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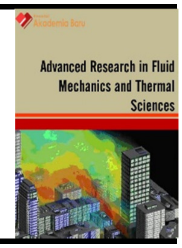

Investigation of Carbon Dioxide Solubility in Aqueous N-methyldiethanolamine (MDEA)-1- butyl-3-methylimidazolium acetate ([bmim][Ac]) Hybrid Solvent

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ABSTRACT

In this research work, aqueous hybrid solvents were prepared at different concentrations of 1-butyl-3-methylimidazolium acetate, [bmim][Ac] as ionic liquids (ILs) and N-methyldiethanolamine (MDEA) for the capturing of carbon dioxide (CO_2). The concentration of MDEA was kept constant at 30 wt% in every hybrid solvent investigated. The solubility of CO_2 in the hybrid solvent was investigated by varying the concentration of [bmim][Ac] in the aqueous hybrid solvent as 10 wt% and 20 wt%. For comparison, the solubility experiment was also conducted for pure aqueous MDEA solvent. Addition of [bmim][Ac] in the hybrid solvent reasonably enhanced the solubility of CO_2 as compared to its solubility in pure aqueous MDEA solvent. The loading capacity of hybrid solvent was also improved significantly with hybrid solvents. Further increasing the concentration of [bmim][Ac] from 10 wt% to 20 wt% has demonstrated a decrease in the solubility of CO_2 into the hybrid solvent. The effect of pressure on loading capacity and rate of absorption was also investigated by increasing the pressure from 10 bar to 20 bar. Both loading capacity and rate of absorption increased with increasing pressure. Promising results were achieved using hybrid solvents for capturing of CO_2.

1. Introduction

Globally, fossil fuel is the major source of energy consumption associated with the emission of carbon dioxide, a major source of greenhouse gases. Carbon dioxide emission related to use of fossil fuel is increasing alarmingly and estimated to reach 43.2 billion metric tons in 2035 as compared to its current 32.1 billion metric tons. This increased concentration of CO_2 results in global warming, polar ice cap melting, glaciers, sea levels rising and shattering weather patterns that can affect life on earth irrecoverably. Among fossil fuel sources, natural gas (NG) is the cleanest

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and one of attractive energy sources as it demonstrated lower emissions of carbon dioxide, nitrogen oxides, and particulates in comparison with other fuels such as oil and coal [1, 2]. However, natural gas reserves are energy sources that are contaminated with substantial amount of CO_2. Research report indicates that more than 50% of the world natural gas reserves are contaminated by more than 2% CO_2 [3]. Prior to its utilization, CO_2 and other acid gasses such as nitrous oxide, hydrogen sulfide need to be separated. As CO_2 has no energy value by itself, its presence in natural gas streams lowers the energy content (calorific value) of natural gas. It also contributes to pipeline and equipment corrosion during storage and transportation [4]. The removal of carbon dioxide from those gases has been carried out by means of several technologies, such as absorption, cryogenic distillation, membrane separation, and adsorption.

Absorption of CO_2 in liquid solvents is the most economical and commercially established technology for purifying large volumes of gas at different level of CO_2 concentration. In existing industrial absorption processes solvents that are widely and commercially applied for CO_2 absorption processes are alkanolamines or its mixture such as monoethanolamine (MEA), diethanolamines (DEA), methyldiethanolamine (MDEA), and Piperazine (Pz) [5, 6]. However, amines have got certain limitations such as high regeneration cost (energy intensive), low loading capacity, equipment corrosion [7-9]. Use of ionic liquid (ILs) in small amount with amines as hybrid solvents is believed to be the better alternative to reduce the limitations posed by amines. ILs especially imidazolium based ILs have high CO_2 selectivity, high reactivity with CO_2 and relatively good thermal stability while overcoming limitations of amines [10-13]. On the other hand, as ILs are expensive, highly viscous to be used as a solvent, its use as a solvent for CO_2 absorption at commercial scale is not justified [14-16]. However, using small amount of ILs in aqueous amine solvents as hybrid solvent is the better option to reduce the limitations of both amines and ILs while utilizing the advantages they offer as CO_2 absorbents. In this research work hybrid solvents were prepared from aqueous MDEA and imidazolium based ILs of 1-butyl-3-methylimidazolium acetate, [bmim][Ac] at different concentrations of [bmim][Ac]. The solubility of CO_2 in hybrid solvents were investigated and the results are compared with pure aqueous MDEA solvent.

2. Materials and Methods

A. Materials and Chemicals

The chemicals and materials used in this research work were N-methyldiethanolamine (MDEA) with a purity of 98% and 1-butyl-3-methylimidazolium acetate, [bmim][Ac] with a purity of > 95% were procured from Merck Sdn Bhd Malaysia. The chemicals were reagent grade and used without any further purification. The samples of the hybrid solvents were prepared using Millipore quality of water. To ensure complete miscibility of components in hybrid solvents, the samples were completely mixed and retained for 24 h. The actual amine concentration in concentrated aqueous solutions were found by means of Karl Fischer titration using 1 mol dm^{-3} of HCl. Carbon dioxide gases premier at 57.3 bar and purified nitrogen at 150 bar were procured from Gas Walkers Sdn. Bhd, Malaysia and used for the investigation of CO_2 solubility in hybrid solvent and performance evaluation.

B. Experimental Methods

Aqueous hybrid solvents at 30 wt% N-methyldiethanolamine (MDEA) and 1-butyl-3-methylimidazolium acetate, [bmim][Ac] as ionic liquids (ILs) at concentration of 10 wt% and 20 wt% were formulated and its thermophysical properties were investigated as presented in our work

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elsewhere [8]. CO_2 absorption capacity of aqueous hybrid solvent samples were investigated at three different pressures of 10 bar, 15 bar, and 20 bar while keeping the temperature constant at of 30°C using High Pressure Solubility Cell (HPSC). The HPSC mainly consists of one mixing vessel (MV), two equilibrium cell (EC_1 and EC_2), magnetic stirrer, pressure sensor, and gas storage tank. Concentration of MDEA was kept constant at 30 wt% MDEA in all of aqueous hybrid solvents under investigation.

The CO_2 solubility in hybrid solvents was measured using pressure decay method with the assumption that all changes in the gas pressure were due to the mass sorption of CO_2 into the hybrid solvents inside a fixed volume system. Since two equilibrium cells were available, two samples were tested at a time. The total volume of EC_1 was 50 ml and 10% of the total volume of EC_1 was accommodated by sample and the remaining 90% of the total volume was filled by CO_2 gas purged from MV. The total volume of EC_2 is 70 ml and similar ratio of sample to CO_2 gas was used in EC_2. In order to ensure an even distribution of CO_2 in the equilibrium cell, the speed of magnetic stirrer used was set at 300 rpm. The pressure and temperature of MV, EC_1 and EC_2 were recorded by a digital indicator. Figure 1 shows the schematic diagram of High Pressure Solubility Cell used in CO_2 solubility experiment of the present work.

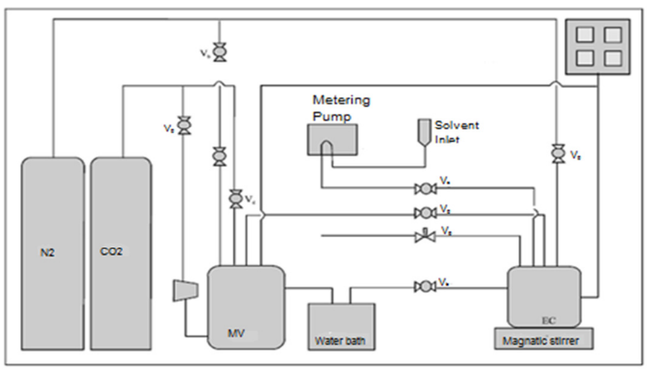

Fig. 1. High Pressure Solubility Cell schematic diagram

It was considered that equilibrium of absorption was achieved when EC pressures became constant. Then, the amount of CO_2 mole transferred from MV to EC was determined using equation (1):

$$n_{CO_2} = \frac{V_T}{RT_a}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \tag{1}$$

where: V_T = MV volume, R = Gas constant = 8.31446 cm^3.MPa/mol.K, T_a = Ambient temperature (K), P_1 = Pressure of MV before transferring CO_2 to EC (MPa), P_2 = Pressure of MV after transferring CO_2 to EC (MPa), Z_1 = Compressibility factor at P_1, Z_2 = Compressibility factor at P_2.

The CO_2 compressibility factors, Z_1 and Z_2 were calculated using *Peng Robinson Equation of State (EOS)*. Equilibrium pressure of CO_2 was determined using equation (2):

$$P_{CO_2} = P_T - P_V \tag{2}$$

where: P_T = EC total pressure (MPa), P_V = Vapor pressure of sample in EC (MPa)

The mole of CO_2 in gas phase in EC was obtained from equation (3):

$$n_{g,CO_2} = \frac{V_g P_{CO_2}}{Z_{CO_2} RT}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \quad (3)$$

where: V_g = Volume of gas in EC (ml), P_{CO2} = CO_2 Equilibrium pressure (MPa), = Z_{CO2} Compressibility factor at P_{CO2}, R = Gas constant = 8.31446 cm^3.MPa/mol.K, T = Equilibrium EC temperature (K)

On the other hand, the amount of absorbed CO_2 in hybrid solvent (liquid phase) was determined using equation (4):

$$n_{l,CO_2} = n_{CO_2} - n_{g,CO_2} \quad (4)$$

The mount of hybrid solvents (MDEA-[bmim][Ac]) in moles after absorption process was determined from equation (5):

$$n_{MDEA-[bmim][Ac]} = \sum \frac{m\rho V_l}{MM} \quad (5)$$

where: m = Mass fraction of MDEA-[bmim][Ac] , ρ = Density of hybrid solvent, V_l = Volume of sample inside EC, MM = Molar mass of MDEA-[bmim][Ac]

The CO_2 loading capacity of the hybrid solvent was obtained using equation (6):

$$\alpha_{CO_2} = \frac{n_{l CO_2}}{n_{MDEA-[bmim][Ac]}} \quad (6)$$

3. Results and Discussion

A. CO_2 Solubility in Aqueous MDEA-[bmim][Ac] Hybrid Solvents

Solubility of CO_2 in aqueous MDEA-[bmim][Ac] hybrid solvents was experimentally investigated at different pressures of 10, 15 and 20 bar and [bmim][Ac] concentration of 10 wt% and 20 wt%, respectively. The concentration of MDEA was kept constant at 30 wt% in the aqueous hybrid solvent throughout the investigation. For comparison results were compared with pure 30 wt% MDEA solvents. As presented in Figure 2, better solubility of CO_2 was observed in hybrid solvents prepared from a mixture of aqueous MDEA and [bmim][Ac] as compared to CO_2 solubility in pure aqueous amine solvents. The result indicates addition of [bmim][Ac] in aqueous MDEA solvent enhances the absorption of CO_2 into the hybrid solvents. It was also observed that increasing pressure from 10 bar to 20 bar drastically increases the solubility of CO_2 in the hybrid solvents. Figure 2 demonstrated that [bmim][Ac] as ILs and pressure have a combined effect in improving the solubility of CO_2 into the hybrid solvent. At aqueous 30 wt% MDEA-10wt% [bmim][Ac] hybrid solvent and operation pressure of 10 bar, the solubility of CO_2 in the hybrid solvent was increased by 53.92% as compared to its solubility in pure 30 wt% aqueous MDEA solvent. When the pressure was further increased to 20 bar, the solubility of CO_2 in hybrid solvents was drastically increased by 201.76%. This is because at higher pressure, more CO_2 molecules were forced to diffused into the liquid phase MDEA-[bmim][Ac] hybrid solvent to relief higher pressure force exerted on CO_2 inside closed vessel of equilibrium cell (EC) where by CO_2 become more soluble in the solvents.

On the other hand, increasing the concentration of [bmim][Ac] from 10 wt% to 20 wt% exhibited a decrease in the solubility of CO_2 in the hybrid solvent as illustrated in Figure 2. This is because as the concentration of [bmim][Ac] in the hybrid solvent increases the hybrid solvent become more viscous as [bmim][Ac] is highly viscous solvent. This viscous effect of [bmim][Ac] suppresses the loading capacity of CO_2 in the hybrid solvent. Hence, systematic investigation is very important to determine the optimum concentration of [bmim][Ac] in the hybrid solvent for better CO_2 solubility.

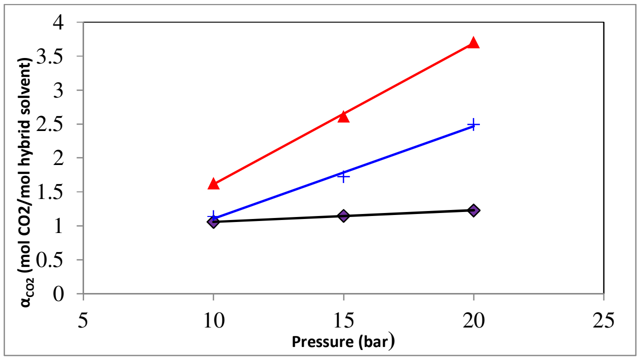

Fig. 2. CO_2 loading capacity in (♦) aqueous 30 wt% MDEA, (▲) 30 wt% MDEA– 10 wt% [bmim][Ac] and (+) 30 wt% MDEA– 20 wt% [bmim][Ac] hybrid solvent at different pressures

B. CO_2 Absorption Kinetics in Hybrid Solvents

Further investigation of the hybrid solvent was conducted in order to observe the CO_2 absorption rate of the hybrid solvents as presented in Figure 3. The study was conducted at 10 wt% and 20 wt% concentration of [bmim][Ac] while keeping MDEA constant at 30 wt%. The absorption pressure and temperature were also kept constant at 20 bar and 30 ^{o}C, respectively while varying the absorption time from 0 to 350 minutes at the interval of 30 minutes until equilibrium is achieved. For comparison, the absorption rate of pure aqueous 30 wt% MDEA was also conducted at the same condition. It was observed that addition of 10 wt% [bmim][Ac] as ILs into aqueous 30 wt% MDEA increase the rate of absorption of hybrid solvent. In only about 50 minutes, the maximum absorption was achieved with hybrid solvent prepared from 10 wt% [bmim][Ac].

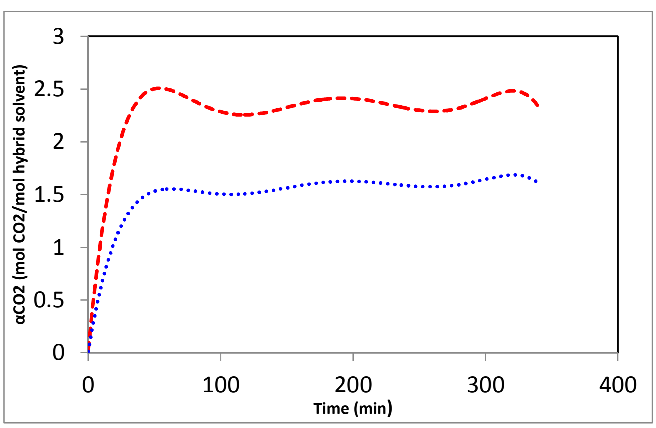

Fig. 3. CO_2 absorption rate in aqueous (—) 30 wt % MDEA, (----) 30 wt% MDEA-10 wt% [bmim][Ac] and (.....) 30 wt% MDEA- 20 wt% [bmim][Ac] hybrid solvent at different time

On the other hand, increasing the concentration of [bmim][Ac] to 20 wt% demonstrated a negative effect on the CO_2 absorption rate as well as CO_2 loading capacity. Increasing the concentration of [bmim][Ac] in the hybrid solvent increases the viscosity as well as the density of the hybrid solvents and results in a decrease in surface tension of the hybrid solvents [8]. Thus, increasing the concentration of [bmim][Ac] in the hybrid solvents reduced both the loading capacity and rate of absorption. It was also investigated that better CO_2 absorption rate was observed when 10 wt% [bmim][Ac] as ILs was added into the solvent as compared to hybrid solvents prepared from aqueous MDEA alone (Figure 3). This indicates at lower concentration of [bmim][Ac], fast solubility of CO_2 in the hybrid solvent can be achieved and it should be carefully evaluated to minimize amount of [bmim][Ac] needed in the hybrid solvent and to avoid its negative effect. The present research work exhibits using amine-ILs hybrid solvent is a promising future for the capturing of CO_2.

4. Conclusion

In this study, for the capturing of CO_2, aqueous hybrid solvents were prepared from the mixture of N-methyldiethanolamine (MDEA) and 1-butyl-3-methylimidazolium acetate, [bmim][Ac] as ionic liquids (ILs)] at different mass ratio. In each aqueous hybrid solvents, the concentrations of MDEA were kept constant at 30 wt% while the concentration of [bmim][Ac] was varied to observe the effect of concentration. Among aqueous hybrid solvents prepared from MDEA and [bmim][Ac], hybrid solvents prepared from 30 wt% MDEA-10 wt% [bmim][Ac] has demonstrated better CO_2 solubility and absorption rate. It was also observed that increasing the concentration of [bmim][Ac] beyond 10 wt% has a negative effect on the solubility of CO_2 in the hybrid solvents due to viscous effect of [bmim][Ac]. The concentration of [bmim][Ac] in the hybrid solvent need to be minimum in order to avoid the negative effect of viscosity. Increasing pressure from 10 bar to 20 bar has exhibited an increase in the solubility of CO_2 in the hybrid solvent as well as an increased rate of absorption. In general, use of hybrid solvents prepared from aqueous amine and ILs is a promising future for the capturing of CO_2.

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