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SOLID-SUPPORTED CO_2 SORBENTS BASED ON AMINE-FREE PHOSPHONIUM CARBOXYLATE IONIC LIQUIDS

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Supervised by Dr Alberto Puga

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Solid-supported CO_2 Sorbents Based on Amine-free Phosphonium Carboxylate Ionic Liquids

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Abstract
Carbon capture is key to minimize the negative effects of CO_2 emissions. There are large numbers of technologies for CO_2 capture. Currently, amine-based CO_2 sorbents are mostly used. Despite the reasonable performance of amine sorbents, they have serious disadvantages such as high energy cost for regeneration and thermal degradability. Thus, new sorbent materials and technologies for CO_2 capture are still intensely sought. Ionic liquids with negligible vapor pressure can be designed to capture CO_2. In this framework, carboxylate ionic liquids, when hydrated, enable a chemical CO_2 sorption with moderate enthalpy, which leads to lower energy cost for regeneration. On the other hand, phosphonium-based ionic liquids exhibit superior thermal stability compared to ammonium counterparts. In this work, tetrabutylphosphonium acetate hydrate ($[P_{4444}][AcO]\cdot H_2O$) was synthesized by simple neutralization of the hydroxide with acetic acid in water characterized by NMR, and its thermal decomposition and glass transition temperatures were recorded. After impregnation on porous silica, a free-flowing solid-supported material ($[P_{4444}][AcO]\cdot H_2O/SiO_2$) was produced and tested for CO_2 sorption-desorption experiments from model flue gas (15% CO_2) in a fixed-bed setup. Performance was compared to polyethyleneimine on silica (PEI/SiO_2) as a competitor amine sorbent material used commercially. Both sorbents showed fast CO_2 sorption, although the capacity of the amine system was higher. Desorption at low temperature (60 °C) was complete and rapid for CO_2-saturated $[P_{4444}][AcO]\cdot H_2O/SiO_2$, while for $PEI\text{-}20/SiO_2$ desorption rate was much slower, and desorption of CO_2 was not complete under same condition. Furthermore, thermogravimetric analysis indicated that $[P_{4444}][AcO]\cdot H_2O/SiO_2$ has thermal stability up to 200°C.

Keywords: Sorption, carboxylate ionic liquids, phosphonium ionic liquids, carbon dioxide capture.

Introduction and Research Proposal

Carbon Capture and Utilization

The increase in the concentration of carbon dioxide in the atmosphere by 31% since the industrial revolution began around 1750, due to anthropogenic emissions, is leading to climate change and other environmental issues, such as ocean acidification [1-3]. In addition, nowadays finding efficient new solutions to overcome the diminishing fossil fuel resources is a major challenge regarding global energy supply [4]. It is thus very important to decrease CO_2 emissions, by direct capture of CO_2 from the atmosphere or from point sources (*e.g.* coal-fired power plants, blast furnaces, natural gas treatment processes, or cement kilns), and to recycle this carbon resource for the production of fuels and chemicals [5, 6].

CO_2 capture technologies

The most common technology for CO_2 capture entails aqueous amine absorption; other approaches include aqueous alkaline absorbents, physically adsorbent solids, membrane separators, and amine-impregnated solids [7, 8]. Current processes for CO_2 capture are associated with some drawbacks, especially high energy consumption and limited stability, resulting in high cost of the recovered CO_2 [9, 10]. Aqueous amine technology is the most widely used method, and commercially implemented in the fields of natural gas purification (sweetening) and ammonia production. However, several issues of this process still remain such as oxidative degradability, high regeneration temperatures (and thus high energy expenditure), volatility losses, and equipment corrosion [7, 8, 11].

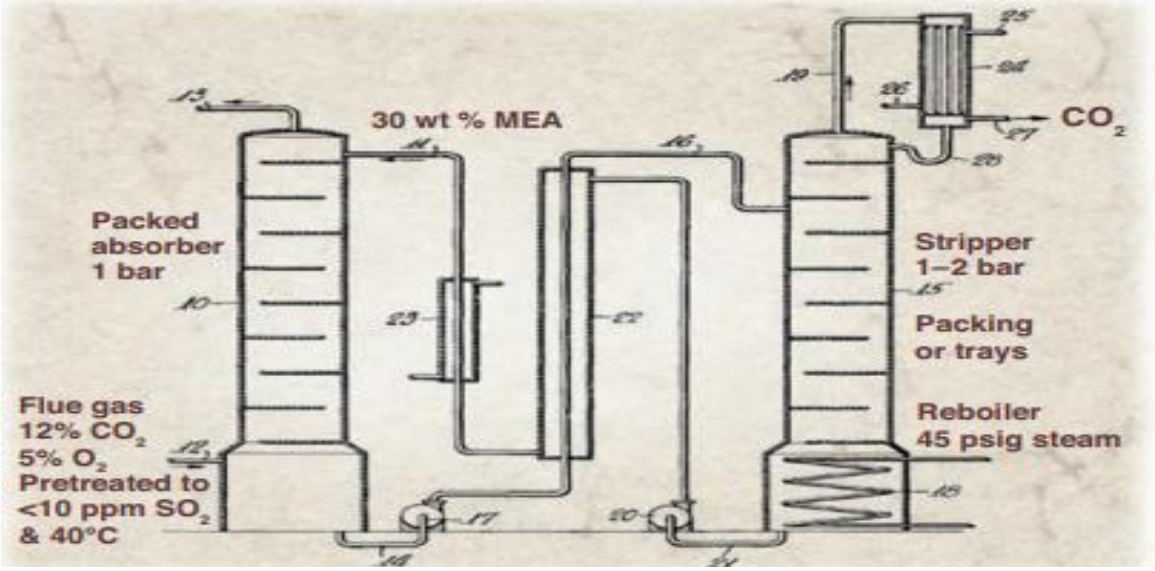


Figure 1. The CO_2 absorption (scrubbing) process invented by Bottoms. Reproduced from reference [15].

Application of amine sorption for flue gas treatment or direct capture of CO_2 from air, whereby the economic benefit is less apparent, is thus seriously hindered by such disadvantages and costs. In consequence, it is very essential to look for alternatives to amine-based CO_2 sorbents. These alternatives must be accompanied by advantageous and more environmentally-friendly features, such as lower regeneration temperature, and cleaner process operation.

Background and State of the Art

Disadvantages of amine CO_2 sorbents

As noted earlier, presently, the favored means of CO_2 capture is chemical scrubbing based on liquid-phase amine absorbents, including primary (*e.g.* monoethanolamine, MEA), secondary (*e.g.* diethanolamine, DEA), or tertiary (*e.g.* methyldiethanolamine, MDEA) [12-14]. The process of CO_2 absorption from flue gas by aqueous amine solutions, and regeneration of the sorbent by stripping with water vapor (at 100 to 120 °C), was patented in 1930 (Figure 1) [15]. Primary and secondary amines react with CO_2 forming carbamate species [14], while tertiary amine groups, having no nitrogen-bonded hydrogen atoms, cannot react with CO_2 directly to form stable carbamates. Conversely, tertiary amines act as a base in CO_2 capture, only in the presence of water, leading to the formation of bicarbonate instead of carbamate. The maximum amine efficiency under dry condition, for primary and secondary amines is 1 mol(CO_2) per 2 mol(N), while for tertiary amines the maximum amine theoretical efficiency is zero (Figure 2) [13, 16].

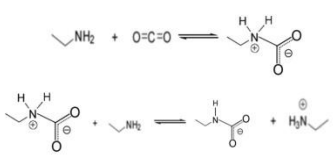
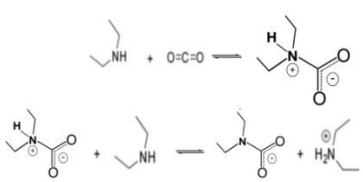
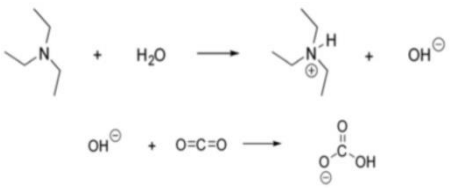
Primary amines	Secondary amines	Tertiary amines
		
Ratio of CO_2/N: 1:2	Ratio of CO_2/N: 1:2	Ratio of CO_2/N: 1:1
Under dry condition	Under dry condition	Under humid condition (ineffective CO_2 capture under dry condition)

Figure 2. Reactions of different type of amines (primary, secondary, and tertiary) with CO_2.

Although amine-based sorbents show high CO_2 sorption capacities, the method involves large enthalpies of reaction [13] (Table. 1). Therefore, a large amount of heat is required for the regeneration step. The regeneration temperature of amine solvents is typically 100-140 °C under near-atmospheric pressures [14], and thus, heat requirements in a CO_2 capture plant can constitute up to 40% of the total operating costs [22]. Other significant drawbacks of amine-based sorbents, as mentioned above, are low thermal stability, the corrosive and reactive characteristics of these materials which raise safety concerns, loss of amine components to the environment due to volatility, and oxidative degradability [14]. As stated above, in order to overcome these problems, it is crucial to look for other alternative CO_2 sorbents.

Design of ionic liquids

Ionic liquids (ILs) are salts which melt at ambient or near-ambient temperatures. By definition, their melting points are lower than 100 °C. Since they are formed entirely by ions, they have negligible vapor pressure and other properties such as ionic conductivity [23]. There are a large number of possible combinations of cations and anions with differences in structure, size, and shape, and this diversity can be used to design ILs with specific chemical and physical properties [24-26]. Furthermore, structural modification by introduction of certain functional groups (such as polar, hydrogen-bonding, hydrophobic, coordinating groups, *etc*.) in the ionic entities of the IL provides certain specific chemical characteristics [27-29]. Thanks to this structural and functional versatilities, ILs have been widely studied in the fields of electrochemistry, catalysis, energy storage, separation processes, extraction, biomass processing and conversion, nanomaterials preparation, etc. [30-37]. Therefore, proper modification of ILs makes them promising substances for use in gas separation technologies, as an example of such large variety of applications.

Ionic liquids as CO_2 sorbents

Ionic liquids can be designed to exhibit marked CO_2 sorption capacity by including ion motifs with tendency to interact with CO_2 via non-covalent binding, or to react with CO_2, for example via acid-base chemistry [19, 24, 26, 38-40]. An important property of ILs in this context is their non-volatility. Since they exhibit negligible vapor pressure, no

Table 1. Reaction enthalpies of adsorption of CO_2 sorbents based on amines or ILs.

Sorbents	*ΔH [kJ mol^{-1}]*	*T [°C]*	*References*
Aqueous amines			
Primary amine (MEA, *aq*, 30% wt%)	−85	-	[17]
Secondary amine (DEA, *aq*, 30% wt%)	−76	-	[17]
Tertiary amine (MDEA, *aq*, 30% wt%)	−62	-	[17]
Solid-supported amines			
Polyethylenimine(33%)/SiO_2	−85	85	[18]
Amine-functionalised ILs			
Trihexyltetradecylphosphonium prolinate ([$P_{6\,6\,6\,14}$][Pro])	−80	25	[19]
Trihexyltetradecylphosphonium metioninate ([$P_{6\,6\,6\,14}$][Met])	−64	25	[19]
Amine-free (carboxylate) ILs			
1-ethyl-3-ethylimidazolium acetate	−38	25	[20]
Triethylhexylphosphonium acetate hydrate (mol ratio = 1:1, [$P_{2\,2\,2\,6}$][AcO].H_2O)	−37	25-50	Unpublished Data
1-butyl-3-methylimidazolium acetate + 14% water	−40	24-80	[21]

contamination of the gas streams (no IL losses) are expected during the overall CO_2 sorption-regeneration process. Regeneration may be safely performed by applying either an increase in temperature or a decrease in pressure [24]. This is a clear advantage over existing commercial sorbents. Therefore, ILs might represent appropriate alternatives for replacing amine sorbents in CO_2 capture processes [19, 40-44].

Amine-functionalised ILs

As mentioned above, solubility of CO_2 in ILs can be tuned by appropriate structural design, including functional groups able to bind CO_2. In this regard, CO_2 solubility could be enhanced by tethering amine functionalities to the constituent ions, resulting in chemical absorption. This was inspired by the widespread use of aqueous amine sorbents. Davis and coworkers reported the potential of using imidazolium-based ILs for CO_2 capture, by functionalizing the imidazolium cation with an amine group as chemical fixation agent to capture CO_2 in the form of carbamate [45]. Fukumoto and coworkers showed the effects of anion structure on the physical properties such as viscosity, density and glass transition temperature of a series of ILs formed by twenty natural amino acid anions, and (3-aminopropyl)tributylphosphonium and 1-ethyl-3-methylimidazolium as cations. They reported that the amino functional groups of these amino acids have the ability to chemically interact with CO_2 [27, 46], in an analogous fashion to classic amines. Nevertheless, these ILs still retain some disadvantages of aqueous amine sorbents due to the presence of amine functionalities, that is, high enthalpies of absorption (see Table 1), high regeneration temperatures, and related chemical degradation issues.

Carboxylate ILs as alternatives to amine-functionalized ILs

Considering amine-free sorbents, carboxylate-based ionic liquids are exclusively suitable, since a

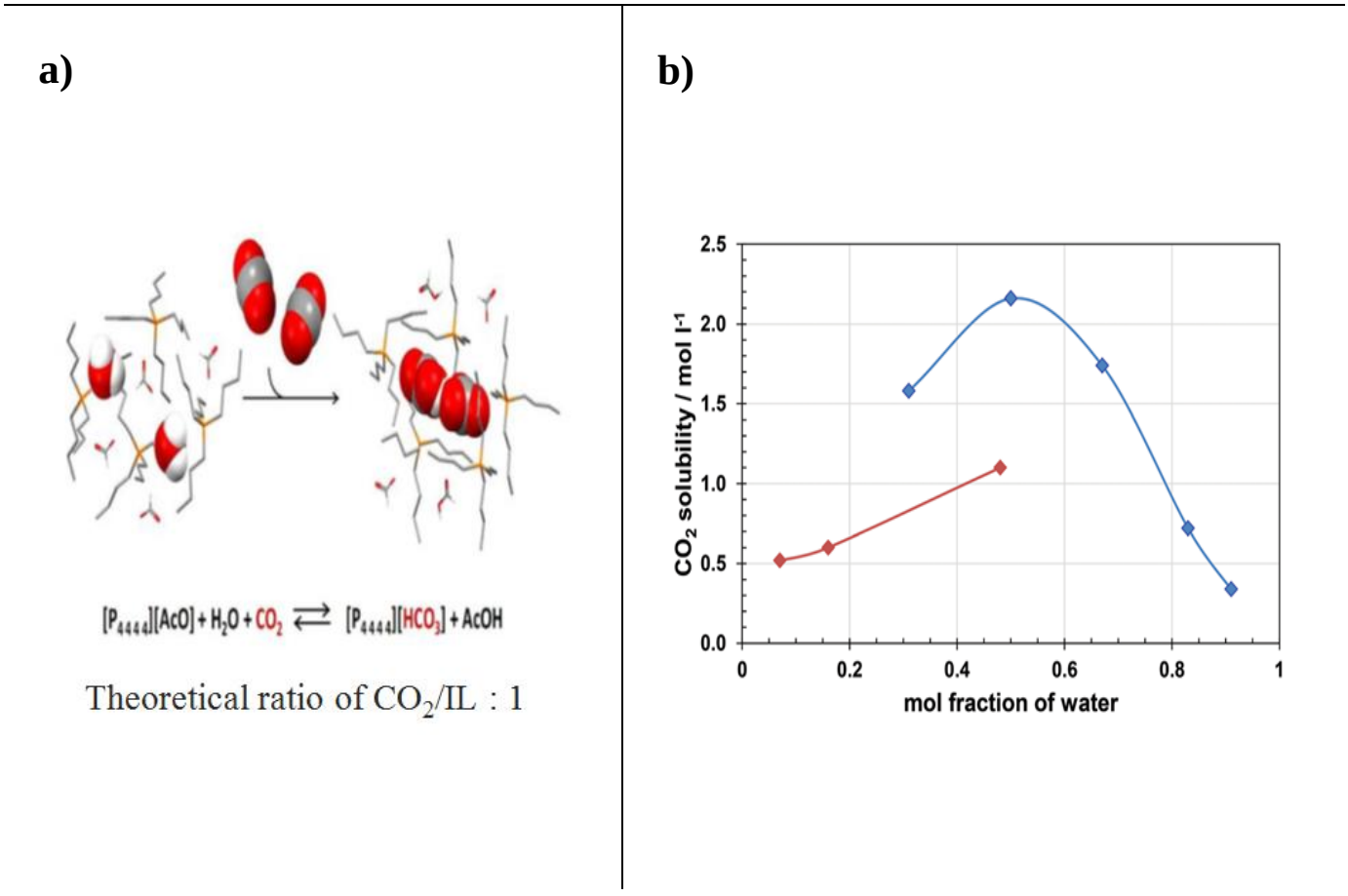


Figure 3. a) Scheme and reaction equation for CO_2 capture on a wet phosphonium carboxylate (red: oxygen; white: hydrogen; gray: carbon; orange: phosphorus). b) CO_2 solubility of hydrated ILs as a function of the molar fraction of H_2O (blue: tetrabutylphosphonium formate; red: trihexyltetradecylphosphonium formate) showing that the maximum CO_2 solubility in the $[P_{4444}][HCO_2]/H_2O$ system is at 1:1 molar ratio of hydrated ILs. Reproduced from reference [48].

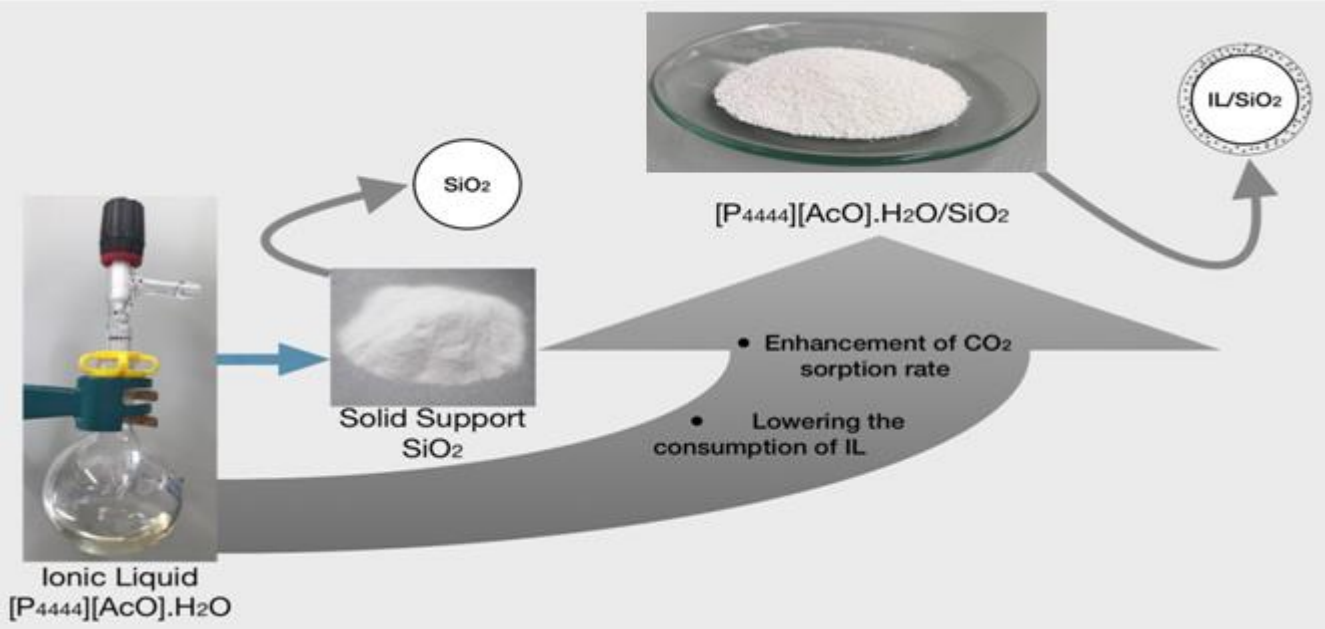
fine adjustment of their reactivity can be accomplished simply by structural design, avoiding the adverse emissions of amine processes [38, 39]. Kirchner and coworkers demonstrated that the acetate anion plays a main role in CO_2 absorption, and also provided evidence that dispersion interactions are present between the cation and the solute [47]. Chinn et al. demonstrated that the volumetric CO_2 absorption capacity of the IL 1-butyl-3-methylimidazolium acetate containing 14 wt% water (≈ 25 m^3/m^3) is lower than that of 30 wt% aqueous MEA solution (≈ 65 m^3/m^3) at equilibrium, under CO_2 at 1 atm partial pressure. However, the enthalpy of reaction of CO_2 in the acetate IL is −40 kJ mol^{-1}, while the enthalpy of reaction of CO_2 in the MEA solution is −85 kJ mol^{-1} (see Table 1), thus suggesting a much lower energy input for the regeneration step using the IL system [21]. Furthermore, CO_2 capture capacity in this set of ILs shows direct relation with the degree of hydration, whereby CO_2 solubility increases as the water content increases up to a maximum at equimolar IL/H_2O ratio, which leads to enabling moisture-adjustable performance by the carboxylate functionality to capture CO_2 in the presence of water to generate trapped bicarbonate (Figure 3) [14, 38, 39, 48]. The most interesting aspect of this is the fact that a true chemical mode of absorption takes place, leading to solubilities attaining one mole of CO_2 per mole of IL at reasonably low pressures. In addition, the energy input for regeneration of phosphonium carboxylate ionic liquids is much lower compared to aqueous amine systems, as discussed above (Table 1). Anderson *et al.* reported that at 70°C (regeneration temperature), tetrabutylphosphonium formate and triethyloctylphosphonium acetate containing water at 1:1 molar ratio ($[P_{4\,4\,4\,4}][HCO_2]\cdot H_2O$ and $[P_{2\,2\,2\,8}][AcO]\cdot H_2O$, respectively) recovered 100 and 90 percent of their CO_2 capacity, respectively, while 30 wt% aqueous MEA only recovered 82% of its CO_2 capacity at 120 °C [48].

Phosphonium ILs have superior thermal stability than ammonium counterparts

Phosphonium carboxylate ionic liquids present higher thermal stabilities than ammonium counterparts. Pena *et al.* reported the thermogravimetric analysis (TGA) of tetrabutylphosphonium acetate ($[P_{4\,4\,4\,4}][AcO]$), observing a decomposition temperature (T_{dec}) of 317 °C under dynamic conditions (increasing temperature). Moreover, they determined that the necessary time for this IL to undergo 1% isothermal decomposition at 70 °C would be 5000 h [49]. In contrast, T_{dec} for triethylbutylammonium acetate ($[N_{2\,2\,2\,4}][AcO]$) was 171 °C under dynamic TGA conditions, as reported by Wang *et al.* This means a significantly lower thermal stability for ammonium as compared to phosphonium ILs. Furthermore, $[N_{2\,2\,2\,4}][AcO]\cdot H_2O$ lost nearly a quarter of its total mass after 24 h at 100 °C, indicating noticeable IL degradation [50]. Tsunashima *et al.* determined T_{dec} data for a series of ILs composed of tetraalkylphosphonium cations and the bis(trifluoromethylsulfonyl)imide (TFSI) anion, and those for their ammonium counterparts. For example, T_{dec} of the triethyldodecylphosphonium ($[P_{2\,2\,2\,12}][TFSI]$) and triethyldodecylammonium ($[N_{2\,2\,2\,12}][TFSI]$) salts were 408 and 390 °C, respectively [51]. Hence, phosphonium ILs are generally more thermally stable as compared to ammonium analogues. For all the reasons mentioned above, tetraalkylphosphonium carboxylate ILs are herein proposed as safe CO_2 sorbents under typical temperature-swing operation, yet at relatively mild conditions.

Solid-supported IL as CO_2 sorbents

ILs are generally associated with high viscosity, a fact that limits mass transfer processes. This may in turn result in slow CO_2 sorption rate due to slow diffusion rate of gas molecules into the viscous liquid media through a relatively small gas-liquid interface. In order to overcome this issue, IL sorbents can be impregnated onto solid support materials such as silica or alumina as an alternative approach [52, 53], as also reported for classic amine sorbents [5, 18, 54-56]. Zhang *et al.* observed that after 2 h the CO_2 absorbed by dual amino-functionalized phosphonium ILs based on the (3-aminopropyl)tributylphosphonium cation and amino acid anions, was as low as 0.2 mol(CO_2)/mol(IL), while materials consisting



Scheme 1. Schematic representation of the formation process for hydrated tetrabutylphosphonium acetate ionic liquid supported on silicon dioxide ($[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$).

on the same ILs impregnated on porous SiO_2 showed almost equimolar ratio of absorption (1 mol(CO_2)/mol(IL)). Moreover, the chemical absorption of CO_2 essentially reached equilibrium after 80 min for such silica-impregnated IL sorbents (SiO_2 absorption subtracted) [57]. Kolding *et al*. used a series of amino acid-based ILs loaded on hydrophobic silica gel to confirm their high performance for CO_2 absorption. Tetrahexylammonium prolinate showed the highest CO_2 adsorption capacity reaching 4.6 wt% CO_2 (at 25° C and 1 bar), thus taking up about 1.23 mole of CO_2 per mole of IL [58]. On the other hand, impregnation of ILs on solid support materials is expected to result in lower amounts of IL consumption in a gas capture process and enhancement of sorption rates (due to enhanced gas-liquid interface) as compared to pure ILs in their liquid state. Hence, this strategy is aimed at lowering costs and improving efficiency in CO_2 capture processes [59]. Zhang *et al*. reported that the CO_2 absorption in tetrabutylphosphonium amine-functionalized glycinate or 2-cyanopyrrolide ILs supported on porous SiO_2 was reversible, and CO_2 absorption rates were much higher than those of the viscous ILs themselves [60]. Despite the interesting research discussed above, most solid-supported IL systems reported to date for CO_2 capture rely on amine-functionalized ions, thus presenting high energetic costs for desorption. Carboxylate ILs, as more readily recyclable and more thermally stable sorbents, have been seldom investigated for this technology.

Research Proposal

In this work, materials based on hydrated tetrabutylphosphonium acetate impregnated onto silicon dioxide ($[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$) were prepared (Scheme 1), and their physicochemical properties were measured. Moreover, their CO_2 sorption and desorption efficiencies were preliminarily investigated at room and moderate temperatures, respectively, and compared with those of polyethyleneimine impregnated onto silicon dioxide (PEI/SiO_2) as a competitor amine sorbent material.

Experimental

Materials and characterization methods

Tetrabutylphosphonium hydroxide solution ($[(CH_3CH_2CH_2CH_2)_4P][OH]$, 40 wt. % in H_2O), polyethyleneimine (PEI, branched, average M_w ~800), tetrabutylammonium acetate ($[N_{4\,4\,4\,4}][AcO]$, 97%) were purchased from Sigma-Aldrich. Acetic acid (CH_3COOH, glacial, extra pure) was obtained from Scharlau. A model flue gas mixture cylinder (CO_2, 15.012%; O_2, 5%; N_2, 80%) was obtained from Carburos Metálicos. Fumed silica powder (SiO_2, AEROSIL® R816) was

obtained from Evonik. All chemicals were used as received unless otherwise stated.

The as-synthesized IL was characterized by ^{1}H NMR spectroscopy on a Varian Gemini 400 spectrometer (400 MHz) using dimethyl sulfoxide-d_6 (dmso-d_6) in a sealed capillary tube as an external standard. Thermal behavior and stability studies were performed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on DSC 3+ STAR^e System and TGA 2 STAR^e System, respectively, Mettler Toledo instruments. The DSC analyses were performed from 50 to −80 °C, and then from −80 to 50 °C, cooling and heating cycles, respectively, at 5 °C min^{-1}, under N_2 (50 mL min^{-1}). The TGA profiles were recorded from 30 to 600 or 800 °C, at 10°C min^{-1}, under air atmosphere (50 mL min^{-1}). Specific surface areas were measured by N_2 physisorption at −196 °C and determined by Brunauer–Emmet–Teller (BET) analysis using a Quantachrome Autosorb instrument.

Synthesis and characterization of [P4444][AcO]

In a typical synthesis of tetrabutylphosphonium acetate ([P4444][AcO]), based on the anion-exchange acid-base neutralization method, an equimolar amount of CH_3COOH (≈ 3.5 g, ≈ 58 mmol) was added drop-wise to a solution of tetrabutylphosphonium hydroxide (40 mL, 40 wt%, ≈ 58 mmol) in distilled water, up to a total volume of 200 mL, in a round bottom flask. The addition of CH_3COOH was carefully performed so as to obtain the calculated final molar equivalence point at pH = 8.98 [61, 62], as measured using a Metrohm pH meter. The mixture was then stirred at room temperature for 24 h. Subsequently, water was distilled off at 60 °C under reduced pressure (around 10-15 mbar) in a rotary evaporator until constant weight. The obtained IL was transferred into a Schlenk-type flask and dried under vacuum (around 10-15 mbar) for extra 24 h at 60 °C to reduce possible traces of water, and then stored under N_2 atmosphere. The faint yellow viscous ILs was observed at the end point of isolation, and the final weight of the [P4444][AcO] was 17.64 g (≈ 96% yield). The lower than expected yield might be due to the loss of IL during transferring IL into another flask, or to inaccuracies in the concentration of the starting commercial tetrabutylphosphonium hydroxide solution.

The structure of [P4444][AcO] was confirmed by ^{1}H NMR spectroscopy, which showed that signal integration matched the expected ratios and ruled out the presence of any noticeable impurities (Figure 4). The water content of the as-synthesized [P4444][AcO] was determined to be 0.8 mol(H_2O)/mol(IL). In this work, the water molar ratio to IL was set to 1 mol(H_2O)/mol(IL), aiming at maximum CO_2 sorption, by adding the appropriate amount of distilled water (0.15 mL) to the total volume of IL, yielding the final [P4444][AcO]·H_2O as a colorless fairly viscous liquid, ready to be used for further experiments.

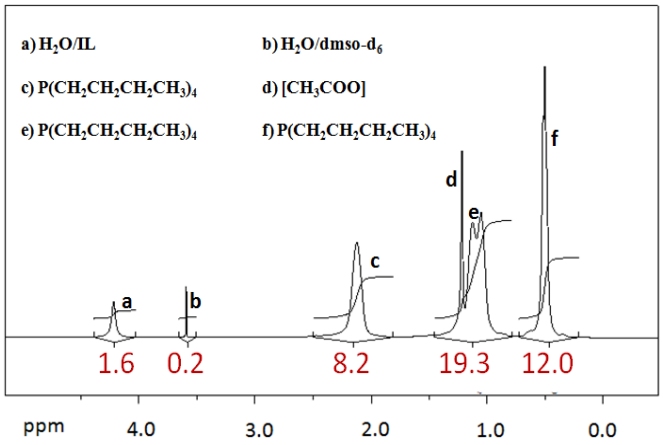
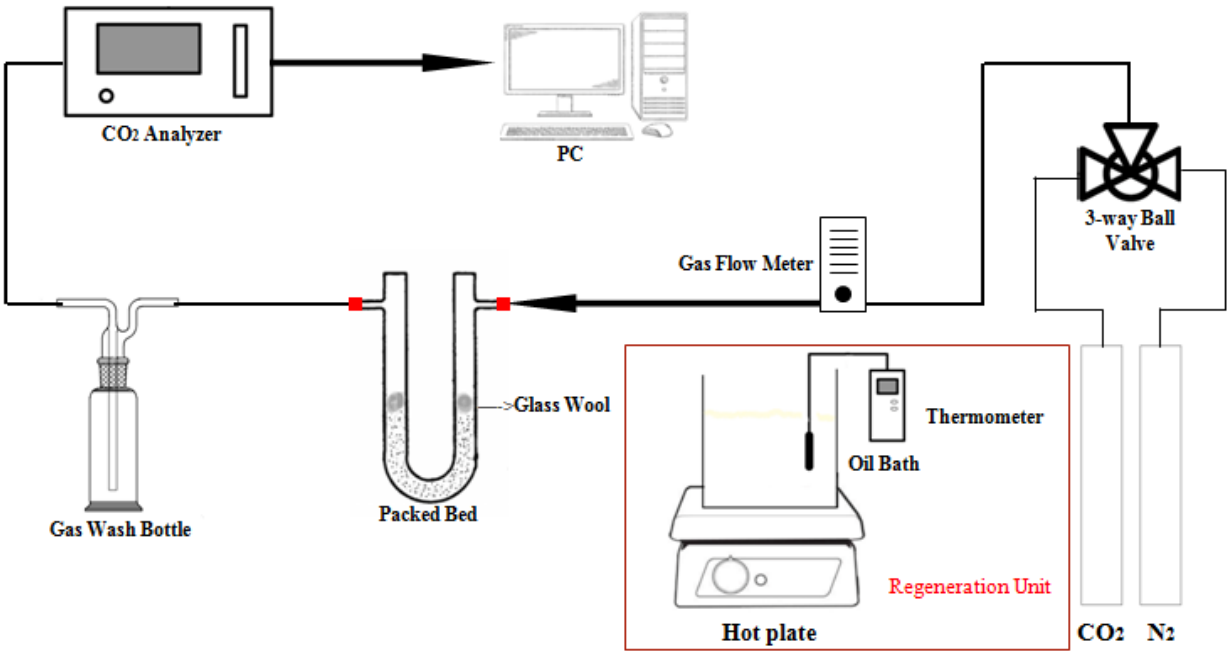


Figure 4. ^{1}H NMR spectrum of the fresh [P4444][AcO]·H_2O (dmso-d_6 external standard, 400 MHz, 25 °C). Integration is indicated below each signal.

Preparation of [P4444][AcO]·H2O/SiO2 and PEI/SiO2

The prepared [P4444][AcO]·H_2O was supported onto silicon dioxide by a conventional impregnation procedure [5, 52, 55]. The fumed silica powder was pressed by means of a hydraulic press into cakes, and then crushed, ground, and sieved. The fraction composed of granules between 0.25 and 0.50 mm in size were separated and employed as solid support for the preparation of impregnated materials (Scheme 1).



Scheme 2. Schematic diagram of the experimental setup.

In a typical procedure to obtain silica-supported sorbent materials (*ca*. 3 g), the desired amount of liquid sorbent ($[P_{4444}][AcO]\cdot H_2O$ or PEI) was dissolved in methanol (≈ 5 mL) in a Schlenk flask and then SiO_2 was added. The mixture was gently shaken and dried off under a gentle N_2 flow at 50 °C resulting in free-flowing granular solids. The following materials, whereby the wt% values are relative to the amount of SiO_2, were prepared:

- **IL-50/SiO_2**, with 50 wt% $[P_{4444}][AcO]\cdot H_2O$.
- **PEI-20/SiO_2**, with 20 wt% PEI.
- **PEI-50/SiO_2**, with 50 wt% PEI.

The solid-supported sorbents were stored under inert atmosphere (N_2) until used for CO_2 capture experiments.

Sorption-desorption performance

Calibration. In order to perform sorption-desorption experiments, the non-dispersive infrared gas analyzer employed (HORIBA VA-5001) was doubly calibrated. Accordingly, the first calibration was performed by passing N_2 flow (300 mL min^{-1}) through of the system in order to obtain 0% CO_2 concentration. Afterward, a second calibration was performed by flowing CO_2 gas mixture (300 mL min^{-1}, 15.012% CO_2) through the gas analyzer. The next step before starting the sorption experiment was to decrease the CO_2 concentration in the gas analyzer to 0% by switching to N_2 flow again until the CO_2 concentration decreased to the baseline level.

Capture. In typical sorption experiment, a custom-designed glass U-tube with an inner diameter of 8 mm containing the desired solid-supported sorbent (*ca*. 3.0 g) was connected into the system, (the solid-supported sorbents were secured on both sides of the U-tube container by inserting glass wool plugs), as indicated in Scheme 2. A N_2 flow was passed as a way to isolate the system from any possible CO_2 contamination that could be caused by contact with atmospheric air while setting up the U-tube. Subsequently, the model flue gas containing 15.012% CO_2 was flowed (300 mL min^{-1}) at nearly atmospheric pressure and room temperature (25.0 ± 0.5 °C) through the solid-supported sorbents in the U-tube glass container, in a fixed-bed-type operation. The concentration of CO_2 in the gas exiting the U-tube fixed-bed was monitored in real time by using the non-dispersive infrared gas analyzer described above, and the data recorded every second. The CO_2 sorption was considered to be completed when the CO_2 concentration of the outlet stream was equal to the inlet one. Afterwards, the glass U-tube was immersed in an ice/salt cooling bath at approximately −15 °C and N_2 flowed (300 mL min^{-1}), in order to remove any CO_2 in the gas-phase remaining in the system, while avoiding

any possible regeneration that could happen at room temperature due to reversal of the CO_2 sorption reaction. This was done until the CO_2 concentration in the system decreased to 0%, before performing CO_2 desorption experiments.

Regeneration. Desorption of CO_2 from saturated sorbents was carried out by monitoring the CO_2 concentration in the same way as described for the sorption method. However, in desorption experiments the sorbents were regenerated by heating at moderate temperature. For this purpose, the U-tube glass container was immersed in an oil bath at 60 °C. Immediately afterwards, N_2 flow at nearly atmospheric pressure (300 mL min^{-1}) was passed through the CO_2-saturated sorbents in the glass container. In this stage, CO_2 was released and increases in CO_2 concentration were observed. The CO_2 desorption was considered to be completed when the CO_2 concentration reading returned down to 0% CO_2 concentration, or no change in CO_2 concentration was observed.

Results and discussion

Physicochemical properties

The aerobic thermal decomposition profiles of $[P_{4444}][AcO]$ and $[N_{4444}][AcO]$ were measured by TGA. According to dynamic TGA data analysis (Figure S1, in supplementary data), at a temperature of 210 °C, $[N_{4444}][AcO]$ showed a significant weight loss (92 wt%) while, $[P_{4444}][AcO]$ had only lost 3.5 wt%. The decomposition temperature was at least 100 °C higher for the latter, thus proving that phosphonium-based carboxylate ILs are more thermally stable than ammonium counterparts. Furthermore, the glass transition temperature of $[P_{4444}][AcO]\cdot H_2O$ having 1 mol(H_2O)/mol(IL) was measured by DSC. The result indicated low glass transition temperature (Figure S2) of the hydrated IL (onset: −72.6 °C, midpoint: −70.9 °C). Moreover, the DSC analysis showed that $[P_{4444}][AcO]\cdot H_2O$ does not have a tendency to be crystallized upon cooling at sub-ambient temperatures. The results obtained from thermochemical analyses, demonstrate the favorable physicochemical properties of the phosphonium-based IL, such as a thermal stability up to 200 °C, and remarkably low glass transition temperature with negligible propensity towards crystallization.

As mentioned above, three solid-supported sorbents were prepared, which include, **IL-50/SiO_2**, **PEI-20/SiO_2**, **PEI-50/SiO_2**. Their thermal properties were recorded by using dynamic TGA. Figure 5 indicates the weight loss of the three samples. The small weight loss that occurred below 150 °C can be ascribed to the removal of pre-adsorbed CO_2 and moisture from the atmosphere. The weight loss of the three samples were almost the same below 200 °C, but as the temperature increased further, the curvature of the TGA traces changed sharply, showing faster weight loss for **PEI-20/SiO_2** and **PEI-50/SiO_2**, indicating decomposition of PEI.

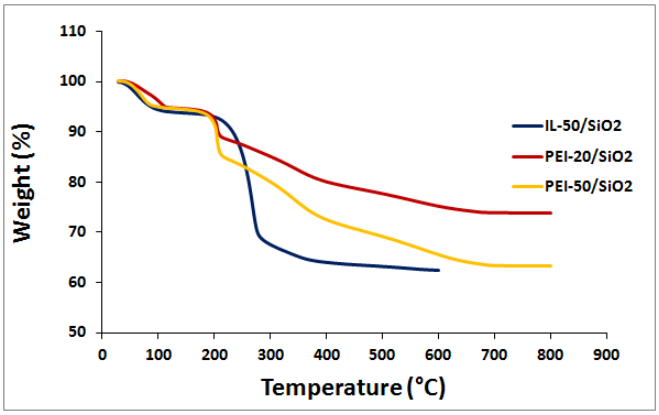


Figure 5. Weight changes of **IL-50/SiO_2**, **PEI-20/SiO_2**, **PEI-50/SiO_2** measured by TGA (10 °C min^{-1}, air flow 50 mL min^{-1}).

On the other hand, **IL-50/SiO_2** showed slower weight loss above 200 °C, indicative of enhanced thermal stability of the amine-free IL sorbent as compared to the polyamine counterparts, even under aerobic conditions employed in the TGA measurements. Decomposition of **IL-50/SiO_2** was largely completed at temperatures below 600 °C, whereas the materials containing PEI required higher temperatures for the total removal of organic components. The content of IL or PEI were calculated from TGA data by subtracting the weight percentage at maximum temperature to that

at 150 °C (after removal of adsorbed H_2O and CO_2). The resulting experimental loadings (listed in Table 2) are reasonably consistent with the theoretical values.

Table 2. Theoretical wt%, experimental wt% from TGA, and surface areas from BET.

Sample	*Theoretical IL or PEI loading [wt%]*	*Experimental IL or PEI loading [wt%]*	*Surface area [$m^2.g^{-1}$]*
IL-50/SiO_2	50	50.3	43.5
PEI-20/SiO_2	20	21.8	82.1
PEI-50/SiO_2	50	49.3	46.2
SiO_2 (blank)	-	-	179.3

The surface areas of **IL-50/SiO_2**, **PEI-20/SiO_2**, **PEI-50/SiO_2** and the pristine fumed silica support (SiO_2, blank) were measured by N_2 physisorption employing the BET method (Table 2 and Figure S3). Surface areas decrease with increasing PEI loading (82.1 and 46.2 $m^2\ g^{-1}$ for 20 and 50%, respectively), whereas the type of liquid sorbent results in similar coverage of the SiO_2 surface (43.5 and 46.2 $m^2\ g^{-1}$ for **IL-50/SiO_2** and **PEI-50/SiO_2**, respectively). These data reveal that the liquid IL or PEI adsorbents were effectively supported on the surface of the SiO_2 nanoparticles.

CO_2 capture-release

To investigate the sorption of CO_2 by solid-supported phosphonium carboxylate ILs, and to compare it with amine based sorbents, the above described **IL-50/SiO_2**, **PEI-20/SiO_2** and **PEI-50/SiO_2** materials have been selected. As a benchmark amine sorbent, PEI has strong CO_2 capture capacity due to the presence of multiple amine sites. In particular, PEI is expected to contain primary/secondary/tertiary amines in a 44:33:23 molar ratio [55]. As discussed above, primary and secondary amines tend to capture 0.5 mol(CO_2)/mol(N), whereas tertiary amines remain unreactive, under dry conditions (see Figure 2). Conversely, chemical absorption by the hydrated IL ([$P_{4\,4\,4\,4}$][AcO]·H_2O) may result in a maximum of 1 mol(CO_2)/mol(IL) (see Figure 3). Under these premises, the theoretical CO_2 capacities of **IL-50/SiO_2**, **PEI-20/SiO_2**, **PEI-50/SiO_2** are 1.0, 1.5 and 3.0 mmol(CO_2) per gram of material, respectively. For a more realistic comparison, the first two materials were studied more in detail in CO_2 capture/release experiments.

The CO_2 sorption in **IL-50/SiO_2** and **PEI-20/SiO_2** was measured at room temperature (25 °C) and nearly atmospheric pressure. The resulting breakthrough curves obtained from monitoring CO_2 concentration in the outlet gas from the sorption unit are shown in Figure 6. According to the breakthrough curve for **IL-50/SiO_2** the concentration of CO_2 during the initial period of the experiment (< 1 min) remained negligible, thus indicating that CO_2 sorption on the material was taking place. This was further proven by comparison to the breakthrough curve of the blank SiO_2, which showed a significantly narrower time frame. After this, the sorbent material began to saturate, and gradual increase in CO_2 concentration in the outlet gas was observed until complete saturation was achieved. On the other hand, it took about 2 min for **PEI-20/SiO_2** to show the increase in CO_2 concentration, and this shift in the breakthrough curve along the x-axis (fraction of time) compared to **IL-50/SiO_2** indicates higher CO_2 sorption, as expected from the higher theoretical capacity and stronger driving force of the amine sorbent, as discussed above.

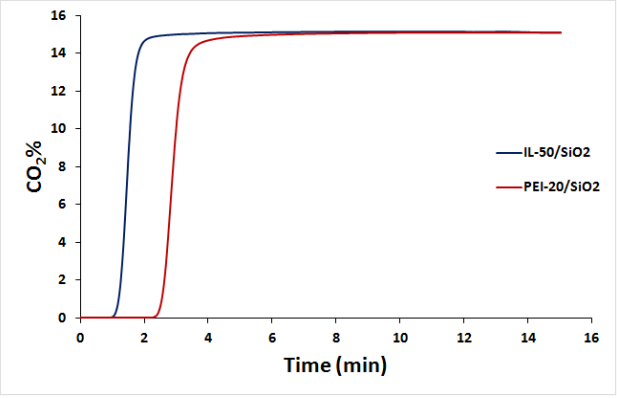


Figure 6. CO_2 sorption breakthrough curve for **IL-50/SiO_2** and **PEI-20/SiO_2**, at room temperature (25 °C) and atmospheric pressure, under CO_2 flow (15.012%, 300 mL min^{-1}).

It should be also noted that the sorption equilibrium for both sorbents was reached within

less than 5 min. This is primarily due to the fact of using solid-supported sorbents, which increase the CO_2 sorption rate compared to the liquid state form of sorbents. As mentioned above, the higher sorption capacity for PEI is expected due to the high CO_2 capture potential of amine-based materials, but considering the high energy input required in the desorption process, the IL-based sorbent might be more advantageous regarding regeneration efficiency. Therefore, CO_2 release experiments at moderate temperature were undertaken, as discussed in the following section.

Desorption of CO_2

The desorption of CO_2 from the studied sorbents (**IL-50/SiO$_2$** and **PEI-20/SiO$_2$**, in addition to SiO_2 as the blank material) was investigated at 60 °C, as shown in Figure 7.

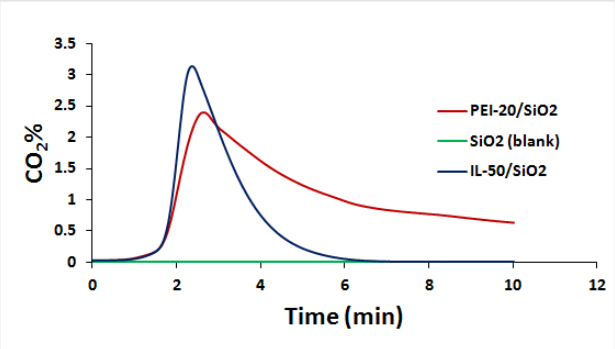


Figure 7. CO_2 desorption curves for **IL-50/SiO$_2$**, **PEI-20/SiO$_2$** and blank SiO_2, at 60 °C and atmospheric pressure under pure N_2 flow (300 mL min^{-1}).

To study the CO_2 desorption behavior aiming at minimizing energy expenditure, short cycles (10 min) were performed at moderate temperature. As can be observed in Figure 7, the CO_2 concentration of the outlet gas for three samples as a function of time show noticeable differences. The blank experiment showed negligible CO_2 release, as clearly seen by the flat line for pristine SiO_2. A maximum value of CO_2 concentration at 3.1% was recorded for **IL-50/SiO$_2$** after *ca.* 2 min, indicating rapid release. Moreover, fast and complete regeneration occurred within 7 min. In contrast, the PEI sample showed a maximum value of 2.1%, and then CO_2 concentration kept decreasing slowly during the remaining regeneration cycle, but it did not reach the baseline level. This means that regeneration of **PEI-20/SiO$_2$** took place to a limited extent, and the rate of desorption was slower than for the IL material.

These preliminary results demonstrate that the regeneration energy input for **IL-50/SiO$_2$** was much lower than for the amine-based competitor. Despite the lower (as expected) total sorption capacity of the IL material, which would require further optimization, the performance under repeated cycles at moderate temperatures might be competitive. These advantages make solid-supported phosphonium carboxylate ILs become promising as energy-efficient CO_2 sorbents.

Conclusions

Carbon dioxide capture is a key factor technology in palliating climate change. Moreover, recycling carbon in the atmosphere or from point sources by direct capture of CO_2, and converting these carbon sources to chemicals and fuels might be a promising solution to overcome the diminishing fossil fuels resources. There are large numbers of various technologies for CO_2 capture. Currently, amine-based CO_2 sorbents are mostly used, but these sorbents are accompanied by several disadvantages such as low thermal stability and high enthalpy of CO_2 reaction with amines, which lead to high energy input in regeneration process. Therefore, it is necessary to look for other alternatives. ILs as non-volatile sorbents with low enthalpy of CO_2 absorption might represent a good alternative to replace amines. In particular, phosphonium carboxylate ILs present higher thermal stabilities than ammonium counterparts. Furthermore, these set of (carboxylate-based) ILs show high CO_2 absorption, up to equimolar ratio, if formulated in the form of monohydrates.

Tetrabutylphosphonium acetate hydrate ([P_{4444}][AcO]·H_2O) was synthesized and impregnated onto silicon dioxide. The physicochemical properties and CO_2 capture-release performance of this solid-supported amine-free IL sorbent were studied and compared to analogous polyethyleneimine materials as competitor amine sorbents. Physicochemical properties of [P_{4444}][AcO]·H_2O/SiO_2 and

PEI/SiO_2 materials were measured, including thermal stability and surface area. The $[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$ showed thermal stability up to 200 °C, that is, higher than that of PEI/SiO_2. The CO_2 sorption capacity of materials containing 50% IL (**IL-50/SiO₂**), and 20% PEI (**PEI-20/SiO₂**), were investigated at room temperature using model flue gas (containing *ca*. 15% CO_2). It was clearly observed that the sorption equilibrium for both sorbents could be reached within 5 minutes, showing the fast capture kinetics of solid-supported materials, but as expected, the PEI sorbent showed higher CO_2 solubility than the IL counterpart. On the other hand, regeneration experiments at 60 °C and flowing N_2 (300 ml min^{-1}) through the CO_2-saturated sorbents showed much better result for **IL-50/SiO₂**, which underwent rapid and total desorption of CO_2 within 7 minutes, while **PEI-20/SiO₂** desorption rate was much slower, and desorption of CO_2 did not completed even after the entire regeneration cycle (10 min). Therefore, the energy input required to regenerate the IL material was much lower than that of a rich CO_2 amine-based PEI benchmark. These results suggest that sorption with solid-supported phosphonium carboxylate IL sorbents might become an energy-efficient CO_2 capture technology.

Future work

Clearly, there is an opportunity for amine-free, carboxylate-based ionic liquids to have a profound impact on CO_2 capture technology by avoiding the noxious emissions of amine processes, exhibiting higher thermal stability, enabling a moisture-adjustable performance, and directing the sorption-desorption process with minimal energy input. Several studies for integrating ionic liquids into CO_2 capture technology should be explored. In the particular case of this study using $[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$, the following ideas could be tested:

- Studying the regenerability of IL sorbents by testing under repeated cycles.
- Spectroscopic characterization of samples before and after CO_2 sorption experiments, in order to identify the different expected species (carbamates, bicarbonates, carbonates, *etc*.).
- Studying the effect of different water ratios in $[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$ materials on CO_2 sorption processes.
- Design and modify the chemical structure of IL, to enhance the CO_2 sorption capacity.
- Optimization of the system by studying the heat required in the regeneration process, the rate of the gas flow in sorption-desorption process and testing various loadings of the IL on SiO_2.
- Exploring the possibility of using $[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$ in large scale CO_2 capture needs to be studied.

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Supplementary Data

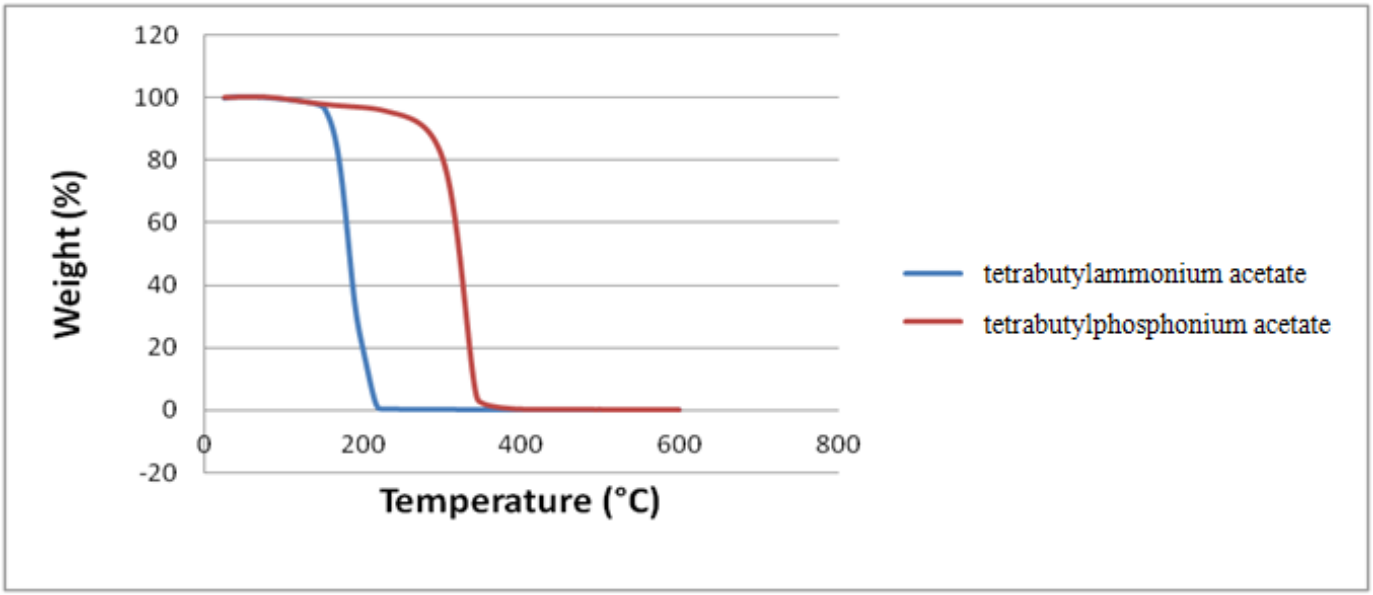


Figure S1. Weight changes of $[N_{4\,4\,4\,4}][AcO]$ and $[P_{4\,4\,4\,4}][AcO]$, measured by TGA (10 °C min^{-1}, air flow 50 mL min^{-1}).

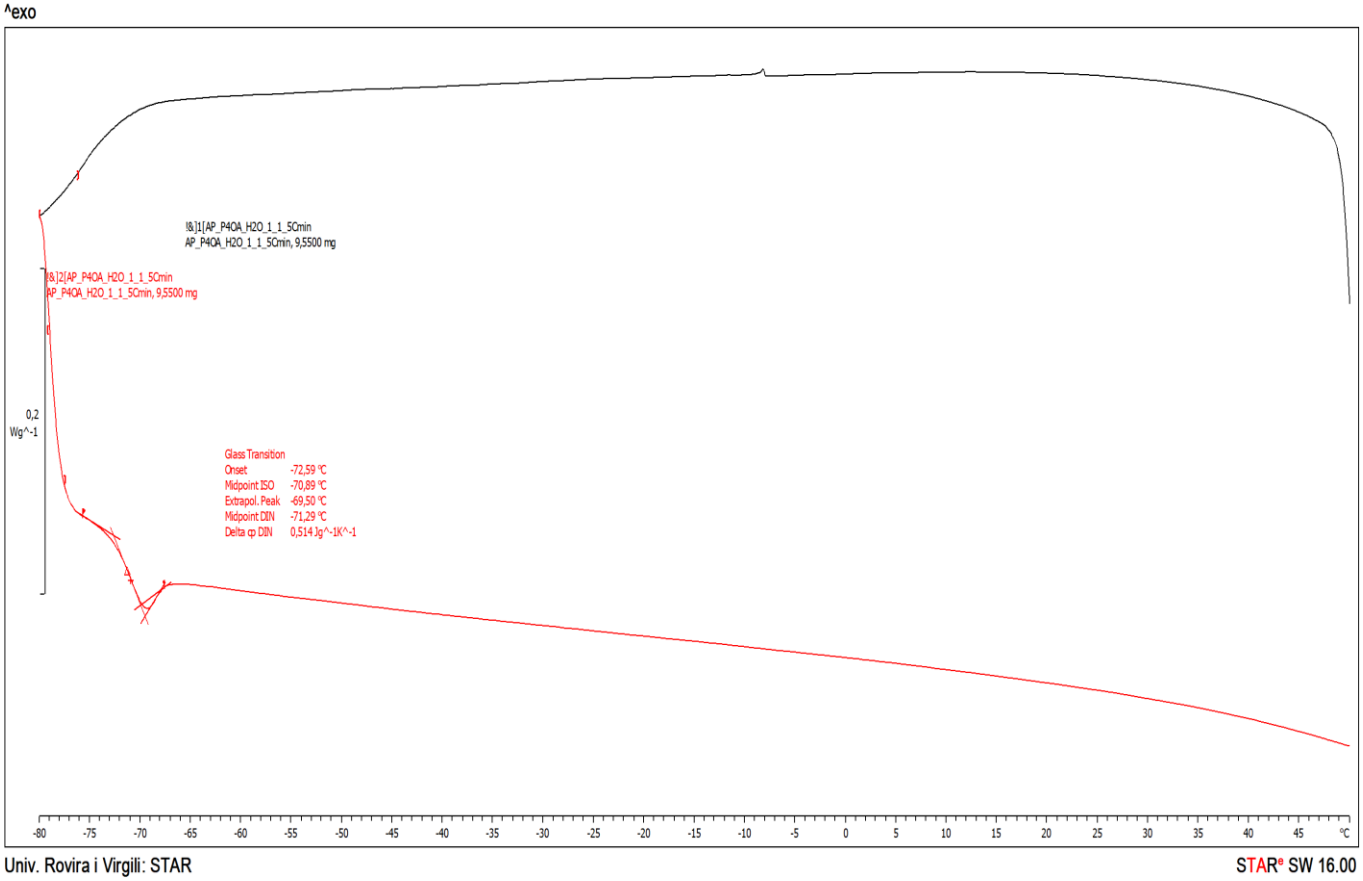
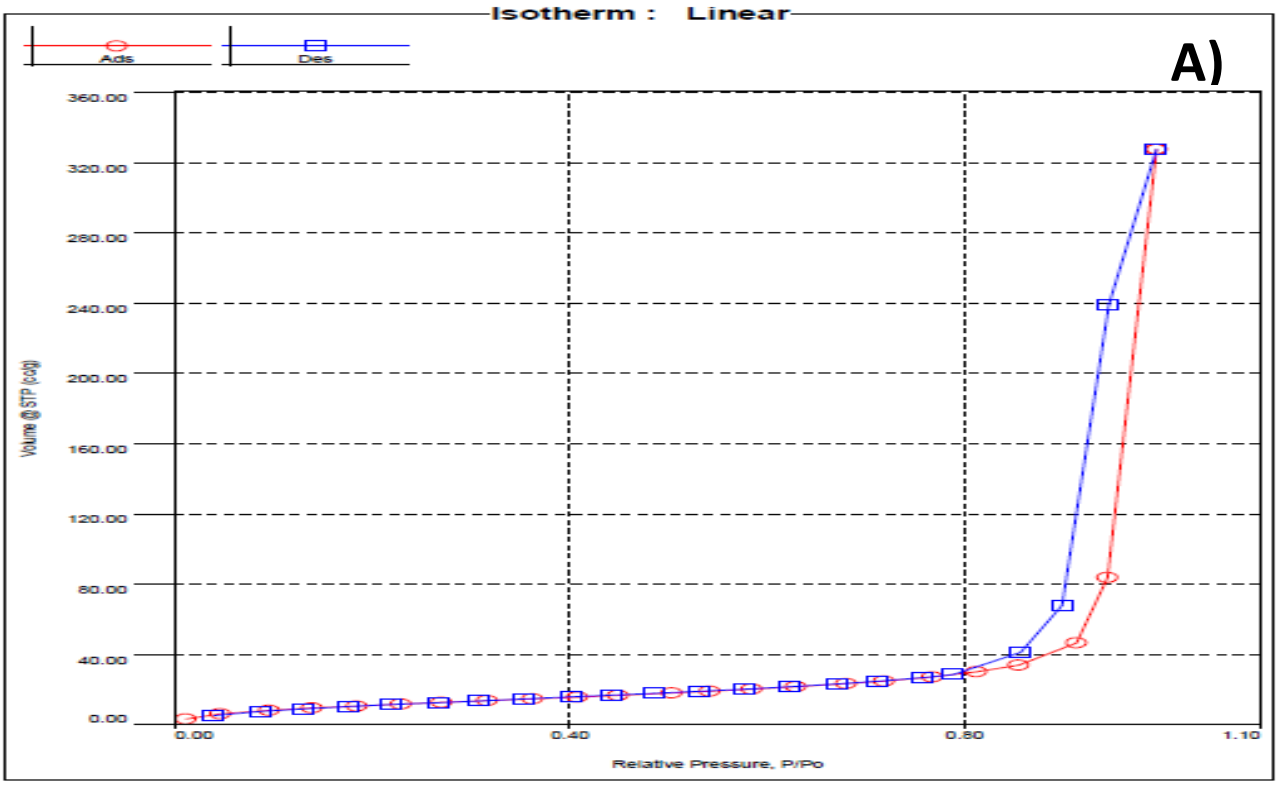
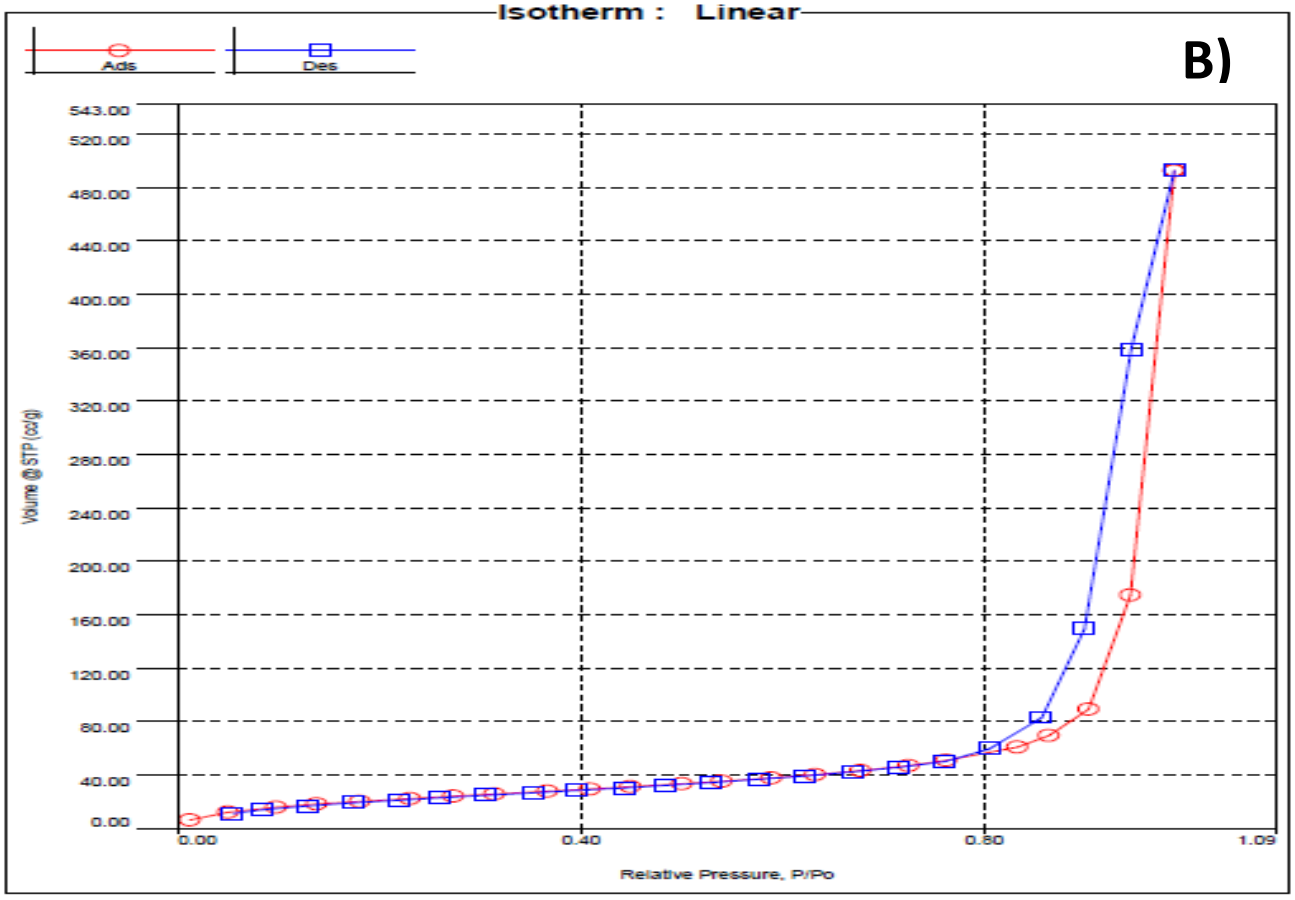
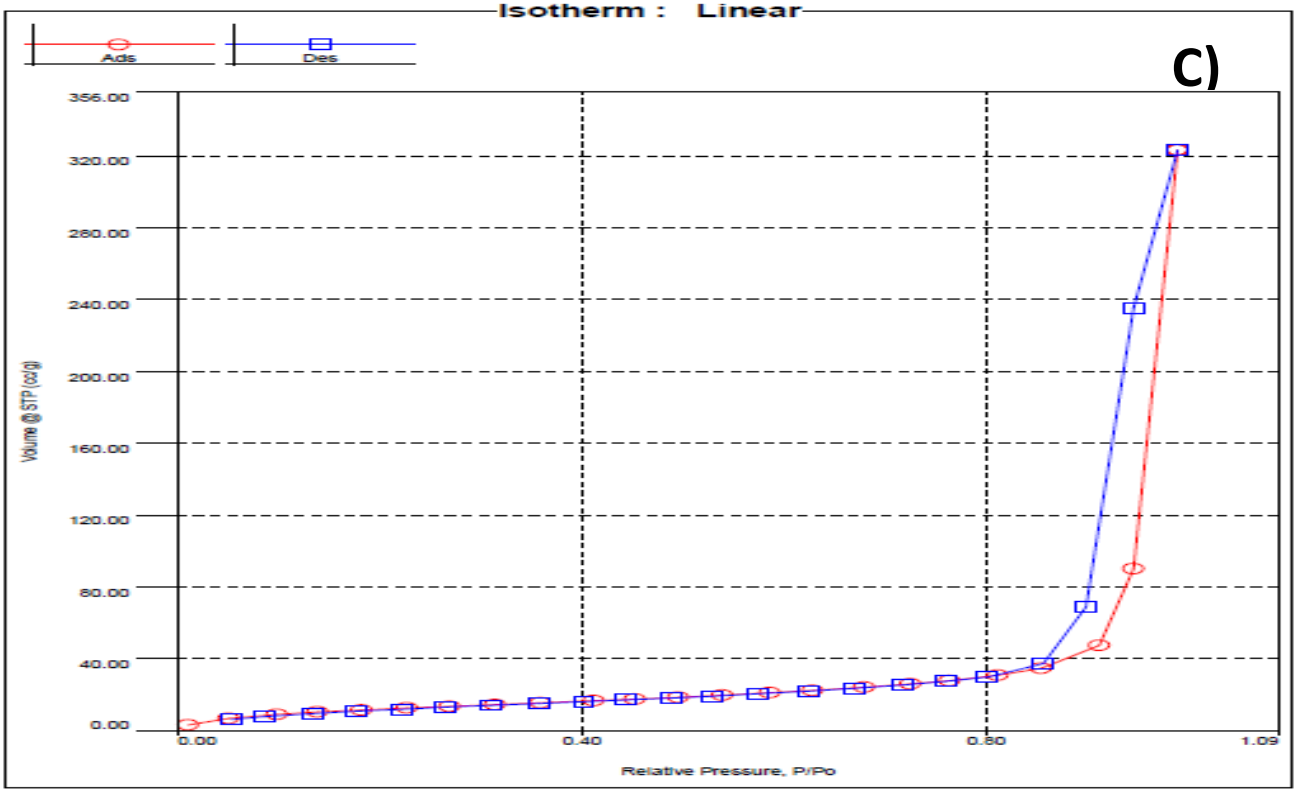


Figure S2. Cooling (black) and heating (red) DSC traces of $[P_{4\,4\,4\,4}][AcO]\cdot H_2O$, showing the glass transition event at −70.9 °C upon heating (5 °C min^{-1}, N_2 flow 50 mL min^{-1}).


Isotherm : Linear
Ads
Des
A)
360.00
320.00
280.00
240.00
200.00
160.00
120.00
80.00
40.00
0.00
Volume @ STP (cc/g)
0.00
0.40
0.80
1.10
Relative Pressure, P/Po


Isotherm : Linear
Ads
Des
B)
543.00
520.00
480.00
440.00
400.00
360.00
320.00
280.00
240.00
200.00
160.00
120.00
80.00
40.00
0.00
Volume @ STP (cc/g)
0.00
0.40
0.80
1.09
Relative Pressure, P/Po



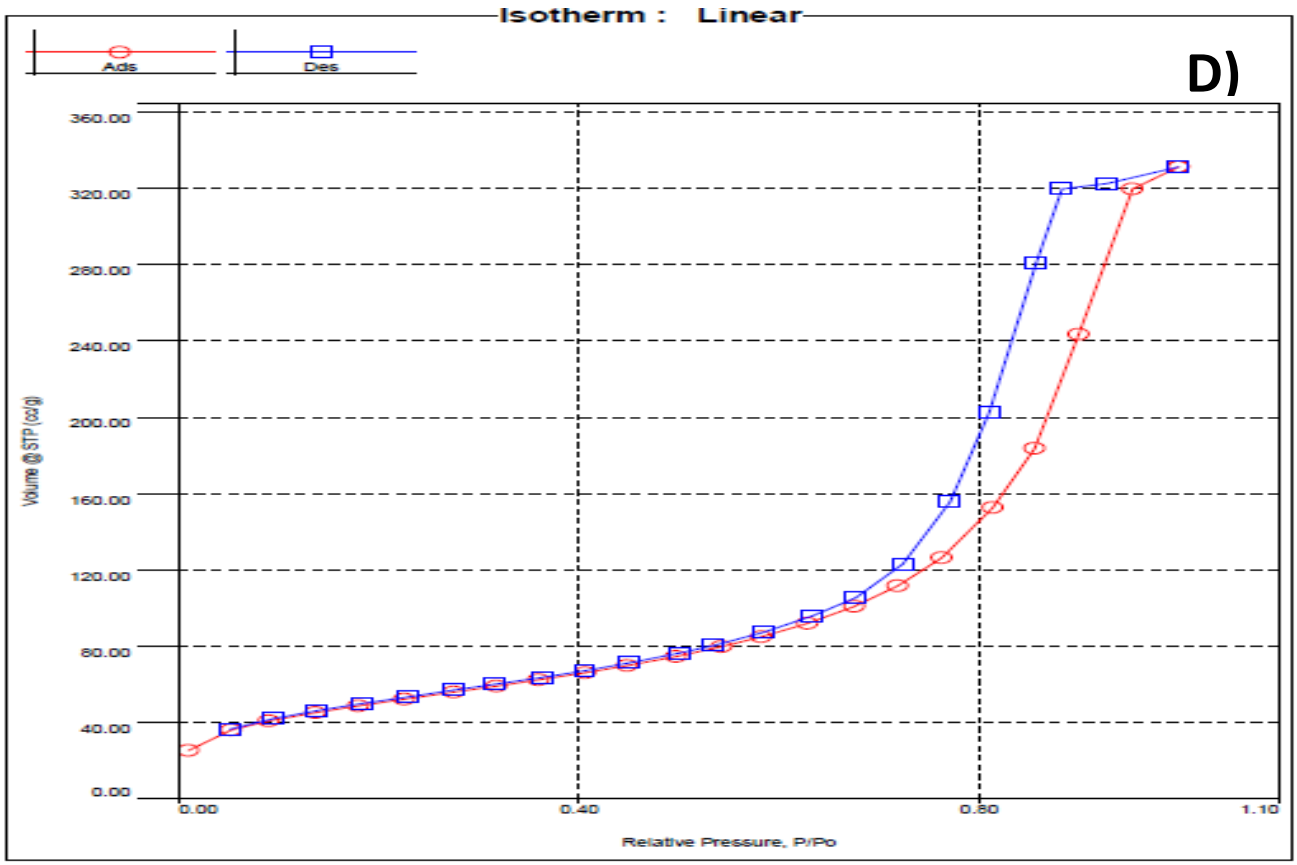


Figure S3. The BET analysis of, A) IL-50/SiO_2, B) PEI-20/SiO_2, C) PEI-50/SiO_2, D) blank sample (SiO_2).