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Separation of CO_2 by Using Aqueous Mixtures of AMP and $[B_3MPYR][BF_4]$ at High Pressure

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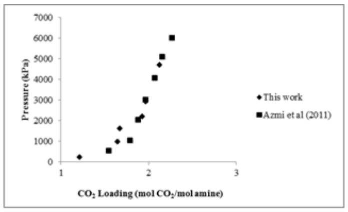
Graphical abstract



Abstract

In this study, CO_2 absorption capacity in aqueous mixtures of 2-amino-2-methyl-1-propanol, (AMP) and N-butyl-3-methylpyridinium tetrafluoroborate, $[B_3MPYR][BF_4]$ was measured at pressures from 200 kPa up to 5000 kPa and temperatures of 303.15 K - 333.15 K. The AMP concentration was maintained at 1 M while the $[B_3MPYR][BF_4]$ concentration ranges from 0.05 M to 0.3 M. It was observed that CO_2 loading capacity increases when the pressure increased. However, increasing of temperature will decrease the CO_2 loading. From the experimental results, a simple correlation, as suggested by Jou and Mather was used to predict the CO_2 loading in the aqueous AMP-$[B_3MPYR][BF_4]$ mixtures. The model were found to be in a good agreement with the experimental results where only 1.66% of the predicted values deviate more than 20% compared to the experimental values.

Keywords: CO_2; loading; mixtures; AMP; $[B_3MPYR][BF_4]$

■1.0 INTRODUCTION

2-amino-2-methyl-1-propanol, (AMP) has twice CO_2 loading capacity as those of any primary and secondary alkanolamine [1]. Besides AMP also has low regeneration energy [2].

Ionic liquids (ILs) are composed of cations and anions and have melting point below 373.15 K. Imidazolium, pyridinium, and phosphonium are some of the cations. While some examples of the anions are tetrafluoroborate, hexafluorophosphate and trifluoromethylsulfonate [3]. Pyridinium based ILs studies are very scarce in the literature compared to imidazolium, however pyridinium has the advantage over imidazolium because pyridinium based ILs are more biodegradeable and cheaper than imidazolium based ILs [4-5].

In this study, AMP and pyridinium based ILs which is N-butyl-3-methylpyridinium tetrafluoroborate, $([B_3MPYR][BF_4])$ were used to capture CO_2.

■2.0 EXPERIMENTAL

AMP and $[B_3MPYR][BF_4]$ were synthesis grade, purchased from MERCK and used as received. The CO_2 gas with purity of 99.9% was obtained from Linde Malaysia Sdn. Bhd. The aqueous AMP-([B3MPYR][BF4]) mixtures were prepared by mixing both solutions where the AMP concentration was set constant at 1 M while [B3MPYR][BF4]) concentrations vary from 0.05 M to 0.3 M. The CO_2 loading data were measured by using high pressure jacketed reactor. In this study, the temperatures were set at 303.15 K - 333.15 K while the pressure ranged from 200 kPa until 5000 kPa. In each run, a measured amount of the solution was placed into the reactor. The CO_2 gas reservoir and the reactor which contains aqueous AMP-$[B_3MPYR][BF_4]$ mixtures were heated up to a desired temperature. Once the desired temperature was achieved, the CO_2 gas was released from the reservoir into the solution and was constantly stirred throughout the experiment. The equilibrium state was reached indicated by a constant pressure for about 30 minutes and the final pressure was recorded. CO_2 loadings were calculated by using Equation 1.

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

where, α is mol CO_2 loading/total amine, P_{Ti} is initial total pressure in vessel, P_f is final pressure after supplied to reactor, V_{vessel} = 1 liter, $V_{reactor}$ is volume of gas in reactor, z is compressibility factor = 1, R is gas constant = 0.08206 L.atm/mol.K, T is temperature (K), P_{eq} is equilibrium pressure in reactor and P_{vi} is vapor pressure.

■3.0 RESULTS AND DISCUSSION

To verify the experimental apparatus used in this study, a number of experiments for CO_2 absorption in 1 M AMP was performed at 313.15 K. From the results, it was found that the average absolute deviation is 4.16 % which specify that the results are close to the literature values reported by Azmi *et al.* (2011) as shown in Figure 1 [6].

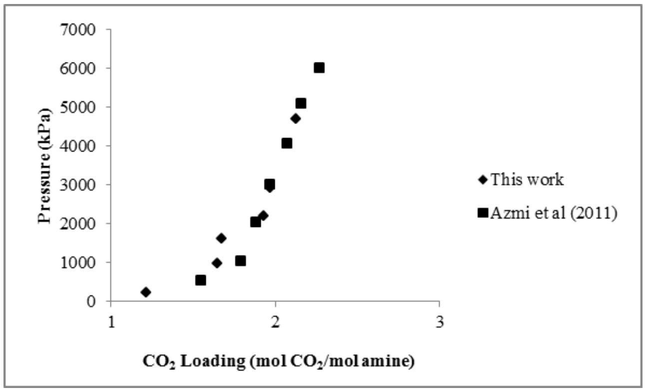


Figure 1 Comparison of CO_2 solubility of this work with literature values at 313.15 K for 1 M AMP [6]

3.1 Effects of Pressure and Temperature on CO_2 Loading

In this work, the CO_2 loading values were obtained from the measured initial and final pressure as calculated in Equation 1. Figure 2 shows the effect of pressure and temperature on CO_2 loading. It illustrated that at constant concentration of AMP–$[B_3MPYR][BF_4]$ mixture and temperature, increasing the pressure will increase the CO_2 loading. This is expected because of high frequency of gas particle collisions occurred at the gas-liquid interfacial area, thus creating more solute particles diffuse into the bulk solution. As a result, more CO_2 gas will be absorbed into the solution. This system obeys the Henry's Law which state that the solubility of a gas in a liquid is directly proportional to the pressure of that gas above the surface of the solution.

It was also observed that the CO_2 loading decreases, as the temperature increases at constant concentration of AMP–$[B_3MPYR][BF_4]$ mixture and pressure. For example, at constant pressure of 2800 kPa the CO_2 loading decreases from 1.46 to 1.26 at temperature of 323.15 K and 333.15 K respectively. This trend is supported by other studies which explained that the increase of kinetic energy at high temperature causing vigorous dynamic motion of the CO_2 molecules hence breaking the intermolecular bonds of CO_2 and the liquid thus escape from the solution [6].

3.2 Effect of ILs Concentration on CO_2 Loading

The CO_2 Loading was calculated in different ILs concentrations using Equation 1. As illustrated in Figure 3, it was observed that at higher concentration of ILs, less CO_2 was absorbed. This is due to the acidity of $[B_3MPYR][BF_4]$ which reduced the basicity of aqueous AMP in the mixture, as a result the driving force for the mass transfer to occur is decreasing [7].

As recommended by Jou and Mather [8], the experimental results of CO_2 loadings were correlated to the partial pressure and temperature as follow:

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

where P is the pressure in kPa, α is mol CO_2 loading/ mol total amine and A and B are functions of temperature in Kelvin. The value of A_i and B_i were determined by plotting ln P (pressure, kPa) against ln CO_2 loading at temperature of 303.15, 313.15, 323.15 and 333.15 K. All the values of A_i and B_i obtained were plotted against the temperature. From these graphs, the coefficients of A_i and B_i were determined. The coefficients are listed in Table 1. Using Equation 2 and the coefficients obtained, it was found that only 1.66% of the predicted CO_2 loading values deviate more than 20% compared to the experimental values thus the Jou and Mather correlation was found to be in a good agreement with the experimental results as shown in Figure 4.

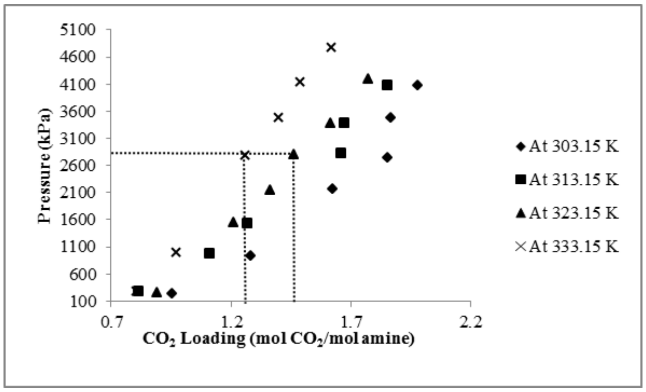


Figure 2 CO_2 solubility at different temperature in 1 M AMP + 0.3 M ILs

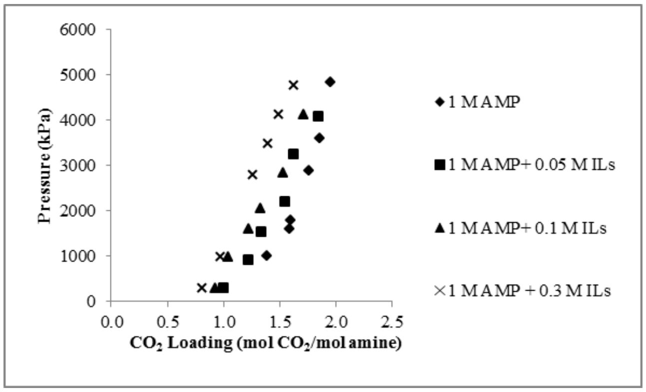


Figure 3 CO_2 solubility in different solution composition at 333.15 K

Table 1 Jou and Mather correlations

System	Correlations	
	A	B
1 M AMP	-0.009T + 7.6266	0.0348T - 6.238
1 M AMP + 0.05 M ILs	0.013T + 0.2464	0.0243T - 2.28
1 M AMP + 0.1 M ILs	0.0012T + 3.912	0.04T- 6.9842
1 M AMP + 0.3 M ILs	-0.0116T + 7.2752	0.0384T- 5.8684

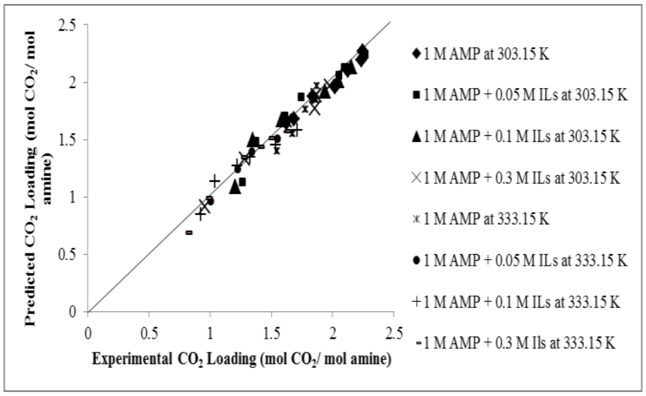


Figure 4 Comparison between correlated and experimental value for CO_2 loading in different solvent concentrations at 303.15 K and 333.15 K

■4.0 CONCLUSION

In this work, it was found that increasing the pressure will increase the CO_2 loading. On the other hand, the rising of temperature will reduce the CO_2 loading. The results also exhibited that the higher the concentration of $[B_3MPYR][BF_4]$ in the aqueous mixtures, the lesser the CO_2 loading due to the reduction of driving force for mass transfer to take place. The Jou and Mather correlation was able to predict the experimental CO_2 loading with only 1.66% predicted data deviated more than 20 % of the experimental values.

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