Application of GC-PC-SAFT EoS to organic sulfur compounds

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Organic sulfur compounds are commonly found as unwanted impurities in products of Fluid Catalytic Cracking (FCC) process. The design and optimization of relevant separation units for desulfurization require knowledge of involved mixtures, such as thermodynamic and phase equilibrium properties which are often determined by thermodynamic models. The reliability of thermodynamic models lies in the availability of accurate experimental data. However, due to the complexity of the systems of interest in industry, experimental measurements are time-consuming and costly. In order to overcome this difficulty, models with predictive features are needed, especially when few or even no experimental data exist in the literature.

Some predictive thermodynamic models have been developed in the last decades. They are mostly based on the Group-Contribution (GC) concept. We cite several examples here: UNIversal Functional-group Activity Coefficients (UNIFAC) [1] and its modified versions [2,3], Predictive Soave-Redlich-Kwong combined with UNIFAC (PSRK-UNIFAC) [4], Predictive 1978 Peng-Robinson EoS (PPR78) [5] and Group Contribution - Statistical Association Fluid Theory EoS (GC-SAFT) [6]. In these models, molecules are divided into pre-defined groups and characterized by a combination of group parameters.

In past years, the GC method proposed by Tamouza et al.[6] were combined with different versions of SAFT EoS to predict the phase equilibria of some organic series, such as n-alkanes, 1-alcohols [6,7], ketones, ethers, aldehydes [8] and amines [9], with satisfactory results. Considering the different types of molecular interactions (dispersion, association and polarity) within organic sulfur compounds, we have chosen the Perturbed – Chain (PC) SAFT EoS [10,11] combined with the dipolar term of Jog and Chapman (JC) [12,13] to model their phase equilibria properties. With the dipolar term, the improvement in the prediction of Vapor-Liquid Equilibria (VLE) of many binary systems was observed by some authors [14–16].

In this work, we apply Tamouza's GC method and make an analogy between organic oxygen compounds and sulfur compounds. The well established group parameters (alkyl) [6] are retrieved in this work. New group parameters of thiol (-SH) and sulfide (-S-) for GC-PC-SAFT-JC EoS are fitted on the vapor pressure and saturated liquid density data of pure compounds. According to the availability and reliability of experimental data, pure compound properties (vapor pressure, liquid density, enthalpy of vaporization etc.) of several thiols and sulfides will be modeled. The EoS will then be extended to binary systems containing sulfur compounds with hydrocarbons and alcohols in a predictive way: binary interaction parameters will be all set to zero. The predicted properties of binary systems will be compared with existing experimental data (VLE, excess enthalpy, excess volume etc.), as well as those obtained by one of the most widely used predictive thermodynamic models in industry: UNIFAC (Dortmund) [2].

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