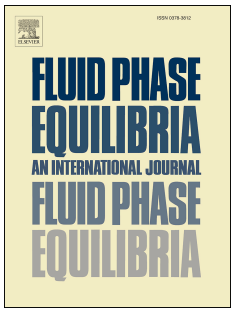

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Prediction of CO2 and H2S solubility and enthalpy of absorption in reacting N-methyldiethanolamine /water systems with ePC-SAFT

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ABSTRACT: The major goal of this work was the prediction of the solubility of CO_2 and H_2S in aqueous methyldiethanolamine (MDEA) reacting systems using the electrolyte equation of state ePC-SAFT with focus on MDEA weight fractions $w_{MDEA} > 0.3$ (related to the binary water/MDEA system). Predictions in this work mean that no parameters were adjusted to the experimental gas solubility data in aqueous MDEA solutions. In order to obtain improved prediction results compared to state-of-the-art literature models, binary interaction parameters k_{ij} between water-$MDEAH^+$, water-HCO_3^-, and water-HS^- were introduced; these k_{ij} values were fitted to osmotic-coefficient data measured in this work and from literature. This new possibility to access these k_{ij} parameters allowed improved predictions of CO_2 solubility, and the predictions were validated by new experimental data at $w_{MDEA} = 0.6$. Even more, the influence of the inert gas CH_4 on CO_2 solubility was predicted reasonably correct. Further, the solubility of H_2S in aqueous MDEA solutions was accurately predicted in the temperature range 298 K < T < 393 K at $w_{MDEA} = 0.32$ and 0.48. In the final part of this work enthalpy of absorption was predicted for 353 K < T < 393 K at $w_{MDEA} = 0.3$ for varying gas loadings. In summary, prediction results were satisfying considering the fact that ePC-SAFT parameters were fitted only to experimental data of pure fluids or binary systems.

1. Introduction

Global-warming-induced new challenges have arisen for the reduction of carbon dioxide (CO_2) in the atmosphere over the past decade[1, 2]. While the removal of CO_2 is the main goal of newly developed methods in process engineering, many exhaust gas streams in chemical engineering consist of more than just one hazardous gas. Hydrogen sulfide (H_2S) for example is a toxic gas, which is a byproduct during the ammonium and petroleum production[3]. Additionally, inert gases such as methane (CH_4) are known to interfere with the CO_2 absorption[4, 5]. A method well suited for CO_2 and H_2S absorption is the use of water-amine based systems[6]. These systems provide a wide variety of different applications in gas-absorption processes. Concerning the single amine systems, monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are commonly used for CO_2 and H_2S absorption processes. For the single amine absorption systems, MDEA is the most commonly used amine, due to its advantages in regard to its high capacity of CO_2/H_2S loading per mole amine and a low enthalpy of absorption[7]. An increased interest in MDEA-based absorption systems[8] leads to the challenge of developing models that are capable of predicting the vapor liquid equilibrium (VLE) of the water-amine-gas system in combination with the enthalpy of absorption to reduce development, plant and operating costs[1, 9, 10].

Literature proposes a number of models that are focused on modeling the ternary water-amine-gas systems based on experimental data for the temperature range of 313 to 413 K and amine weight fractions between 0.19 and 0.6 (related to the binary water/amine system)[11-14]. Most of the models proposed in literature are of empirical nature. They require a large number of experimental data and furthermore neglect speciation caused by reaction equilibrium and only focus on describing the VLE[15, 16]. In contrast, some models were successfully combined with reaction equilibria, e.g., electrolyte Non-Random Two Liquid (eNRTL)[17] and Universal Quasi-chemical model (UNIQUAC)[18]. Especially good modeling results of the VLE of water-amine-gas systems for a wide range of temperature, pressure and amine weight fractions were achieved with the equations of Pitzer[13, 19]. While such activity-coefficient models allow a good interpolation between experimental data, it is well-known that they require a lot of parameters that are fit to experimental data of the ternary amine-gas-water system. These parameters are system-specific and depend on temperature and composition. Thus, these parameters do not allow for de novo predictions [12, 17, 18]. A reduction of experimental effort can be achieved by the use of equations of state such as Cubic Plus Association equation of state (CPA)[20], Statistical Associating Fluid Theory (SAFT)[21], the SAFT-VR[22] or Perturbed-Chain SAFT (PC-SAFT)[23]. These models do not necessarily require