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# Encapsulated amino acid-based ionic liquids for CO<sub>2</sub> capture

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**Abstract:** Ionic liquids have gathered special attention due to their potential for carbon dioxide capture, and their potential as solvents for climate changes mitigation. Following the scope of previous works, amino acid-based ionic liquids encapsulated (ENILs) into carbonaceous submicrocapsules are here proposed as a novel material for CO<sub>2</sub> capture. The ENILs prepared using tetrabutylphosphonium acetate ([P<sub>4,4,4,4</sub>][Ac]), used as reference, (2-hydroxyethyl)trimethylammonium L-phenylalaninate ([N<sub>1,1,1,2(OH)</sub>][L-Phe]), (2-hydroxyethyl)trimethylammonium L-prolinate ([N<sub>1,1,1,2(OH)</sub>][L-Pro]) and tetrabutylammonium L-prolinate ([N<sub>4,4,4,4</sub>][L-Pro]) were characterized by SEM, TEM, elemental analysis, TGA and BET to assess their morphology, chemical composition, porous structure and thermal stability. The absorption of CO<sub>2</sub> on these materials was studied up to 0.5 MPa and 343 K. The desorption of CO<sub>2</sub> from the saturated ENILs was evaluated, at mild conditions, evidencing these materials as promising agents for CO<sub>2</sub> capture from post-combustion sources, with high sorption capacity and fast and complete regeneration.

## Introduction

Mitigation of climate changes and the use of renewable energy sources have been two of the most important societal challenges, particularly when considering the increasing energy demand and average global temperature due to greenhouse gases release. Regarding the increasing average global temperature, predominantly due to accumulation of CO<sub>2</sub> in the atmosphere, innovative post-combustion technologies for CO<sub>2</sub> capture stand as indispensable for a cleaner energy production. Post-combustion stands as the most appealing emission sources due to an easy retrofit of existent and new technologies into existing power plants. Although gas separation has long been used in natural gas industry, counterbalanced by the increased value of the post-treated streams, post-combustion is still seen as a non-efficient, costly and, ultimately, unfeasible process.<sup>[1–4]</sup>

Over the last decade, the research community has been proposing several approaches for the improvement of CO<sub>2</sub> absorption, aiming at developing novel separation technologies suitable for industrial implementation.<sup>[5–10]</sup> Among these, chemical absorption has attracted special interest due to the solvents' high capacity, even at post-combustion low CO<sub>2</sub> partial pressures.<sup>[10–</sup>

<sup>13]</sup> Task-specific ionic liquids (TILs), amino acid-functionalized ILs, IL-mixed solvents and eutectic solvents, are promising materials for this purpose. Within chemisorption driven solvents, those based on amino acids stand out due to their low cost, abundant availability, easy synthesis and low toxicity and biodegradability.<sup>[11,13,22–26,14–21]</sup> However, the use of chemisorption driven solvents present several drawbacks, such as corrosivity, high viscosity of the products resultant from the chemical reaction(s), solvent loss and the high energy requirement for the regeneration processes, leading to high operational costs and ultimately leading to uneconomical, and sometimes technical unfeasible, processes. These drawbacks have hampered the development of separation units and industrial processes capable of fulfilling industry demands. The correct selection of the solvent stands thus, as one of the main challenges for innovative technological development of acid gases post-combustion treatment.<sup>[27]</sup> Furthermore, envisioning the use of green solvents is indispensable for a clean energy production, anthropogenic CO<sub>2</sub> capture, transportation, and/or reconstitution into value-added products. Nonetheless, if one aims at developing a technical and economically viable process for carbon capture, the pursuit on improving CO<sub>2</sub> solubility, viscosity, heat capacity and mass transfer of sorbents must be addressed from a process engineering perspective, as highlighted by Leclaire and Heldebrant<sup>[3]</sup> in their recent 'call to arms' perspective.<sup>[3]</sup> As emphasized by the authors, the community should shift focus from just enhancing equilibrium capacity to focus on the principles of green chemistry and green engineering, to make Carbon Capture, Utilization and Storage (CCUS) a reality.

Although amino acid-based ILs are a promising class of solvents, CO<sub>2</sub> absorption in these solvents presents important kinetic limitations, resultant from their inherent high viscosity or the drastic viscosity, increase upon reaction with CO<sub>2</sub>.<sup>[14]</sup> Nonetheless, many have pursued different approaches aiming at minimizing these limitations, while maintaining the enhanced gas sorption capacity, such as using a solid phase to immobilize the solvents and the use of gas-liquid membrane contactors for gas

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absorption processes.<sup>[17,28]</sup> Recently, the confinement of solvents in nano-porous matrices has been proposed as a promising technique for gas separation, with improved mechanical integrity capable of overcoming the major drawbacks of the bulk solvents, such as high viscosity and slow gas diffusivity, and ultimately, requiring reduced quantities of solvent to achieve the separation.<sup>[20,29–36]</sup> The encapsulated ionic liquids (ENILs) have shown to impose no loss of the solvent absorbent capacity with a drastic enhancement of the CO<sub>2</sub> sorption rate, both for physical or chemical sorption driven solvents.<sup>[20,31,36,37]</sup>

Here, aiming at further enhancing the CO<sub>2</sub> solubility and the fast sorption and desorption kinetics, amino acid-based ILs encapsulated in hollow carbonaceous submicrocapsules are evaluated for gas separation at temperatures ranging from 303 to 343 K, for CO<sub>2</sub> partial pressures ranging from 0 to 0.5 MPa.

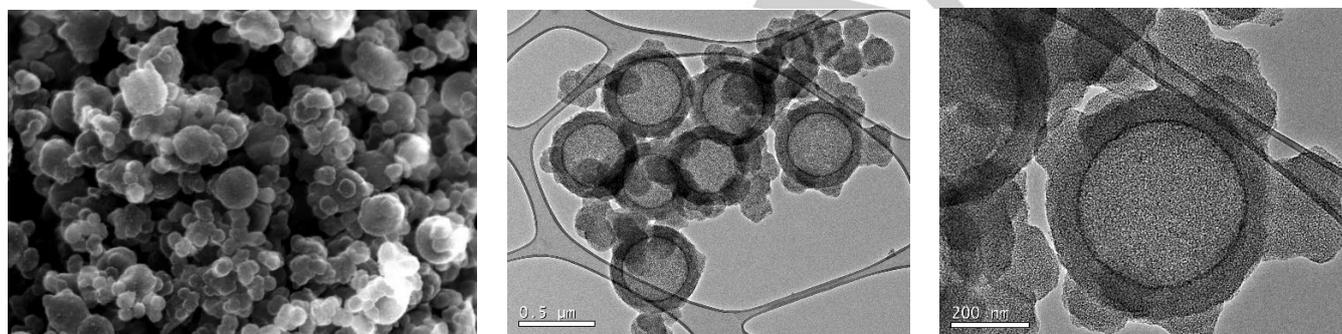


Figure 1. SEM (a) and TEM (b), (c) images of the C<sub>cap</sub> used for the ENIL preparation.

Table 1. Characterization of the C<sub>cap</sub> and ENILs prepared with different load of IL.

Material	EA			IL Load (% w/w)	Textural properties A <sub>BET</sub> (m <sup>2</sup> /g)
	%C	%H	%N		
C <sub>cap</sub>	87.67	1.8	0.0		1721
[P <sub>4,4,4,4</sub> ][Ac]	58.67	5.1	0.0	60.2	
[N <sub>1,1,1,2(OH)</sub> ][L-Phe]	59.57	6.8	6.3	51.2	
[N <sub>1,1,1,2(OH)</sub> ][L-Pro]	60.83	6.4	5.7	58.9	
[N <sub>4,4,4,4</sub> ][L-Pro]	62.02	6.7	8.4	60.9	

Adsorption–desorption isotherms of N<sub>2</sub> at 77 K were used to analyse the porous structure of the C<sub>cap</sub>. The results of the BET analysis are reported in Table 1 and Figure 2, showing a type IV adsorption isotherm with an inflection (or Knee) with the monolayer formation.

## Results and Discussion

## ENILs Characterization

The carbon capsules (C<sub>cap</sub>) with a micro/mesoporous shell structure and hollow core were studied by SEM and TEM. As depicted in Figure 1 spherical capsules were obtained containing high carbon content (~90%w/w) and homogeneous morphology (~500 nm of diameter and ~150 nm of shell thickness). Elemental analysis allowed quantifying the incorporation of IL in the C<sub>cap</sub>, by measuring the percentage of N in the final material, which can be related to the uptake of the cations and amino acid anions.<sup>[38]</sup> The EA results, reported in Table 1, confirm the adequate incorporation of the ILs (50–62% in mass).

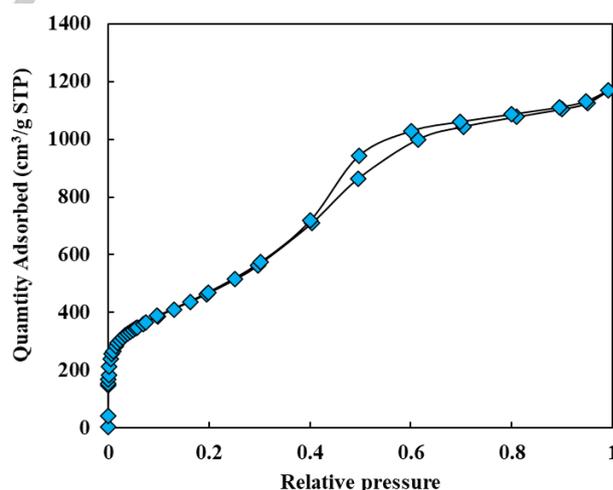


Figure 2. Nitrogen adsorption–desorption BET isotherm of capsules used in this work.

They show a highly developed porous structure (A<sub>BET</sub> = 1721 m<sup>2</sup>/g), with contributions of micro- and meso-porosity, as indicated by the high amount of nitrogen adsorbed in the whole relative pressure range, which is completely lost after incorporation of the IL in the C<sub>cap</sub> (Table 1); *i.e.*, the IL besides de

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capsule, also completely fills the pores of the capsule structure. As reported in previous publications,<sup>[31,38]</sup> the amount of IL confined inside the carbon capsules can be determined through a linear regression between the percentage of elemental nitrogen, obtained by EA, and the weight percentage of IL incorporated on the support.

**CO<sub>2</sub> solubilities**

The sorption isotherms of CO<sub>2</sub> in the neat ILs was not possible to be determined using the apparatus and methodology here adopted due to the high viscosity of the reaction product(s) of the carbon dioxide and the ILs. In fact, the initial contact and absorption of the CO<sub>2</sub> in the IL lead to the formation of a solid-like interface, at the gas-liquid interface, that did not allow for additional CO<sub>2</sub> to absorb and diffuse to the IL bulk. Nonetheless, when confined within the C<sub>cap</sub> the ILs did not present the behaviour observed in the neat IL solubility measurements, thus, ENIL sorption measurements were feasible within all the pressure and temperature ranges evaluated. The only exception was [P<sub>4,4,4,4</sub>][Ac] that is solid at temperatures below 333 K. The encapsulation of IL not only enhances the mass transport properties but also lets us use ILs that would not reach the thermodynamic equilibrium under reasonable conditions due to the kinetic limitations.<sup>[20]</sup> This improvement is due to the large increase of the contact surface area between the gas phase and the amino acid IL, upon dispersion of the absorbent in submicrodrops, in good agreement with previous results.<sup>[20,34,35,39,40]</sup>

The sorption isotherms of CO<sub>2</sub> in the ENILs were determined at five temperatures, namely 303, 313, 323, 333 and 343 K, for the amino acid-based ILs and at three temperatures, namely 333, 343 and 353 K, for the [P<sub>4,4,4,4</sub>][Ac], as depicted in **Figure 3** – with the CO<sub>2</sub> mole fractions calculated based on the moles of IL encapsulated. The results reported indicate an initial region with low equilibrium pressure, typical of chemical sorption, followed by physical absorption regime with a fast increase of the equilibrium pressure with the CO<sub>2</sub> content. Furthermore, the ILs not only remain liquid during CO<sub>2</sub> sorption but also maintain a high CO<sub>2</sub> absorption capacity and kinetics (**Figure 4**) when encapsulated. This approach of creating ‘microsolid’ droplets of IL allows to overcome the problems associated to the use of neat ILs.

Acetate-based ILs are known to play an important role in conditioning chemical reactions with CO<sub>2</sub> with reaction products with low viscosity, compared to most chemisorption solvents.<sup>[41–44]</sup> Although most of the work focus on the imidazolium cation, with

the sorption mechanism well described and accepted,<sup>[42,43]</sup> Shi et al.<sup>[41]</sup> have shown that for the tetrabutylphosphonium acetate IL the anion controls the large CO<sub>2</sub> solubility by chemisorption, with the cation contributing mostly for the physisorption regime. As depicted in **Figure 3** and **4**, the L-Proline-based IL, a secondary amine, presents higher CO<sub>2</sub> solubility than the L-Phenylalaninate-base IL, a primary amine, at pressures below 0.5 MPa – inverting the behaviour observed for higher CO<sub>2</sub> pressures. Although, secondary amines tend to present lower solubility and higher effective CO<sub>2</sub> mass transfer rates than primary amines, the amine pK<sub>a</sub>, degree of sterical hindrance or hybridization are known to present a significant impact on the gas absorption.<sup>[45][46,47]</sup>

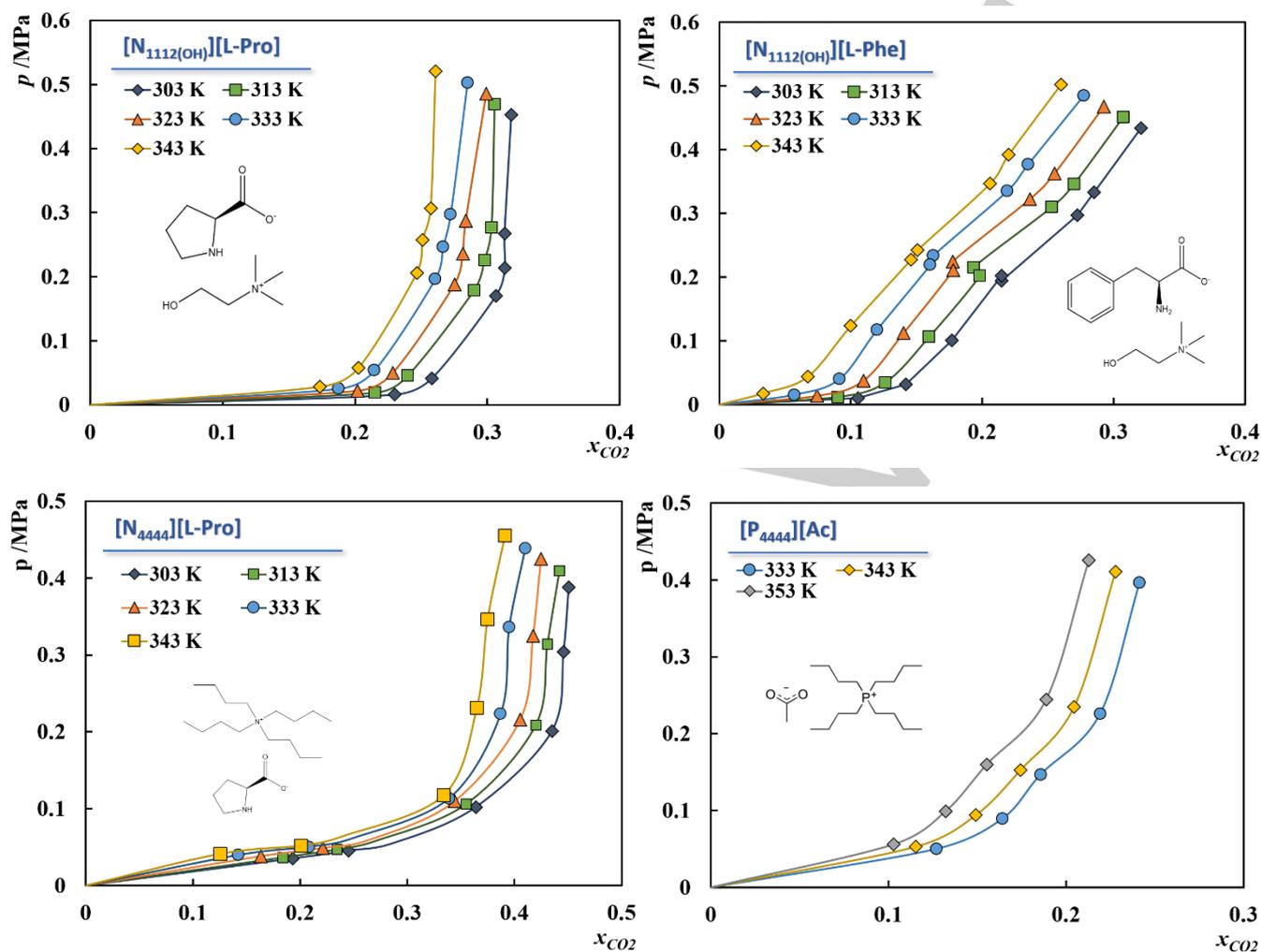
Furthermore, secondary hindered amines present higher absorption rates than most primary amines but, primary and secondary amines with similar pK<sub>a</sub> and hindrance tend to present similar CO<sub>2</sub> solubility.<sup>[45]</sup> Here, the anion charge delocalization, anion hinderance, and aromaticity, seem to impose additional complexity that translates into higher solubilities, in mole fraction, of the [N<sub>1,1,1,2(OH)</sub>][L-Pro] and [N<sub>4,4,4,4</sub>][L-Pro], compared to the [N<sub>1,1,1,2(OH)</sub>][L-Phe] and [C<sub>4</sub>C<sub>1im</sub>][L-Pro] reported in a previous publication<sup>[20]</sup> (**Figure S9**). Moreover, the higher degree of sterical hindrance and higher charge delocalization of the [N<sub>1,1,1,2(OH)</sub>][L-Pro] cation translates into a lower CO<sub>2</sub> sorption capacity, than that of the [N<sub>4,4,4,4</sub>][L-Pro]. However, when the molecular weight effect is removed from the analysis by comparing the solubility in molalities, the differences and trends of the solubilities change.

As depicted in **Figure 4**, the [N<sub>1,1,1,2(OH)</sub>][L-Pro] presents the highest solubility, at 343 K, followed by the [P<sub>4,4,4,4</sub>][Ac], [N<sub>4,4,4,4</sub>][L-Pro] and [N<sub>1,1,1,2(OH)</sub>][L-Phe]. Nonetheless, as one would expect, within the physisorption regime the molecular weight becomes the dominant factor with the higher molecular weight ILs presenting higher solubility.<sup>[6]</sup> The experimental data are reported in **Table S1** in SI.

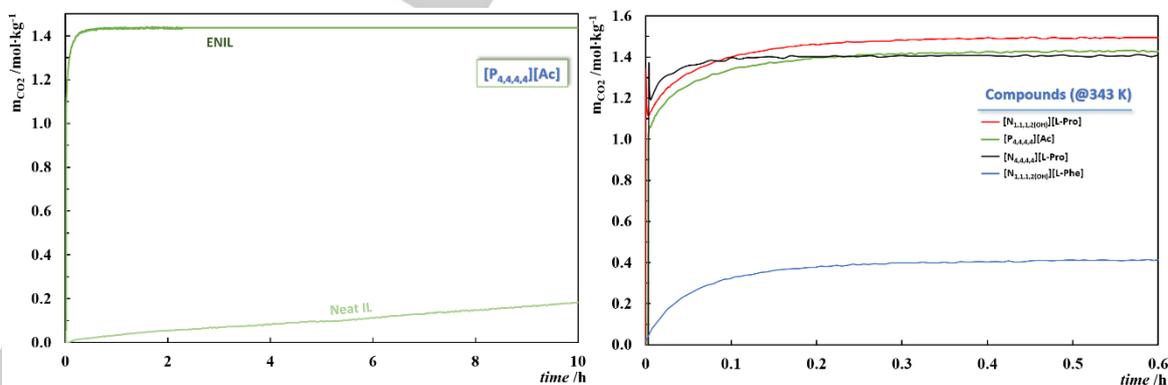
To ensure a successful industrial application one must ensure an easy and low energy demanding regeneration. Thus, the sorption capability of ENILs prepared with [P<sub>4,4,4,4</sub>][Ac], [N<sub>4,4,4,4</sub>][L-Pro], [N<sub>1,1,1,2(OH)</sub>][L-Pro] and [N<sub>1,1,1,2(OH)</sub>][L-Phe], was evaluated during four cycles of sorption-desorption. The desorption cycles were performed after each sorption cycle at 1 Pa, 343 K during 2 h, while the sorption was performed with an initial pressure of (0.2 ± 0.05) MPa. As depicted in **Figure 5**, the regeneration of the ENIL was successful with the solubility essentially constant after the various regeneration cycles, the deviations observed being within the experimental uncertainty. Furthermore, <sup>1</sup>H and <sup>13</sup>C NMR was performed after the sorption cycles showing no degradation of the ILs either due to

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immobilization, solvent evaporation or gas sorption/desorption cycles, as depicted in Figure S10 of the Supporting Information.

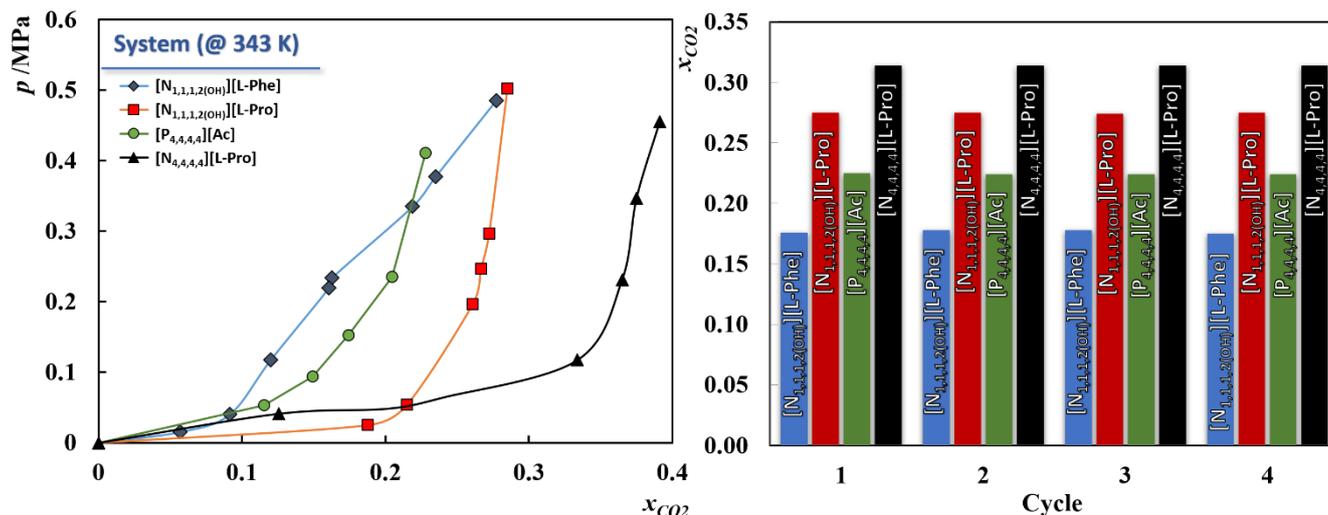


**Figure 3.** Pressure-composition diagram of the binary systems  $CO_2 + [N_{1,1,1,2(OH)}][L-Pro]$ ,  $CO_2 + [N_{1,1,1,2(OH)}][L-Phe]$ ,  $CO_2 + [N_{4,4,4,4}][L-Pro]$  and  $CO_2 + [P_{4,4,4,4}][Ac]$ . The lines are guides for the eyes.



**Figure 4.** Molality – absorption time diagrams of (left)  $CO_2 + [P_{4,4,4,4}][Ac]$  and (right) the studied ENILs.

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**Figure 5.** Pressure-composition diagram of the binary systems CO<sub>2</sub> + [P<sub>4,4,4,4</sub>][Ac], CO<sub>2</sub> + [N<sub>4,4,4,4</sub>][L-Pro], CO<sub>2</sub> + [N<sub>1,1,1,2(OH)</sub>][L-Pro] and CO<sub>2</sub> + [N<sub>1,1,1,2(OH)</sub>][L-Phe] (left) and sorption (333 K and 0.2 MPa for the phosphonium IL and 323 K and 0.2 MPa for the remaining ILs) and desorption (343 K and 1 Pa) cycles (right). The lines are guides for the eyes.

## Conclusion

Encapsulated amino acid-based ionic liquids (ENILs) were prepared for CO<sub>2</sub> capture from post-combustion and their performance evaluated by means of an isochoric pressure cell. The confinement of specific ILs into the carbon submicrocapsules resulted in ENILs with high CO<sub>2</sub> sorption capacities and thermal stabilities. Furthermore, contrary to the neat ILs, whose reaction with CO<sub>2</sub> lead to the formation of a solid-like interface that blocked further gas sorption and diffusion to the IL bulk, the ENILs remain liquid and absorbing the CO<sub>2</sub> within the pressure range studied with fast sorption kinetics. The incorporation of the ILs into the carbon submicrocapsules increases their performance when compared with the neat IL, due to the increase of the surface contact area, promoting higher mass transfer rates. In addition, ENILs were successfully regenerated at mild conditions and used in successive CO<sub>2</sub> capture-desorption cycles. Therefore, these results highlight ENILs as new separating agents with promising characteristics for industrial application in CO<sub>2</sub> capture technologies, with good thermal stability, high CO<sub>2</sub> sorption capacities, and low energy demanding in regeneration steps.

## Experimental Section

### Materials

The tetrabutylammonium L-prolinate, [N<sub>4,4,4,4</sub>][L-Pro], the (2-hydroxyethyl)trimethylammonium L-phenylalaninate, [N<sub>1,1,1,2(OH)</sub>][L-Phe], (2-hydroxyethyl)trimethylammonium L-prolinate, [N<sub>1,1,1,2(OH)</sub>][L-Pro], and the tetrabutylphosphonium acetate [P<sub>4,4,4,4</sub>][Ac] ILs were synthesized

following the procedure reported by Allen et al.<sup>[48]</sup> and Santis et al.<sup>[49]</sup> The ionic liquids were synthesized by the neutralization of [N<sub>4,4,4,4</sub>][OH] or [N<sub>1,1,1,2(OH)</sub>][OH] with the respective amino acid/organic acid, namely the L-phenylalanine, L-proline and acetic acid.

Succinctly, [P<sub>4,4,4,4</sub>][OH] or [N<sub>4,4,4,4</sub>][OH] (1 equiv, 40 wt% in aqueous solution) were added dropwise to an aqueous solution of acetic acid or respective amino acid, with a molar excess of 1.1 equivalent, at room temperature. The reaction mixture was constantly stirred at room temperature for [P<sub>4,4,4,4</sub>][Ac] and for [N<sub>4,4,4,4</sub>][L-Pro], and protected from light for 2 hours, producing the respective ionic liquid and water as the by product. The water was then removed under reduced pressure (2 kPa). For [N<sub>4,4,4,4</sub>][L-Pro], the resultant residue was dissolved in acetonitrile and filtered to remove the unreacted amino acid. Finally, the acetonitrile was removed under reduced pressure and the obtained compound was dried under high vacuum for at least 48 h. The ILs were further dried under high vacuum (0.1 Pa) and moderate temperature (303 K) for at least 48 hours in order to remove the remaining solvents. [N<sub>1,1,1,2(OH)</sub>][OH] (1 equiv, 45 wt% in methanol solution) was added dropwise to an aqueous solution of amino acid, with a molar excess of 1.1 equivalents, at room temperature for [N<sub>1,1,1,2(OH)</sub>][L-Pro] and at 333 K for [N<sub>1,1,1,2(OH)</sub>][L-Phe]. The reaction mixture was stirred for 2 hours and protected from light. The solvents were then removed under reduced pressure (2 kPa). A solution of acetonitrile/methanol (9:1, v/v) was then added under vigorous stirring in order to precipitate the excess of amino acid. The mixture was left stirring for 1 hour and the excess of amino acid was then filtrated. In a final step, the acetonitrile and methanol were evaporated initially under reduced pressure (2 kPa) and then high vacuum (0.1 Pa) and moderate temperature (303 K) for at least 48 hours. The water mass fraction of the ionic liquids was determined by coulometric Karl Fischer titration (Metrohm, model 831) and shown to be less than 0.05 wt%. The structure of all compounds was evaluated by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, showing purity higher to 99% for all the ionic structures, as reported in **Figures S1**

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to S8 in Supporting Information. The properties of four selected ILs in this work are present in Table 2.

Tetrabutylammonium hydroxide ( $[N_{4,4,4,4}]OH$ , in aqueous solution at 40 wt%), the tetrabutylphosphonium hydroxide ( $[P_{4,4,4,4}]OH$ , in aqueous solution at 40 wt%), the (2-hydroxyethyl)trimethylammonium hydroxide ( $[N_{1,1,1,2(OH)}]OH$ , in methanol solution at 45 wt%), L-phenylalanine (99 wt% of purity) and acetic acid (99.99 wt% pure) were acquired from Sigma-Aldrich. L-proline (99 wt% of purity) was acquired from Acros Organics. Methanol (HPLC grade) and acetonitrile (99.9 wt% of purity) were acquired from VWR. The water used was ultrapure water, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus.

The sorption experiments were carried out using carbon dioxide ( $CO_2$ ) supplied by Air Liquide Portugal with a purity of 99.999%.

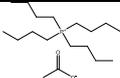
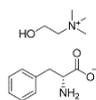
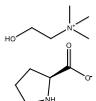
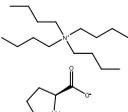
### Preparation of the ENILs

The carbon submicrocapsules ( $C_{cap}$ ) were synthesized following the template method described in detail in previous works.<sup>[32,34,36,39,50,51]</sup> A model of a silica sphere with a solid core and mesoporous shell were used as template. A volume of 15 mL of tetraethoxysilane (TEOS) was added to a reaction medium of an ethanolic solution composed of 185 mL of ethanol, 20 mL of distilled water and 12 mL of ammonia and maintained with vigorous stirring at 303 K for at least 1 hour. Then, a mixture containing 17.5 mL of TEOS and C18TMS (2.5:1 v/v) was added to previous solution to form the mesoporous shell around them. This step was repeated twice in order to increase the thickness of the mesoporous shell. After 1 hour of reaction, the resulting material was filtered and calcinated in air at 823 K for 6 hours. The silica spheres were then impregnated by a solution consisting on 0.27 g of  $AlCl_3 \cdot 6H_2O$  per gram of template and calcinated again under the same conditions. A phenol-

formaldehyde resin was used as carbon precursor to obtain the desired carbon microcapsules. A mixture of 0.374 g of phenol/g template was added to the template and maintained in agitation for 14 hours at 373 K through a rotary evaporated. Then, 0.238 g of paraformaldehyde/ g of template was added, and the temperature was increased to 403 K and maintained under vacuum for 24 hours. The resulting material was heated under a nitrogen atmosphere for 5 hours at 433 K in a vertical furnace, and then, pyrolyzed at 1123 K for 7 hours. The silica template was removed by washing it with hydrofluoric acid solution (48 %v/v). The resulting  $C_{cap}$  support material was washed with deionized water until reach pH 7 and dried at 373 K for 24 hours. Phenol (99%), paraformaldehyde (95-100%), aluminium trichloride (95-100%), ammonia (38%), absolute ethanol (99%) and hydrofluoric acid (48%) used were provided by Panreac. Tetraethylorthosilicate (98%, TEOS) and octadecyltrimethoxysilane (90%, C18TMS) were supplied by Sigma-Aldrich. Then, the ENIL materials were prepared by incipient wetness impregnation with the corresponding ILs, dissolved in ethanol to reduce the viscosity and assure good dispersion. To ensure a homogeneous penetration, into the pores, the IL solution was added drop wise over the  $C_{cap}$ , followed by vacuum evacuation, to remove the solvent, at 333 K and 1 Pa over 24 h. The procedure followed allowed to impregnate ~60% of IL (wt., ENIL basis) in the ENIL. The amount of IL loaded was determined by weight difference between the final ENIL and the weight of  $C_{cap}$ .

Elemental analysis (EA) was used to validate the IL impregnation. The IL impregnation percentage was derived from the linear relationship, proposed in a previous publication,<sup>[38]</sup> using the percentage of elemental nitrogen, in the supported-IL materials and the weight percentage of the IL supported on porous carbons. All the ENILs prepared had the resemblance and behaviour of a powdered material, allowing one to infer that all the IL was encapsulated.

**Table 2.** Name, acronym, chemical structure and molecular weight of the four ILs studied in this work.

Name	Acronym	Chemical Structure	Mw /g.mol <sup>-1</sup>
Tetrabutylphosphonium acetate	$[P_{4,4,4,4}][Ac]$		318.48
(2-Hydroxyethyl)trimethylammonium L-phenylalaninate	$[N_{1,1,1,2(OH)}][L-Phe]$		268.27
(2-Hydroxyethyl)trimethylammonium L-prolinate	$[N_{1,1,1,2(OH)}][L-Pro]$		218.32
Tetrabutylammonium L-prolinate	$[N_{4,4,4,4}][L-Pro]$		356.60

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## Characterization of the ENILs

The morphology and microstructure of  $C_{\text{cap}}$  and ENILs were studied by scanning and transmission electron microscopy (SEM and TEM). SEM micrographs were obtained using a HITACHI SU-70 operating at 25 kV. The samples were previously coated with a carbon film using an Emitech K950X carbon evaporator. TEM analyses were performed by means of a Philips 420 JEM-2000 FX microscope. The porous structure was characterized in a Micromeritics apparatus (Tristar II 3020 model) by nitrogen adsorption-desorption isotherms at 77 K using the Brunauer-Emmett-Teller (BET) equation using the methodology reported in a previous publication and **equation 1** (detailed description is given in the Supporting Information).<sup>[32]</sup>

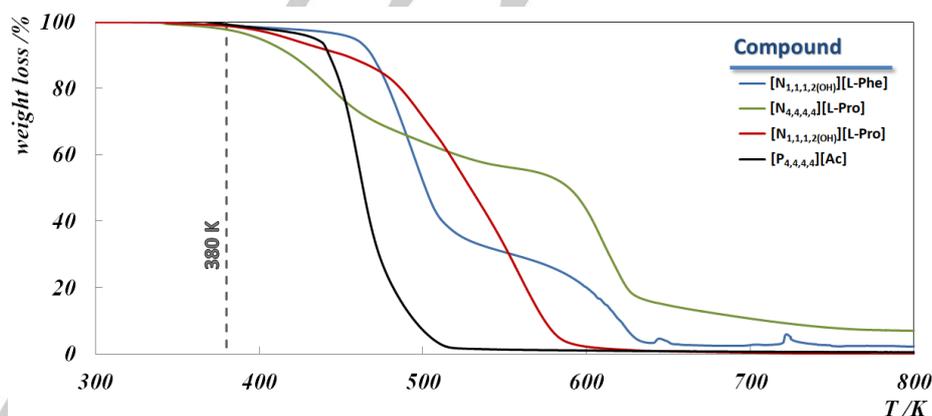
$$S_a = \frac{v_m N_a a_m}{v_m m_s} \quad (1)$$

where  $S_a$  is the specific surface area,  $N_a$  is the Avogadro's number,  $V_m$  is the amount of gas adsorbed if a monolayer was formed,  $a_m$  is the effective cross-section area of one adsorbed molecule,  $v_m$  is the molar volume of one adsorbed molecule (22400 mL of volume occupied by mol of adsorbate gas at STP conditions) and  $m_s$  is the mass of adsorbent.

Elemental analyses (EA) of  $C_{\text{cap}}$  and ENILs were carried out in a LECO CHNS-932 analyser to obtain C, H and N content. A macro-sized sample is weighed (2-5 mg) into a ceramic boat, placed in the loader and transferred to a sealed purge chamber, where entrained atmospheric gas

is removed. The purged sample is transferred to the furnace and to ensure complete and rapid combustion (oxidation) of the sample the furnace environment is composed of pure oxygen with a secondary oxygen flow directed to the sample via a ceramic lance. The combustion gases are swept from the furnace through a thermoelectric cooler or an anhydron reagent, to remove moisture, and collected in a thermostatically controlled ballast volume. The gases equilibrate and mix in the ballast before a representative aliquot of the gas is extracted and introduced into a flowing stream of inert gas for analysis.

Thermogravimetric analyses (TGA) of ILs and ENILs were conducted in a Setaram SETSYS Evolution 1750 thermobalance under nitrogen atmosphere. A dynamic method was used with a temperature range from (298–835) K at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen flow of 200 ml min<sup>-1</sup>. The accuracy of temperature and mass measurements was 0.1 K and 10<sup>-3</sup> mg, respectively. Aluminium pans were used to hold an initial mass between 4 and 12 mg. In all TGA runs, the derivative curves (DTG) were obtained for more in-depth interpretation and DTG temperatures. TDTG (K) was assigned to IL decomposition in the solid supports from the DTG curve. As depicted in **Figure 6**, the studied ILs are thermally stable up to 380 K and afterwards a sharp decomposition was observed in the temperature range of 380–680 K. The respective ENIL exhibits a weight loss with a similar pattern to the neat IL, however the peak appears at somewhat lower temperatures, denoting worse thermal stability due to the encapsulation, similar to that reported in a previous publication.<sup>[31]</sup>



**Figure 6.** Thermogravimetric analysis (TGA) of the studied ILs.

CO<sub>2</sub> Solubility

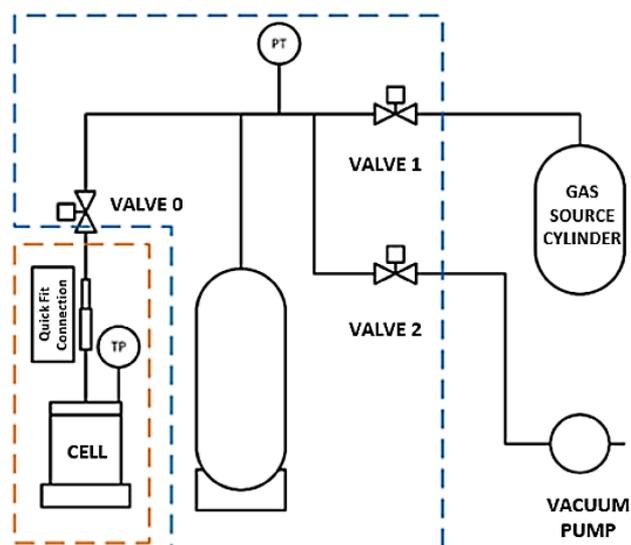
The CO<sub>2</sub> solubility was evaluated using a constant temperature-volume equilibrium cell made of stainless steel, reported in detail elsewhere.<sup>[31]</sup> The isochoric equilibrium cell consists of a fixed volume cell connected to a gas line, as depicted in **Figure 7**. The gas line, also with a known volume, consists of a large volume cylinder, a pressure transducer (*Swagelok S Model*), able to operate up to 1 MPa with an uncertainty of

0.2%, and valves that allow controlling the gas addition. The experimental setup, except for the pressure transducer, is placed inside an oven with a temperature stability of 0.5 K. The pressure transducer is placed outside the oven to assure no influence of the temperature on the pressure uncertainty.

A fixed amount of ENIL, whose exact mass is determined by weight using a high weight/high precision balance (Sartorius LA200P) with an

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accuracy of 1 mg, is introduced into the cell. The ENIL is then kept under vacuum overnight, while heating at 353 K, in order to remove atmospheric gases absorbed during manipulation. The gas is introduced on the gas section (dashed blue section, **Figure 7**) up to the desired pressure. The amount of gas (number of moles) present in the gas line is calculated using the Peng-Robinson EoS knowing the gas-phase volume and system pressure once the temperature equilibration is reached. The initial temperature is set to 353 K and once the equilibrium is reached the valve that connects the gas section with the solvent containing cell is open, allowing the gas to get in contact with the ENIL. The pressure decay is then monitored and logged, until new pressure equilibrium is reached. Knowing the cell gas phase volume and pressure, at equilibrium, the number of moles is determined. The number of moles adsorbed into the ENIL is then calculated by the difference to those initial added. The temperature is then decreased to a new set point allowing for additional gas to adsorb in the ENIL. Once the new equilibrium is reached the number of moles adsorbed into the ENIL is again calculated. After the equilibrium pressure is determined for all temperatures, the IL is regenerated by applying reduced pressure (1 Pa) and moderate temperature (353 K) for a period never shorter than 4 hours. Once regenerated the adsorption procedure is then repeated with a different initial pressure of the gas, allowing thus, to determine additional equilibrium points and better describe the system phase diagram. The determined equilibrium points are remeasured, normally in triplicate, aiming to minimize, identify and remove measurement and manipulation errors. For the sorption/desorption cycles, after each pressure equilibrium is reached, the system is degassed at 1 Pa and 353 K for 2 h and the sorption methodology repeated.



**Figure 7.** Diagram of the isochoric method apparatus used in this work.

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**Keywords:** Post-combustion • Carbon dioxide capture • Encapsulated ionic liquids • Amino acid-based ionic liquids

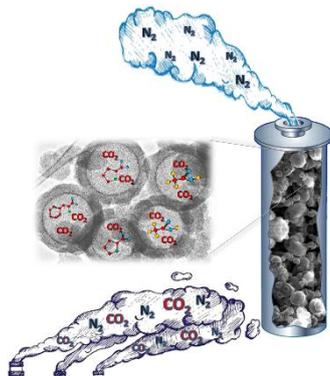
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The absorption of CO<sub>2</sub> on amino acid-based ionic liquids, encapsulated (ENILs) into carbonaceous submicrocapsules are proposed as a novel promising agents for CO<sub>2</sub> capture from post-combustion sources, with high sorption capacity and fast and complete regeneration.

**Key Topic:** amino acid-based ionic liquids; IL encapsulation into carbonaceous submicrocapsules