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Equilibrium Solubility of CO_2 in Alkanolamines

Muhammad Waseem Arshad[a], Philip Loldrup Fosbøl[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*

Abstract

Equilibrium solubility of CO_2 were measured in aqueous solutions of Monoethanolamine (MEA) and *N,N*-diethylethanolamine (DEEA). Equilibrium cells are generally used for these measurements. In this study, the equilibrium data were measured from the calorimetry. For this purpose a reaction calorimeter (model CPA 122 from ChemiSens AB, Sweden) was used. The advantage of this method is being the measurement of both heats of absorption and equilibrium solubility data of CO_2 at the same time. The measurements were performed for 30 mass % MEA and 5M DEEA solutions as a function of CO_2 loading at three different temperatures 40, 80 and 120°C. The measured 30 mass % MEA and 5M DEEA data were compared with the literature data obtained from different equilibrium cells which validated the use of calorimeters for equilibrium solubility measurements.

* Corresponding author. Tel.: +45 4525 2860; fax: +45 4588 2258.
  E-mail address: kth@kt.dtu.dk

1. Introduction

Post combustion carbon capture by absorption is one of the most feasible industrial technologies available today. Various 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 carbamate 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.

The experimental data of equilibrium solubility of CO_2 in aqueous alkanolamine solutions are necessary for the design of unit operations in the carbon capture process. Equilibrium cells are generally used for the measurement of vapor-liquid equilibrium (VLE) of CO_2 with aqueous amine solutions [3-7]. Extensive CO_2 solubility data are available in the literature for various amine systems measured with different equilibrium cells by using either static or circulation method [8]. In the static method, a known amount of amine solution to be tested is taken in the equilibrium cell, CO_2 is injected and the system is allowed to reach the equilibrium. When the equilibrium is established, equilibrium pressure is recorded and the two phases (liquid and gas phases) are analyzed for different components of the system. In the circulation method, the amine solution is taken in the cell followed by the injection of nitrogen and the system in equilibrated at a preset temperature. The equilibrium pressure is recorded and CO_2 is injected to the equilibrium cell. Then the vapor phase is circulated with the help of a circulating pump and the gas is bubbled through the liquid phase. When the equilibrium is achieved, the total pressure of the system is recorded and CO_2 partial pressure is calculated from the difference between the total pressure and the equilibrium pressure before introducing any CO_2 in the system [8].

This work presents experimental measurement of VLE of CO_2 in aqueous solutions of MEA and DEEA using a calorimeter. Calorimeters are generally used for the measurement of heat of absorption. Our previous work with the calorimeter presented the enthalpy of CO_2 absorption in amine solutions [2]. In the present work, equilibrium measurements of CO_2 solubility with aqueous MEA and DEEA solutions are presented. To validate the method, the measured CO_2 solubility data were compared with the data available in the literature obtained from different equilibrium cells. The method has an advantage of measuring both heat of absorption and CO_2 equilibrium solubility over aqueous amine solutions at the same time.

2. Experimental Section

2.1. Materials

MEA (purity ≥ 99%) and DEEA (purity ≥ 99%) were supplied by Sigma-Aldrich and CO_2 (purity ≥ 99.99%) was supplied by AGA. All chemicals were used as received with no further purification. The amine solutions were prepared from deionized water using analytical balance.

2.2. Working Procedure

A schematic diagram of the experimental setup is given in Figure 1. The equipment was previously described by Kim and Svendsen [1]. The operating procedure is similar to that of heat of absorption measurements. It consists of a jacketed reaction calorimeter (reactor volume of 2000 cm^3) model CPA 122 from ChemiSens AB, Sweden, attached to two CO_2 storage cylinders through a mass flow controller, a vacuum pump, feed solution bottle and data acquisition unit (VRC200).

The reactor was evacuated first to remove any inert gas and the sample solution was fed to the reactor at a preset temperature. When the system attained equilibrium, small amount of CO_2 was injected to the reactor from CO_2 storage cylinders by monitoring their pressure difference and the system was allowed to reach a new equilibrium. The thermostat medium (reactor jacket) added or removed heat from the system to keep the isothermal conditions in the reactor. The system took about 60-90 min to reach the new equilibrium and the reactor was fed again with CO_2 for another cycle. The reactor was continuously fed with CO_2 until the amine solution is fully saturated. All the operating parameters were logged against time and equilibrium pressures were noted down. A sample of logged data against time for one complete experiment is shown in Figure 2. The measurements were made at 40, 80 and 120°C. The CO_2 added in each feeding interval was calculated using the Peng-Robinson equation of state. The equilibrium partial pressures of CO_2 were obtained from the difference between the total pressure and the equilibrium pressure before injecting CO_2 into the reactor. The details of experimental setup and working procedure can be found elsewhere [1,2].
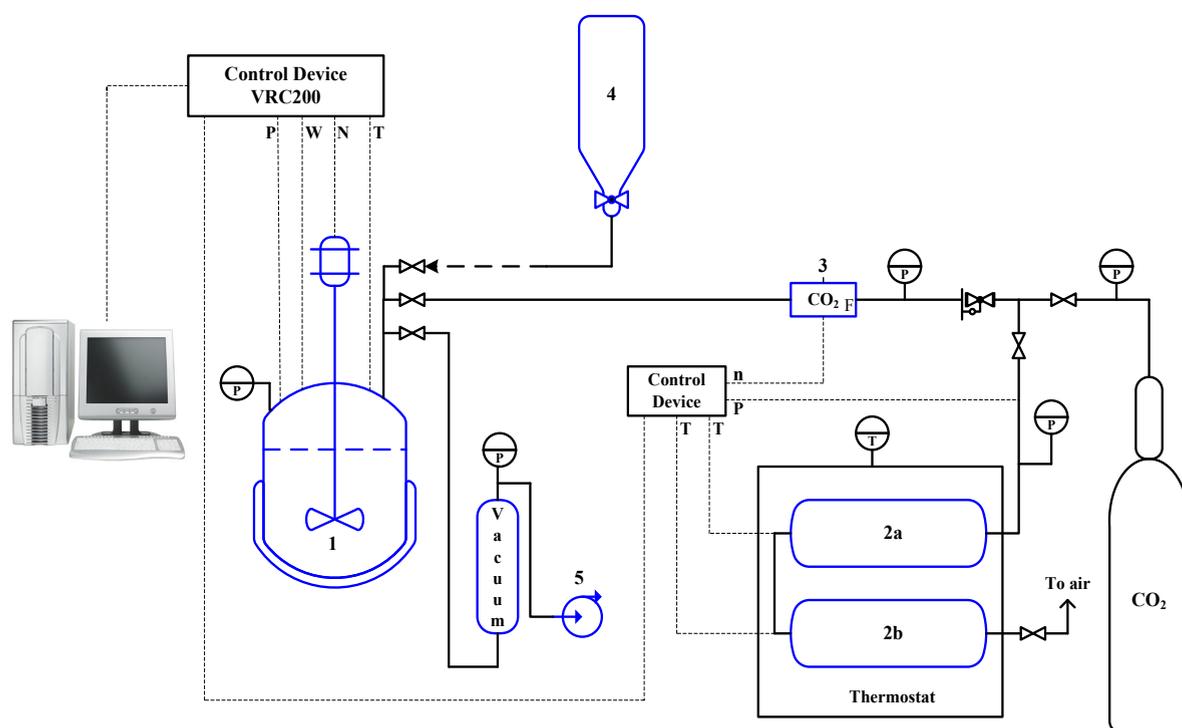

Figure 1: Experimental setup: 1 - reaction calorimeter; 2a, 2b - CO_2 storage cylinders; 3 - CO_2 mass flow controller; 4 - amine solution feed bottle; 5 - vacuum pump.
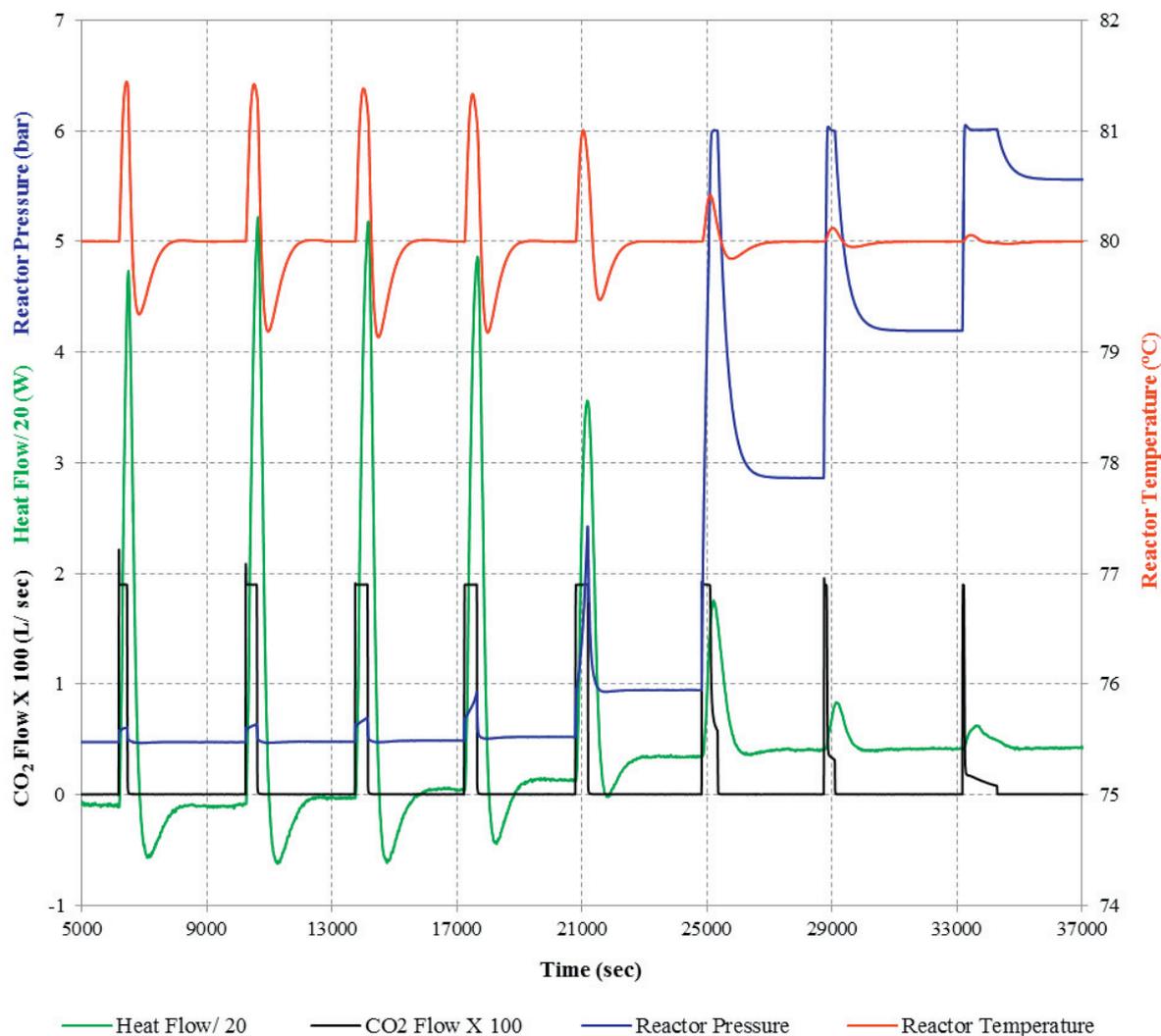
Figure 2: An example of different parameters (reactor temperature and pressure, heat flow and CO_2 flow in the reactor) recorded as function of time for one complete experiment. In order to plot the logged data in one axis, heat flow values were divided by 20 and CO_2 flow values were multiplied by 100.

3. Results and Discussion

The equilibrium solubility data of CO_2 in 30 mass% MEA solutions were measured at 40, 80 and 120°C. The measured data are presented graphically in Figures 3, Figure 4 and Figure 5 together with the literature data measured from different equilibrium cells by using the static and/ or the circulation method. It can be seen that the measured equilibrium CO_2 partial pressure data are in good agreement with the literature data at all the temperatures which validates the use of calorimeter for CO_2 solubility measurements.
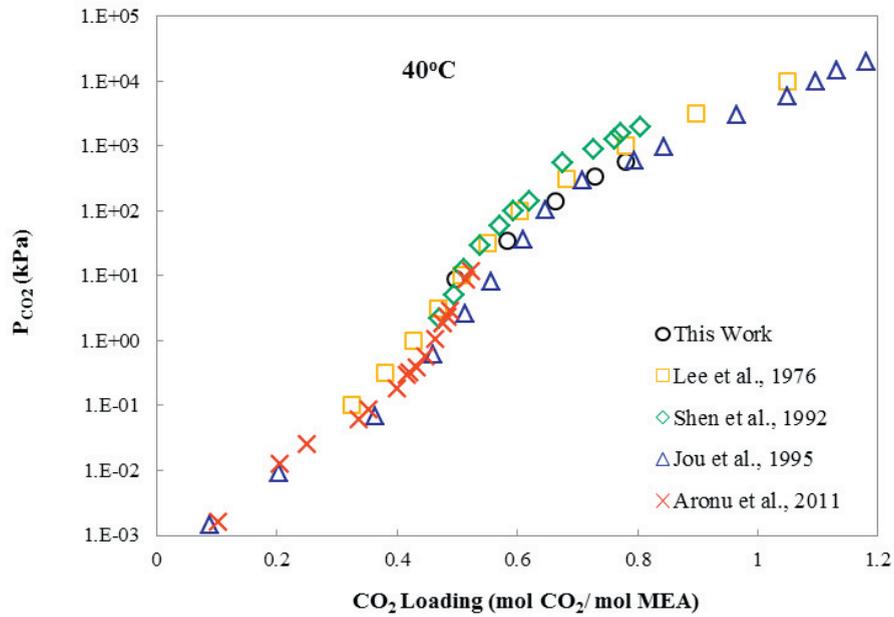
Figure 3: Equilibrium solubility of CO_2 in 30% MEA at 40°C from this work and the data available in literature.
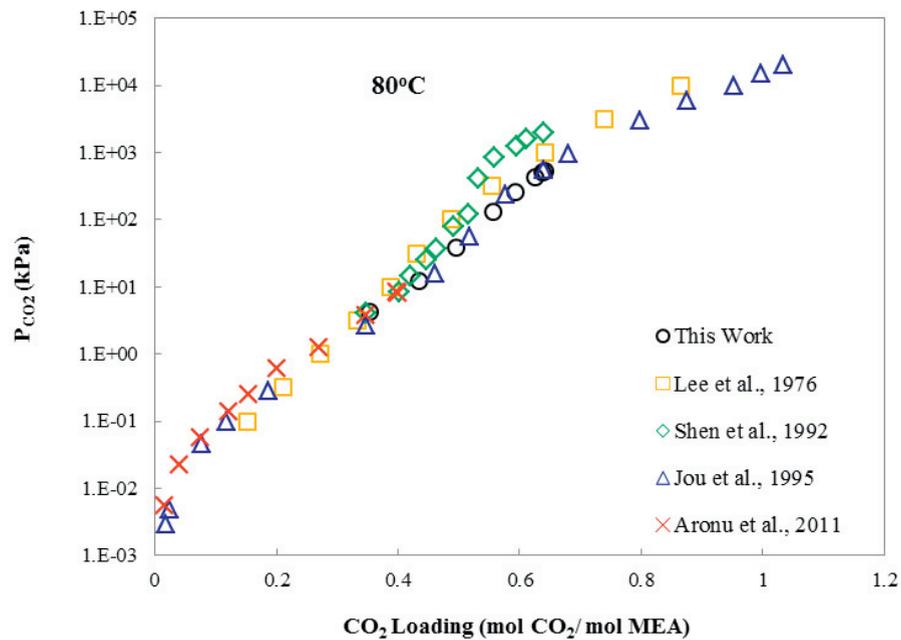

Figure 4: Equilibrium solubility of CO_2 in 30% MEA at 80°C from this work and the data available in literature.
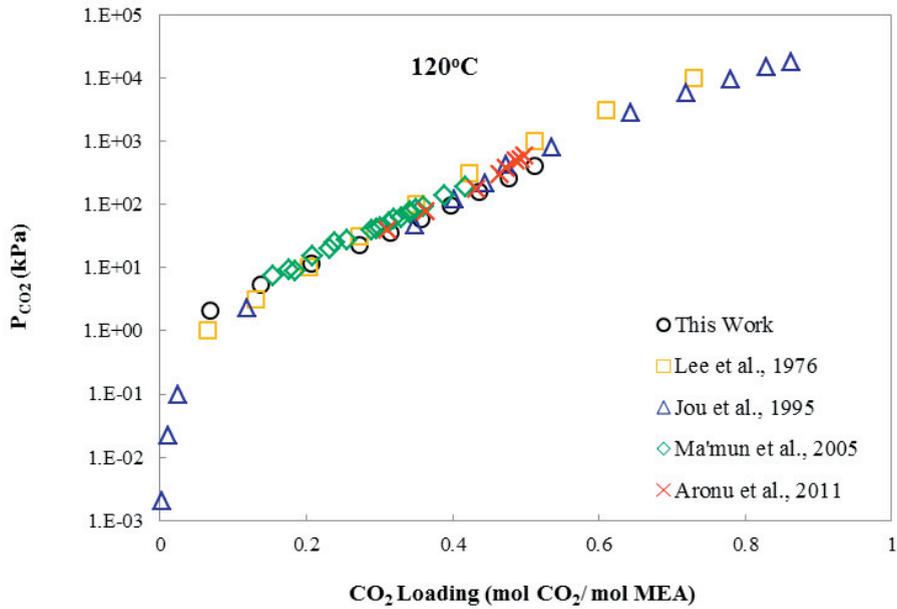
Figure 5: Equilibrium solubility of CO_2 in 30% MEA at 120°C from this work and the data available in literature.

The solubility data of CO_2 were also measured in 5M DEEA at 40, 80 and 120°C. The results are given in Figure 6. The measured total pressure data from this work are also compared with the total pressure data from Monteiro et al. [9] which shows a very good agreement between the two sets of data.
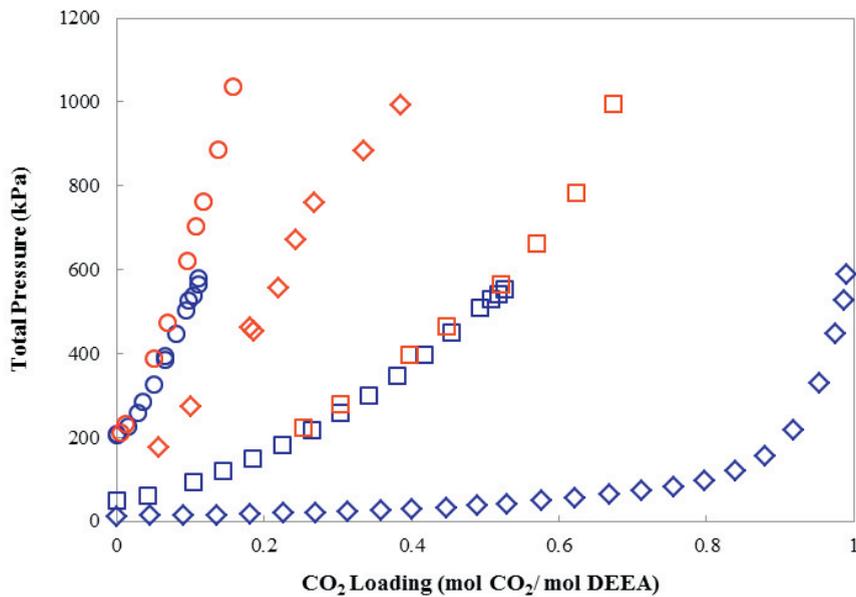

Figure 6: Equilibrium solubility of CO_2 in 5M DEEA at 40, 80 and 120°C. This work (blue color points): ◊, 40°C; □, 80°C and O, 120°C. Monteiro et al. [9] (red color points): □, 80°C; ◊, 100°C and O, 120°C.

4. Conclusions

Equilibrium solubility of CO_2 were measured in aqueous solutions of Monoethanolamine (MEA) and *N,N*-diethylethanolamine (DEEA). Equilibrium cells are generally used for these measurements. In this study, the equilibrium data were measured from the calorimetry. For this purpose a reaction calorimeter (model CPA 122 from ChemiSens AB, Sweden) was used. The advantage of this method is being the measurement of both heats of absorption and equilibrium solubility data of CO_2 at the same time. The measurements were performed for 30 mass % MEA and 5M DEEA solutions as a function of CO_2 loading at three different temperatures 40, 80 and 120°C. The measured 30 mass % MEA and 5M DEEA data were compared with the literature data obtained from different equilibrium cells which validated the use of calorimeters for equilibrium solubility measurements. The measured data can be used in the thermodynamic modeling.

Acknowledgements

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