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Absorption of Carbon Dioxide in the aqueous solution of Diethanolamine (DEA) blended with 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate [BmPyrr][OTf] at high pressure

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Abstract. Solubility data of carbon dioxide (CO_2) in aqueous Diethanolamine (DEA) blended with 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate [Bmpyrr][OTf] were measured at temperature 313.15K, 323.15K, 333.15K and pressure from 500psi up to 700 psi. The experiments covered over the concentration range of 0-10wt% for [Bmpyrr][OTf] and 30-40wt% for DEA. The solubility of CO_2 was evaluated by measuring the pressure drop in high pressure stirred absorption cell reactor. The experimental results showed that CO_2 loading in all DEA-[BmPyrr][OTf] mixtures studied increases with increasing of CO_2 partial pressure and temperature. It was also found that the CO_2 loading capacity increase significantly as the concentration of [Bmpyrr][OTf] increases. Jou and Mather model was used to predict the solubility of CO_2 in the mixtures where the experimental data were correlated as a function of temperature and CO_2 partial pressure. It was found that the model was successful in predicting the solubility behavior of the aqueous DEA-[Bmpyrr][OTf] systems considered in this study.

1. Introduction

The growth in worldwide carbon dioxide emission has become a big threat to our environment. Fossil fuels consumption has been found to increase significantly nowadays caused by rapid development of industry as well as population growth. International Energy Agency (IEA) predicts that 40.2GT of fossils fuels utilization by the year 2030 [1]. As a result, it has led to global warming and drastic climate change. Excessive of CO_2 emission consequently will be disastrous to humankind and also a great threat to disrupt. Thus, effective method to capture CO_2 is urgently needed to mitigate this environmental problem [2][3].

Presently, several methods have been implemented for CO_2 removal purposes including absorption, adsorption, membrane separation and cryogenic process [2][3][4][5]. Among these methods, absorption using chemical solvents such as aqueous alkanolamine is one of the most matured and effective methods since it has significant experience for CO_2 capture process besides cost effective for large-scale separations. Diethanolamine (DEA) is one of the common alkanolamine used in the industries due to their high reactivity and low cost however, low loading of this amine developed

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researcher's interest to explore new amines/solvents which may improve loading capacity of CO_2 gas [6].

Recently, Ionic Liquids (ILs) has attracted considerable attention due to their significant advantages over basic aqueous alkanolamine [7][8]. ILs possess low vapour pressure, low regeneration energy, tuneable nature and thermally stable over wide range of temperature. These advantages make ILs useful medium for capturing CO_2 [7]. However, most of ILs have revealed that it is not always cost effective, thus developing the most efficient hybrid solvent for CO_2 capture technologies is urgently needed.

In this work, the idea of aqueous amines blended with ionic liquid was comprehensively investigated. The equilibrium CO_2 solubility into aqueous Diethanolamine (DEA) blended with 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate [BMPyrr][OTf] mixtures experiments were performed at temperature range of 313.15K-333.15K over CO_2 partial pressure range from 500 psi up to 700 psi using different weight percent of [BmPyrr][OTf] (0–10 wt%) and the DEA 30–40 wt%. Jou and Mather model was employed to predict the CO_2 solubility in the mixtures.

2. Experimental

2.1. Material
Purified CO_2 (purity $\geq$ 99.95%) was obtained from Linde Malaysia Sdn Bhd. 1-Butyl-Methylpyrrolidinium Trifluoromethanesulfonate [Bmpyrr][OTf] (purity $\geq$ 98%) and Diethanolamine (DEA) with minimum purity of 99.5% used in this study were purchased from Merck and used as received without further purification. Figure 1 shows the chemical structure for these two types of solvents. Distilled water was used as diluter solvents for all experiments. For this study, the mixtures were prepared by adding [BmPyrr][OTf] at different concentration from 0 to 10wt % to aqueous DEA solutions.
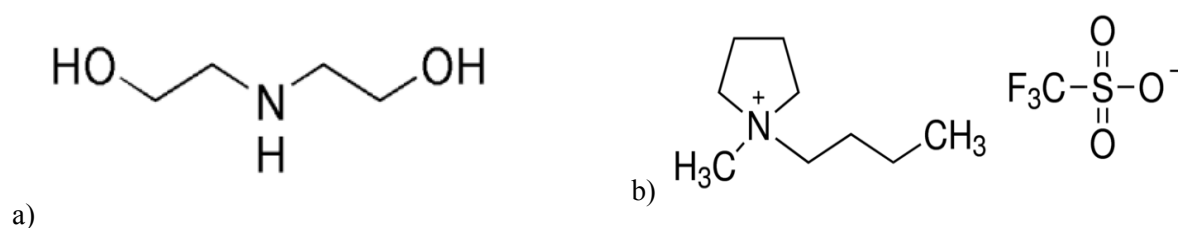

a)
b)

Figure 1. Chemical structure of a) Diethanolamine (DEA), b) 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonates [BmPyrr][OTf].

2.2. Methods
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 was measured using high-pressure jacketed reactor, which equipped with magnetic stirrer, glass liner and thermocouple. For this work, the temperatures were set in the ranges of 313.15K-333.15K while pressure up to 700 psi. In each run, 20ml of solvent mixtures was placed into the reactor. The CO_2 gas reservoir and the reactor were heated to the desired temperature. Once temperature was stable, CO_2 gas was released into the reactor and constantly stirred throughout the experiments. Equilibrium was achieved indicated by a constant pressure. Finally, the CO_2 loading for equilibrium cell was calculated based on pressure drop using equation (1).

$$\alpha = \frac{\frac{(PTi - Pf) \times Vvessel}{zRT} - \frac{(Peq - Pvi) \times Vreactor}{zRT}}{n_{total}}$$

(1)

Where α is mol CO_2 loading/ total amine, P_{Ti} is initial total pressure on the vessel (atm), P_f is final pressure in the vessel (atm), V_{vessel} is 1 litre, $V_{reactor}$ is gas volume in reactor (litre), Z is gas compressibility factor, R is gas constant, P_{eq} is equilibrium pressure in reactor (atm), P_{vi} is vapor pressure (atm) n_{total} is no of moles of amine and T is temperature (K)

3. Result

In this work, to validate the experimental data, the solubility of CO_2 in aqueous solution of 1M concentration of 2-Amino-2-Methyl-1-Propanol (AMP) was measured at 333.15K and compared with the literature [9]. Figure 2 demonstrated that the measured data exhibit good agreement with the literature where the average absolute deviation is only 4.28%.
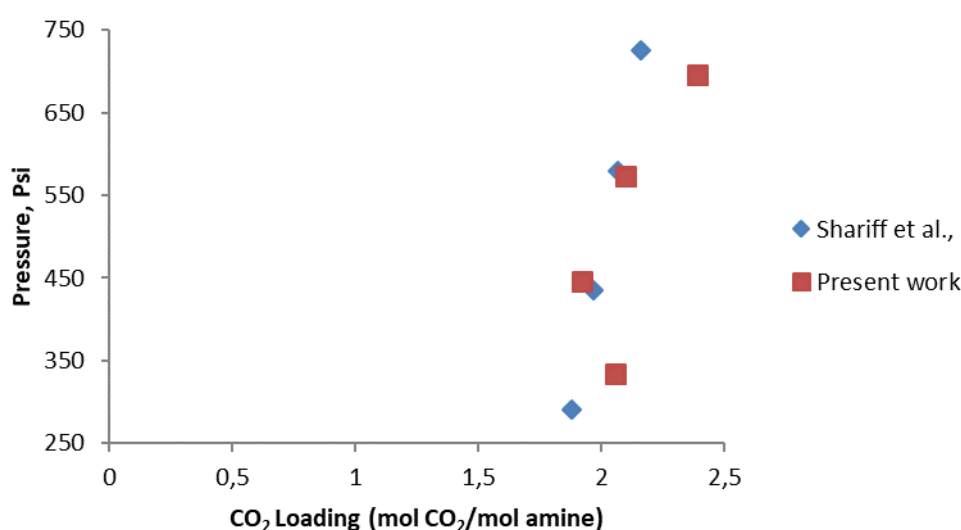

Figure 2. Solubility comparison of this work with literature values at 333.15K for 1M AMP.

3.1. Effect of [BmPyrr][OTf] concentration on CO_2 loading

The experimental focusing on the effect of ILs concentration on CO_2 loading was performed. The results indicated that the addition of [BmPyrr][OTf] into aqueous DEA enhanced the absorption capacity of CO_2. This can be seen from Figure 3 where the uptake of CO_2 into aqueous mixtures of [DEA][BmPyrr] was greatly increased compared to aqueous DEA alone. Addition of 5wt% of [BmPyrr][OTf] to the aqueous DEA increased the CO_2 loading by 56.5% at temperature 333.15K compared to the CO_2 loading in aqueous DEA. In the three aqueous mixtures of [DEA][BmPyrr][OTf] solution studied, the most CO_2 absorption capacity uptake was recorded for 30wt% DEA + 10wt% ILs aqueous solution which is 1.82 mol CO_2/mol amine at pressure 700psi. Therefore, this observation demonstrates that an increase in the concentration of ILs in the solution leads to an increase in CO_2 loading.
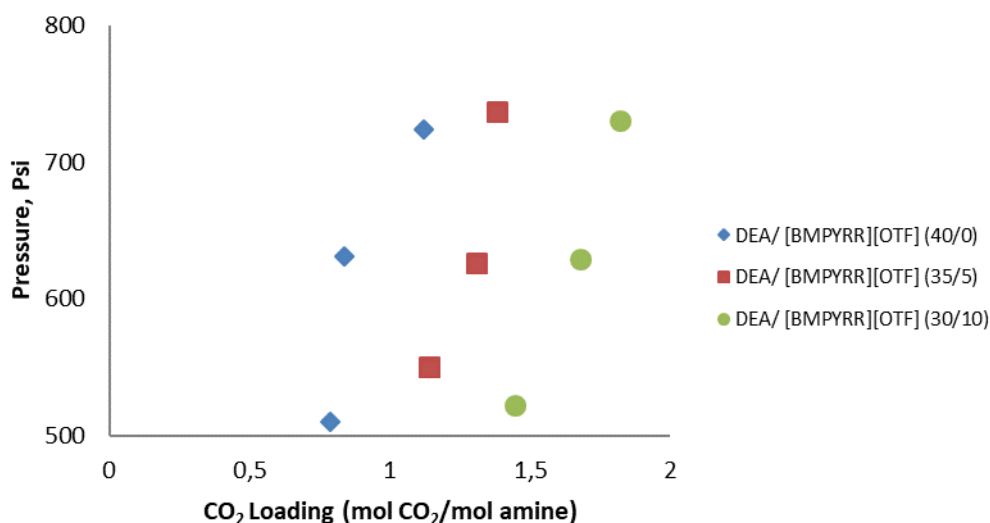
Figure 3. CO_2 loading for aqueous mixtures of DEA + [BmPyrr][OTf] with different composition at 333.15K.

3.2. Effect of temperature and pressure

The experimental results of temperature and pressure effect on CO_2 loading in the aqueous DEA is shown in Figure 4. As expected similar to other single amines behaviour, the result shows that CO_2 solubility decreases with increasing temperature in aqueous DEA solution. There is a clear trend of decreasing CO_2 absorption performance where the curve shifted to the left when the temperature increases indicating that less CO_2 absorbed by the solutions. This CO_2 solubility pattern is in agreement with the findings of other researchers [10][11][12][13]. This behaviour demonstrated that more gas is present in the solution with lower temperature, besides that the increasing of kinetic energy at high temperature has led to vigorous dynamic motion of CO_2 molecules causing the breaking of the intermolecular bond between CO_2 and the solution [14]. As a result, less CO_2 will be absorbed since more CO_2 was escaped from the solutions. This trend can be explained by the understanding of the vapor pressure concept, which increase with temperature [9]
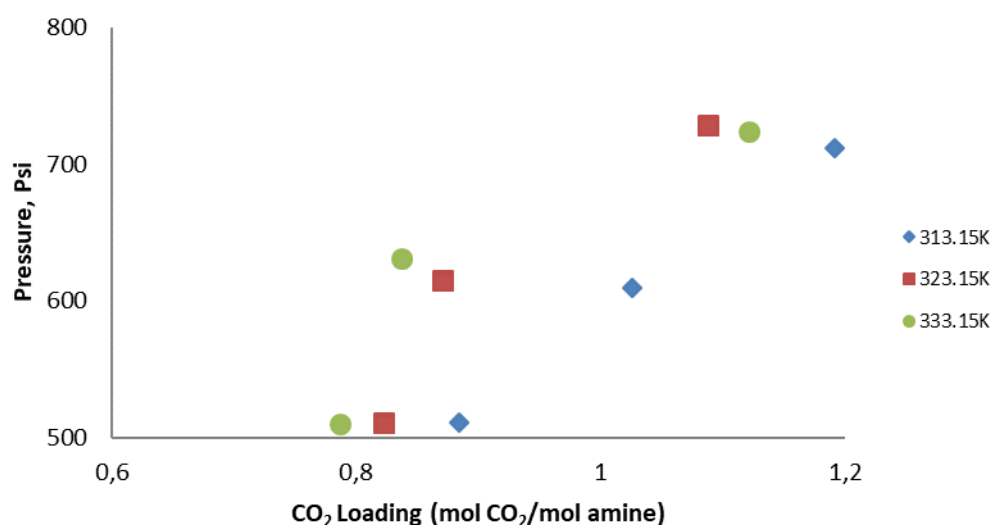

Figure 4. CO_2 loading of 40wt% of aqueous of DEA at different temperature.

However, contrast trends was found for aqueous DEA-[BmPyrr][OTf] mixtures where the CO_2 solubility increases as temperature increases. Figure 5 shows that the curve shifted to the right side when the temperature increases from 313.15K to 333.15K indicating that more CO_2 absorbed by the solutions. This behaviour showing that there is an interaction between water and [BmPyrr][OTf] that consequently causing the absorption process increase with temperature .
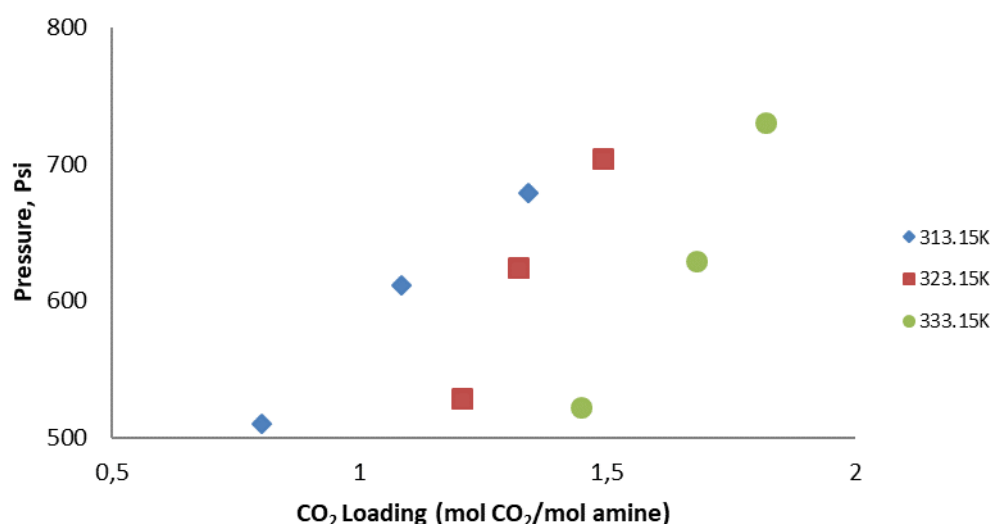

Figure 5. CO_2 loading of 30wt% DEA + 10wt% [BmPyrr][OTf] at different temperature.

In terms of pressure effect toward CO_2 absorption performance, positive impact was observed for aqueous mixtures of DEA + [BmPyrr][OTf] where CO_2 solubility increases with the increasing of the CO_2 partial pressure. This is because the gas pressure increases the number of collision between the gas molecules and the solution surface, therefore more gas is dissolved as the pressure increased [12][15]. This system obeys the Henry's Law concept where the solubility of gas in a liquid is directly proportional to the pressure of the gas above the surface of the solution.

3.3. Correlations of solubility as a function of pressure and temperature
The experimental data of CO_2 loading suggested by Jou and Mather [16] model were correlated linearly fitted as function of CO_2 partial pressure and temperature according to Equation 2 as follow:

$$\ln P = A \ln \alpha + B$$
(2)

where P is the pressure in Psi, α is mol CO_2 loading/ mol total amine and A and B were determined by plotting ln P against ln α at temperature of 313.15K, 323.15K and 333.15K. Once the values of A and B were obtained these values were plotted against the temperature to get the coefficients of A and B. The coefficients were listed in Table 1.

Table 1. Jou and Mather coefficients.

System	Coefficients	
	A	B
40 wt% DEA	-0.0137T + 5.4557	0.0083T + 4.5871
35 wt% DEA + 5 wt% [BmPyrr][OTf]	-0.0208T + 8.0386	-0.0617T + 26.558
30 wt% DEA + 10 wt% [BmPyrr][OTf]	0.0438T − 13.052	-0.0312T + 16.41

The solubility correlations as a function of temperature at various pressures were conducted to determine the CO_2 loading measurement. The model was further quantified by determining the average absolute deviation (AAD) using Equation (3) as follows:

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

(3)

Comparisons between the predicted and experimental values of CO_2 solubility are shown in Figure 6.
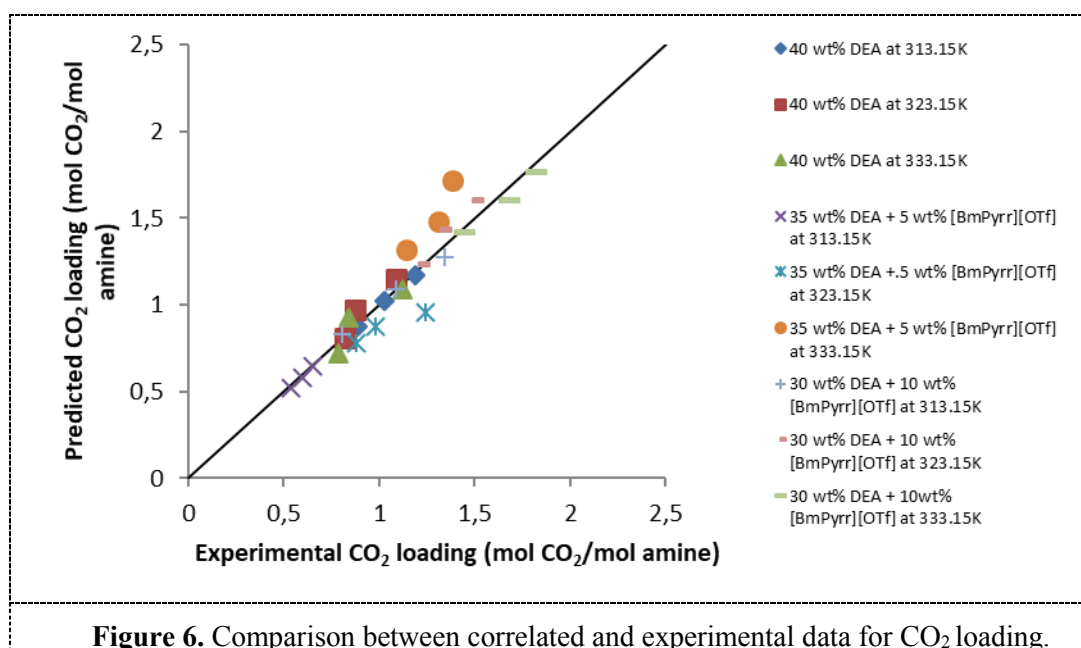

Figure 6. Comparison between correlated and experimental data for CO_2 loading.

It was found that the correlation of CO_2 solubility has AAD percentages of 6.936%. Thus, it shows good agreement between the experimental and predicted data.

4. Conclusion

In this work, the absorption of CO_2 into aqueous DEA blended with [BmPyrr][OTf] was measured. It has been found that addition of small amount of [BmPyrr][OTf] to the aqueous DEA can significantly enhance the CO2bsorption capacity compared to the conventional aqueous single amine. Aqueous solution with 30wt% of DEA + 10wt% of [BmPyrr][OTf] has the highest CO_2 uptake capacity compared with other aqueous mixtures solutions that have been investigated. It was found that increasing the pressure has led to increasing of CO_2 loading and increasing of temperature increases the CO_2 solubility performances for aqueous DEA-[BmPyrr][OTf] mixture however absorption performances reduces for aqueous DEA when temperature rises. Predicted CO_2 solubility using Jou and Mather model was found to be in good agreement with the experimental data.

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