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Solubility of Carbon Dioxide in Piperazine-activated Methyldiethamolamine and 2-Amino-2-Methyl-1-Propanol

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Abstract: Carbon dioxide (CO_2) is one of the major causes of accelerating global warming. It is thus important to employ an efficient method to capture CO_2. Absorption is the most established technique to separate CO_2 and amines are most commonly used as solvent. Methyldiethanolamine (MDEA), which is a tertiary amine, is known for its high equilibrium CO_2 loadings. Similar to MDEA, sterically hindered amine, such as 2-amino-2-methyl-l-propanol (AMP) which also demonstrates high CO_2 solubility, was proposed as a new commercially attractive solvent for CO_2 removal. In recent years, many studies were carried out on piperazine (PZ) as an activator to enhance CO_2 absorption. This study aims to extend the experimental data for solubility of CO_2 in aqueous solutions of AMP/PZ and MDEA/PZ at higher pressures. In present study, CO_2 solubility in aqueous mixture AMP/PZ and MDEA/PZ systems was measured at varying pressures, temperatures and concentrations. The experiments were conducted at temperatures 303.15 and 333.15 K and at pressures 4, 8, 12 and 16 bar. The AMP and MDEA concentration ranges from 25-50 mass % while PZ concentration varies from 0-8 mass %. Solubility of CO_2 was determined from the pressure drop due to absorption of CO_2 into solvent within a high pressure equilibrium cell. Substantial increase in CO_2 loading was observed when a small amount of PZ was added to the amine solutions, proving PZ an effective promoter to enhance CO_2 absorption. Mixture AMP/PZ shows higher CO_2 absorption capacity than MDEA/PZ at the same pressure and temperature.

Key words: CO_2 loading, amines blend, absorption

INTRODUCTION

In recent years it has been shown that carbon dioxide (CO_2) is one of the major factors accelerating global warming. It is thus crucial to develop and employ efficient methods for acid gas treatment. Apart from the recognition of greenhouse gas, CO_2 is also known as acid gas, which is one of the impurities in natural gas. The CO_2 reacts with water to form carbonic acid that is corrosive to pipeline and equipment. Besides, CO_2 removal is important to increase heating value of natural gas and optimize pipeline capacity. There are several techniques to separate CO_2 from process gas streams, such as absorption, adsorption, cryogenic separation and membrane. Absorption is acknowledged as the most effective method for bulk removal of CO_2. Amines have long been identified as commercial solvents for removal of carbon dioxide in natural gas industry. Carbon dioxide reacts with alkanolamines, either directly or through an acid-base buffer mechanism and forms non-volatile ionic species such as carbonates, bicarbonates and carbamates. Numerous alkanolamines were proposed for this purpose, monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) being the most commonly used in industry (Kadiwala *et al*., 2010; Kohl and Nielsen, 1997). Methyldiethanolamine (MDEA) has high equilibrium CO_2 loadings due to its lack of N-H bond and low reaction enthalpy, which leads to less regeneration cost required (Kumar *et al*., 2003). The AMP, a sterically hindered amine, was proposed as a new, commercially attractive solvent for CO_2 capture. Similar to MDEA, AMP has stoichiometric CO_2 loading of 1 mole AMP per mole of CO_2 and requires low regeneration energy (Sartori and Savage, 1983).

Using amine blends allows an improved absorption capacity and absorption rate while reducing the energy requirement which leads to lower operation cost (Chakravarty *et al*., 1985; Samanta and Bandyopadhyay, 2009). Recently, PZ is being intensively studied as

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additive and has shown great potential in acid gas removal. The major advantages of PZ are its high resistance to thermal and oxidation degradation (Song *et al*., 2012). Previous studies demonstrate that PZ markedly accelerates CO_2 absorption and increases the enhancement factor when a small amount is added into alkanolamine solutions (Dang and Rochelle, 2003; Hamborg *et al*., 2010; Samanta and Bandyopadhyay, 2009, 2011; Sun *et al*., 2005). Thermodynamic equilibrium of such solvents is one of the important parameters to design CO_2 removal system. Carbon dioxide solubility in the solvent determines cyclic capacity, which affects sizing of absorption column. Experimental results for CO_2 solubility in MDEA/PZ and AMP/PZ solutions at lower pressure have been published. Solubility of CO_2 in aqueous solutions of PZ activated MDEA has been investigated for CO_2 partial pressures ranging from 0.1-100 kPa (Ali and Aroua, 2004). Derks *et al*. (2010) presented experimental equilibrium data on the solubility of CO_2 into aqueous solutions of MDEA and PZ at atmospheric pressure. Yang *et al*. (2010) carried out VLE measurements of CO_2 in PZ and AMP mixture up to 152 kPa. Solubility of CO_2 in aqueous mixture containing different concentrations of AMP and PZ has been reported by Dash *et al*. (2011) in pressure range of 0.1-140 kPa.

The present investigation aims to extend the experimental database created in previous work by other researchers for the solubility of CO_2 in aqueous solutions of AMP/PZ and MDEA/PZ at elevated pressures. In this study, the solubility of solvents was measured at the temperatures 303.15 and 333.15 K and at pressures 4, 8, 12 and 16 bar. The measurements were reported for AMP and MDEA concentration ranges from 25-50 mass % blended with piperazine at concentration varying from 0-8 mass %.

MATERIALS AND METHODS

Materials: Carbon dioxide with purity of 99.8% was purchased from Air Product Malaysia Sdn. Bhd. MDEA, AMP and PZ of reagent grade (95, 98 and 99%, respectively) were purchased from Merck, Malaysia. Bi-distilled water was used to prepare aqueous solutions of MDEA and AMP. All the solutions were prepared gravimetrically using analytical balance (Mettler Toledo AS120S) within ±0.0001 g.

Experimental setup and procedure: In this study, CO_2 solubility in aqueous AMP/PZ and MDEA/PZ systems was measured at temperatures and pressures ranging at 303.15 and 333.15 K and 4, 8, 12 and 16 bar, respectively. The AMP and MDEA concentration ranged from 25-50 mass % while piperazine concentration was from 0-8 mass %. Solubility experiments were conducted in a high pressure solubility cell, similar with the one used by Harris *et al*. (2008). Setup of the experiment is shown in Fig. 1.

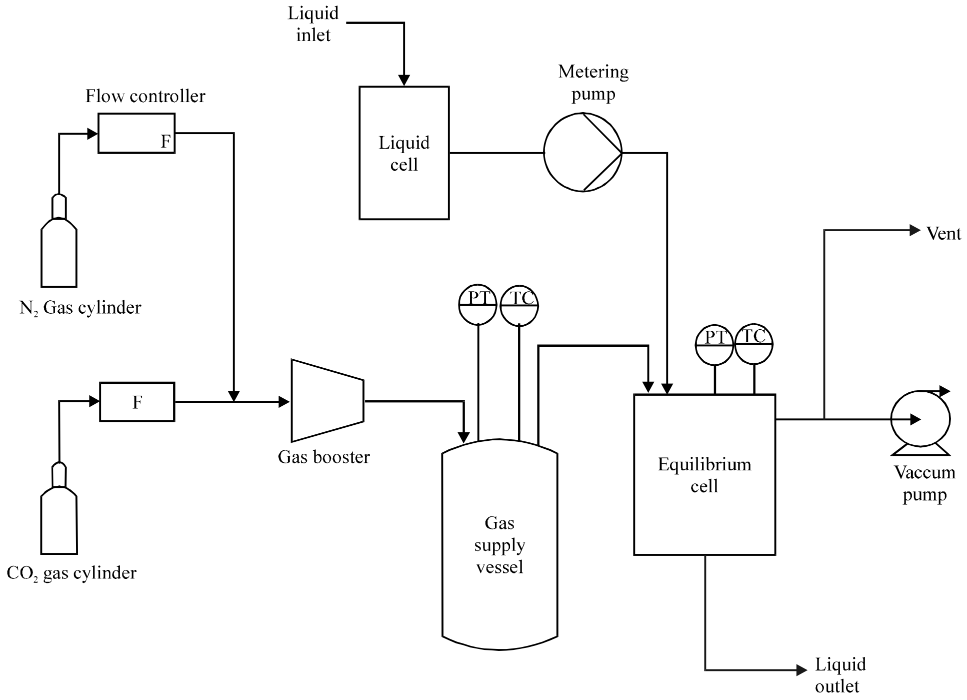

Fig. 1: Set up of physical solubility experiment

Two pressure vessels were used in this experiment, namely Gas Supply Vessel (GSV) to elevate gas pressure and Equilibrium Cell (EC) was used, where the gas and solvent were mixed and reacted. Both of the vessels were thermo regulated with water bath set at the required temperatures. Gas booster was used to pressurize the gas in a gas supply vessel to achieve the desired CO_2 pressure. Then, 6 mL of solvent was injected into equilibrium cell and the solvent was degassed by applying vacuum for a short period. After that, the valve between gas supply vessel and equilibrium cell was opened to allow gas transfer into an equilibrium cell. The valve was closed when pressure of both vessels stabilized. Pressure of the gas supply vessel before and after gas transfer was recorded. When no pressure drop was observed indicating equilibrium was attained, pressure of equilibrium cell was taken. This method was repeated for different pressures, temperatures and concentrations of solvent. The CO_2 loading was determined from the ratio of mole of CO_2 absorbed and mole of amine in solvent.

RESULTS AND DISCUSSION

The CO_2 loading of aqueous MDEA and piperazine activated MDEA solution as well as aqueous AMP and piperazine activated AMP solution for four different pressures and two temperatures at various concentrations were presented in Table 1-4.

It was observed that solubility of CO_2 in amine blends shows an increasing trend with pressure at a fixed temperature. This is because the partial pressure of the gas dictates the number of collisions between the gas molecule and the surface of the solution, consequently, more dissolved gas is obtained as the pressure is increased since the number of collisions increases (Zumdahl and DeCoste, 2010).

Besides, amine solvents with piperazine activator exhibited a significant increase in CO_2 solubility. Due to its cyclic and diamines attribute, piperazine has higher capacity of dissolving CO_2 chemically (Bishnoi and Rochelle, 2000). With increasing mass percentage of piperazine in total amine blend, CO_2 solubility increased at a particular MDEA or AMP concentration. For both MDEA and AMP, solubility of CO_2 decreased as concentration of amine increases.

Figure 2 illustrates the effect of temperature on CO_2 loading in 8% piperazine in MDEA and AMP solutions. Absorption capacity of CO_2 is higher at 303 K compared to 333 K. This phenomenon is due to higher vapor pressure that results from higher kinetic energy of the molecules in the liquid at high temperature (Zumdahl and DeCoste, 2010). Besides, from Fig. 2 it could be seen that AMP has better CO_2 solubility than MDEA at the same concentration of piperazine.

Table 1: Carbon dioxide (CO_2) loading for aqueous MDEA and mixture of MDEA+PZ at 303 K

	Pressure (bar)			
Concentration (mass %)	4	8	12	16
25% MDEA	0.761	0.977	1.242	1.349
25% MDEA+2% PZ	1.825	2.478	3.054	3.814
50% MDEA+2% PZ	1.077	1.762	2.497	3.245
25% MDEA+8% PZ	2.270	2.800	3.390	4.121
50% MDEA+8% PZ	1.193	1.907	2.625	3.496

Table 2: Carbon dioxide (CO_2) loading for aqueous MDEA and mixture of MDEA+PZ at 333 K

	Pressure (bar)			
Concentration (mass %)	4	8	12	16
25% MDEA	0.631	0.802	1.019	1.141
25% MDEA+2% PZ	1.403	2.004	2.624	3.485
50% MDEA+2% PZ	0.864	1.375	1.999	2.704
25% MDEA+8% PZ	1.769	2.354	2.987	3.789
50% MDEA+8% PZ	1.086	1.580	2.194	2.952

Table 3: Carbon dioxide (CO_2) loading for aqueous AMP and mixture of AMP+PZ at 303 K

	Pressure (bar)			
Concentration (mass %)	4	8	12	16
25% AMP	0.848	1.073	1.340	1.497
25% AMP+2% PZ	2.035	2.698	3.456	4.260
50% AMP+2% PZ	1.231	1.908	2.699	3.555
25% AMP+8% PZ	2.382	3.001	3.828	4.624
50% AMP+8% PZ	1.325	2.166	2.794	3.653

Table 4: Carbon dioxide (CO_2) loading for aqueous AMP and mixture of AMP+PZ at 333 K

	Pressure (bar)			
Concentration (mass %)	4	8	12	16
25% AMP	0.717	0.859	1.114	1.376
25% AMP+2% PZ	1.794	2.398	3.096	3.890
50% AMP+2% PZ	0.978	1.521	2.293	3.018
25% AMP+8% PZ	2.125	2.711	3.372	4.289
50% AMP+8% PZ	1.197	1.784	2.470	3.361

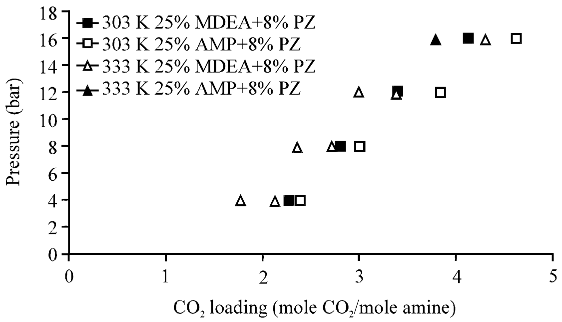

Fig. 2: Solubility of CO_2 in piperazine activated MDEA and AMP solutions at 303 and 333 K

CONCLUSION

A new set of experimental data of CO_2 solubility in aqueous MDEA and AMP solutions with piperazine as an activator over temperature range from 303.15-333.15 K at pressures 4, 8, 12 and 16 bar were presented. The measurements were reported for AMP and MDEA concentration ranges from 25-50 mass % blended with piperazine at concentration varying from 0-8 mass %. In this investigation it was found that CO_2 loading increase substantially when a small amount of piperazine was added into the amines' solutions, proving piperazine an effective promoter to enhance CO_2 absorption. Aqueous blend of AMP and piperazine has higher absorption capacity as compared to piperazine activated MDEA solution.

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