Equilibrium Solubility of Carbon Dioxide in Aqueous 2-Amino-2-Methyl-1-Propanol (AMP) Blended with 2-Methylpiperidine (2MPD) at High Pressure

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ABSTRACT

In this study, a new experimental data on CO_2 absorption capacity in aqueous mixtures of 2-Amino-2-Methyl-1-Propanol (AMP) and 2-Methylpiperidine (2MPD) was measured at temperature conditions of 313.15K, 323.15K and 343.15K and pressure ranges of 400psi up to 700psi. The experiments were carried out with 0-10wt% of 2MPD and 20-30wt% of AMP. It was found that the CO_2 loading capacity increased with increasing CO_2 partial pressure and with decreasing temperature. The results indicated that addition of 2MPD to the aqueous AMP solution greatly enhanced the CO_2 loading capacity by 0.93% up to 45.41%. Simple correlations of solubility as a function of temperature and CO_2 partial pressure suggested by Jou and Mather Model was used to predict the solubility of CO_2 in the mixtures and found to be in a good agreement with the experimental value.

Keywords: *Carbon Dioxide, Solubility, 2-Amino-2-Methyl-1-Propanol (AMP), 2-Methylpiperidine (2MPD).*

Introduction

Carbon dioxide (CO_2) is an odorless gas composed of two oxygen atoms each covalently doubles bonded to a single carbon atom and classified as non-toxic gas. However, anthropogenic CO_2 emissions have led to global climate change that eventually affects human life and disrupting our ecosystem

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[1][2]. Major sources of CO_2 generally come from the use of natural gas, power plants, petrochemical and steel production industries [3][4][5]. Hence, CO_2 removal and recovery are urgently needed to maintain safe and secure environment by implementing carbon capture and storage (CCS) [6][7].

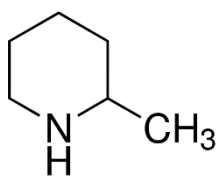
Among the various technique available for efficient CO_2 removal, absorption based process using alkanolamine has received a great interest and so far has been effective in capturing CO_2. Among the aqueous solutions of amine, 2-Amino-2-Methyl-1-Propanol (AMP) is considered as one of promising absorbents for carbon capture process with sterically hindered structure and has an equilibrium CO_2 loading that can reach twice of any primary and secondary alkanolamine [8][9]. AMP has also been used in the industry for having a potential of high CO_2 loading, selectivity and efficient regeneration [10][11][12].

In this work, mixed solvents of AMP with 2MPD as a chemical activator were tested for CO_2 solubility performance to improve the CO_2 absorption reaction capacity of AMP. The effects of pressure, temperature and concentration of 2MPD on CO_2 solubility performance were studied. The experiments were conducted within a temperature range of 313.15K – 343.15K and pressure ranging up to 700psi. Three different compositions of solvent mixtures were used which included 27.5wt% of AMP + 2.5wt% of 2MPD, 25wt% of AMP + 5wt% of 2MPD and 20wt% of AMP + 10wt% of 2MPD. The solubility data obtained has been correlated as a function of CO_2 partial pressure and temperature as suggested by Jou and Mather model.

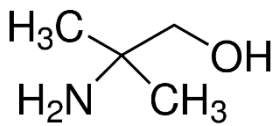
Materials and Method

Materials

Purified CO_2 (purity ≥ 99.995%) was obtained from Linde Malaysia Sdn. Bhd. The ionic liquids 2-Methylpiperidine (2MPD) with a minimum purity of 98% and 2-Amino-2-Methyl-1-Propanol, AMP (purity ≥ 95) were purchased from MERCK and used as received. The structure of the 2MPD and AMP is shown in Figure 1.



(a)



(b)

Figure 1: Chemical Structure of a) 2-Methylpiperidine (2MPD) and b) 2-Amino-2-Methyl-1-Propanol (AMP)

Method

The aqueous solutions were prepared by adding distilled water to the solvent mixtures at the desired concentration in all of the experiments. The CO_2 solubility measurements were carried out using high-pressure jacket reactor which is equipped with magnetic stirrer, glass liner and thermocouple. For this study, temperature was set at 313.15K, 323.15K and 343.15K while pressure ranges from 400psi to 700psi. In each run, 20ml of solvent mixtures was placed into the reactor. The CO_2 gas reservoir and the reactor, which contain aqueous mixtures of AMP and 2MPD, were heated to the desired temperature. Once the temperature was stable, CO_2 gas was released into the reactor and constantly stirred throughout the experiments. Equilibrium was achieved that was indicated by a constant pressure. This procedure was repeated for other solvent mixtures concentration. Finally, the CO_2 loading for the equilibrium cell was calculated based on the pressure drop using equation (1).

$$\alpha = \frac{\frac{(P_{Ti}-P_f)\times V_{vessel}}{zRT} - \frac{(P_{eq}-P_{vi})\times V_{reactor}}{zRT}}{n_{total}} \quad (1)$$

where α = mol CO_2 loading/ total amine, P_{Ti} = initial total pressure in the vessel (atm), P_f = final pressure in the vessel (atm), V_{vessel} = 1(litre), $V_{reactor}$ = volume of gas in reactor (litre), Z = compressibility factor, (based on temperature), R = gas constant, 0.08206 L.atm/mol.K, P_{eq} = equilibrium pressure in reactor (atm), P_{vi} = vapor pressure (atm).

Results and Discussion

The validation of equipment used was conducted by using 2-Amino-2-Methyl-1-Propanol (AMP) at 333.15K with 1M AMP concentration to verify the accuracy of measurement used in this work. Based on the results, it was

found that the measured data were in good agreement with the literature [13] with an average absolute deviation of 4.28%. The data were plotted as shown in Figure 2.

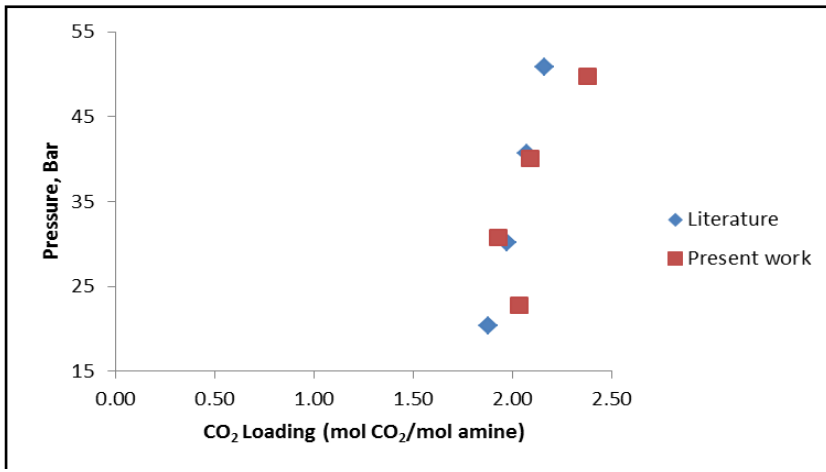


Figure 2: Comparison of solubility of this work with literature values at 333.15K for 1M AMP

Effect of pressure and temperature

In this work, the CO_2 loading values were calculated using equation (1). The CO_2 solubility was measured at temperature range of 313.15K to 343.15K. The similar trend of amine mixtures behavior was observed where the CO_2 solubility in the AMP + 2MPD mixtures decreases with the increasing of temperature. Figure 3 shows that the curve shift to the left side as the temperature increased indicating less CO_2 captured by the AMP + 2MPD mixture. This behavior demonstrates that more CO_2 gas is present in the solution at lower temperature compared to higher temperature. Besides that, the high temperature effect leads to increase the kinetic energy causing the vigorous dynamic motion of CO_2 molecules; thus, breaking the intermolecular bond of CO_2 and the liquid. As a result, more CO_2 gas escaped from the solutions. This trend can be explained by the understanding of the vapor pressure concept which increases with temperature [13][14]. These similar trends were also reported by other research findings [15][16][17].

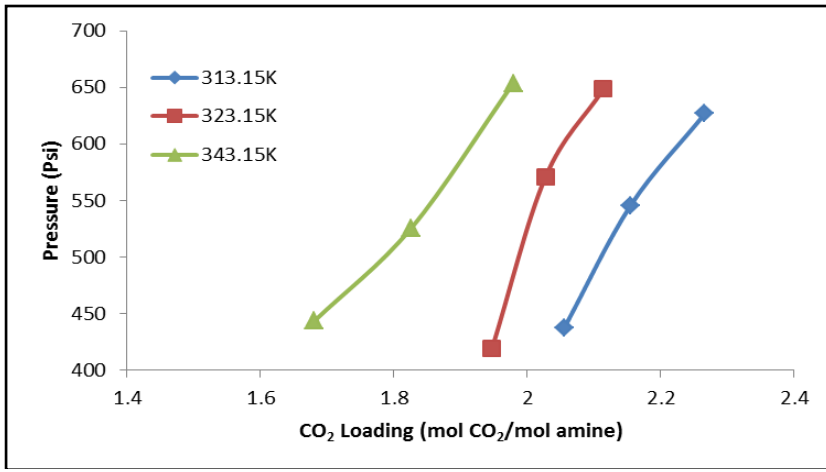


Figure 3: CO_2 loading with different temperature at concentration of AMP/2MPD (20/10)

In terms of pressure effect toward CO_2 absorption performance, it was observed that CO_2 solubility increases directly proportional to the increasing of the CO_2 partial pressure. This is because at a high pressure, more solute particles diffuse into bulk solution since the high frequency of gas particle collisions occur at the gas-liquid interfacial area. Hence, the solution will absorb more CO_2 gas into it [18][19][20].

Effect of 2MPD concentration on CO_2 loading

The solubility of CO_2 was measured at various weight percent of 2MPD in the aqueous AMP solutions of 30wt% + 0wt%, 27.5wt% + 2.5wt%, 25wt% + 5wt% and 20wt% + 10wt% respectively.

As shown in Figure 4, the results indicated that the addition of 2MPD into aqueous AMP enhanced the absorption capacity of CO_2. Increasing the concentration of 2MPD will increase about 0.93% to 45.41% of CO_2 solubility in the aqueous AMP + 2MPD solutions for this research experiment. This phenomenon can be explained by steric hindrance effect on AMP that creates carbamates instability which causes the hydrolysis reaction to go faster and lead to the formation of bicarbonates [11][21]. Clearly, 2MPD structure also exhibits similarly to sterically hindered amine absorbents due to methyl group attached to the ortho position of the cyclic amine; thus, the addition of 2MPD into aqueous AMP increases the amount of bicarbonate allowing for higher CO_2 absorption capacity [8][22][23].

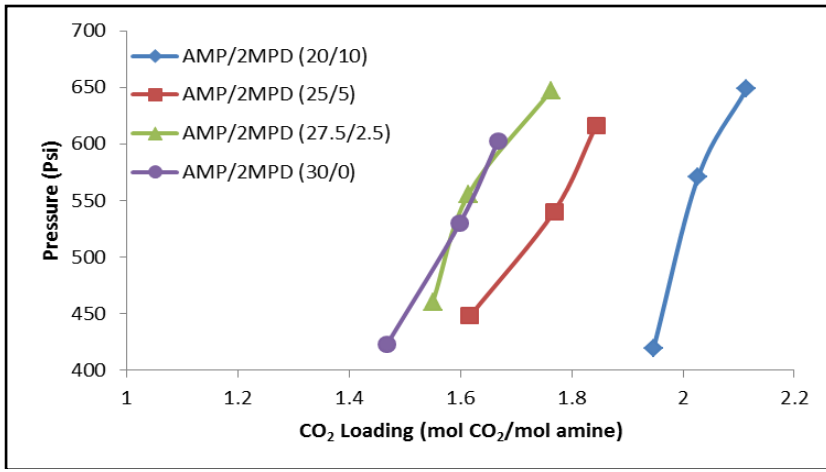


Figure 4: CO_2 loading with different concentration of blended AMP/2MPD at 323.15K

Correlations of solubility as function of pressure and temperature

Linear regression approach was used to model the CO_2 solubility experimental data as a function of partial pressure and temperature. The equation of the model is shown in Equation (2) as suggested by Jou and Mather.

$$\ln P = A \ln \alpha + B \tag{2}$$

where P is the pressure, α is mol CO_2 loading/ mol total amine and A and B were determined by plotting ln P against ln α at different temperatures. Once the values of A and B were obtained, it was plotted against the temperature to obtain the coefficient of A and B. The coefficients are listed in Table 1.

Table 1: Jou and Mather correlation

System	Correlations	
	A	B
30 wt % AMP	-0.0162T+7.6093	0.0248T-2.8081
27.5 wt% AMP + 2.5 wt% 2MPD	-0.041T+15.643	0.0364T-6.7091
25 wt% AMP + 5 wt% 2MPD	0.0249T-5.6532	-0.0007T+5.1191
20 wt% AMP + 10 wt% 2MPD	-0.058T+22.723	0.0566T-14.867

The correlations of solubility as a function of temperature at various pressures were used to determine the CO_2 loading. Figure 5 shows the comparison between calculated and experimental CO_2 loading for all solvent systems at various temperatures and concentrations. The model was further quantified by determining the average absolute deviation (AAD) using equation (3) as follows:

$$AAD = \frac{\sum_{i-1}^{N} \left| (\alpha_{\text{exp}} - \alpha_{\text{cal}}) / \alpha_{\text{exp}} \right|}{N} \times 100 \qquad (3)$$

where N is the number of data points. The average absolute deviation percent for the whole data measured was found to be ±1.93%. It shows that there is a good agreement between the experimental and predicted data.

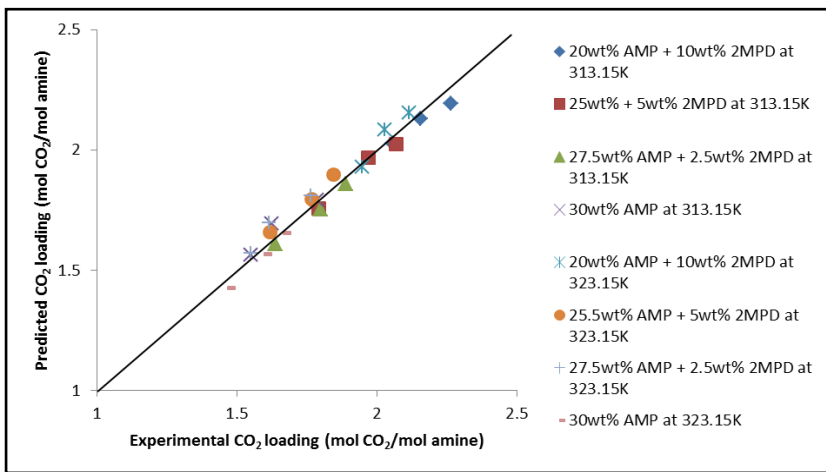


Figure 5: Comparison between predicted and experimental value for CO_2 loading

Conclusion

In this work, the solubility of CO_2 in mixtures of AMP and 2MPD was measured. It was found that increasing the pressure has led to the increasing of CO_2 loading. On the other hand, increasing the temperature reduced the CO_2 solubility performance. The results exhibited that addition of 2MPD to the aqueous AMP solution greatly enhanced the CO_2 loading capacity. Simple correlation by Jou and Mather was utilized to predict the CO_2 loading with only ±1.93% average absolute deviation.

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