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Equilibrium in the H$_2$O-MEA-CO$_2$ system:
new data and modeling

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1. Introduction

Several studies have been carried out on the solubility of CO$_2$ in aqueous MEA solution. The experimental data of Jou et al., 1995 covers a wide range of temperatures, pressures and loadings, however it is available only for 30 mass % MEA. Of all the numerous work on MEA, only Mason and Dodge(1936) and Atadan (1954) measured CO$_2$ solubility in MEA at concentrations higher than 30mass %. These data are old and quite few. There is also a strong need for more data in the very low loading and pressure regions for modeling purposes. Thus an up-to-date VLE data set for the H$_2$O-MEA-CO$_2$ system, spanning a large concentration range, is clearly needed. All model implementations of H$_2$O-MEA-CO$_2$ system were based on data of not more than 30 mass % MEA concentration, except for Hessen (2010) who applied the r-e-NRTL model to predict experimental VLE results of 60mass % MEA up to 80°C. None of the existing models have used the solubility of N$_2$O in MEA which by utilizing the so-called N$_2$O analogy (originally proposed by Clarke, 1964) gives a measure of the physical solubility, or Henry’s law constant, of CO$_2$ in the aqueous MEA solution. Through the physical solubility of CO$_2$, the activity coefficient of CO$_2$ can be calculated. Hessen (2010) showed that existing models give CO$_2$ activity coefficients which are far from the N$_2$O analogy derived values.

The objectives of this work are to present a consistent VLE data set for MEA through experimental VLE measurements for 15, 30, 45 and 60 wt% MEA in the low and high CO$_2$ loading regions from 40 to 120°C, and to
use these data together with CO$_2$ solubility data based on the N$_2$O analogy, to provide a rigorous equilibrium model based on the extended UNIQUAC model framework (Thomsen and Rasmussen, 1999).

2. Equilibrium experiments and model parameters regression

VLE experiments for preloaded aqueous MEA solutions were conducted from 40 to 80°C using a low temperature/atmospheric vapor-liquid equilibrium apparatus while equilibrium total pressure data at 100 and 120°C for the systems were obtained using a high temperature apparatus. The data set used for regression of model parameters are; the experimental determined CO$_2$ partial pressures and total pressure measurements from this work as well as data for solubility of N$_2$O into 30wt% MEA from Hartono, 2009.

3. Results

The extended UNIQUAC model results for the N$_2$O (physical) solubility of 30 wt% MEA are shown in figure 1. The average absolute relative deviation (AARD) value of 2.7% indicates a very good representation of experimental data. Sample model results and experimental CO$_2$ partial pressures from this work as functions of loading and temperature are given in figure 2. The model correlates well CO$_2$ partial pressures over MEA solutions for 15, 30, 45 and 60 wt% MEA and adequately predicts pCO$_2$ down to 0.5wt% MEA. The AARD of 18.8% for the fit to own data shows that the model gives a good representation of the experimental data. Figure 3 shows the concentration dependency of CO$_2$ partial pressure for the MEA system. It is clear from the figure that CO$_2$ partial pressures over MEA solution are strongly dependent on the MEA concentration.

![Figure 1](image1.png)

**Figure 1:** (a) Solubility of N$_2$O in 30wt% MEA partialy loaded with CO$_2$. Experimental points, Hartono 2009; —, e-UNIQUAC this work. (b) Parity plot between experimental and model predicted N$_2$O solubility in 30wt% MEA.

![Figure 2](image2.png)

**Figure 2:** CO$_2$ partial pressure as function of loading for MEA. Experimental data; ○, 40°C; ●, 60°C; □, 80°C; △, 100°C; ◆, 120°C; —, e-UNIQUAC. (a) 30wt% MEA. (b) 60wt% MEA.
Figure 3: Concentration dependency of equilibrium CO₂ partial pressure of MEA at 40°C

4. Conclusions

New experimental data for vapor-liquid equilibrium of CO₂ in aqueous monoethanolamine solutions are presented for 15, 30, 45 and 60 mass % MEA and from 40 to 120°C. CO₂ partial pressures over loaded MEA solutions were measured using a low temperature equilibrium apparatus while total pressures were measured with a high temperature equilibrium apparatus. The extended UNIQUAC model framework was applied; model parameters were fitted to the new experimental VLE data and physical solubility data from the literature. The model gives a good representation of the experimental VLE data for all MEA concentrations with an average absolute relative deviation (AARD) of 18.8 % and also of the physical solubility data with an average absolute relative deviation (AARD) of 2.7 %. Further, the model predicts well liquid phase speciation results determined by NMR and experimental data for freezing point depression and excess enthalpy.

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