ij}$  values considering CO<sub>2</sub> with the 2B or the 4C association schemes.

CO <sub>2</sub> +	T/K	4C			2B		
		$k_{ij}$	AAD %		$k_{ij}$	AAD %	
			x	y		x	y
Pentane [83]	277.65	0.1123	0.6	1.0	0.1096	5.3	0.1
	311.04		0.6	1.0		1.4	0.2
	344.15		0.5	0.9		0.9	0.9
	377.59		0.4	0.8		3.4	0.1
Hexane [84]	313.15	0.0954	4.4	0.2	0.1245	4.4	1.0
	353.15		4.0	0.8		4.8	2.6
	393.15		2.5	2.5		3.4	0.7
Heptane [85]	310.65	0.0731	3.4	0.7	0.0817	3.4	0.7
	352.59		1.1	0.5		1.2	0.5
	394.26		4.1	0.8		4.0	4.0
Octane [86]	313.15	0.0999	2.7	0.2	0.1095	4.0	0.2
	328.15		3.9	0.3		2.2	0.3
	348.15		3.5	0.6		3.1	0.7
Nonane [87]	315.12	0.0999	2.2	0.1	0.0869	2.4	0.1
	344.53		1.8	0.4		3.5	0.4
	373.28		3.7	0.8		4.4	0.8
	418.82		3.7	0.4		4.2	0.1
Decane [88]	344.25	0.0895	1.4	0.2	0.0694	5.2	0.3
	377.55		2.9	0.3		26	0.3
Undecane [87]	314.98	0.0961	4.0	0.1	0.0993	3.7	0.1
	344.46		5.2	0.6		5.0	0.6
	373.13		2.3	0.8		2.2	0.8
	418.30		3.9	0.9		3.9	1.2
Tetradecane [89]	344.30	0.0957	0.8		0.0874	1.0	
Pentadecane [90]	313.15	0.0957	1.9		0.1026	0.5	
Hexadecane [90]	313.15	0.0920	2.1		0.0921	2.1	
Nonadecane [91]	313.15	0.0740	4.8		0.0756	5.0	
	333.15		2.9			2.8	
Eicosane [92]	323.15	0.0626	3.0		0.0506	8.8	
	373.20		8.0			4.8	
Heneicosane [91]	318.15	0.0466	5.8		0.0471	6.5	
	338.15		4.1			3.8	
Docosane [93]	348.15	0.0351	3.7		0.0341	4.0	
	373.15		5.2			4.5	
Tetracosane [94]	373.15	0.0299	3.1	0.6	0.0235	3.5	0.4
	573.15		10.8	0.4		21.4	0.2
Octacosane [92]	373.20	−0.0178	9.1		−0.0152	9.1	
	423.20		7.3			7.2	
Dotriacontane [94]	373.15	−0.0135	5.9		−0.023	4.6	
	573.15		10.7			24.0	
Hexatriacontane [92]	423.20	−0.1170	7.2		−0.1353	7.9	
Tetratetracontane [92]	423.20	−0.1400	9.1		−0.1600	9.1	

for the description of CO<sub>2</sub> thus has no impact on the description of the second virial coefficient. Therefore, in this work, the VLE calculations were performed using both approaches attempting at identifying the best approach to the description of CO<sub>2</sub>.

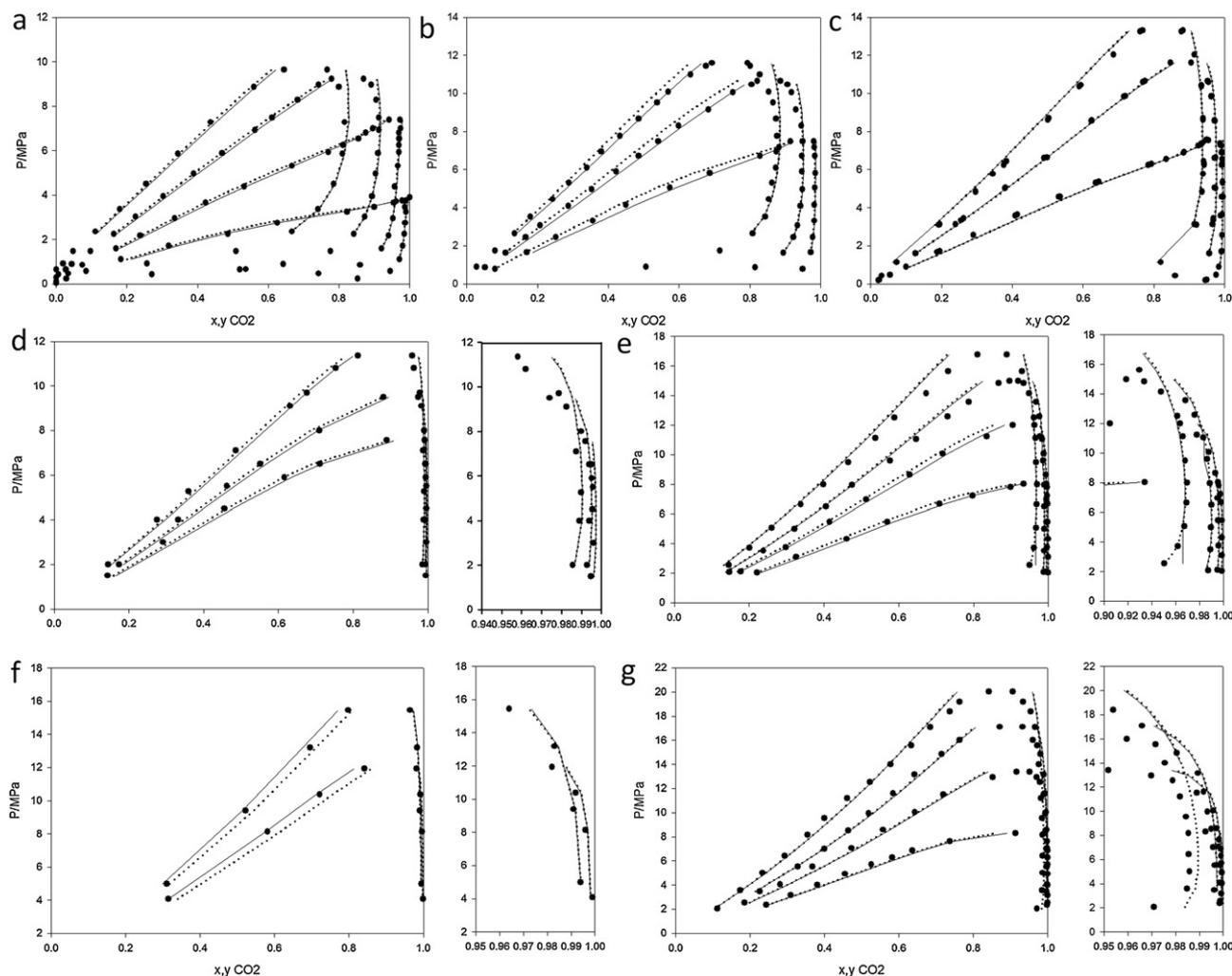
### 3.3. Description of the phase equilibria of CO<sub>2</sub> + Alkane systems

Experimental high pressure data are available, amongst others, for the systems: CO<sub>2</sub> + pentane [83], CO<sub>2</sub> + hexane [84], CO<sub>2</sub> + heptane [85], CO<sub>2</sub> + octane [86], CO<sub>2</sub> + nonane [87], CO<sub>2</sub> + decane [88], CO<sub>2</sub> + undecane [87], CO<sub>2</sub> + tetradecane [89], CO<sub>2</sub> + hexadecane [1,90], CO<sub>2</sub> + nonadecane [91], CO<sub>2</sub> + eicosane [1,92], CO<sub>2</sub> + heneicosane [91], CO<sub>2</sub> + docosane [93], CO<sub>2</sub> + tetracosane [1,94], CO<sub>2</sub> + octacosane [1,92], CO<sub>2</sub> + dotriacontane [1,94], CO<sub>2</sub> + hexatriacontane [92] and CO<sub>2</sub> + tetratetracontane [92].

For modeling the available experimental data, CO<sub>2</sub> was considered as an inert and as a self-associating molecule, with the 2B and the 4C association schemes.

Considering CO<sub>2</sub> as self-associating, the CPA EoS was able to provide a very good description of all the binary systems considered above (Table 3 and Figs. 2–4), with single and temperature independent binary interaction parameters. Moreover, the  $k_{ij}$  values have a constant value up to eicosane and follow a linear dependency with the *n*-alkane carbon number for higher alkanes, as shown in Fig. 5. The phase equilibria description and the  $k_{ij}$  values are very similar for the 4C and for the 2B association schemes.

Temperature independent, positive and almost constant binary interaction parameters illustrate the improvement of explicitly considering the specific polar interactions between CO<sub>2</sub> molecules in the model. In contrast, when using the CPA EoS and considering CO<sub>2</sub> as inert, higher binary interaction parameters are required



**Fig. 2.** CO<sub>2</sub>/*n*-alkane VLE. Experimental—symbols and CPA results—lines (dotted line for CO<sub>2</sub> 2B, solid line for CO<sub>2</sub> 4C). (a) CO<sub>2</sub>/pentane at 277.65, 311.04, 344.15 and 377.59 K; (b) CO<sub>2</sub>/hexane at 313.15, 353.15 and 393.15 K; (c) CO<sub>2</sub>/heptane at 310.65, 352.59 and 394.26 K; (d) CO<sub>2</sub>/octane at 313.15, 328.15 and 348.15 K; (e) CO<sub>2</sub>/nonane at 315.12, 344.53, 373.28 and 418.82 K; (f) CO<sub>2</sub>/decane at 344.25 and 377.55 K; (g) CO<sub>2</sub>/undecane at 314.98, 344.46, 373.13 and 418.3 K.

and their alkane chain length dependency is much less evident (Fig. 5).

These results are expected since Coutinho et al. [22] previously showed, when not taking into account those interactions, temperature dependent binary interaction parameters are necessary while applying the SRK EoS to model the phase equilibria of CO<sub>2</sub> + hydrocarbon systems. The SRK EoS binary interaction parameters,  $k_{ij}$ , have a quadratic temperature dependency with respect to  $1/T$  and a high scattering with respect to the *n*-alkane carbon number [22].

In comparison to previous works performed for these systems using association equations of state, the binary interaction parameters obtained in this work are quite similar to the ones reported by Gross and Sadowski [33], who applied the PC-SAFT model to this kind of systems (up to C<sub>7</sub>). However, Gross and Sadowski did not mention any kind of chain length dependency for the binary interaction parameters, as was obtained with the CPA EoS.

Tang and Gross [36] showed the improvement of the PCP-SAFT over the PC-SAFT model, while correlating CO<sub>2</sub> + *n*-alkane systems up to C<sub>10</sub>. Comparing these results with the ones obtained here with the CPA EoS, binary interaction parameters are slightly smaller with the PCP-SAFT than with the CPA EoS, but the mole fraction composition deviations are similar.

Our results are also comparable to the ones from Nguyen-Huynh et al. [38,39] and Le Thi et al. [37] that applied the group-

contribution SAFT with a  $k_{ij}$  correlation method based on London's theory and with a  $k_{ij}$  group contribution method, respectively, to model several systems of the series CO<sub>2</sub> + *n*-alkane.

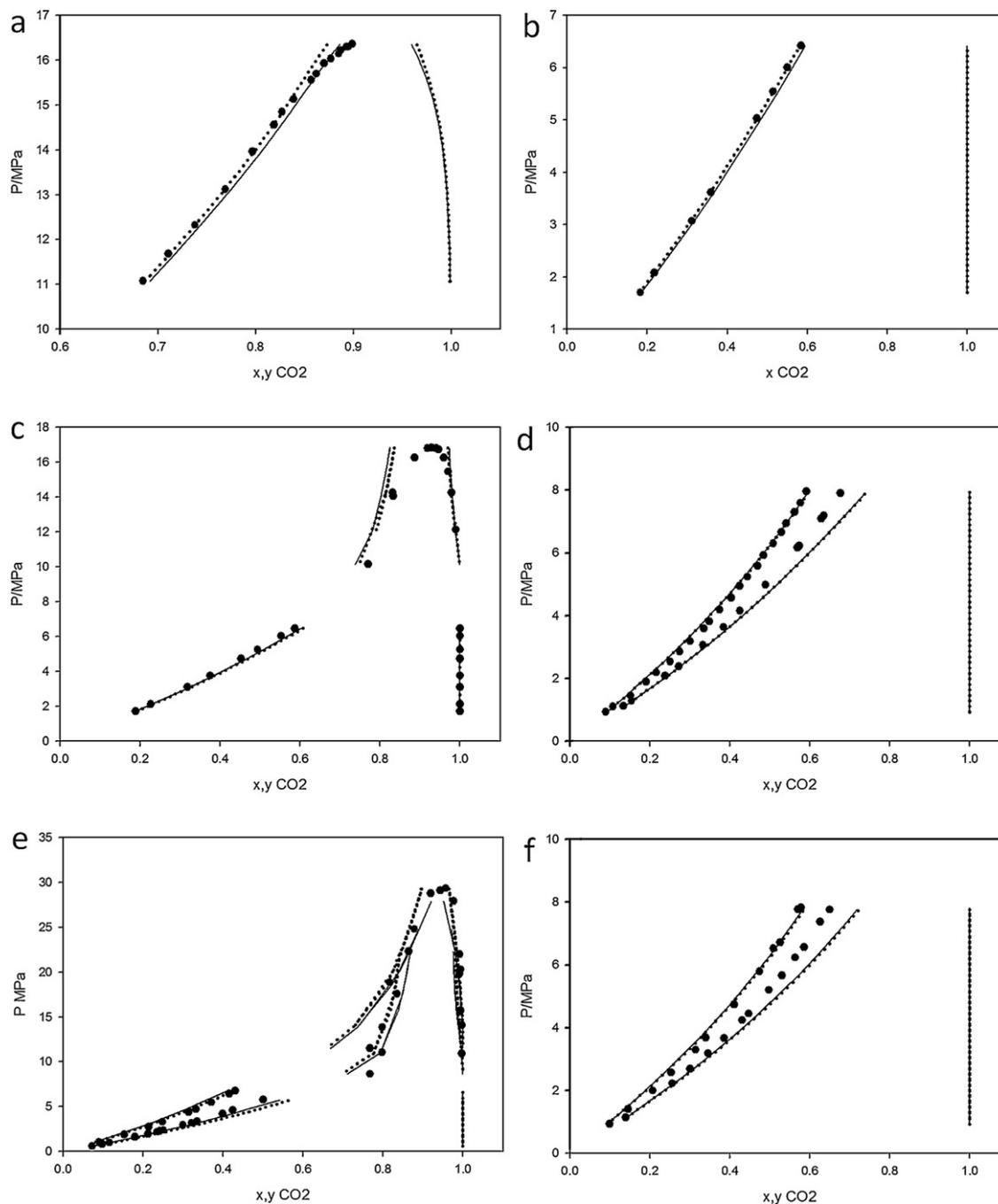
In addition, the fitted  $k_{ij}$  values were applied to successfully predict phase equilibria data at pressures of up to 30 MPa for the systems containing hexadecane, eicosane, tetracosane, octacosane and dotriacontane, as seen in Figs. 2–4.

These results show that the CPA EoS is able to provide an excellent description of CO<sub>2</sub> + *n*-alkane systems with less pure compound parameters than most association equations of state and with temperature independent and chain length dependent binary interaction parameters.

### 3.4. Description of the vapor–liquid equilibria of CO<sub>2</sub> + alcohol systems

Experimental high pressure VLE was selected for the systems: CO<sub>2</sub> + methanol [40], CO<sub>2</sub> + ethanol [40], CO<sub>2</sub> + propanol [95], CO<sub>2</sub> + butanol [42], CO<sub>2</sub> + pentanol [96], CO<sub>2</sub> + hexanol [97], CO<sub>2</sub> + octanol [40], CO<sub>2</sub> + nonanol [40], CO<sub>2</sub> + tetradecanol [98], CO<sub>2</sub> + hexadecanol [98] and CO<sub>2</sub> + octadecanol [98].

CO<sub>2</sub> was considered as inert, as inert but capable of solvation (following the procedure proposed by Folas et al. [61]) and as a self-associating molecule, with the 2B and the 4C association schemes. Temperature dependent and independent binary inter-



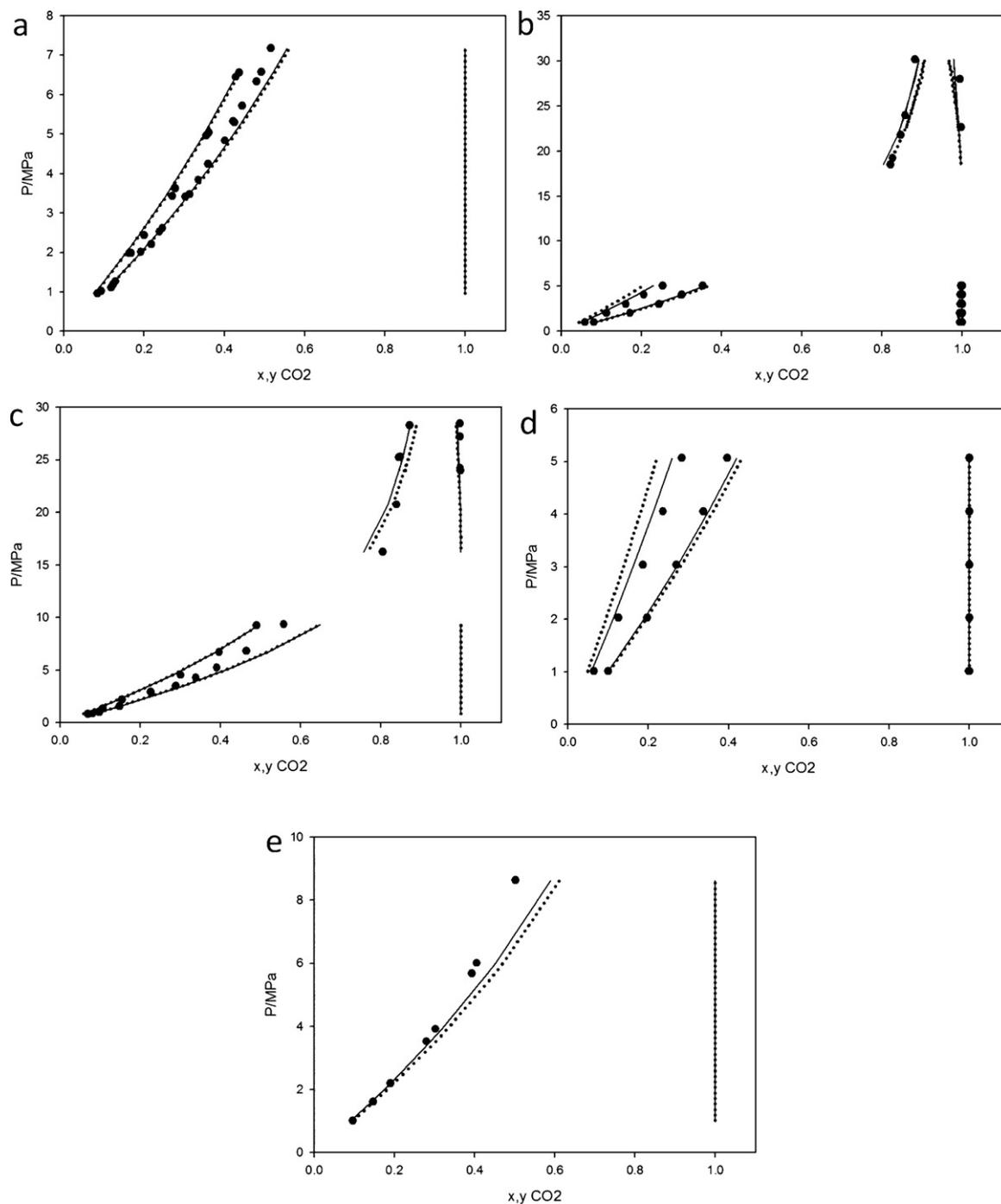
**Fig. 3.** CO<sub>2</sub>/*n*-alkane VLE. Experimental—symbols and CPA results—lines (dotted line for CO<sub>2</sub> 2B, solid line for CO<sub>2</sub> 4C). (a) CO<sub>2</sub>/tetradecane at 344.3 K; (b) CO<sub>2</sub>/pentadecane at 313.15 K; (c) CO<sub>2</sub>/hexadecane at 313.15 and 323.15 K; (d) CO<sub>2</sub>/nonadecane at 313.2 and 333.15 K; (e) CO<sub>2</sub>/eicosane at 320.60, 323.2, 348.30 and 373.2 K; (f) CO<sub>2</sub>/heneicosane at 318.15 and 338.15 K.

action parameters were estimated using the experimental VLE data.

Deviations in the VLE expressed in mol fractions and the corresponding binary interaction parameters are presented in Tables 4–6. It can be seen that there is no significant improvement in the VLE description by using temperature dependent  $k_{ij}$ 's. In addition, and as already observed for CO<sub>2</sub> + *n*-alkane systems, there is no major difference between the 2B and 4C association schemes for CO<sub>2</sub>, global average deviations of 12% for the liquid phase and of 1% for the vapour phase when using the 4C association scheme and of 11% for the liquid phase and of 1% for the vapour phase with the 2B scheme,

and temperature independent  $k_{ij}$ 's. Only a minor improvement in the liquid phase description is observed when using the 2B scheme.

Only for methanol, ethanol and propanol containing systems, considering CO<sub>2</sub> a cross-associating molecule improves the VLE representation, reducing the global average deviations in the liquid phase composition from about 10 to 6%. Particularly for the methanol containing system, negative binary interaction parameters are required to provide a good representation of the VLE, when not considering CO<sub>2</sub> as a self- and as a cross-associating molecule, suggesting that the existing interactions must explicitly be taken into account.



**Fig. 4.** CO<sub>2</sub>/*n*-alkane VLE. Experimental—symbols and CPA results—lines (dotted line for CO<sub>2</sub> 2B, solid line for CO<sub>2</sub> 4C). (a) CO<sub>2</sub>/docosane at 348.15 and 373.15 K; (b) CO<sub>2</sub>/tetracosane at 351.70, 373.15 and 573.15 K; (c) CO<sub>2</sub>/octacosane at 373.20, 423.20 and 357.00 K; (d) CO<sub>2</sub>/dotriacontane at 373.15 and 573.15 K; (e) CO<sub>2</sub>/hexatriacontane at 423.2 K.

For the heavier alcohols systems, considering CO<sub>2</sub> an inert compound provides similar results to the approach that considers the CO<sub>2</sub> as a self- and/or cross-associating molecule, even with temperature independent binary interaction parameters, with average deviations inferior to 14%.

The important role of association between CO<sub>2</sub> molecules, and between small alcohols and CO<sub>2</sub>, is further confirmed when considering CO<sub>2</sub> as a non-associating molecule but capable of solvating with polar compounds. The results for methanol and ethanol systems are improved when considering CO<sub>2</sub> as self-associating molecule (and thus cross-associating with alcohols). When consid-

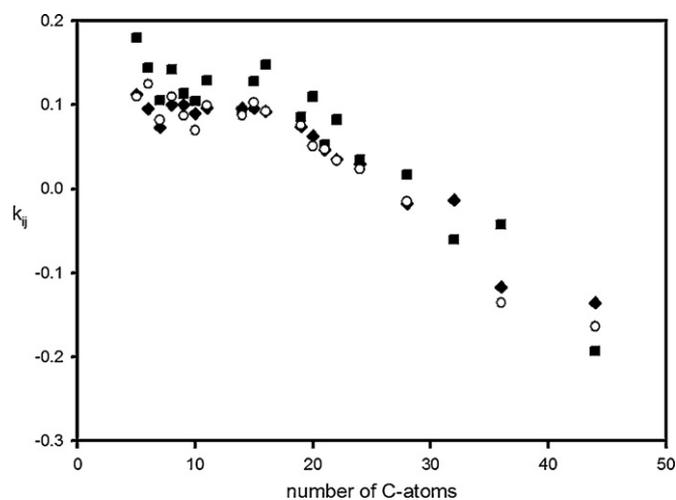
ering CO<sub>2</sub> as a non-associating molecule but capable of solvation, the global average deviations in the liquid phase composition are reduced to about 8% and negative binary interaction parameters are only needed at the lowest temperatures (Table 1 in the Supplementary Data). These results are in agreement with Kontogeorgis et al. [73] that observed an improvement in the description of phase equilibria when considering the solvation phenomena for the CO<sub>2</sub> + methanol system.

These conclusion implying the presence of strong interactions between small alcohols, namely methanol, ethanol and propanol, and CO<sub>2</sub> are in agreement with spectroscopic studies. Experimen-

**Table 4**CPA composition deviations in the VLE of CO<sub>2</sub> + *n*-alcohol systems with the 4C association scheme for CO<sub>2</sub>.

CO <sub>2</sub> +	T/K	T independent $k_{ij}$			T dependent $k_{ij}$		
		$k_{ij}$	AAD %		$k_{ij}$	AAD %	
			x	y		x	y
Methanol [28]	291.15	0.1059	33.1	0.2	0.0413	2.6	0.3
	298.16		12.9	0.4	0.1148	12.6	0.4
	303.18		11.3	0.3	0.1066	10.6	0.3
	308.15		8.9	0.3	0.0953	8.8	0.3
	313.4		8.9	0.2	0.1042	8.8	0.2
Ethanol [28]	291.15	0.1285	31.8	0.7	0.054	4.9	0.8
	298.17		24.2	0.6	0.0599	7.9	0.7
	308.11		7.0	6.0	0.1247	6.5	6.1
	313.14		10.6	0.5	0.1412	5.2	0.5
Propanol [95]	315	0.1421	5.4	0.1	0.1411	5.4	0.1
	326.6		6.7	0.2	0.1445	6.4	0.2
	337.2		4.1	0.2	0.143	4.0	0.2
Butanol [30]	293.15	0.1228	14.8	0.8	0.1465	11.5	1.1
	303.15		17.7	0.5	0.1396	17.7	0.5
	313.15		9.2	0.1	0.1265	8.8	0.1
	324.15		14.5	0.2	0.1208	14.3	0.2
Hexanol [97]	353.93	0.0693	19.3	4.1	0.0592	3.5	4.0
	397.78		7.9	2.0	0.0354	6.2	1.9
	403.39		9.5	4.5	0.0688	9.4	4.5
Octanol [28]	308.11	0.1298	6.7	0.1	0.1307	6.5	0.2
	318.91		7.9	0.1	0.1283	7.7	0.1
	328.15		9.2	0.9	0.1172	6.2	0.8
Nonanol [28]	308.14	0.1265	7.4	0.1	0.1422	6.7	0.2
	318.13		6.9	0.4	0.1167	6.5	0.4
	328.18		7.5	0.5	0.1115	6.4	0.4
Tetradecanol [98]	373.15	0.0681	10.0	0.3	0.0958	0.9	0.3
	423.15		18.1	0.7	0.0197	2.3	0.7
	473.15		8.5	0.5	0.0228	2.2	0.5
Hexadecanol [98]	373.15	0.0477	10.7	0.4	0.0768	3.0	0.4
	473.15		13.1	0.4	-0.0269	1.9	0.4
	573.15		13.2	0.7	-0.0689	1.3	0.8
Octadecanol [98]	373.15	0.0350	11.6	0.1	0.0677	2.0	0.1
	473.15		8.8	0.4	-0.0237	3.5	0.4
	573.15		16.4	0.4	-0.1161	2.8	0.3

tal spectroscopy observations put in evidence the presence of strongly attractive ethanol/methanol (OH group)-CO<sub>2</sub> interactions, due to highly stable complexes formed through the sp<sup>3</sup> O-donating atoms [99–102]. *Ab initio* calculations also support the notion of



**Fig. 5.**  $k_{ij}$  trend with the *n*-alkane carbon number (◆, 4C CO<sub>2</sub>; ○, 2B CO<sub>2</sub>; ■, inert CO<sub>2</sub>).

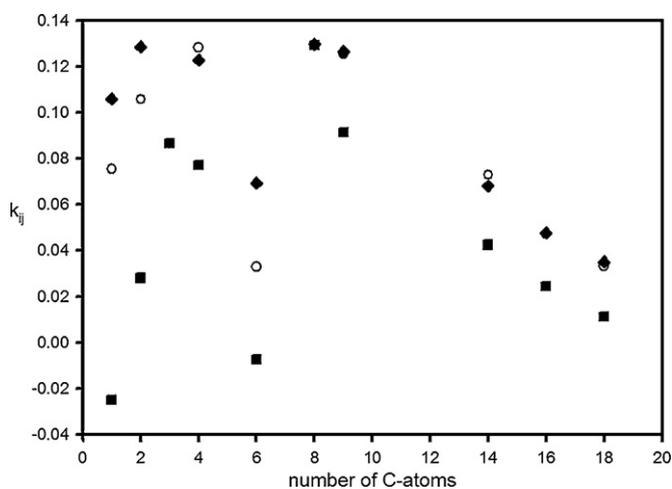
the formation of an electron donor-acceptor interaction, in which the carbon atom of CO<sub>2</sub> is the electron acceptor and the oxygen atom of the hydroxyl group is the electron donor [99]. In addition, the Kamlet-Taft solvatochromic parameters show that methanol, ethanol and propanol have strong “acid” characters. The Kamlet-Taft acid parameters are 0.93, 0.83 and 0.78 for these alcohols [103], which suggests the possibility of a strong solvation through an electron donor-acceptor interaction between these short alcohols and CO<sub>2</sub>.

As expected from the poor solvation observed between the heavier *n*-alcohols and CO<sub>2</sub>, the self-association character of alcohols dominates and considering CO<sub>2</sub> as inert with the CPA EoS provides equally good results with no need to use temperature dependent binary interaction parameters. The binary interaction parameters are plotted against the *n*-alcohol carbon number in Fig. 6. Similar results are obtained when using the 2B or the 4C association schemes. The interaction parameters seem to depend on the alcohol carbon number, rendering the model to be a predictive tool for alcohol + CO<sub>2</sub> systems. For inert CO<sub>2</sub> some scattering is observed as also occurred for the *n*-alkane containing systems.

A higher degree of scattering is observed for the binary interaction parameters with the alcohol than with the alkane carbon number. In order to analyse the scatter effect, two different chain length and temperature independent binary interaction parameters were applied to model alcohol + CO<sub>2</sub> VLE data, with the 2B association scheme. Characteristic results are obtained as pre-

**Table 5**  
CPA composition deviations in the VLE of CO<sub>2</sub> + *n*-alcohol systems with the 2B association scheme for CO<sub>2</sub>.

CO <sub>2</sub> +	T/K	T independent $k_{ij}$			T dependent $k_{ij}$		
		$k_{ij}$	AAD %		$k_{ij}$	AAD %	
			x	y		x	y
Methanol [28]	291.15	0.0754	21.7	0.3	0.0293	3.1	0.3
	298.16		9.4	0.5	0.0800	9.3	0.4
	303.18		10.1	0.3	0.0823	9.5	0.3
	308.15		9.6	0.3	0.0866	8.0	0.3
	313.4		14.7	0.3	0.1032	7.0	0.3
Ethanol [28]	291.15	0.1058	24	0.7	0.0491	4.4	0.8
	298.17		18.3	0.7	0.0630	7.3	0.7
	308.11		7.9	6.1	0.1150	5.8	6.1
	313.14		17.5	0.5	0.1421	5.2	0.5
Propanol [95]	315	0.1421	5.9	0.1	0.1363	5.6	0.1
	326.6		6.6	0.2	0.1402	5.6	0.1
	337.2		4.3	0.3	0.1404	4.1	0.3
Butanol [30]	293.15	0.1283	11.5	0.8	0.139	10.6	0.8
	303.15		17.4	0.5	0.1333	17.3	0.5
	313.15		8.9	0.1	0.1252	8.9	0.1
	324.15		16	0.2	0.1220	14.9	0.2
Hexanol [97]	353.93	0.0331	5.8	4.0	0.0497	3.9	4.1
	397.78		6.2	1.9	0.0355	6.0	1.9
	403.39		8.9	4.4	0.0496	8.7	4.4
Octanol [28]	308.11	0.1294	6.7	0.1	0.1385	6.0	0.2
	318.91		7.9	0.1	0.1176	6.9	0.1
	328.15		9.1	0.9	0.1066	6.3	0.9
Nonanol [28]	308.14	0.1254	7.4	0.1	0.1409	6.7	0.2
	318.13		6.8	0.4	0.1198	6.4	0.4
	328.18		7.4	0.5	0.121	6.7	0.5
Tetradecanol [98]	373.15	0.0729	7.9	0.3	0.0948	0.9	0.3
	423.15		12	0.7	0.0192	2.4	0.7
	473.15		9.3	0.5	0.0236	2.2	0.5
Hexadecanol [98]	373.15	0.0471	10.4	0.4	0.0730	2.9	0.4
	473.15		12.9	0.4	-0.0235	1.8	0.4
	573.15		13	0.7	-0.0652	1.3	0.8
Octadecanol [98]	373.15	0.0335	11.7	0.1	0.0661	2.0	0.1
	473.15		8.2	0.4	-0.0135	2.0	0.1
	573.15		16.1	0.4	-0.1142	2.8	0.5



**Fig. 6.**  $k_{ij}$  trend with the *n*-alcohol carbon number (◆, 4C CO<sub>2</sub>; ○, 2B CO<sub>2</sub>; ■, inert CO<sub>2</sub>).

sented in Table 1 in the Supplementary Data. Global average deviations of 16 and of 26% for the liquid phase compositions were obtained when using the binary interaction parameters of 0.1044 and of 0.07, respectively, showing the predictive ability of the CPA EoS.

In conclusion, the CPA EoS is able to correctly consider the CO<sub>2</sub> different behaviour when dealing with small or heavy *n*-alcohols. For small alcohols, the CO<sub>2</sub> self- and cross-association must be taken into account, and the simpler 2B association scheme can be used for CO<sub>2</sub> along with temperature independent binary interaction parameters. For alcohols above propanol, CO<sub>2</sub> can be treated as inert with temperature independent binary interaction parameters.

### 3.5. Description of the phase densities of CO<sub>2</sub> + Alcohol systems

As an additional part of our investigation for understanding which is the best association scheme for CO<sub>2</sub>, the two (2B) and the four (4C) site association schemes were evaluated for density calculations of CO<sub>2</sub> binary systems with methanol, ethanol, octanol and nonanol [40]. Satisfactory and similar results were obtained for all the approaches, leading to the same conclusions as from

**Table 6**  
CPA composition deviations in the VLE of CO<sub>2</sub> + *n*-alcohol systems considering CO<sub>2</sub> as non-associating.

CO <sub>2</sub> +	T/K	T independent $k_{ij}$			T dependent $k_{ij}$		
		$k_{ij}$	AAD %		$k_{ij}$	AAD %	
			x	y		x	y
Methanol [28]	291.15	-0.0249	11.2	0.4	-0.0553	11.2	0.5
	298.16		13.1	0.6	-0.0219	13.4	0.6
	303.18		12.5	0.6	-0.0203	11.0	0.5
	308.15		14.3	0.6	-0.0220	13.5	0.6
	313.4		17.4	0.6	0.0037	9.2	0.6
Ethanol [28]	291.15	0.0282	21.0	0.8	-0.0217	5.6	0.8
	298.17		18.2	0.8	0.0128	11.8	0.8
	308.11		7.9	6.2	0.0317	7.4	6.2
	313.14		14.0	0.7	0.0588	10.2	0.7
Propanol [95]	315	0.0866	9.4	0.2	0.0769	8.0	0.2
	326.6		8.6	0.3	0.0808	8.4	0.3
	337.2		6.3	0.4	0.0851	6.1	0.4
Butanol [30]	293.15	0.0771	16.5	0.8	0.0838	14.1	0.8
	303.15		21.2	0.5	0.0811	20.6	0.5
	313.15		11.3	0.1	0.0791	11.3	0.1
	324.15		17.5	0.3	0.0568	16.9	0.3
Hexanol [97]	353.93	-0.0071	4.9	4.5	-0.0070	4.9	4.5
	397.78		6.4	2.0	-0.0057	6.3	2.0
	403.39		9.3	4.4	0.0035	9.1	4.4
Octanol [28]	308.14	0.0987	6.4	0.1	0.0911	7.7	0.2
	318.13		10.1	0.2	0.0925	9.2	0.2
	328.18		12.7	1.1	0.0730	7.1	1.0
Nonanol [28]	308.14	0.0915	8.5	0.2	0.1039	6.8	0.2
	318.13		7.5	0.4	0.0876	7.3	0.4
	328.18		7.9	0.6	0.0775	7.3	0.5
Tetradecanol [98]	373.15	0.0424	9.8	0.3	0.0701	0.8	0.3
	423.15		9.7	0.7	-0.0023	2.6	0.7
	473.15		6.3	0.5	0.0065	2.4	0.5
Hexadecanol [98]	373.15	0.0247	9.5	0.4	0.0578	3.4	0.4
	473.15		11.8	0.4	-0.0372	1.8	0.3
	573.15		11.1	0.8	-0.0691	1.3	0.8
Octadecanol [98]	373.15	0.0114	10.7	0.1	0.0508	3.5	0.1
	473.15		7.2	0.4	-0.0324	3.3	0.4
	573.15		14.4	0.5	-0.1174	2.8	0.5

**Table 7**  
Deviations in the phase densities of CO<sub>2</sub> + *n*-alcohol systems obtained from CPA using T dependent  $k_{ij}$ 's.

CO <sub>2</sub> +	T/K	AAD %					
		4C		2B		Non-associating	
		$\rho^V$	$\rho^L$	$\rho^V$	$\rho^L$	$\rho^V$	$\rho^L$
Methanol [40]	291.15	26.6	5.4	26.4	5.9	26.5	6.6
	298.16	11.5	2.5	11.4	3.4	11.3	6.3
	303.18	14.5	3.3	14.4	3.6	14.3	6.0
	308.15	13.8	3.3	13.4	3.7	13.2	6.2
	313.40	14.0	2.9	14.4	3.1	14.8	5.2
Ethanol [40]	291.15	79.1	5.6	79.1	5.9	79.0	5.8
	298.17	22.5	4.2	22.7	4.1	22.5	5.0
	308.11	14.4	2.9	14.7	2.8	14.7	3.1
	313.14	13.8	3.7	13.3	3.3	12.9	3.0
Octanol [40]	308.11	124.0	1.0	127.2	1.1	129.3	1.3
	318.91	9.5	1.3	9.9	0.7	9.7	4.1
	328.15	4.1	0.4	4.9	0.5	3.0	2.4
Nonanol [40]	308.14	132.6	1.6	131.7	1.5	131.2	1.4
	318.13	3.4	0.7	3.4	0.6	3.0	0.7
	328.18	2.0	0.6	1.9	0.5	1.5	0.5

**Table 8**  
CPA composition deviations in the VLE of CO<sub>2</sub> + ester systems and respective binary interaction parameters.

CO <sub>2</sub> +	T/K	$k_{ij}$	$\beta_{ij}$	AAD %		$k_{ij}$	$\beta_{ij}$	AAD %		
				x	y			x	y	
Ethyl butanoate [104]	4C	308.45	0.1134	0.0136	1.2	0.1	0.1175	0.0103	1.9	0.1
		313.45	0.1165	0.0218	4.3	0.1			4.6	0.1
		318.55	0.1095	0.0147	3.4	0.2			4.7	0.1
	2B	308.45	0.1117	0.0142	1.7	0.1	0.1115	0.0122	2.2	0.1
		313.45	0.1128	0.0418	3.9	0.1			4.0	0.1
		318.55	0.1133	0.0293	3.2	0.2			3.2	0.2
	non-associating	308.45	0.1210	–	1.9	0.1	0.1292	–	2.8	0.1
		313.45	0.1243	–	3.5	0.1			4.4	0.1
		318.55	0.1249	–	3.3	0.2			3.5	0.2
Ethyl hexanoate [105]	4C	308.20	0.0180	0.1469	1.9	0.03	0.0151	0.0100	2.4	0.03
		318.20	0.0218	0.0597	1.6	0.04			2.4	0.04
		328.20	0.0272	0.2596	1.4	0.04			1.8	0.04
	2B	308.20	0.0195	0.1983	1.7	0.03	0.0164	0.0131	2.2	0.03
		318.20	0.0242	0.0854	1.5	0.04			2.5	0.04
		328.20	0.0226	0.1295	1.5	0.04			1.8	0.04
	non-associating	308.20	0.0257	–	2.0	0.02	0.0345	–	3.2	0.03
		318.20	0.0337	–	1.4	0.04			1.4	0.03
		328.20	0.0296	–	1.7	0.03			1.9	0.04
Ethyl decanoate [105]	4C	308.20	0.0306	0.1141	2.7	0.02	0.0402	0.1878	2.2	0.02
		318.20	0.0363	0.2412	2.2	0.02			2.8	0.02
		328.20	0.0224	0.03	2.8	0.01			3.4	0.01
	2B	308.20	0.0395	0.2868	2.2	0.02	0.0253	0.1742	4.9	0.02
		318.20	0.0339	0.4107	4.0	0.02			4.1	0.02
		328.20	0.0232	0.0035	2.8	0.01			3.0	0.01
	non-associating	308.20	0.0406	–	2.2	0.02	0.0374	–	2.7	0.02
		318.20	0.0403	–	2.2	0.02			2.3	0.02
		328.20	0.0394	–	2.5	0.01			2.4	0.01

the VLE studies (Table 7). It is also worthy to point out the large deviations obtained for the vapour densities of the octanol and nonanol containing systems at 308 K, that contrast with the very good results obtained for the higher temperatures, raising some questions about the quality of the experimental data at the lowest temperature.

### 3.6. Description of the vapor–liquid equilibria of CO<sub>2</sub> + ester systems

Experimental high pressure VLE are available, amongst others, for: CO<sub>2</sub> + methyl myristate [12], CO<sub>2</sub> + methyl palmitate [12], CO<sub>2</sub> + methyl oleate [12], CO<sub>2</sub> + ethyl butanoate [104], CO<sub>2</sub> + ethyl hexanoate [105] and CO<sub>2</sub> + ethyl decanoate [105].

For the shorter ester-containing systems, up to ethyl decanoate, a very good description of both vapor and liquid phases is obtained considering CO<sub>2</sub> as inert, inert but cross-associating or as self-associating with the 2B and the 4C schemes (Table 8). When esters are considered as non-associating compounds that can cross-associate, the procedure proposed by Folas et al. [61] was used.

There are no main differences in the results revealing that CO<sub>2</sub> self and cross-associations do not necessarily need to be taken into consideration by the CPA EoS. Both CO<sub>2</sub> and esters can be considered as inerts and it is only necessary to use single, small and positive binary interaction parameters to obtain a good description of the VLE of these systems at different temperatures.

Theoretical and spectroscopic studies have showed the existence of a specific Lewis acid–base interaction between CO<sub>2</sub> and the carboxyl oxygen of esters, where the geometry and strength of the interaction varies depending on the adjacent groups [102,106–107]. Danten et al. [101] also suggested that CO<sub>2</sub> complexes with alcohols, formed through sp<sup>3</sup> O-donating atoms, are more stable than complexes between CO<sub>2</sub> and esters, formed by sp<sup>2</sup>

O-donating atoms. This substantiates the fact that for CO<sub>2</sub> + short ester systems it is not necessary to explicitly take into account association with the CPA EoS, as is required for systems containing small alcohols.

Additionally, very good results were obtained with temperature independent binary interaction parameters, showing again the good predictive character of the CPA EoS.

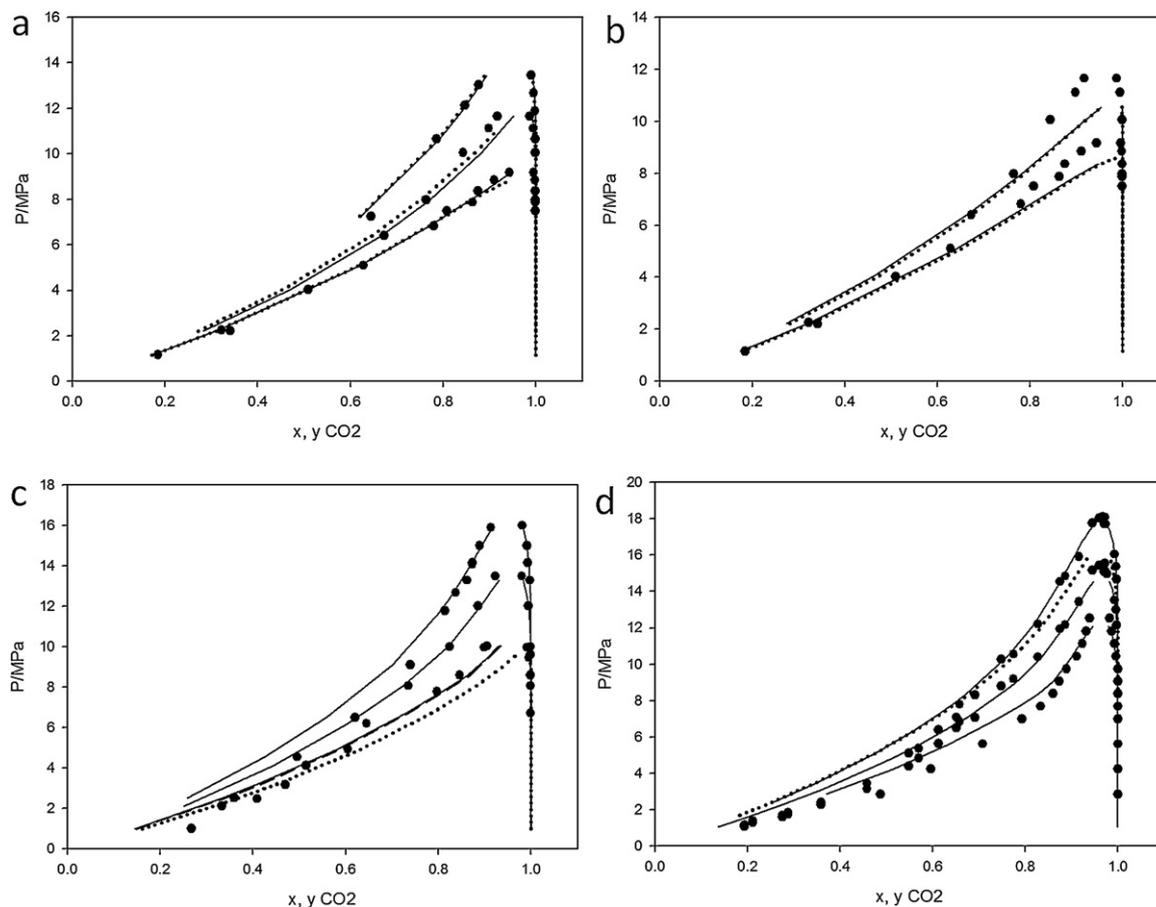
For systems of heavier esters the critical region cannot be described when considering CO<sub>2</sub> as inert and with parameters fitted to vapour pressure and liquid density data, as shown in Fig. 7. The same is observed for the 4C association scheme for CO<sub>2</sub>, where the  $\beta_{ij}$  value must be excessively high to describe the system accurately.

In order to enhance the typically poor description of the critical region provided by equations of state, the pure component critical properties were considered instead of the regressed CPA pure compound parameters. Using the CO<sub>2</sub> critical properties there is an improvement in the description of this region, and using the critical properties for both components the enhancement is even greater. However, this is observed for methyl myristate and methyl palmitate containing systems but not for the system with methyl oleate.

Overall, the results obtained for heavy esters containing systems may reveal the lower quality of the experimental VLE data, bearing in mind the good results obtained for small esters containing systems.

### 3.7. Description of the vapour–liquid equilibria of CO<sub>2</sub> + acid systems

Experimental high pressure VLE for CO<sub>2</sub> + propanoic acid, CO<sub>2</sub> + hexanoic acid [108], CO<sub>2</sub> + octanoic acid [109] and CO<sub>2</sub> + oleic acid [110] was chosen.



**Fig. 7.** CO<sub>2</sub>/ester VLE. Experimental—symbols and CPA results—lines. First two figures of CO<sub>2</sub>/methyl myristate at 313.15, 323.15 and 333.15 K ((a) full line using critical properties for CO<sub>2</sub> and dotted line using critical properties for both components, (b) full line 4C for CO<sub>2</sub> and dotted line considering CO<sub>2</sub> non-associating); (c) CO<sub>2</sub>/methyl palmitate at 313.15, 323.15 and 333.15 K, full line using critical properties for CO<sub>2</sub>, dotted line using critical properties for both components and small dotted line considering CO<sub>2</sub> non-associating; (d) CO<sub>2</sub>/methyl oleate at 313.15, 323.15 and 333.15 K, full line using critical properties for CO<sub>2</sub>, dashed line using critical properties for both components and dotted line considering CO<sub>2</sub> non-associating.

For the acids containing mixtures very good descriptions of the experimental data were obtained with all the approaches considered for the CO<sub>2</sub> molecule. Only a slight improvement is seen for the 2B scheme, but it is too small to consider that association is essential to be taken into consideration (Fig. 8; Table 9).

More detailed conclusions can only be reached when more and reliable experimental data becomes available for these systems. Even so, it can be concluded that the CPA EoS by considering self-association for acids is capable of correctly describe the VLE of these systems with positive binary interaction parameters.

**Table 9**

CPA liquid phase composition deviations in the VLE of CO<sub>2</sub> + *n*-acid systems and respective binary interaction parameter values.

CO <sub>2</sub> +		T/K	<i>k<sub>ij</sub></i>	AAD %
Propanoic acid [108]	4C	313.20	-0.0180	12.8
	2B	313.20	-0.0222	7.1
	non-associating	313.20	-0.0859	16.8
Hexanoic acid [108]	4C	308.15	0.0582	5.6
	2B	308.15	0.0466	5.2
	non-associating	308.15	0.0191	12.7
Octanoic acid [109]	4C	308.15	0.0751	6.7
	2B	308.15	0.0691	4.6
	non-associating	308.15	0.0402	12.1
Oleic acid [110]	4C	308.15	0.0716	6.7
	2B	308.15	0.0713	7.1
	non-associating	308.15	0.0343	8.0

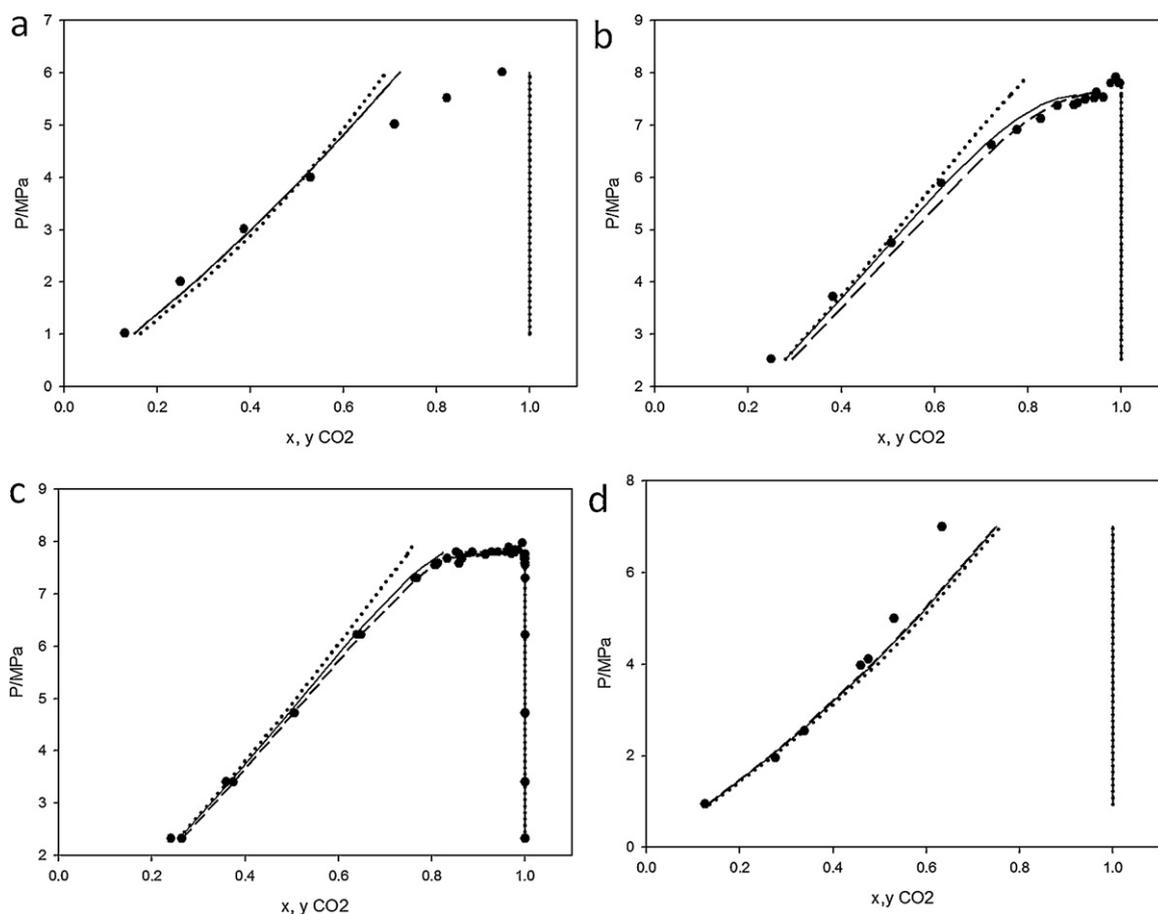


Fig. 8. CO<sub>2</sub>/n-acyl VLE: Experimental—symbols and CPA results—lines (full line 4C CO<sub>2</sub>; dashed line 2B CO<sub>2</sub>; dotted line inert CO<sub>2</sub>). (a) CO<sub>2</sub>/propanoic acid at 313.15 K; (b) CO<sub>2</sub>/hexanoic acid at 308.15 K; (c) CO<sub>2</sub>/octanoic acid at 308.15 K; (d) CO<sub>2</sub>/oleic acid at 308.15 K.

#### 4. Conclusions

In this work, the ability of the CPA EoS to describe high pressure VLE of several binary CO<sub>2</sub> containing systems, in a broad range of temperatures and pressures, was investigated. We here considered 19CO<sub>2</sub> + *n*-alkanes, 11CO<sub>2</sub> + *n*-alcohols, 6CO<sub>2</sub> + esters and 4CO<sub>2</sub> + *n*-acids systems.

A detailed study regarding the importance of considering CO<sub>2</sub> as a self and/or a cross-associating molecule was performed. The reported results indicate that CO<sub>2</sub> self or cross-association does not necessarily have to be considered here in order to describe pure CO<sub>2</sub> and the VLE of CO<sub>2</sub>/heavy alcohol, ester and acid systems. On the other hand, CO<sub>2</sub> self and cross-association is required to correctly describe the VLE of CO<sub>2</sub>/alkane and CO<sub>2</sub>/small alcohol systems.

Positive, small and temperature independent binary interaction parameters were sufficient for a correct description of high pressure VLE data of all the systems here considered.

Further advances on this field can be achieved as more solubility data becomes available as well as more data from spectroscopic and computational studies. In this regard, it is expected that molecular simulation calculations of non-bonded fractions may help to achieve a better understanding of CO<sub>2</sub> interactions.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.supflu.2010.09.036.

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