Activated Carbon Supported Amine Functionalized Ionic Liquids for CO$_2$ Sorption

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Abstract. Ionic liquids (ILs) have been proven to produce promising results in CO$_2$ capture. However, ILs suffer the problem of having high viscosities which limit the application. Impregnation of ILs into porous solid support may be an alternative to overcome this problem. In this study, the wet impregnation method was used and this was confirmed by surface area, pore volume and pore size before and after impregnation. Activated carbon impregnated with 10wt% of [hmim][NTf$_2$], [vbtma][gly] and poly[vbtma][gly] were prepared to study the CO$_2$ sorption. The results showed that activated carbon impregnated with [vbtma][gly] gives higher CO$_2$ sorption with 19.91 mmol/g at 20 bar. Therefore, a series of activated carbon impregnated with 10wt%, 20wt% and 30wt% of [vbtma][gly] were prepared to study the optimum composition of [vbtma][gly] for CO$_2$ sorption. The CO$_2$ sorption studied showed the optimization occurred at 20wt% of poly[vbtma][gly] and CO$_2$ uptake increased with pressure increased.

1. Introduction
Development of technologies in the separation of carbon dioxide (CO$_2$) is very important especially in the natural gas processing and fossil fuel power plant [1]. A commercial solvent such as aqueous ammonia is the most common solvent used to absorb CO$_2$ [2]. Currently, the new alternative solvent so called ionic liquids (ILs) are getting wide attention because of their green properties such as non-volatile, non-corrosive, chemically stable, thermally stable, non-flammable, and low vapor pressure. ILs also show very promising results in the process of CO$_2$ removal [3].

ILs as an alternative solvent to capture CO$_2$ have been proven to give promising results in CO$_2$ capture applications. Shahrom et al. [4] reported that their synthesized amino acid-based polymerized ionic liquids (AAPILs) was capable of capturing CO$_2$ more than the task specific ionic liquid and polymerized ionic liquid due to the functionalized amine tethered at the anion. In another report by Vijayraghavan et al. [5], a series of protic ionic liquids were employed for CO$_2$ capture which resulted higher absorption capacities compared to MEA. However, the viscosity of functionalized ILs is high which can limit the mass transfer of molecules in the ILs [2]. The use of water to reduce the viscosity however leads to ILs loss due to evaporation and corrosion problem [6]. Impregnation of ILs into porous solid support may be an alternative to overcome this problem.

The use of solid support to impregnate ionic liquids has received many attentions lately. Yu et al. [7] who reviewed quite a number of solid supports from various works found that amine-impregnated solid support has high CO$_2$ adsorption capacity. Romanos et al. [8] on the other hand has proposed a novel supported ionic liquid phase systems (inverse SILPs). SILPs are usually formed by filling the ILs to the nanoporous materials such as silica nanoparticles. This prepared inverse SILPs exhibited very promising CO$_2$ absorption capacity and fast kinetics since the latter was attributed to the high dispersion of the ILs phase which was stabilized between the silica particles. The CO$_2$ sorption
capacity of 1.5-3.3 mmol/g and the CO/N₂ selectivity achieved above 200 suggested that it is a promising candidate for CO₂ capture in industrial scale.

In this study, three types of ILs have been chosen to impregnate with activated carbon which is [hmim][NTf₂], [vbtma][gly] and the polymer, poly[vbtma][gly]. By using amino acid (glycinate) with functionalize amine at anion, it would increase the CO₂ sorption as compared to non-functionalized amine, [hmim][NTf₂]. However, these functionalized ILs suffer the problem of high viscosity in monomer, and sticky material due to hygroscopic nature in polymer. Therefore, by impregnating these ILs on activated carbon would enhance the properties of material. The amine functionalities can be study by comparing with non-functionalize ILs which is [hmim][NTf₂]. These ILs were impregnated on activated carbon via wet impregnation method and was confirmed by surface area and porosity using BET and further for CO₂ adsorption studies.

2. Experimental Method

2.1. Chemicals

The chemicals used in the synthesis of [vbtma][gly] are (vinylbenzyl)trimethylammonium chloride, [vbtma][Cl] 99%, glycine, Amberlyst A-26 (hydroxide, OH form) were purchased from Sigma Aldrich, Malaysia. The solvents, methanol, and acetonitrile were purchased from Merck, Malaysia. To polymerize the [vbtma][gly], radical initiator used was α,α′-Azobisisobutyronitrile (AIBN) and it was purchased from R&M, Malaysia. The 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide 99% ([hmim][NTf₂]), was purchased from Merck and used without further purification. Activated carbon was used in pellet form.

2.2. Methodology

2.2.1. Preparation of solid supported ionic liquids

[vbtma][gly] and poly[vbtma][gly] was synthesized as reported in previous literature [4]. Activated carbon was heated at 200 ºC for 3 h to remove any moisture. To prepare 10wt% of ILs, a solution of appropriate amount of ILs with methanol was prepared. Then, appropriate amount of activated carbon was added to the solution of ILs. The mixture was gentle stirred for 24 h at room temperature. After that, the methanol was removed using the rotary evaporator which created a physical immobilization of ILs on the solid support. Then, the activated carbon supported with ILs were dried in oven for 1 day at 70 ºC.

3. Results and Discussions

3.1. Morphological analysis by FESEM

The morphological analysis for pure activated carbon (AC), AC-[hmim][NTf₂], AC-[vbtma][gly] and AC-poly[vbtma][gly] was determined by Field Emission Scanning Electron Microscopy (FESEM). The magnification used was 10,000×. Figure 1 shows the FESEM images pure AC and AC impregnated with ILs.
Figure 1. Morphology of (a) pure AC, (b) AC-[hmim][NTf$_2$] and (c) AC-[vbtma][gly] (d) AC-poly[vbtma][gly]

Figure 1 shows the FESEM morphology of pure AC and AC after impregnated with ILs i.e. AC-[hmim][TfN], AC-[vbtma][gly] and AC-poly[vbtma][gly]. For pure AC, it can be observed that the surface possessed a porous surface and after ILs were added, the surface of AC impregnated ILs were smooth compared to pure AC.

3.2. Surface area and Porosity Analysis

The surface area, pore size and pore volume were determined by SAP analyzer. Activated carbon (AC) was impregnated with 10wt% [hmim][NTf$_2$], [vbtma][gly] and poly[vbtma][gly] through wet impregnation method.

| Sample                  | Surface Area (m$^2$/g) | Pore size (nm) | Pore volume (cm$^3$/g) |
|-------------------------|-------------------------|----------------|------------------------|
| Activated carbon (AC)   | 767.97                  | 1.936          | 0.372                  |
| AC-[hmim][NTf$_2$]      | 519.26                  | 2.139          | 0.277                  |
| AC-poly[vbtma][gly]     | 721.97                  | 2.171          | 0.411                  |
| AC-[vbtma][gly]         | 426.3                   | 2.32           | 0.248                  |

From Table 1, it can be seen that after impregnation, the surface area and porosity were lower than pure AC which confirmed the impregnation occurred. This is due to less nitrogen adsorbed by AC-impregnated since the pores were filled with ILs making it to have less pores available for nitrogen adsorption thus lower the surface area. The reduction in surface area and pore volume were also observed by previous literature [9]. Pore size however increased due to the filling of the smaller micropores by ILs to the AC.

However, the surface area after activated carbon impregnated with poly[vbtma][gly] was almost similar and slightly less than pure AC as compared with the monomer, [vbtma][gly] and [hmim][NTf$_2$]. This is probably due to the leaching of poly[vbtma][gly] on AC during wet impregnation process. This is because, poly[vbtma][gly] is not well dissolved in methanol solvent, thus it gives gel type solution. Therefore, full impregnation of poly[vbtma][gly] on AC was not achieved.

Figure 2 shows the isotherm plot of AC impregnated ILs. The plot shows that the Type I isotherm which is characterized by an initial increased rapidly in the amount adsorbed and produced a long nearly flat region at higher pressure. This isotherm is characterized by micropore adsorbent and the mechanism involved was the micropore filling.
3.3. \textit{CO$_2$} adsorption by SSILs

\textit{CO$_2$} sorption can be determined by high pressure manometric sorption system at 5, 10, 15 and 20 bar pressures and at 298. The system used was a ‘volumetric type’ based on a pressure drop method. The calculation to determine the mole of \textit{CO$_2$} captured is shown in Equation 1.

\begin{equation}
n = \frac{P_{ini} \cdot V_{tot} - P_{eq} \cdot (V_{tot} - V_{sample})}{Z_{ini} \cdot R \cdot T_{ini}}
\end{equation}

where $n$ = Mol \textit{CO$_2$} captured, $P_{ini}$ = Initial pressure, $V_{tot}$ = Total of volume system, $Z_{ini}$ = Compressibility factor ($P_{ini} \times T_{ini}$), $Z_{eq}$ = Compressibility factor ($P_{eq} \times T_{eq}$), $P_{eq}$ = Equilibrium pressure, $V_{sample}$ = Sample volume, $R$ = 8.314 kPa.L/mol.K, $T_{ini}$ = Initial temperature and $T_{eq}$ = Equilibrium temperature. The compressibility factor was taken by using the \textit{Peng-Robinson} equation of state. Experiments were repeated three times and standard deviation of \textit{CO$_2$} absorption data was less than 0.05 \%.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Pressure (bar) & AC (pure) (mmol/g) & AC-[hmim][NTf$_2$] (mmol/g) & AC-[vbtma][gly] (mmol/g) & AC-poly[vbtma][gly] (mmol/g) \\
\hline
5 & 3.18 & 4.09 & 5.87 & 3.7 \\
10 & 5.19 & 6.58 & 12.73 & 7.1 \\
15 & 6.81 & 8.68 & 16.50 & 8.5 \\
20 & 8.08 & 10.67 & 19.91 & 12.11 \\
\hline
\end{tabular}
\caption{\textit{CO$_2$} sorption of AC (pure) and 10wt\% of [hmim][NTf$_2$], [vbtma][gly] and poly[vbtma][gly] impregnated on activated carbon}
\end{table}
From Table 2, it can be seen that the CO$_2$ sorption increased with increasing pressure for all SSILs from 5 bar to 20 bar. This is expected because when the pressure increases, it will force the gas into the ILs [10].

Figure 3 shows the adsorption capacity from the CO$_2$ adsorption experiment. For pure AC, CO$_2$ captured might be due to physisorption occurring within its pore structure [11]. However, after impregnated, CO$_2$ adsorption was higher than pure AC. This is due to the ability of the impregnated ILs [hmim][NTf$_2$], [vbtma][gly] and poly[vbtma][gly] to attract and adsorb CO$_2$ into the pores.

The adsorption capacity of AC-[vbtma][gly] is higher than the polymer itself, AC-poly[vbtma][gly] and AC-[hmim][NTf$_2$]. This is because, the amine functional group in glycinate as anion contributed to the attraction of CO$_2$ to the ILs thus increases the CO$_2$ sorption [12]. After polymerization, the CO$_2$ sorption was lower than the monomer, [vbtma][gly] because well impregnation did not occur due to the low dissolution of polymer in methanol solvent during the impregnation process. Although the impregnation of activated carbon with poly[vbtma][gly] did not successfully occur, the CO$_2$ sorption was still higher than [hmim][NTf$_2$] due to the functionalized amine which attracted with CO$_2$. The polymer structure also contributed to increase the CO$_2$ sorption due to the multiple linkage of [vbtma][gly].

AC-[hmim][NTf$_2$] produced low CO$_2$ sorption capacity as compared to AC-functionalized ILs due to the effect of amine in ILs which attracted more CO$_2$ thus adsorbed into the pores. Furthermore, this AC impregnated ILs can be recycled and regenerated by pressure swing adsorption.

Overall, the promising results can be observed for AC-[vbtma][gly]. Therefore, AC impregnated with 10wt%, 20wt% and 30wt% [vbtma][gly] were prepared to study the optimization for CO$_2$ sorption. Figure 4 and Table 3 shows the CO$_2$ sorption results of AC impregnated [vbtma][gly] with various composition.
Figure 4. CO$_2$ sorption on 10wt%, 20wt% and 30wt% AC- [vbtma][gly]

Table 3. CO$_2$ sorption of 10, 20 and 30wt% AC-[vbtma][gly]

| Pressure (bar) | 10wt% (mmol/g) | 20wt% (mmol/g) | 30wt% (mmol/g) |
|---------------|----------------|----------------|----------------|
| 5             | 5.87           | 6.06           | 1.28           |
| 10            | 12.73          | 14.0           | 10.0           |
| 15            | 16.50          | 20.53          | 16.57          |
| 20            | 19.91          | 30.90          | 20.09          |

Figure 4 shows that when the pressure was increased, the gas solubility increased. This explained that the CO$_2$ sorption increased with increasing pressure for all SSILs from 5 bar to 20 bar. This is expected as when the pressure increases, it will force the gas into the ILs.

Lower adsorption for 10wt% indicated that less impregnation loading did not help to increase the adsorption capacity. This might be due to the stronger AC and [vbtma][gly] interaction rather than with CO$_2$. The optimum capacity can be seen at 20wt% [vbtma][gly] which the result showed higher CO$_2$ sorption at 30.90 mmol/g at 20 bar. This might be because the 20wt% loading produced good interaction with AC and CO$_2$. However, at 30wt%, the CO$_2$ sorption decreased due to blockage of pores with ILs due to saturated pores and fully adsorption occurred at adsorbent thus the CO$_2$ sorption uptake decreased [13].

Figure 5 shows the CO$_2$ sorption at 20 bar for 20wt% AC-[vbtma][gly] in function of time. From Figure 5, it can be seen that the CO$_2$ sorption reached equilibrium approximately in 15 hours.
Figure 5. CO₂ sorption of AC-20wt%[vbtma][gly] in function of time

4. Conclusion
From the experimental work, the CO₂ sorption capacity increased by using AC impregnated with ILs as compared to pure AC. The wet impregnation method had successfully impregnated the ILs loading inside the porous support which was confirmed through surface area and pore size analyses. However, since poly[vbtma][gly] did not dissolve well in any solvents, hence full impregnation could not be achieved. Despite that, the CO₂ sorption in AC-poly[vbtma][gly] was still higher than AC-[hmim][NTf₂] due to the amine functional group in glycine which plays a major role in the attraction of CO₂ to the SSILs. Thus, the monomer [vbtma][gly] with successfully impregnated showed higher CO₂ sorption than the polymer itself. The optimum composition was at 20wt% [vbtma][gly] since at 30wt%, the CO₂ sorption capacity decreased due to blockage of pores with CO₂ thus saturated occurs. From here, it can be concluded that, AC impregnated with functionalised amine ILs could increase the CO₂ sorption intake capacity.

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