# Correlation and Prediction of Vapor-Liquid-Liquid Equilibrium using the e-NRTL model applied to the MAPA-DEEA-$CO_2$-Water System

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## Introduction

In gas processing, removing acids components, e.g. $CO_2$ and $H_2S$, from natural, refinery and synthesis gas streams is an important operation (Kundu and Bandyopadhyay, 2006). Gas sweetening operations have been widely used for many decades; however, these operations are becoming more and more needed with $CO_2$ recognized as a greenhouse gas and the need to have its emissions restricted. One of the main causes for $CO_2$ emissions is human activity, and most of the anthropogenic $CO_2$ comes from combustion of fossil fuels. Nonetheless, great efforts are being made to reduce its presence in the atmosphere resulting in several studies on $CO_2$ capture and storage (CCS) processes (Hessen *et al*., 2010).

Chemical processes are known to be the most reliable and economical for $CO_2$ removal. Aqueous alkanolamines have been extensively used for this purpose. Nevertheless, both capital costs (capex) and operational costs (opex) are still high when this technology is applied to industrial plants (Singh *et al*., 2009; Jenab *et al*., 2005).

In order to design or optimize CCS facilities, good thermodynamic models should be used, mainly, to describe the vapor liquid equilibrium, the solution speciation and the heat evolved when $CO_2$ is absorbed. Sundry works have been published in this field during the last decades; however, there are still many unsolved issues (Hessen *et al*., 2010). A wide range of equilibrium data for alkanolamines-water and alkanolamines-water-$CO_2$ systems can be found in the literature. A reliable depiction of these data is required to design and optimize the CCS facilities, allowing engineers to interpolate and extrapolate in the data (Austgen *et al*., 1989).

Correlations for vapor liquid equilibrium data require a reliable excess Gibbs energy model to predict activity coefficients. Chen and Evans (1986), Bollas *et al* (2008) and Hessen *et al* (2010), for instance, have shown the electrolyte NRTL model to represent the excess Gibbs energy of aqueous multi-component electrolyte systems. Austgen *et al*. (1989) show results for the electrolyte NRTL model for tertiary and quaternary systems.

This work presents a complex system composed by DEEA, MAPA, water and $CO_2$. A solution of DEEA 5M + MAPA 2M was loaded with $CO_2$ at different temperatures, namely, 40 ℃, 60 ℃ and 80 ℃. A screening apparatus, consisted of 1 liter glass absorber, a thermocouple, a LAUDA circulating heater (type E103), a Rosemount BINOS 100 IR $CO_2$-analyzer and three BRONKHHORST HI-TEC $N_2$/$CO_2$/$H_2S$ mass flow controllers (type E7100), was used to

perform these tests. LabVIEW was used for data acquisition. A synthetic gas mixture composed of $CO_2$ and $N_2$ was passed through the absorber (glass vessel) containing 750 ml of mixed absorbent. The inlet and outlet concentrations were compared, so the process would be automatically terminated when the concentration difference of $CO_2$ at the inlet and outlet of the absorber became 5 %, i.e., if 95 % of the inlet $CO_2$ concentration was achieved at the absorber outlet.

During the experiment, it was noted that the initial clear mixture at a certain point turned turved and by observing the walls of the reactor/absorber closely it could be noted droplets, like oil droplets dispersed in water, indicating a two phase region. By the end of the experiment a two liquid phase was formed. Further analysis revealed that MAPA concentration was higher in the lower phase and DEEA concentration was higher in the upper phase.

Vapor liquid equilibrium experiments were performed on the lower phase and data (pressure, temperature and composition) were stored. The electrolyte NRTL model presented by Hessen *et al*. (2010) will be used to calculate the activities coefficients of the species present in the solution. NRTL parameters were fit minimizing the absolute deviation over the summation of calculated and experimental pressure, temperature and composition over all data (binary, ternary and quaternary data), subject to (1) vapor liquid-liquid constraint, (2) chemical equilibrium constraint and (3) material balance constraints. Particle swarm optimization (PSO) was used on the MEA-H2O-CO2 system to estimate the NRTL parameters with good prediction. Therefore, the same method will be used on the quaternary system. The correlation should provide a reliable vapor liquid-liquid equilibrium fit within the experimental data.

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