Prediction of surface properties of binary, sulfur containing mixtures

Christian Bühl, Andreas Danzer, Sabine Enders[*]

KIT, Institute of Technical Thermodynamics and Refrigeration Engineering, Engler-Bunte-Ring 21, D-76131 Karlsruhe, Germany

ARTICLE INFO

ABSTRACT

This work aims to the prediction of the surface tensions of binary mixtures relevant to enhanced oil recovery or bio gas production, in the case, where no or only a very limited number of experimental data are available in the open literature, especially for mixtures, where sulfur-containing compounds are present. We focus our attention to mixtures made of $CO_2 + SO_2$ and $CO_2 + H_2S$. The predictions were performed with help of density gradient theory (DGT) combined with the perturbed chain statistical associating fluid theory (PC-SAFT) in order to model phase behavior and interfacial properties, simultaneously. The employed PC-SAFT-EOS is able to calculate the phase diagram close to experimental data taken from the literature. The influence parameter of the pure components, required in the DGT-approach, was fitted to the surface tension at one temperature. For the estimation of the influence parameter of the mixture the geometrical combining rule was applied. Additionally, density profiles and consequently, enrichments effects in the surface were calculated. Finally, polynomial expressions for the surface tension as function of the liquid composition and temperature are provided.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Recently [1—8], we have shown the ability of prediction of interfacial properties related to liquid—vapor equilibria (VLE) as well as liquid—liquid equilibria (LLE) using the density gradient theory (DGT) [9—11] in combination with a physical sound equation of state (EOS), like the perturbed chain statistical associating fluid theory equation of state (PC-SAFT EOS) [12], for polar and non-polar mixtures. The predicted surface tensions are mostly in excellent agreement with experimental data [1—3], if no water is present in the mixture. This paper concentrates on the prediction of surface tensions for mixtures, where no experimental data or a very limited number of data points are available in the open literature. This situation is true for mixtures with sulfur-containing compounds, for example SO_2 and H_2S. Both types of molecules are undesirable components of natural gases, but may be present up to relatively high percentages, making the gas sour. They can deactivate the catalyst in the catalytic cracking process and can cause the deposition of heavy organic molecules such as asphaltenes, which leads to corrosion in wells, pipelines and refining equipment. Caused by the toxicity and the corrosive properties of these substances, the measurements are very challenging. Additionally, for mixtures made of $CO_2 + SO_2$ and $CO_2 + H_2S$ low temperatures are required for establishing a VLE. The mixture $CO_2 + SO_2$ is very corrosive and due to this, very little experimental data related to the VLE [13—15] and only two data points related to the surface tension [16] are available. Caused by the toxicity of the system $H_2S + CO_2$ there are also a limited amount of VLE-data available [17]. On the other hand, these data are very important in the field of enhanced oil recovery or in the field of biogas upgrading, because sulfur-containing compounds are present in the system. As with CO_2, the need for greater natural gas production has increased the production of acid reservoirs, and removal of H_2S and SO_2 has become increasingly important. The procedures for gas sweetening require accurate knowledge of phase behavior and interfacial properties. Justified by the experimental problems, it would be desirable to have reliable information on the interfacial properties of these mixtures from a theoretical approach.

Thermodynamic models representing phase diagrams of these pure substances [18—42] or mixtures with CO_2 [21,23,25,34,36, 37,40] have already been proposed earlier, and SAFT-type models were recommended due to their physical background. Using SAFT-type models different approaches for the molecules of interest are possible. H_2S can be described as non-associating molecule [24,27,29,31,32,34,35,41], or as associating molecule [18,19,21, 25—30,34,38,39,42], where different types of association were discussed, or as dipolar molecules [37] or as dipolar and associating

* Corresponding author.
 E-mail address: Sabine.Enders@kit.edu (S. Enders).

substance [20,22,25]. The similar situation occurs for SO_2 [23,26,33,34,36,42].

In contrast to the phase behavior, the interfacial properties are studied very seldom. For the system $CO_2 + SO_2$, Fu et al. [23] performed calculations of the surface tension using density gradient theory in combination with PC-SAFT. However, they predict a liquid−liquid phase transition at low temperatures, which is not found experimentally. The predicted surface tension data were not compared to the experimental data from the literature [16]. Khosharay et al. [41] calculated the surface tension of $H_2S + H_2O$ using density gradient theory in combination with simplified PC-SAFT-EOS. They [41] were able to reproduce the surface tension in a good agreement with experimental data.

Obtaining knowledge on the interfacial properties is extremely important to improve the technical processes related to biogas production or enhanced oil recovery. Our goal in this contribution is to provide surface tension data for both mixtures useful in the process simulation software. To achieve this aim, the gradient theory is coupled with PC-SAFT-EOS. The model parameters were tested by comparison to available experimental data related to bulk-properties and for the $CO_2 + SO_2$ mixture to the two experimental surface tension data points [16]. In the light of this idea, we fit polynomial parameter to express the surface tensions as function of temperature and liquid composition. These polynomials can be incorporated in the process simulation software, like ASPEN.

2. Theory

The DGT [9–11] is an approach to describe the interfacial properties of a two-phase-system in equilibrium. In contrast to earlier theories, the DGT describes the interfacial properties of a system in equilibrium involving the thickness of the interface. The fundamental assumption of this theory is to consider the partial densities and its derivatives as independent variables [10]. Thus the density gradient theory is able to determine the interfacial properties of a binary system using the bulk properties and the surface tension of the respective components.

The PC-SAFT-EOS [12] for the Helmholtz Energy f is written as a sum of the ideal gas contribution f^{id}, the hard chain reference fluid contribution f^{hc}, the contribution of dispersive interactions f^{disp}, a contribution for the interactions of associating molecules f^{assoc} and the contribution of the interactions of polar molecules f^{polar} [43,44]:

$$f = f^{id} + f^{hc} + f^{disp} + f^{assoc} + f^{polar}. \quad (1)$$

The density gradient theory has been used for mixtures of hydrocarbons [1,11,45–50], polar compounds [2–8,51–53] and further mixtures including polymers [54–58]. The detailed equation can be found in literature [e.g. 1,2,48].

In the case of a non-associating substance the EOS requires three pure-component parameters: the segment diameter (σ), the interaction energy related to the dispersion interaction (ε), and the number of segments of the chain molecule (m). In the case of associating molecules it is necessary to add the bonding energy related to hydrogen bonding (ε^{AB}) and the association volume of the molecule (κ^{AB}). It is also necessary to define an appropriate association scheme. Further details about possible association models can be found in the paper of Huang and Radosz [59]. The parameters can be obtained by fitting to vapor pressure and liquid densities data of the pure substance. More details can be found in the original paper of Gross and Sadowski [12]. The polar term, f^{polar}, can be applied for molecules carry on a dipole momentum [44] or a quadrupole momentum [43] and does not require additional adjustable pure-component parameters.

The main goal of this paper is the description of mixtures of $CO_2 + SO_2$ as well as $CO_2 + H_2S$.

For the description of CO_2 exists two possibilities [3,12,43]. The two possibilities differ in the negligence of the quadrupole moment (CO_2-a in Table 1) [12] or the consideration (CO_2-b in Table 1) [3,43]. It could be recognized the improvement of the calculation results, if the quadrupole of CO_2 is included in the theoretical framework, especially in the critical region [3,43]. The improvement of the calculated liquid volumes leads to an improvement in the calculated surface tension in the critical region [3].

The correct model for H_2S in the SAFT framework is still under intense debate [18−30,34−39,41,42]. H_2S will posses polar and association interactions. Experimental data obtained by spectroscopic measurements of H_2S [61] indicate that H_2S forms dimers through hydrogen bonding. The simplest approach is the negligence of the self-association and the polar moments resulting in model H_2S-a [24] in Table 1. The model H_2S-a was used to calculate phase behavior of sour natural gas systems [35] as well as the surface properties of the system $H_2S + H_2O$ [41]. However, for the correlation of the phase behavior in the system $H_2S + H_2O$ a strongly temperature-depended k_{ij}-value (polynomial of with degree of three) was required. Ramos et al. [20,22] modeled H_2S by a four site association model as a dipolar hard sphere with an embedded dipole moment. Llovell et al. [33] suggested a model of H_2S with three associating sites in the Soft-SAFT approach: two for the sites of type H for the hydrogen atoms and one site of type E for the electronegativity of the sulfur. Aparicio-Martínez and Hall [18] studied the phase diagram of mixtures containing light alkanes and H_2S over a large temperature and pressure range and found similar correlative ability of the association models (2B, 3B and 4C according the nomenclature of Huang and Radosz [59]). Tang and Gross [25] have adopted two, three, and four association sites for H_2S and evaluated mixtures of H_2S with n-alkanes, branched alkanes, and cyclohexane. Additionally, they investigated also the impact of the dipole and the quadrupole moment. The result for the mixtures of all three parameterization was practically identically. The association volume κ^{AB} is generally strongly correlated to the association energy ε^{AB}. Therefore, the association volume was fixed and only the association energy was included in the parameter fitting procedure [25] (model H_2S-b in Table). Diamantonis and Economou [29] figured out that the derivative properties (i.e. isobaric heat capacities) with two and four associating sites were significantly less accurate then calculations using the one site model. Additionally, they [29] recognized that explicit account for association results in marginal improvement of the correlation of some of derivative properties over the nonassociating model. However, the incorporation of the association improves the saturated liquid density calculated with PC-SAFT-EOS [29] while higher deviations were observed for the vapor pressure. Diamantonis et al. [34] recommended the treatment of H_2S as non-associating molecule in the PC-SAFT framework (model H_2S-a in Table 1). The parameters (m, σ and ε/k) used in this work (H_2S-a and H_2S-b in Table 1) are very similar to the pure-component parameter provided by Diamantonis and Economou [29] and Diamantonis et al. [34]. Differences occur in the association energy and in the association volume due to the fact that both parameters were fitted to experimental data in contrast to the approach used by Tang and Gross [25], where the association volume were fixed. The model H_2S-b with the parameter in Table 1 was already successfully used for the calculation of the solubility in ionic liquids [38]. A model taking into account the association forces, but with slightly different pure-component parameters, was adopted for the investigation of the hydrate dissociation [19] or the binary phase equilibria in contact with n-alkanes or aromatics [21]. H_2S is a very interesting molecule to study the influence of the permanent