



## Modeling phase equilibria for acid gas mixtures using the CPA equation of state. Part II: Binary mixtures with CO<sub>2</sub>

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### ABSTRACT

In Part I of this series of articles, the study of H<sub>2</sub>S mixtures has been presented with CPA. In this study the phase behavior of CO<sub>2</sub> containing mixtures is modeled. Binary mixtures with water, alcohols, glycols and hydrocarbons are investigated. Both phase equilibria (vapor–liquid and liquid–liquid) and densities are considered for the mixtures involved. Different approaches for modeling pure CO<sub>2</sub> and mixtures are compared. CO<sub>2</sub> is modeled as non self-associating fluid, or as self-associating component having two, three and four association sites. Moreover, when mixtures of CO<sub>2</sub> with polar compounds (water, alcohols and glycols) are considered, the importance of cross-association is investigated. The cross-association is accounted for either via combining rules or using a cross-solvation energy obtained from experimental spectroscopic or calorimetric data or from *ab initio* calculations. In both cases two adjustable parameters are used when solvation is explicitly accounted for. The performance of CPA using the various modeling approaches for CO<sub>2</sub> and its interactions is presented and discussed, comparatively to various recent published investigations. It is shown that overall very good correlation is obtained for binary mixtures of CO<sub>2</sub> and water or alcohols when the solvation between CO<sub>2</sub> and the polar compound is explicitly accounted for, whereas the model is less satisfactory when CO<sub>2</sub> is treated as self-associating compound.

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### 1. Introduction – applications of thermodynamics of CO<sub>2</sub>-containing mixtures

The knowledge of the thermodynamics of mixtures with H<sub>2</sub>S or CO<sub>2</sub> is crucial for the rational design and operation of many processes. An extensive discussion has been presented in Part I of this series of articles [1]. In particular, phase equilibria of supercritical fluids including acid gases like CO<sub>2</sub> and H<sub>2</sub>S in mixtures with water, alcohols and glycols are of great importance in numerous processes in the oil and gas and chemical industries [2–4]. Water, typically found in petroleum reservoirs, or brine may cause reduction of the amount of gas available for mixing with hydrocarbons and this effect increases with pressure and the amount of the aqueous phase (while it decreases with salinity). Understanding of the phase behavior of gas (methane, CO<sub>2</sub>)/water (brine)/oil is, thus, of importance for the design of these processes.

Moreover, during the last years, there is a need to reduce atmospheric emissions of acid gases, especially CO<sub>2</sub>, because of environmental regulations. An option for the CO<sub>2</sub> disposal is to re-inject it into the underground zone of the reservoir. Such treatment

or transport requires a good knowledge of the phase behavior of mixtures with hydrocarbons, water or other fluids such as alkanols and glycols. In this direction the modeling of the phase behavior of CO<sub>2</sub> containing mixtures is of importance for the rational design of these oil related processes.

In the chemical industry, supercritical fluid extraction is a separation process which may in the future replace, to some extent, environmentally less friendly processes such as distillation and liquid–liquid extraction. One potential application is the recovery of alcohols especially ethanol from aqueous solutions using CO<sub>2</sub> [5]. Satisfactory pilot plant results have been obtained. Extraction or removal of other compounds from aqueous solutions e.g. phenols and other organic pollutants has been reported [5].

In the first part [1] of this series of articles, the CPA equation of state has been applied to binary and multicomponent systems containing H<sub>2</sub>S with other compounds, both non-polar (alkanes, CO<sub>2</sub>) and polar ones (water, methanol and glycols). The interactions of H<sub>2</sub>S with polar compounds (water, methanol and glycols) were modeled assuming presence or not of cross-association interactions. It was shown that, using interaction parameters obtained solely from binary systems, CPA can predict satisfactorily phase equilibria of multicomponent H<sub>2</sub>S-systems. The best results are obtained when the solvation between H<sub>2</sub>S and water or methanol is explicitly accounted for, especially when the cross-association

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**Table 1**  
Interaction energy values for the CO<sub>2</sub>–H<sub>2</sub>O cross association.

Interaction	Interaction energy	Technique	Reference
H <sub>2</sub> O...CO <sub>2</sub>	–25.7 kJ/mol	<i>Ab initio</i> calculations	[10]
O=C=O...HOH	–12.1 kJ/mol		
H <sub>2</sub> O...CO <sub>2</sub>	–10.9 kJ/mol	<i>Ab initio</i> calculations	[9]
O=C=O...HOH	–4.2 kJ/mol		
H <sub>2</sub> O...CO <sub>2</sub>	–9.2 to –11.7 kJ/mol	<i>Ab initio</i> calculations	[11]
O=C=O...HOH	–5.0 to –6.7 kJ/mol		
H <sub>2</sub> O...CO <sub>2</sub>	–14.0 ± 0.2 kJ/mol	Calculated from calorimetric experimental data	[12]

energy is taken from experimental spectroscopic studies. However, equally good results are obtained when a self-associating H<sub>2</sub>S molecule is assumed (using the 3B association scheme), when the cross-association energy, which characterizes cross-interactions with polar molecules, is taken from experimental spectroscopic studies.

As a follow-up of Part I (on H<sub>2</sub>S mixtures) [1], the purpose of this work is to present a comprehensive investigation of the performance of an association model, the CPA equation of state, to mixtures containing CO<sub>2</sub> and mostly polar compounds. The ultimate target is to conclude on the best approach for modeling CO<sub>2</sub>-containing multicomponent mixtures. The results for CO<sub>2</sub> binary mixtures are summarized in this work, while the results for multicomponent mixtures will be presented in the third part of this series of articles.

## 2. The nature of CO<sub>2</sub> and its interactions with polar chemicals – literature studies on thermodynamics of CO<sub>2</sub> containing mixtures

### 2.1. Interactions of CO<sub>2</sub> with polar chemicals

The understanding of CO<sub>2</sub> interactions with other organic molecules has been the subject of many experimental and theoretical studies, mainly due to the large variety of supercritical CO<sub>2</sub> applications (extractions, materials processing, reactions, etc.). It is well known that CO<sub>2</sub> can play either the role of proton acceptor forming hydrogen bonds or the role of electron acceptor or electron donor according to the nature of the organic molecule.

The increased solubility of alcohols in CO<sub>2</sub> compared with their solubility in other gases, such as light hydrocarbons or nitrogen, suggests increased association, which can be explained by strong specific interactions between CO<sub>2</sub> and alcohol molecules. Reilly et al. [6] studied the formation of carbon dioxide–methanol-*d* complexes using FT-IR spectroscopy. In methanol-*d*-CO<sub>2</sub> liquid mixtures there was no experimental indication for interaction between methanol's hydrogen (of the hydroxyl group) and CO<sub>2</sub> oxygen atoms. They concluded that all specific interactions between CO<sub>2</sub> and methanol molecules are of Lewis acid–base type. Such interactions are formed between the CO<sub>2</sub> carbon atom and the oxygen atom in methanol. According to the authors, one CO<sub>2</sub> molecule is more likely to accept an electron pair than donate one.

Lalanne et al. [7] performed IR experimental study of dilute ethanol-*d*-scCO<sub>2</sub> mixtures. Results were also analyzed using *ab initio* calculations. The IR study revealed that there is a strong attractive interaction between ethanol and CO<sub>2</sub>. *Ab initio* calculations revealed a relatively strong specific interaction between ethanol's oxygen atom and CO<sub>2</sub> carbon atom. The interaction energy of this complex was calculated to be around –2.96 kcal/mol. Moreover, Saharay and Balasubramanian [8] studied various ethanol–CO<sub>2</sub> mixtures using molecular dynamics. They observed relatively strong specific interactions between ethanol and CO<sub>2</sub> molecules. These interactions are of the two types: hydrogen bonding interactions (between ethanol's hydroxyl proton and CO<sub>2</sub> oxygen atoms) and Lewis electron donor–acceptor interactions

(interaction between ethanol's oxygen and CO<sub>2</sub> carbon atom). However, according to the authors, Lewis electron donor–acceptor interactions are much stronger than hydrogen bonding interactions. According to their results the dimerization energy is around –2.6 kcal/mol and –0.84 kcal/mol for the former and latter interaction, respectively. Lewis acid/base interactions shift CO<sub>2</sub> molecules from linearity to an O=C=O angle equal to 170°.

The nature of CO<sub>2</sub>–water interactions has been studied both from experimental and theoretical (mainly using *ab initio* calculations) point of view. Such interactions are due to dispersive and dipole–quadrupole forces. Recently, a Lewis acid–base type of interaction has been put in evidence [9]. In this, the carbon atom in CO<sub>2</sub> molecule acts as electron acceptor, while the oxygen atom in H<sub>2</sub>O molecule plays the role of an electron donor. On the other hand, hydrogen bonding interactions between the CO<sub>2</sub> oxygen atoms and the H<sub>2</sub>O protons can also be present, but are less stable than the electron donor–acceptor interactions [9,10]. Calculated and experimental values for the energy of CO<sub>2</sub>–water specific interactions are presented in Table 1.

### 2.2. Literature studies on thermodynamics of CO<sub>2</sub> containing mixtures

The importance of the thermodynamics of CO<sub>2</sub>-containing systems is clearly reflected in the large number of publications and models applied to different types of phase equilibria and a variety of CO<sub>2</sub> mixtures (with hydrocarbons, polar and associating compounds). As typically high pressures are involved, mostly equations of state have been used, either cubic equations of state or recent approaches e.g. those based on SAFT. This section briefly reviews both approaches illustrating the current status and applicability of the models.

#### 2.2.1. Cubic equations of state

Cubic EoS has been applied to both CO<sub>2</sub>–hydrocarbons and to CO<sub>2</sub>–polar mixtures. In the cases of mixtures with hydrocarbons only, the van der Waals one fluid mixing rules and classical combining rules are often used. Non-zero binary interaction parameters ( $k_{ij}$ ) are needed, of magnitude around 0.12–0.15 for CO<sub>2</sub>/alkanes (with SRK). Generalized correlations of interaction parameters with e.g. acentric factor and reduced temperature have been developed for specific EoS e.g. for a translated modified PR EoS by Kordas et al. [13], for PR by Trebble et al. [14] and for SRK by Moysan et al. [15]. It is noted that for cubic EoS the  $k_{ij}$  decreases with carbon number for CO<sub>2</sub>–alkanes (data available up to C<sub>44</sub>) and there is a U-type temperature dependency. The performance of cubic EoS for CO<sub>2</sub>–alkane mixtures depends on the  $k_{ij}$  values used. For example, PR with  $k_{ij}=0$  cannot predict the azeotropic behavior of CO<sub>2</sub>–ethane, while an excellent correlation is possible with a large positive value of  $k_{ij}$ . At low temperatures, higher  $k_{ij}$  values are needed and the performance of the model is worse. These results may indicate an importance of quadrupole effects, especially at low temperatures. At even lower temperatures and for some systems e.g. for CO<sub>2</sub>–decane, liquid–liquid equilibria are observed, which cannot be represented well with cubic equations of state using

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