Solubility of CO_2 in Aqueous Solutions of 2-Amino-2-Methyl-1-Propanol at High Pressure

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Abstract—Carbon dioxide is one of the major green house gases. It is removed from different streams using amine absorption process. Sterically hindered amines are suggested as good CO_2 absorbers. Solubility of carbon dioxide (CO_2) was measured in aqueous solutions of 2-Amino-2-methyl-1-propanol (AMP) at temperatures 30 ^{o}C, 40 ^{o}C and 60 ^{o}C. The effect of pressure and temperature was studied over various concentrations of AMP. It has been found that pressure has positive effect on CO_2 solubility where as solubility decreased with increasing temperature. Absorption performance of AMP increased with increasing pressure. Solubility of aqueous AMP was compared with mo-ethanolamine (MEA) and the absorption capacity of aqueous solutions of AMP was found to be better.

Keywords—Global warming, Carbon dioxide, Amine, Solubility

I. INTRODUCTION

GLOBAL warming is becoming a public concern due to escalation of global CO_2 emission to 80 % from 1970 to 2004 [1]. This increase in CO_2 emission is due to rapid usage of fossil fules; coal, natural gas and petroleum. This contribution due to fuel usage reaches to 86 % of the global CO_2 emission. Many programs are launched to bring the awareness as well as to find solutions to minimize the global CO_2 around the world by different organizations. These initiatives include, International Panel of Climate Change (IPCC), the Global Climate Change initiatives and the United Nations Framework Commission on climate Change [2].

The agenda of all above mentioned initiatives is to provide strategies to meet energy requirements while reducing the green house emissions in line with the Global targets. There are three CO_2 separation areas are focused currently. These areas include; separation from power plant flue gas, separation from fuel gas, and separation from natural gas. In pre-combustion process CO_2 is removed at high pressure up to 40 bar and in some cases at 60 bar range of gas pressure by aqueous solutions of alkanolamines [2]. The traditional amines used for acid gas removal include; mono-ethanolamine (MEA), di-ethanolamine (DEA) and N-methyldiethanolamine (MDEA) [3]. Conventional amines used for removing CO_2 have their operational and absorption limitations. Recently a new class of amines, sterically hindered amines is suggested as one of the attractive amine for acid gas removal due to their relatively higher CO_2 absorption capacity and higher values of rate constant [4]. One of the sterically hindered amine is 2-amino-2-methyl-1-propanol (AMP). This hindrance is caused by the presence of bulky group adjacent to the amino group. Sterically hindered amine (AMP) is the potential absorbent for CO_2 removal with relatively high CO_2 loading, selectivity and efficient regeneration due to unstable carbamate formation [5-8]. The available open literature on the CO_2 absorption in AMP reveals that most of the work is reported on low pressure conditions [9-10]. However, sweetening of natural gas and pre combustion processes require high pressure CO_2 removal. Therefore, in this work, the CO_2 absorption capacity in aqueous AMP solutions is evaluated at high pressure in order to provide a real time data to avoid operational issues. The absorption capacity is investigated in terms of CO_2 solubility or CO_2 loading. The effect of pressure and temperature is studied on CO_2 solubility. The data is reported for a pressure range of 5 bar to 60 bar and at three different temperatures ranging from (30 to 60) ^{o}C. The three different concentrations of AMP are studied in order to get the efficient CO_2 removal from gaseous streams.

II. EXPERIMENTAL SECTION

A. Materials

Carbon dioxide with a purity of 99.99 % was purchased from Malaysian Oxygen Behrad (MOX Gases). AMP 95 % was purchased from Merck, Malaysia. It was used without further purification. The bi-distilled water was used to prepare solutions. All the solutions were prepared gravimetrically using an analytical balance (Mettler Toledo AS120S) with measuring accuracy of ±0.0001 g. The total amine concentration was also experimentally determined by titration with 0.5 M HCl using methyl orange indicator and the concentrations were accurate with in ± 0.1 %.

B. Apparatus and Procedure

The solubility measurements were conducted in a high pressure solubility cell (SOLTEQ BP -22) as used by Haris et al. [12]. The schematic diagram of solubility cell is shown in Figure 1. The set up consist of two vessels, mixing vessel (3 L) where the gas pressure was raised up to 60 bar and equilibrium cell (50 mL) where the solubility measurements were made. Initially both vessels were purged with nitrogen and then mixing vessel was pressurized from 5 to 60 bar. The pressure of the system was measured using digital pressure indicator (Druck DPI 150) with a precision of ± 1.0 bar for a range of 0 bar to 100 bar. The temperature of the system was controlled by thermostat water bath Julabo by ± 0.1 ^{o}C and the inside temperature of mixing vessel and solubility cell was measured with YOKOGAVA (7653) digital thermometer with an accuracy of ± 0.01 ^{o}C. The solubility measurement method was similar as adopted by Jenab et. al. [13]. Vacuum was created in equilibrium cell and 5 mL of the aqueous solution was introduced using metering pump. The temperature of the cell was then adjusted to the desired value and pressure was

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noted. At this stage, solvent exists under its own vapor pressure P_v. The CO_2 was transferred from mixing vessel to the equilibrium cell and the stirrer was turned on. The moles of CO_2 n_{co2} transferred were calculated using drop in pressure, volume of vessel and temperature by the following Eq.

$$n_{CO2} = \frac{V_T}{RT_a}\left(\frac{P_1}{z_1} - \frac{P_2}{z_2}\right)$$

Where V_T is the volume of the gas container (mixing vessel), z_1 and z_2 are the compressibility factors for each pressure (P_1 and P_2), R is the real gas constant and T_a is the ambient temperature. The compressibility factors were calculated using Peng Robinson equation of state (EOS) . When there was no further drop in pressure inside equilibrium cell indicating thermodynamic equilibrium is achieved, pressure value was recorded.

The equilibrium pressure (P_{CO2}) was calculated by the following Eq.

$$P_{CO_2} = P_T - P_V$$

Where P_T represents the total pressure and P_v represents vapor pressure of solutions. The remaining moles of CO_2 in the gas phase n_g were calculated by equilibrium pressure (P_{CO2}), temperature and overhead gas volume by using the following Eq.

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{Z_{CO_2} RT}$$

Where V_g is the gas volume in the equilibrium cell and T is the operating temperature. The moles of CO_2 in the liquid phase were then calculated from

$$n_{CO2}^l = n_{CO_2} - n_{CO2}^g$$

The solubility was then calculated as mol of CO_2 per mol of amine by using the following equation

$$\alpha = \frac{n_{CO_2}^l}{n_{AM}}$$

Where n_{AM} represents the moles of AHPD in the liquid and calculated by the following Eq.

$$n_{AM} = \frac{\rho V_l m_{AHPD}}{M_{AHPD}}$$

Where ρ is the density of the aqueous solution of AHPD, V_l is the liquid volume in the cell, m_{AHPD} is the mass fraction of AHPD and M_{AHPD} is the molecular weight of AHPD.

III. RESULTS AND DISCUSSION

To validate the experimental method, the solubility of 10 mass % AHPD aqueous solutions at 40 °C was measured and compared with the literature. These results along with the literature [11] values are presented in Table 1 and illustrated in Figure 1. The measured data was in good agreement with the literature with average absolute deviation (AAD) of less than 3

%. The AAD was calculated using Eq. 1.

$$\%AAD = \frac{1}{n}\sum\left|\frac{X_{exptl} - Y_{lit.}}{Y_{lit.}}\right| * 100$$

Where n is the number of data points, X_{exptl} measured physical property and Y_{lit} physical property values from literature.

The solubility of AMP was measured over the wide range of concentrations of industrial importance (1, 2 and 3) molar and at elevated pressure of up to 60 bar. The measurements were made at three temperatures (30, 40 and 60) °C. The measured solubility data is presented in Tables 2 to 4 as a function of pressure and concentration at various temperatures. The expected general trend of increasing solubility with increasing pressure and decreasing with increasing temperature is observed. It can be observed from Figure 3 that pressure has a positive effect on CO_2 loading as solubility of CO_2 increases while increasing pressure. However, it decreases while increasing temperature at any given concentration. This could be due to high vapor pressure at high temperatures. The effect of pressure on CO_2 solubility is independent of concentration as shown in Figure 4. It represents the CO_2 loading for all three concentrations at 30 °C and solubility shows increasing trend for all concentrations. Solubility of 1M AMP aqueous solution was also compared with commercially used MEA [14] solvent and results are presented in Fig 5. It can be observed from Fig 5 that solubility of 1M aqueous solution of AMP is better than MEA. Keeping in view the reported performance of AMP in this work, it can be used as an effective solvent for CO_2 removal from different gaseous streams where the process is carried out especially at high pressures.
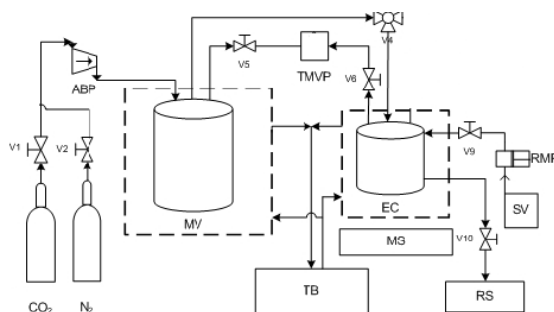

Fig. 1 Schematic diagram of high pressure gas solubility equipment
ABP: Air driven gas booster pump
MV: Mixing vessel
TB: Thermostat bath
EC: Equilibrium cell
MS: Magnetic stirrer
TMVP: Turbo-molecular vacuum pump
SV: Sample vessel
MP: Metering pump

TABLE I
SOLUBILITY OF CO_2 IN 10 % MASS AHPD AND COMPARISON WITH LITERATURE

Literature (11)		Present work	
P/bar	α	P/bar	α
1.273	0.749		
1.676	0.918	1.51	0.896
3.42	0.992	3.45	0.974
6.02	1.12	6.10	1.101
10.52	1.21	10.45	1.113
15.06	1.286	15.00	1.271
		19.85	1.385

TABLE II
SOLUBILITY (MOL_{CO2}/MOL_{AMP}) FOR 1 M AMP AT VARIOUS TEMPERATURES

P (bar)	30 °C	40 °C	60 °C
5.2	1.66	1.55	1.43
10.4	1.95	1.79	1.59
20.3	2.08	1.88	1.68
30.1	2.19	1.97	1.84
40.7	2.29	2.07	1.96
50.8	2.37	2.16	2.05
60.1	2.49	2.27	2.15

TABLE III
SOLUBILITY (MOL_{CO2}/MOL_{AMP}) FOR 2 M AMP AT VARIOUS TEMPERATURES

P (bar)	30 °C	40 °C	60 °C
5.6	1.37	1.26	1.19
10.8	1.59	1.45	1.29
20.5	1.78	1.63	1.43
30.7	1.92	1.76	1.58
40.9	2.13	1.91	1.75
50.1	2.19	1.97	1.84
60.8	2.28	2.08	1.92

TABLE IV
SOLUBILITY (MOL_{CO2}/MOL_{AMP}) FOR 3 M AMP AT VARIOUS TEMPERATURES

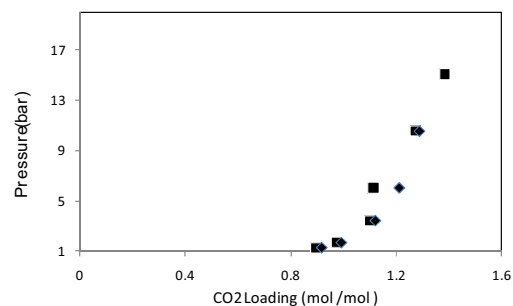| P (bar)	30 °C	40 °C	60 °C
5.3	1.11	1.06	0.99
10.4	1.52	1.38	1.23
20.7	1.69	1.51	1.35
30.7	1.82	1.67	1.46
40.2	1.95	1.77	1.55
50.9	2.09	1.93	1.71
60.6	2.18	2.06	1.82

Fig. 2 Comparison of CO2 solubility in 10 mass % AHPD at 50 °C: ■ , This work, ◆ ,Park et. al. [11]
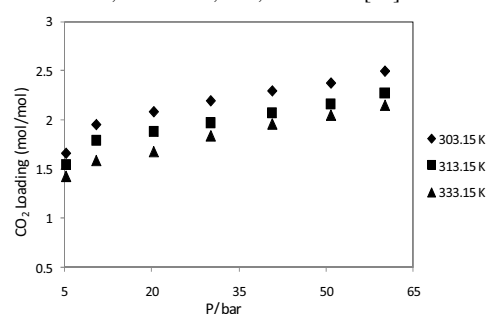

Fig. 3 Effect of Pressure and Temperature on CO2 loading for 1 Molar AMP
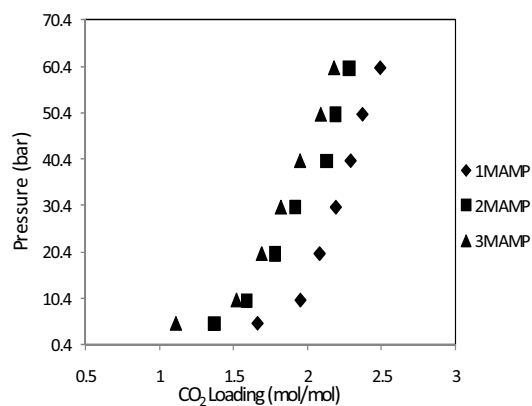

Fig. 4 Effect of Concentration on CO2 loading at 30 oC for all three concentrations of AMP
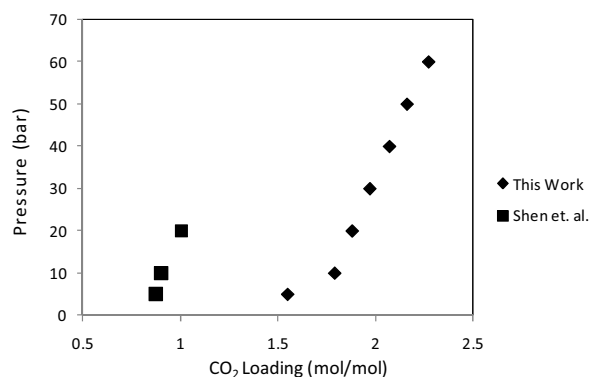

Fig. 5 Comparison of CO_2 solubility in 1M AMP aqueous solution and 15.3 wt% MEA solution at 40 °C

IV. CONCLUSION

Solubility of CO2 in aqueous solutions of 2-Amino-2-methyl-1-propanol (AMP) was measured over the wide range of pressure of industrial interest. The pressure was varied up to 60 bar and measurements were made for three temperatures. (30, 40, 60)°C. It is found that solubility increase with the increase of CO_2 pressure and decrease by increasing temperatures. Higher AMP concentrations are found to have less CO_2 absorption capacity. The absorption capacity was also compared with conventional amine MEA, and AMP CO_2 absorption capacity was found to be better. Solvent, AMP can be potential CO_2 removing source.

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