Thermodynamic Equilibrium Solubility of Diethanolamine – N-Butyl-1-Methylpyrrolidinium Dicyanamide [DEA-BMPYRR DCA] Mixtures for Carbon Dioxide Capture

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Abstract. Solubility data of carbon dioxide (CO₂) in aqueous Diethanolamine (DEA) blended with pyrrolidinium-based ionic liquid: N-Butyl-1-Methylpyrrolidinium Dicyanamide [Bmpyrr][DCA] are presented at various temperatures (313.15K-333.15K) and pressure up to about 700 psi. The concentration of [Bmpyrr][DCA] ranges from 0-10wt% and 30-40wt% for DEA. The solubility of CO₂ was evaluated by measuring the pressure drop in high pressure stirred absorption cell reactor. The CO₂ loading in all studied mixtures increases with an increase in CO₂ partial pressure and decreases with temperature. It was also found that the CO₂ loading capacity decrease as the concentration of [Bmpyrr][DCA] increases. The experimental data were correlated as a function of temperature and CO₂ partial pressure to predict the solubility of CO₂ in the mixtures. It was found that the model predicted results in a good agreement with experimental value.

1. Introduction
Antropogenic CO₂ emissions is a big threat to the environment and has led to global climate change since CO₂ concentration has been increasing over the year due to rapid usage of natural gas, coal, petroleum and etc. One of the alternatives to mitigate the excessive CO₂ amount in the atmosphere is by applying post combustion capture technology onto the power plants. Chemical absorption technique using alkanolamine is the most extensively used benchmark technology in the industries. DEA (secondary amine) 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 researchers interest to explore new amines/solvents which may have a better loading capacity of CO₂ gas [1]. Other than that, owing to volatility and corrosive nature of the amine with high energy required for regeneration make this solvent unattractive thus efficient alternative routes urgently needed [2][3].

Nowadays, Ionic liquids (ILs) have received much attention and considered as one of the promising absorbents for capturing CO₂ since its have advantages over basic aqueous alkanolamine such as high thermal stability, low vapor pressure with added benefit of minimal solvent loss and corrosion [4]. These great advantages of ionic liquids make it suitable to be mix with amine solvent. Nevertheless, most ILs are not always cost effective, thus developing the most efficient hybrid solvent for CO₂ capture technologies is urgently needed. The objective of this work is to measure the total CO₂ loading in aqueous Diethanolamine (DEA) solutions mixed with N-Butyl-1-Methylpyrrolidinium Dicyanamide [Bmpyrr][DCA] over wide range of CO₂ partial pressure, temperature and concentration. A simple model of solubility was performed to predict the CO₂ solubility in the mixtures.
2. Experimental

2.1. Materials

Purified CO\textsubscript{2} (purity ≥ 99.95\%) was obtained from Linde Malaysia Sdn Bhd. N-Butyl-1-Methylpyrrolidinium Dicyanamide [Bmpyr][DCA] with minimum purity of 98\% and Diethanolamine, DEA (purity ≥ 99.5\%) were purchased from Merck and used as received. The structure of DEA and [BmPyr][DCA] is shown in Figure 1. Aqueous DEA solutions were prepared by adding distilled water to the desired concentration. Then [BmPyr][DCA] was added to the aqueous DEA at different concentration from 0 to 10wt\%. The mixtures were listed in Table 1.

![Figure 1. Chemical structure of a) Diethanolamine (DEA), b) N-Butyl-1-Methylpyrrolidinium Dicyanamide [BmPyr][DCA].](image)

Table 1. Mixtures of DEA with different weight percentage of [BmPyrr][DCA].

| Sample                  | DEA Concentration (wt %) | [BmPyrr][DCA] Concentration (wt %) |
|-------------------------|--------------------------|-----------------------------------|
| Aqueous DEA +           | 40                       | 0                                 |
| [BmPyrr][DCA]           | 35                       | 5                                 |
|                         | 30                       | 10                                |

2.2. Methods

The CO\textsubscript{2} solubility was measured using high-pressure jacketed reactor which equipped with magnetic stirrer, glass liner and thermocouple. For this work, temperature 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. Operation was started by heating up the CO\textsubscript{2} gas reservoir and the reactor to the desired temperature. Once temperature was stable, CO\textsubscript{2} gas was released into the reactor and constantly stirred throughout the experiments. Equilibrium was achieved indicated by a constant pressure. Finally, the CO\textsubscript{2} loading for equilibrium cell was calculated based on pressure drop using equation (1).

\[
\alpha = \frac{(P_{Ti} - P_f) V_{vessel}}{Z RT} - \frac{(P_{eq} - P_{vi}) V_{reactor}}{Z RT} \quad \text{n}_{total}
\]

Where \(\alpha\) is mol CO\textsubscript{2} loading/ total amine, \(P_{Ti}\) is initial total pressure on the vessel, \(P_f\) is final pressure in the vessel, \(V_{vessel}\) is 1 litre, \(V_{reactor}\) is gas volume in reactor, \(Z\) is gas compressibility factor, \(R\) is gas constant, \(P_{eq}\) is equilibrium pressure in reactor, \(P_{vi}\) is vapor pressure.

3. Results and Discussion

In order to verify the reliability of equipment and the deviation of equilibrium experimental data, the CO\textsubscript{2} solubility experiment was measured at 313.15K using 1M concentration of AMP and compared with the literature [5]. Figure 2 demonstrated that the measured data exhibit good agreement with the literature where the average absolute deviation is only 4.28\%. 

![Table 1. Mixtures of DEA with different weight percentage of [BmPyrr][DCA].](image)
3.1. Effect of [BmPyrr][DCA] concentration on CO$_2$ loading

In this work, the CO$_2$ loading were measured at various weight percent of ILs [BmPyrr][DCA] in aqueous DEA solution. The composition of DEA+ [BmPyrr][DCA] mixtures are 40wt% DEA, 35wt% DEA + 5wt% ILs and 30wt% DEA + 10wt% ILs respectively.

The results indicated that the addition of [BmPyrr][DCA] into aqueous DEA reduced the absorption capacity of CO$_2$. This can be seen from the data on Figure 3 since the uptake of CO$_2$ into aqueous mixtures of DEA+[BmPyrr][DCA] was decreased compared to aqueous DEA alone. This behavior can be explained the main reason of reducing CO$_2$ loading due to reduced water which replaced by ILs. Since the water content on the mixture was reduced, the CO$_2$ cannot react directly with the alkanolamine for absorbing CO$_2$. Other than that, this is due to the acidity of [BmPyrr][DCA] which reduced the basicity of aqueous DEA in the mixture, as a result the driving force for the mass transfer to occur is decreasing.
3.2. Effect of temperature and pressure
The temperature and pressure effect toward CO2 loading were conducted within temperature range of 313.15K-333.15K and pressure range up to 700psi. From Figure 4 and Figure 5, there is a clear trend of decreasing CO2 absorption performance in amine-ILs mixtures when the temperature increases. This CO2 solubility pattern is in agreement with the findings of other researchers [6][7][8][9]. The results show that the curve shift to the left side when the temperature increases from 313.15K to 333.15K indicating that less CO2 absorbed by the solutions. 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 CO2 molecules causing the breaking of the intermolecular bond between CO2 and the solution [10]. As a results, less CO2 will be absorbed since more CO2 was escaped from the solutions. In terms effects of pressure toward CO2 absorption, CO2 solubility increased with increasing of CO2 partial pressure as shown in Figure 4 and Figure 5. 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 [8][11]. The similar trends with respect to temperature and pressure was also observed for 35wt% DEA + 5wt% [BmPyrr][DCA].

![Figure 4. CO2 loading of 40wt% of DEA + 0wt% of [BmPyrr][DCA] at different temperature.](image1)

![Figure 5. CO2 loading of 30wt% of DEA + 10wt% of [BmPyrr][DCA] at different temperature.](image2)

3.3. Correlations of solubility as a function of pressure and temperature
Linear regression approach was used to model the experimental data of CO2 solubility as a function of temperature and partial pressure. Equation 2 is used to correlate the data according to Jou and Mather model [12]. Where P is the pressure in Psi, $\alpha$ is mol CO2 loading/ mol total amine and A and B were determined by plotting ln P against ln $\alpha$ 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 2.

$$\ln P = A \ln \alpha + B$$  \hspace{2cm} (2)

| System | Correlations |
|--------|--------------|
|        | A            | B            |
| 40 wt% DEA | -0.0103T + 4.3473 | 0.0070T + 4.1978 |
| 35 wt% DEA + 5 wt% [BmPyrr][DCA] | 0.0015T + 0.4177 | 0.0184T + 0.7509 |
| 30 wt% DEA + 10 wt% [BmPyrr][DCA] | 0.0177T + 5.1241 | 0.0160T + 1.3955 |

Table 2. Jou and Mather correlations.
The solubility correlations as a function of temperature at various pressures were conducted to determine the CO\textsubscript{2} loading measurement. Comparison between the predicted and experimental values of CO\textsubscript{2} solubility is shown in Figure 6. The model was further quantified by determining the average absolute deviation (AAD) using (3) as follows:

\[
AAD = \frac{\sum_{i=1}^{N} |(\alpha_{\text{exp}} - \alpha_{\text{cal}})/\alpha_{\text{exp}}|}{N}
\]

It was found that the correlation of CO\textsubscript{2} solubility has average absolute deviation (AAD) percentages of 5.427%. Thus, it shows good agreement between the experimental and predicted data.

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**Figure 6.** Comparison between correlated and experimental data for CO\textsubscript{2} loading.

4. Conclusions
In this work, the absorption of CO\textsubscript{2} into aqueous DEA blended with [BmPyrr][DCA] was measured. The results exhibit that addition of [BmPyrr][DCA] into aqueous DEA reduced the CO\textsubscript{2} loading capacity. On the other hand, it was found that increasing the pressure has led to increasing of CO\textsubscript{2} loading and increasing of temperature reduces the CO\textsubscript{2} solubility performances. Predicted CO\textsubscript{2} solubility using Jou and Mather model was found to be in good agreement with the experimental data.

Acknowledgement
The authors would like to thank the Ministry of Higher Education (MOHE) and Universiti Teknologi MARA (UiTM) for financial support given through the Fundamental Research Grant Scheme (FRGS) (600-RMI/FRGS 5/3 (91/2014)) for completing this research project.

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