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EQUILIBRIUM SOLUBILITY OF CO$_2$ IN ALKANOLAMINES

Muhammad Waseem Arshad$^a$, Philip Loldrup Fosbol$^a$, Nicolas von Solms$^a$, Hallvard Fjøsne Svendsen$^b$, Kaj Thomsen$^{a,**}$

$^a$Technical University of Denmark, Department of Chemical and Biochemical Engineering, Center for Energy Resources Engineering (CERE), Søltofts Plads Building 229, DK-2800 Kongens Lyngby, Denmark

$^b$Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, NO-7491 Trondheim, Norway

*Corresponding author’s e-mail address: kth@kt.dtu.dk

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Introduction

Post combustion carbon capture by absorption is one of the most common industrial technologies available today. Recent techno-economic studies indicate that the technology will remain competitive in the coming future. Alkanolamines are the most common chemical absorbents used for capturing CO$_2$ from the flue gas streams. Aqueous solutions of monoethanolamine (MEA), a primary alkanolamine, have been extensively studied for this purpose due to fast reaction rate, low solvent cost, ease of reclamation and relatively low solubility of hydrocarbons in the solutions. The disadvantages are high heat of absorption due to formation of stable carbamates leading to high energy consumption for solvent regeneration in the desorber, formation of degradation products, solvent losses due to high vapor pressure, relatively high corrosiveness and the limit of loading capacity of up to 0.5 mol CO$_2$/ mol amine [1]. On the other hand, aqueous solutions of N,N-diethylethanolamine (DEEA), a tertiary alkanolamine, have high loading capacity (1.0 mol CO$_2$/ mol amine) [2] and low heat of absorption due to formation of carbonates leading to low desorption energy. The major disadvantage of DEEA is the slow rate of reaction. However, DEEA can be blended with a suitable promoter to get reasonably fast reaction rate along with other favorable properties required for the cost effective CO$_2$ capture.

Experimental data on the equilibrium solubility of CO$_2$ in aqueous alkanolamine solutions are necessary for the design of unit operation in the carbon capture process. Equilibrium cells are generally used for the measurement of vapor-liquid equilibrium (VLE) of CO$_2$ over aqueous amine solutions [3-7]. Extensive CO$_2$ solubility data are available in the literature for various
amine systems measured with different equilibrium cells. This work exhibits experimental measurement of solubility of CO₂ in aqueous solutions of MEA and DEEA using a calorimeter. Calorimeters are generally used for the measurements of heat of absorption. But in the present work, besides heat of absorption data which was presented earlier [2], VLE of CO₂ over aqueous MEA and DEEA solutions were measured. To validate the method, the measured CO₂ solubility data were compared with the data available in the literature obtained from different vapor-liquid equilibrium cells. The method has an advantage of measuring both heat of absorption and CO₂ equilibrium solubility over aqueous amine solutions at the same time.

**Experimental**

The vapor liquid equilibrium of CO₂ in aqueous solutions of MEA and DEEA was conducted in a reaction calorimeter (model CPA 122 from ChemiSens AB, Sweden). The equipment was previously described by Kim and Svendsen [1]. The 2-L mechanically agitated reactor is attached to the CO₂ storage cylinders through a mass flow controller, a vacuum pump, feed solution bottle and data acquisition unit. Sample solution was fed to the reactor and CO₂ was injected to the reactor in several small steps. The experiments were conducted in an isothermal mode while the total pressure inside the vessel varied from the amine plus water vapor pressure before the first loading of CO₂ at the start of experiment to a maximum total pressure (amine + water vapor + CO₂) of ~ 6 bars during the last loading. The system continuously logged all the necessary parameters (reactor temperature and pressure, CO₂ storage cylinders pressure etc.) as a function of time. The CO₂ added in each feeding interval was calculated using the Peng-Robinson equation of state. The measurements were performed at temperature ranging from 40 to 120°C.

The solubility of CO₂ in 30 mass % MEA solutions were measured and presented in Figure 1 and Figure 2 respectively for 40 and 120°C. The measured data in this work (using calorimeter) are in good agreement with the literature data [3-7] obtained from different vapor-liquid equilibrium cells. Similarly, the equilibrium solubility of CO₂ with 5M DEEA was also measured at temperature ranging from 40 to 120°C and compared with the data available in the literature.

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Figure 1: Equilibrium solubility of CO₂ in 30% MEA at 40°C from this work and data available in literature.

Figure 2: Equilibrium solubility of CO₂ in 30% MEA at 120°C from this work and data available in literature.
References