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# Ice-templated fabrication of porous imidazole based polymers for $CO_2$ adsorption

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Poly-n-vinyl imidazole and its low-cost derivatives have been synthesized using ice-templation method and the synthesized porous organic polymeric material has been employed for $CO_2$ capture at room temperature. Simple modification of the monomer introducing –OH and –$NH_2$ groups followed by polymerization lead to two new polymers. All the three polymers have been characterized thoroughly using NMR and mass spectrometry. Ice-templated method has been found to create fibrous porous network inside the material as can be revealed by scanning electron microscopy. Thermal stability of porous polymeric network has been signified through TGA. Introduction of hetero atoms like oxygen and nitrogen in the polymeric matrix show improved $CO_2$ uptake due to increase in number of $CO_2$-philic sites as demonstrated by BET adsorption isotherm.

**Keywords**: Poly-n-vinyl imidazole, $CO_2$ capture, adsorption, BET adsorption isotherm

According to United Nation report appealing to control excessive emission of greenhouse gases, scientific workers are taking great efforts to reduce the global temperature by capturing greenhouse gases using different technologies[1]. As automobile industries and other sources like burning fossil fuels, emitting $CO_2$ significantly, there is an urgent need to tackle with an anthropogenic $CO_2$ emission in order to make environment clean and safe[2]. The challenge of controlling global warming has been accepted by industrial and academic scientific workers and came with an alternative of carbon capture and storage[3,4]. Very first attempt towards carbon capture and storage is an absorption by liquid amines called 'amine–scrubbing process' where aqueous solution of amines have been used as an absorber[4,5]. Although the process provides high efficiency, but includes various disadvantages like amine evaporation, corrosive nature, energy dissipation and non-regeneration[6-8]. Therefore, the condition offers a route for the development of an alternative for carbon capture and storage to overcome the bottlenecks of amine-scrubbing process.

From the existing alternatives, adsorption by solid and porous adsorbents has been found to be most prominent and fascinating one as it offers numerous advantages namely, free from volatility and corrosion issues. In addition to this, porous adsorbents are associated with high adsorption capacity, high thermal stability and can be handled and regenerated easily[9,10]. A series of porous adsorbents have been developed to obtain highest uptake including activated carbons, zeolites, metal oxides, metal organic frameworks, covalent organic frameworks and porous organic polymers (POPs)[11-14]. Due to versatile nature of POPs, they are established as a state of art with potent class in the field of carbon capture and storage. The versatility of POPs involves diversity in structures and synthetic processes that leads to the wide range of modifications, physicochemical stability, high surface area and inherent porosity[12-16].

It is known that the $CO_2$ capture capacity of porous organic polymers improved not only due their structural framework and arrangements but also the availability of functional sites. Functionally diverse skeleton plays pivotal role in enhancing modification in the structural motif in order to increase the uptake[17-24]. It has been well established that due to lone pairs in the functional group polarizes the acidic $CO_2$ molecule. This Lewis acid-base interaction concept has been applied to develop a wide range of porous polymeric adsorbents by incorporating Nitrogen and Oxygen moieties in the polymeric networks[25-27]. The development towards the synthesis of nitrogen framework containing polymeric adsorbents carried out significantly with few shortcomings like multi-step synthesis, post polymerization still required for modification, use of usual monomers[28-32]. To scale-up the synthetic process, recently, Kuan Huang et. al.[33] has developed solvothermal process to synthesize nitrogen tuned nanoporous organic polymers by different nitrogen – containing monomers for selectively enhancing the carbon capture. Therefore, there is always a scope for scientific workers to upgrade synthetic routes for obtaining porous polymers with ease of synthesis using simple monomers.

The method of Ice-templating has been well established so far and it is further extended to fabricate porous polymers for adsorption of flue gas at atmospheric pressure without any prior and post treatment. This involves freeze -drying process that leads to porosity by means of sublimation of soluble solvent which dissolves polymer. Various co-workers have synthesized porous polymer using ice-templating process for demonstrating ice-segregation induced self-assembly capabilities, providing a rigid macroporous scaffold, preparing composites for water adsorbers[34-36].

Herein, we report the facile synthesis of nitrogen and oxygen-functionalized fibrous POPs from one-step homo-polymerization followed by lyophilisation (freeze – drying) of Poly-N-vinyl imidazole and its polymeric derivatives under normal conditions using Azobisisobutyronitrile (AIBN) initiator. All the three materials have shown good carbon dioxide capture capacity.

## Experimental Section

### Chemicals

All chemicals used were of AR grade.N-vinylimidazole (VIm) and dimethylformamide were purchased from Alfa Aesar. N-vinylimidazole was taken in a cone-shaped RB flask and then vacuum distilled at 90 $^0$C and collected in a round bottom flask containing dry KOH pallets. Dimethylformamidewas taken in a cone-shaped round bottom flask and then vacuum distilled at 150 $^0$C and collected in a RB flask containing dry molecular sieves. 2,2’-Azobis(2-Methylpropionitrile) (AIBN) and n-butyl lithium were purchased fromSigma Aldrich. AIBN was recrystalized from hot methanol and then used for polymerization. Sodium borohydride, ammonium acetate, zinc dust, triethylamine, di-tert-butyl dicarbonate, trifluoroacetic acid (Spectrochem), hydroxylamine hydrochloride (Loba Chemie) sodium carbonate, liq. ammonia (Merck) were used without further purification. Methanol was obtained from Merck, India and dried with Karl-Fisher reagent before use.

### Instruments

The solution state $^1$H NMR spectra were recorded on Bruker Avance III 500 MHz NMR spectrometers. Electron spray ionization high resolution mass spectrometry (ESI-HRMS**)** was carried out on Bruker Daltonics MicroTOF-Q-II Mass Spectrometer using acetonitrile as solvent.

Thermogravimetric analysis was carried out using Perkin Elmer TGA-6000 instrument. The surface morphology of all polymers were examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope (FESEM). The SEM samples were prepared by sprinkling (~0.5 mg) polymers (powdered form) on aluminium stub using silicon wafer over an adhesive carbon tape. All samples were coated with a thin layer of sputtered gold prior to imaging. FESEM was carried out using an accelerating voltage of 5 kV and 10 kV.

All the gas adsorption measurements were executed on Autosorb QUA211011 (Quantachrome) equipment. Adsorption Isotherms plots was analyzed using ASIQwin software.

### Preparation of monomers

#### 1-Vinylimidazole-2-carbaldehyde

2 mmole N-vinylimidazole (VIm) was converted into 1-vinylimidazole-2-carbaldehyde using reported method[37]. In a typical experiment, VIm wastaken in a round bottom (RB) flask containing plastic bead using glass syringe followed by the addition of 5 mL dry tetrahydrofuran (THF). The RB flask was cooled at -78$^0$C with degassing by $N_2$ for 30 minute. 20 mmole of n-butyl lithium was added dropwise in the presence of $N_2$ gas using glass syringe. Mixture was stirred for 60 minute. The slightly yellowish reaction mixture was then kept at room temperature. After 5 minutes, 4 mmole of dry dimethyl formamide (DMF) was the added in the reaction mixture in the presence of $N_2$ gas using glass syringe. Reaction mixture was stirred at room temperature for 3 hour. After the confirmation of completion of reaction through TLC, reaction mixture was transferred into a separating funnel containing ethyl acetate-water mixture. Compound was extracted 4 times and then solvent was evaporated using rotary evaporator, yellowish oil obtained was further purified by column chromatography (40% yield).

### 1-Vinylimidazole-2-methyl alcohol

2.6 mmole yellowish oil (1-vinylimidazole-2-carbaldehyde) was takenin a 10 mL RB flask and dissolved in a 2.6 mL Karl Fischer dried methanol followed by the addition of 10.4 mmole sodium borohydride into it in dry condition. The reaction mixture was kept for stirring in water bath for 6 hours. After the completion of reaction as observed through TLC, the compound (1-vinylimidazole-2-methylalcohol) was further purified by column chromatography. Yield of the product VIm-OH obtained was 94 %.

### 1-Vinylimidazole-2-methylamine

1.64 mmole hydroxylamine hydrochloride and 0.82 mmole sodium carbonate were dissolved in 1.6 mL distilled water. Reaction mixture was then placed in ice bath. 1.64 mmole1-vinylimidazole-2-carbaldehyde dissolved in 0.8 mL ethanol was added dropwise in the reaction mixture. The resulting white suspension was stirred for 1.5 hours in ice bath. After the completion of reaction observed through TLC, the reaction mixture was centrifuged and filtered. Solid white precipitate obtained was then dried and transferred into RB flask and dissolved in 6.5 mL ethanol. It was added with 266 mg ammonium acetate and 5 mL aqueous ammonia followed by addition of 440 mg zinc dust and the reaction mixture was refluxed at $85^0$C for 3 hours. After completion of reaction, the mixture was filtered to remove zinc dust. Filtrate was then concentrated on rotary evaporator. The slight yellowish product (1-vinylimidazole-2-methylamine) was further purified by column chromatography. Yield of the product $VIm-NH_2$ obtained was 85%.

## Preparation of polymers

### Polymerization of Vinylimidazole (VIm)

The polymerization of VIm was carried out in accordance with the method suggested by Srivatava et al[38]. In a 25 mL sealed tube,6 mmole VIm was dissolved in 5 mL methanol (Karl Fischer dried) and reaction mixture was purged with $N_2$ gas for 1 hour. 0.2 mmole AIBN was then added into it in an inert condition and again purged the reaction mixture for 1 hour with $N_2$. The properly sealed tube under positive $N_2$ pressure was heated at 65 $^o$C for 24 hours. After 24 hours of heating, reaction mixture was allowed to cool at room temperature and precipitated the product with cold diethyl ether. Precipitation process was repeated 3 times by decanting the solvent. The compound obtained was then dissolved in water and then dialysed with distilled water using cellulose acetate membrane with MW cut-off of 10 kDafor 9 hours. The water was changed every 2 hours. After dialysis, white-brownish viscous compound obtained was lyophilized for 3 days. After lyophilisation, white foam like polymer *PVIm* was obtained.

### Polymerization of 1-Vinylimidazole-2-methyl alcohol (VIm-OH)

In a 25 mL sealed tube,2.4 mmole *VIm-OH* was dissolved in 4 mL methanol and reaction mixture was purged with $N_2$ for 1 hour. 0.08 mmole AIBN was then added into it in an inert condition and again purged the reaction mixture for 1 hour with $N_2$. The sealed tube sealed properly under positive $N_2$ pressure and heated at 65 $^o$C for 24 hours. After 24 hours of heating, reaction mixture was allowed to cool at room temperature and precipitated the product with cold diethyl ether. Precipitation process was repeated 3 times by decanting solvent. The compound (precipitate) obtained was then dissolved in water-isopropanol (9:1) system and then dialysed against distilled water using cellulose acetate membrane with MW cut-off of 10 kDafor 9 hours. The water was discarded every 2 hours interval. After dialysis, white-brownish viscous compound was obtained then lyophilized for 3 days due to excess water taken for solubility of compound. After lyophilisation, white foam like solid *PVIm-OH* was obtained.

### Polymerization of 1-Vinylimidazole-2-methylamine ($VIm-NH_2$)

This polymerization was carried out in three steps:

### Step 1: BOC protection of 1-Vinylimidazole-2-methylamine

In order to polymerize this compound, it was firstly protected by BOC anhydride. In 100 mL round bottom flask, 4.04 mmole $VIm-NH_2$was dissolved in 20 mL dry methanol. 6.06 mmole triethylamine was then transferred using 1 mL plastic syringe. After 15 min, 12.12 mmole di-tert-butyl dicarbonate was added into it using 1 mL plastic syringe and reaction mixture was stirred for 6 hours at room temperature. After the completion of reaction, the mixture was concentrated on rotary evaporator. The product was extracted using dichloromethane and further purified by column chromatography. Yield of this Boc-protected product $Boc-VIm-NH_2$ was 73 %.

### Step 2: Polymerization of BOC protected 1-Vinylimidazole-2-methylamine

2.04 mmole of Boc-protected compound was transferred into 50 mL sealed tube followed by the addition of 4 mL dry methanol and the reaction mixture was heated at 60 °C until clear solution was observed. After the complete dissolution of compound, reaction mixture was purged with $N_2$ gas for 1 hour. 0.034 mmole AIBN was added in the reaction mixture and again purged for 1 hour. Reaction was kept on stirring at 65 °C for 2 days. After 2 days, reaction mixture was concentrated on rotary evaporator and precipitated using cold diethyl ether, centrifuged 3 times to obtain a brown precipitate. It was then dissolved in a mixture of water-isopropanol (9:1) and then dialysed in distilled water using cellulose acetate membrane with MW cut-off of 10 kDafor 9 hours. Water was discarded at every 2 hour interval. After dialysis, whitish brown precipitate was obtained. The precipitate was dissolved in water-isopropanol (9:1) mixture and kept for lyophilization for 24 hours to get a foam-like polymeric compound Poly-*Boc-VIm-NH*$_2$.

### Step 3: Deprotection of Poly-Boc-VIm-NH$_2$

The compound was then deprotected as follows. In a 25 mL dry RB flask, 300 mg polymer was taken and kept in an ice bath. 10 mL trifluoroacetic acid was added using 20 mL glass syringe drop-wise in the ratio of 30 mg per mL in an inert condition. The RB flask was removed from ice bath and stoppered with the guard tube. The brownish reaction mixture was stirred for 8 hours at room temperature and concentrated on rotary evaporator to remove excess TFA. Resulting brownish liquid was dissolved in distilled water and clear brownish solution was dialysed in distilled water using cellulose acetate membrane with MW cut-off of 10 kDafor 9 hours by making whole surrounding basic (pH=8-10) using 1N NaOH solution. Dialysed water was discarded every 2 hour interval. After dialysis, clear brownish solution was transferred into 50 mL plastic beaker and kept for lyophilisation for 3 days. Brownish cotton-like polymer *PVIm-NH*$_2$ obtained was then characterized by Mass and NMR spectroscopy.

### Ice templated fabrication of porous PVIm and hierarchical homopolymers

All the three polymers were taken in two different concentrations as 0.025 mol $L^{-1}$ and 0.0125 mol $L^{-1}$ in aqueous media with the help of sonication. The sample beakers were covered with aluminium foil and pricked it with small syringe (approximately 400 holes) and then kept at -20 °C for 12 hours followed by lyophilisation at -45 °C for 3 days. White cotton like compound obtained was then stored in desiccator under vacuum and used for BET analysis.

The synthesis schemes have been depicted in Figure 1.

## Results and Discussion

### Characterization

### 1-Vinylimidazole-2-carbaldehyde

The $^1$H NMR (500 MHz) was recorded in $CDCl_3$ and all peaks were standardized using TMS as an internal standard (Figure S1, a). The characteristic peak obtained at δ 9.85 corresponds to the CHO group. The peak obtained at δ 7.93 was splitted into doublet of doublet due to ethylene protons present on carbon attached to ring nitrogen. The peaks corresponds to δ 7.52 and δ 7.32 were belongs to aromatic region of imidazole ring while both ethylene protons splitted into doublet of doublet due to coupling with adjacent proton and peaks obtained at δ 5.40 and δ 5.10 respectively. m/z ESI-MS 122 (100%).

### 1-Vinylimidazole-2-methyl alcohol

The $^1$H NMR (500 MHz) was recorded in $CDCl_3$ and all peaks were standardized using TMS as an internal standard (Figure S1, b). The characteristic peak obtained at δ 7.15 and δ 7.08 corresponds to aromatic proton from imidazole ring. The splitted doublet of doublet obtained at δ 6.93 was due to ethylene proton present on the carbon attached to ring nitrogen. Two doublet of doublet obtained at δ 5.18 and δ 4.85 were corresponds to ethylene proton splitted due to adjacent proton. The characteristic peak obtained at δ 4.20 was due to methylene proton attached to imidazole ring as well as OH group. Hydroxyl proton singlet obtained at δ 6.32. m/z ESI-MS 124 (100%).

### 1-Vinylimidazole-2-methylamine

The $^1$H NMR (500 MHz) was recorded in MeOD and all peaks were standardized using TMS as an internal standard (Figure S1, c). The characteristic peak obtained at δ 8.13 and δ 7.77 due to imidazole ring protons. The splitted doublet of doublet obtained at δ 7.46 was due to ethylene proton directly attached to the ring nitrogen while the doublet of doublet obtained at δ 6.02 and δ 5.63 were due to ethylene protons. The characteristic peak obtained at δ 4.70 was due to methylene proton attached to ring as well as $NH_2$ group. m/z ESI-MS 123 (100%).

### BOC protection of 1-Vinylimidazole-2-methylamine

The $^1H$ NMR (500 MHz) was recorded in $CDCl_3$ and all peaks were standardized using TMS as an internal standard (Figure S2, a). The characteristic peak obtained at δ 7.18 and δ 6.97 corresponds to the imidazole ring protons. The splitted doublet of doublet obtained at δ 7.10 was due to ethylene proton directly attached to the ring nitrogen while the doublet of doublet obtained at δ 5.22 and δ 4.93 were due to ethylene protons. The doublet obtained at δ 4.44 corresponds to methylene proton directly attached to $NH_2$ group while the singlet obtained at δ 5.37 corresponds to amide proton. Intense singlet containing nine proton corresponds to methyl group of boc anhydride.

### Polymerization of BOC protected 1-Vinylimidazole-2-methylamine

The $^1H$ NMR (500 MHz) was recorded in MeOD and all peaks were standardized using TMS as an internal standard (Figure S2, b). The characteristic peak obtained in the aromatic region as well as in the aliphatic region got broadened. The sharp peak obtained in the aliphatic region corresponds to all methyl groups of boc anhydride. The peak obtained at δ 4.48 was due to residual solvent i,e water.

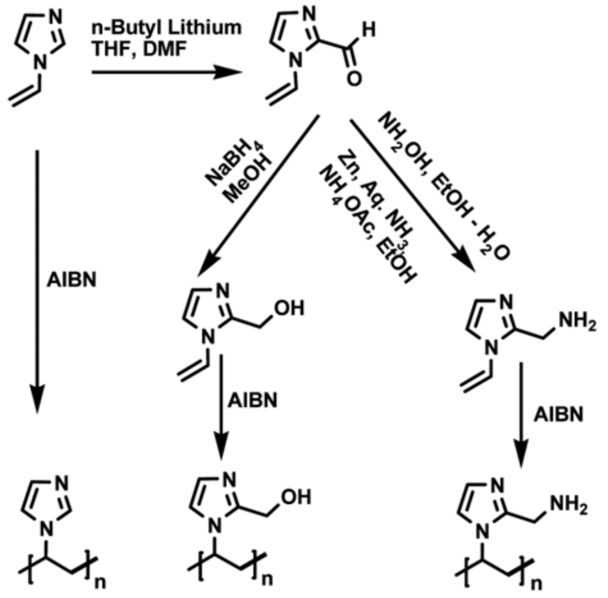

Figure 1 — Synthetic scheme of PVIM based homopolymers

### Deprotection of Poly-Boc-VIm-$NH_2$

The $^1H$ NMR (500 MHz) was recorded in DMSO-D6 and all peaks were standardized using TMS as an internal standard. The Characteristic peak obtained in the aromatic region as well as in the aliphatic region got broaden. The sharp peak in the aliphatic region correspond to all methyl group of boc anhydride was removed that confirmed the deprotection. The peak obtained at δ 3.5 was due to residual solvent i,e water.

All the three polymers were characterized using $^1H$-NMR, electron spray ionization high resolution mass spectrometry (ESI-HRMS), scanning electron spectrometry (SEM) and thermogravimetric analysis (TGA).

The $^1H$-NMR spectra have been depicted in Figure S3. These spectra clearly show broadened peaks due to polymerization. The HRMS data obtained for all the three polymers. The charge spectra have shown the mass of 701.4903 with charge state of 36 (suggesting 36 sites of protonation in polymer), which after deconvoluted mass of 25218.3404. With this, there are other deconvoluted mass obtained as 14735.7415, 20397.1629, and 26503.0450 respectively indicating the heterogeneity of the synthetic polymers. The HRMS spectra are depicted in Figure S4, Figure S5 and Figure S6 respectively.

After ice-templated synthesis, all polymers have been investigated for their thermal stability. TGA was carried out using Perkin Elmer TGA-6000 instrument (Figure 2). The sample was heated from 30 $^oC$ to 900 $^oC$ under nitrogen atmosphere at a rate of 10 $^oC$ $min^{-1}$. From the TGA, it was found that PVIm shows highest stability as it is showing its degradation started at 450 $^oC$ while PVIm-OH shows its thermal degradation started at 350 $^oC$. PVIM-$NH_2$ shows its degradation started at more than 300 $^oC$.

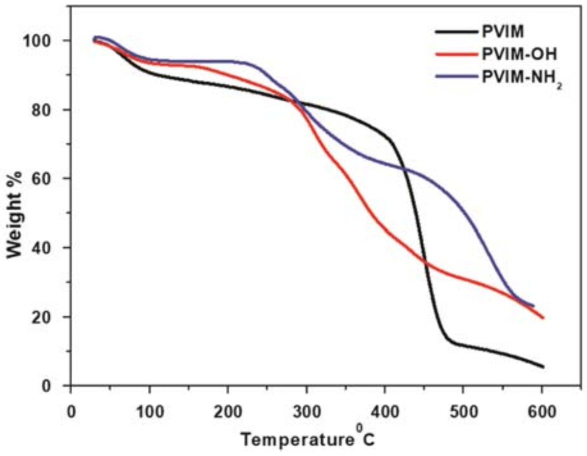

Figure 2 — TGA curves of PVIm, PVIm-OH and PVIm-$NH_2$

The surface morphology of all polymers was examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope. Samples for microscopy were prepared by sprinkling (~ 0.5 mg) polymers (powdered form) on aluminium stub using silicon wafer over an adhesive carbon tape. All samples were coated with a thin layer of sputtered gold prior to imaging. FESEM was carried out using an accelerating voltage of 5 kV and 10 kV. It was observed that PVIm contains broad threadlike structure along with enough voids and spaces in the structure (Figure 3a). Since it is having free space in the structure that facilitates capture of $CO_2$ molecules in its surface. From SEM images of PVIm-OH (Figure 3b)., it is observed that it contains dry leaflike structure having various pore in it. In case of PVIM-$NH_2$ SEM images reveals about porous structure having various pores in its surface (Figure 3c).

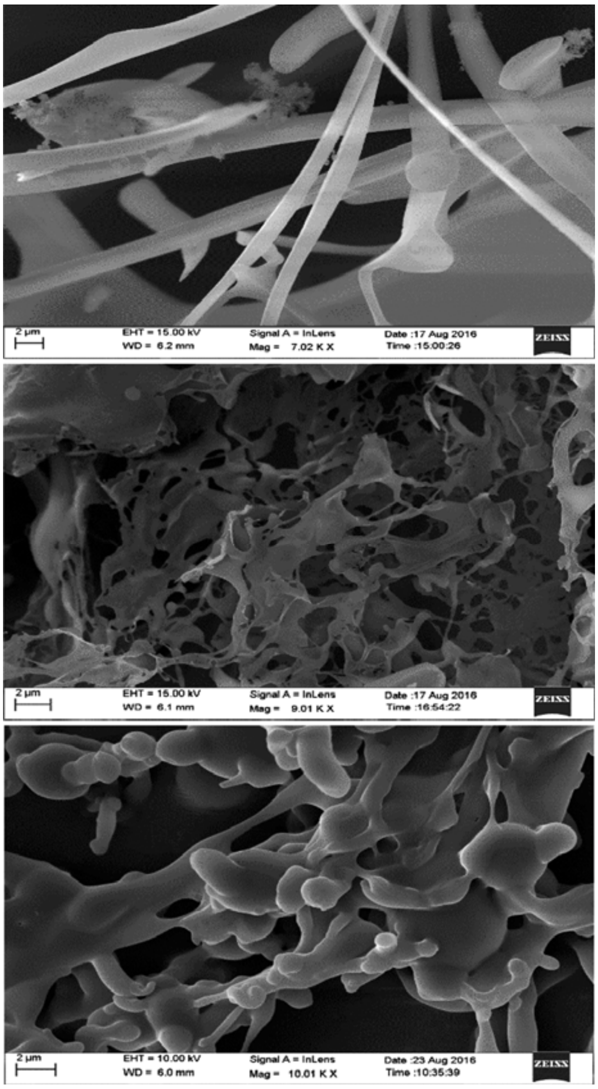

Figure 3 — SEM images of (a) PVIm, (b) PVIm-OH and (c) PVIm-$NH_2$

## Gas adsorption studies

All the gas adsorption measurements were performed on Quantachrome Autosorb QUA211011 equipment. Adsorption measurements was done at 298 K. Isotherms were analyzed using ASIQwin software. The heat of adsorption plots were obtained using ASIQwin software. All the samples were treated at a temperature of 80 °C for 24 h under high vacuum before the analysis.

Basic moieties like nitrogen and oxygen present on the polymers are playing an important role behind adsorption of carbon dioxide. As the synthesized polymers are rich in nitrogen content, they are interacting with carbon dioxide by involving Lewis acid-base concept. Since polymers are abundant with such basic moieties they are having strong capability to have an interaction with acidic carbon dioxide. Adsorption isotherm has been shown in Figure 4. The experiment was conducted using both prepared concentration system as shown in ice templated system. But at the lower concentration (0.0125M) system adsorption of carbon dioxide was not satisfactorily while at higher concentration i.e. at 0.025M concentration, adsorption of carbon dioxide was significant as shown in Figure 4. From the adsorption curve, it is observed that there was not a notable difference in adsorption of hydroxyl modified PVIm in comparison with the simple PVIm. This might be due to less basic characteristic of hydroxyl group. But when we compare adsorption of Amine modified PVIm, there was an appreciable adsorption of carbon dioxide. The

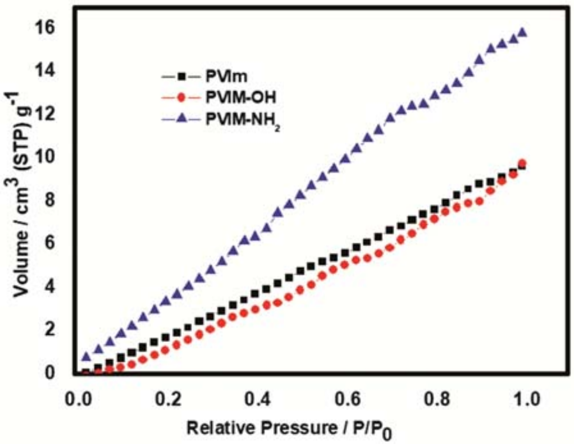

Figure 4 — Adsorption isotherm of $CO_2$ on all three polymers

increase in carbon capture capacity of PVIm-$NH_2$ is due to stronger Lewis acid base interaction of $NH_2$ moiety with $CO_2$ since it is having acidic character.

## Conclusions

Porous organic fibrous polymer structures are promising substrates for amine-based adsorbents for $CO_2$ capture. The synthesized polymers were found to have nice fibrous structure with reasonably high thermal stability as revealed from the SEM and TGA studies. All the three polymers had good uptake of $CO_2$ at low pressures. The Nitrogen moieties and most probably the fibrous nature played an important role in the adsorption of $CO_2$. The quantitative modification of the polymers to optimize and balance the heat of adsorption, uptakes, selectivity's and cycling behaviours could be an important aspect for future studies.

## Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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