Encapsulated Protic Ionic Liquids as Sustainable Materials for CO₂ Separation

Liliana P. Silva, Emanuel A. Crespo, Mónia A. R. Martins, Paula C. Barbosa, Ramesh L. Gardas, Lourdes F. Vega, João A. P. Coutinho, and Pedro J. Carvalho*

Cite This: https://doi.org/10.1021/acs.iecr.1c04335

ABSTRACT: Protic ionic liquids (PILs) have been suggested as promising solvents for CO₂ capture; however, their high viscosity and consequent poor mass transfer coefficients hinder their large-scale industrial application. To overcome this limitation, PILs (neat or encapsulated) can be incorporated into polymers coated on hollow fiber membranes, to be implemented in gas–liquid contactor units. However, before the immobilization of PIL-based solvents on membranes, fundamental studies on the CO₂ sorption process in PILs are still mandatory. Here, the carboxylate-based PILs' ability for CO₂ absorption was evaluated using an isochoric solubility cell in a wide range of temperatures (303−343 K) and CO₂ partial pressures (0−0.8 MPa). The experimental data revealed the existence of a distinct sorption mechanism than that typically observed in other low-volatile physical solvents, where the solubility was mainly affected by entropic effects. The soft-SAFT equation of state was further applied for modeling of the sorptivity data, which allowed us to infer the influence of the anion’s structure on the system’s interactions. Aiming to improve the process kinetics, the PILs were encapsulated in carbonaceous submicrocapsules, herein proposed as an efficient material for CO₂ separation. To characterize the composition, morphology, porous structure, and thermal stability of the solvents used, SEM, TEM, TGA, BET, and elemental analyses were performed. The adsorption of CO₂ on these materials showed that these materials retained the same sorption capacity as their neat counterparts and with considerably increased sorption rates. These materials also retained their performance after various sorption–desorption cycles and showed fast and complete regeneration and high sorption capacity, thus indicating their potential for CO₂ capture.

1. INTRODUCTION

The increasing concentration of greenhouse gases (GHGs) in the atmosphere, especially carbon dioxide (CO₂), is particularly concerning with erratic climate changes, such as the increasing average global temperature, flooding, and extreme drought, as evident from recurrent global events.¹,² Currently, more than 50% of the total GHG emissions are derived from industrial sources, with a large share being related to the use of fossil fuels as a major energy source.³ Decarbonization of industrial processes has been urged by governments and environmental agencies worldwide, leading to the enforcement of more restrictive legislations and collaborative programs to encourage researchers to develop highly efficient technologies capable of mitigating CO₂ emissions.⁴

There are several ways to mitigate CO₂ emissions in the atmosphere, including the replacement of fossil fuel-based energies by renewable sources, the development of higher-efficiency processes for energy production, and the most promising strategy of implementation of carbon capture and storage (CCS) technologies.⁵ CCS has the potential for trapping up to 90% of CO₂ emissions from current industrial power plants. These CCS technologies target capturing anthropogenic CO₂ emissions from large point sources prior to their release into the atmosphere, with the main foreseen implementation being the coal-fired power plants. Currently, CCS is seen as the most practical and direct strategy and an established short to medium term solution to mitigate climate changes until renewable energy technologies become mature. Among these strategies, postcombustion capture processes are particularly advantageous because they can be implemented in existing or new power plants.⁶,⁷ In addition, the solvents used in this processes are usually well documented in the literature, and the technology has been successfully applied in natural gas treatment and in ammonia production processes, for example, ref ⁵ and ⁷. The most relevant postcombustion technologies used to capture/separate CO₂ include amine-based chemisorption, adsorption onto porous solids, and membrane and

Received: November 2, 2021
Revised: February 28, 2022
Accepted: February 28, 2022
cryogenic separation,\textsuperscript{8–12} with amine-based absorption being often acknowledged as the most efficient and mature technology with a large implementation at an industrial scale.\textsuperscript{13} However, despite their advantages, like high reactivity and high absorption, these solvents still present important environmental and economic concerns due to their corrosive nature, volatility, and their high-energy requirements for regeneration.\textsuperscript{11} Thus, there is an increasing demand for novel solvents for CO\textsubscript{2} capture with good absorption capacity, high selectivity, low regeneration penalty, and low volatility. Among several potential CO\textsubscript{2} absorbents, ionic liquids (ILs) have been highlighted due to their remarkable combination of intrinsic properties, such as negligible vapor pressure, thermal and chemical stabilities, low flammability, and high sorption capacity.\textsuperscript{16–18} However, their key feature is their adeptness to, by an appropriate choice of a cation/anion pair, tune their physical properties aiming at a specific application. Consequently, a large amount of work has been carried out on their experimental determination and theoretical understanding of gas sorption, including CO\textsubscript{2}.\textsuperscript{19–24} Among different aspects, the impact of chemical functionalization, with ether, alkyl, hydroxyl, fluorine, and nitrile groups, on the gas solubility in aprotic ILs was thoroughly investigated.\textsuperscript{19–21,25–29} Over the last decade, increasing attention has been devoted to protic ionic liquids (PILs), a class of ILs formed by the simple neutralization of a Lewis or Brønsted acid and a base, which are acknowledged as promising solvents for CO\textsubscript{2} absorption.\textsuperscript{14,30,31} This attention comes from the PILs’ unique properties, such as low cost, easy preparation, and a variable proton activity.\textsuperscript{32} Of special relevance is that PILs’ CO\textsubscript{2} regeneration can be accomplished at reasonably low temperatures, substantially minimizing the required energy, avoiding the loss of absorbents, and the formation of toxic compounds.\textsuperscript{33,34} Recently, Martins et al.\textsuperscript{35} reported a screening of more than 200 systems, using the COSMO-RS activity coefficient model,\textsuperscript{36} showing that the [C\textsubscript{4}C\textsubscript{1}im][DMP] or [C\textsubscript{4}C\textsubscript{1}im][NTf\textsubscript{2}] ILs mixed with a range of 6 carboxylate-based PILs demonstrate higher excess molar volumes, thus foreseeing increased CO\textsubscript{2} solubility due to the mixtures’ increased free volume and lower viscosity than that observed for the PILs.\textsuperscript{35} However, one of the principal drawbacks of using PILs is their intrinsic viscosity, which results in low mass transfer coefficients that hinder their industrial application in conventional absorption processes and ultimately result in unfeasible large separation units. Despite the limiting properties exhibited by the ILs, researchers tend to concentrate on improving their sorption capacity, neglecting other important characteristics, such as their poor transport properties, which often make the processes not viable due to high capital and operating costs. Hence, to develop a cost-effective process for carbon capture, the viscosity, diffusivity, and heat capacity must be tackled from a process-engineering standpoint, as these thermophysical properties highly affect the performance and scaling of the process.\textsuperscript{37} Recently, distinct approaches have been pursued aiming at minimizing the impact of solvents’ viscosity and thus the mass transfer and kinetic limitation on a feasible separation unit while

<table>
<thead>
<tr>
<th>Compound, acid:base molar ratio</th>
<th>Chemical Structure</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
</table>
| [DEEA][Ace], 1:1                | \( \begin{array}{c}
N,N\text{-diethylethanolammonium acetate} \\
M_w=177.24\text{g mol}^{-1} \\
x > 98\%; w_{HO}=0.3^b
\end{array} \) |  |  |
| [DEEA][Prop], 1:1              | \( \begin{array}{c}
N,N\text{-diethylethanolammonium propanoate} \\
M_w=191.27\text{g mol}^{-1} \\
x > 99\%; w_{HO}=0.2^b
\end{array} \) |  |  |
| [DEEA][But], 1:1               | \( \begin{array}{c}
N,N\text{-diethylethanolammonium butanoate} \\
M_w=205.30\text{g mol}^{-1} \\
x > 99\%; w_{HO}=0.4^b
\end{array} \) |  |  |
| [DEEA][Pent], 1:1              | \( \begin{array}{c}
N,N\text{-diethylethanolammonium pentanoate} \\
M_w=219.33\text{g mol}^{-1} \\
x > 99\%; w_{HO}=0.3^b
\end{array} \) |  |  |
| [DEEA][Hexa], 1:1              | \( \begin{array}{c}
N,N\text{-diethylethanolammonium hexanoate} \\
M_w=233.35\text{g mol}^{-1} \\
x > 98\%; w_{HO}=0.3^b
\end{array} \) |  |  |

\textsuperscript{a}Estimated by NMR. \textsuperscript{b}Determined by Karl Fisher titration.
maintaining their enhanced gas absorption capacity and selectivity. The use of solid matrices to support the solvents and their incorporation into gas–liquid membrane contactors are two of the most promising alternatives. The immobilization of solvents on nanoporous matrices stands as a potential alternative for gas capture, with enhanced mechanical integrity, ability to overcome the resistance to mass transfer inherent to the compounds’ high viscosity, and the slow gas diffusivity of bulk solvents, while requiring lower amounts of solvents to attain the same separation capacity. Despite their advantages, the encapsulated solvents cannot be used directly in traditional separation columns because their size and thus the small bed void will lead to increased, unworkable pressure drop. Thus, picturing their use on a separation unit, one needs to address these issues before the scale-up and industrial application. One way to overcome these limitations is to use a physical support for immobilization of the encapsulated solvents. While the support should not present resistance to the gas diffusivity or even block the access of the gas to the solvent, it must ensure an increased area for mass transfer and small amounts of solvent per area of the support. This approach will allow us to take advantage of the two technologies such as the high solubility and selectivity related to the solvents and high mass transfer area of membranes. However, prior to the immobilization of PIL-based solvents on membranes, fundamental studies on the CO2 sorption process in encapsulated protic ionic liquids (ENILs) are still required.

In this work, CO2 absorption isotherms of five different neat carboxylate-based PILs were investigated from 303 to 343 K, using an isochoric equilibrium cell. Then, the impact of PIL encapsulation, using hollow carbonaceous submicroparticles, on CO2 absorption was assessed through equilibrium and time-dependent sorption measurements in the same isochoric equilibrium cell. The experimental solubility data were further described using the soft-SAF equation of state (EoS), providing useful insights into the solubility behavior, while establishing a thermodynamic model of these systems for later use in process simulators. Furthermore, the stability and regeneration of the prepared ENILs were analyzed over successive sorption–desorption cycles.

2. EXPERIMENTAL METHODS AND MODELING

2.1. Chemicals. Five protic ILs based on the N,N-diethylethanolammonium ([DEEA]⁺) cation and the anions: acetate ([Ace]⁻), propanoate ([Prop]⁻), butanoate ([But]⁻), pentanoate ([Pent]⁻), or hexanoate ([Hexa]⁻) were synthesized following the Bronsted acid/base neutralization method. The synthesized PILs are summarized in Table 1, along with their chemical structure, molecular weight, average water content, and purity. 1H NMR analysis was carried out to evaluate the purity of the synthesized compounds (Figures S1–S5).

The individual compounds used to synthesize the protic ILs were used as received. N,N-Diethylethanolamine, acetic acid, propionic acid, butyric acid, pentanoic acid, and hexanoic acid were acquired from Acros Organics, Sigma-Aldrich, Acros Organics, Prolabo, Riedel-de Haen, and Aldrich, respectively, all with mass fraction purities greater than 99%.

2.2. Synthesis of PILs. The synthesis of the carboxylate-based protic ILs studied in this work was based on the Bronsted acid/base neutralization method, as reported by Sharma et al. and Chennuri et al. in which the acid is added drop-by-drop to an equimolar quantity of a base under room-temperature conditions and under a nitrogen atmosphere and vigorous stirring. No additional purification steps, such as using vacuum and moderate temperatures, were performed in order to prevent the reported formation of azeotropes. A coulometric Karl Fischer titration (Metrohm, model 831) was carried out to determine that the PILs’ water content was lower than 0.5 wt % (Table 1). The structure of the synthesized PILs was evaluated by 1H and 13C NMR spectroscopy, as reported in Figures S1–S5, Supporting Information.

2.3. Preparation of ENILs. 2.3.1. Chemicals. The compounds used to prepare the capsules, namely phenol (99%), paraformaldehyde (95–100%), aluminum trichloride (95–100%), ammonia (38%), absolute ethanol (99%), and hydrofluoric acid (48%), were used as provided by Panreac. Tetraethylorthosilicate (98%, TEOS) and octadecyltrimethoxysilane (90%, C18TMS) were supplied by Sigma-Aldrich.

2.3.2. Synthesis of Capsules. The carbon submicroparticles (Ccap) were prepared following the template method described in detail in previous publications.

The procedure is divided into three steps: (i) the preparation of a silica template, (ii) the formation of carbon capsules, and (iii) the washing step. Briefly, in the first step, a model of silica sphere with a double wall was synthesized, calcined, and used as the template in the following steps. Next, the silica template was functionalized with Al and calcined. A phenol–paraformaldehyde resin was synthesized, added to the silica template, and then pyrolyzed. In the last step, the silica template was rinsed with a hydrofluoric acid solution (48% v/v) and the material was washed until a neutral pH was reached.

2.3.3. Encapsulation of PILs. The impregnation of the corresponding PIL was made by its dilution in ethanol to reduce viscosity and assure good dispersion. Then, the solution was added dropwise over the carbon capsules and the solvent was removed under vacuum. The amount of PIL immobilized in Ccap was determined by elemental analysis through a linear relationship between the nitrogen wt % of the support versus IL.

2.4. Characterization of Neat and Encapsulated PILs. Scanning and transmission electron microscopy (SEM and TEM) analyses were used to characterize the microstructure and morphology of the Ccap and the ENILs. SEM micrographs were obtained using a HITACHI SU-70, operating at 25 kV. TEM analyses were performed with a Philips 420 JEM-2000 FX microscope. The porous structure of submicroparticles was characterized on a Micromeritics apparatus (Tristar II 3020 model) by nitrogen adsorption–desorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) equation and the methodology reported in a previous publication.

Elemental analyses (EA) of the Ccap and the ENILs were carried out using a LECO CHNS-932 analyzer to obtain C, H, and N contents. For that, a small known (analytical determined) amount of the sample was combusted in a furnace, in a pure oxygen environment to ensure a fast oxidation, and a representative aliquot of the gas was characterized.

Thermogravimetric analysis (TGA) of PILs and ENILs was conducted on a Setaram SETSYS Evolution 1750 thermobalance under a nitrogen atmosphere. A dynamic method was used in a large temperature range (298–835 K) with a heating rate of 10 °C min⁻¹ and under a nitrogen flow of 200 mL min⁻¹. The
The accuracy of temperature and mass measurements was of 0.1 K and \(10^{-3}\) mg, respectively. The differential thermogravimetric analysis was carried out to determine the PIL decomposition in the solid supports from the derivative curves. As depicted in Figure 1, the investigated PILs are thermally stable up to 325 K for [DEEA][Ace] and up to 345 K for the remaining PILs. A sharp decomposition is observed in the temperature range of 345–350 and 400–430 K.

After the encapsulation, the thermostability of the studied PILs increases 23 K for [DEEA][Ace] and [DEEA][But] and 35 K for [DEEA][Prop], [DEEA][Pent], and [DEEA][Hexa]. The shape obtained for the respective ENILs is similar to those observed for the neat PILs; however, a peak appears at slightly higher temperatures, demonstrating a better thermal stability.

2.5. Soft-SAFT EoS Modeling. The CO\(_2\) solubility data measured in this work was modeled using the soft-SAFT EoS to provide further insights into the thermodynamic behavior of the system and how the PIL/gas interactions are affected by the PIL’s molecular structure.

When compared with the classic cubic EoSs, soft-SAFT has the advantage of explicitly accounting for the presence of strong associating or polar interactions, which is particularly important when dealing with PILs (due to the propensity for proton transfer) and CO\(_2\) that contains a permanent quadrupole. A thorough description of the model’s theory can be found in its original publications and in our previous work, where a coarse-grained (CG) model for the PILs investigated in this work was first proposed.

Using high-pressure density data measured for the neat PILs to obtain the corresponding molecular parameters and employing a 2/2 association scheme to account for the hydrogen bonding behavior of the ILs, an accurate description of their physical behavior was achieved. CO\(_2\) was also recently parameterized in the framework of polar soft-SAFT, the most recent extension of the soft-SAFT model to deal with polar systems, which is also applied in this work. Thus, in this work, both the PILs and CO\(_2\) are described using pure-component parameters from previous publications in a transferable manner, whose values are summarized in Table 2.

The extension to mixtures is accomplished by applying the van der Waals one-fluid theory to the reference term in eq 1, with the unlike size and energy LJ parameters given by the Lorentz–Berthelot mixing rules

\[
\sigma_{ij} = \eta_i \left( \sigma_i + \sigma_j \right) / 2 \\
\epsilon_{ij} = \eta_i \sqrt{\sigma_i \sigma_j} \approx \eta_i^{6/5} \sigma_i \sigma_j^{1/2}
\]

In the mixing rules expressed by eqs 1 and 2, \(\eta_i\) and \(\sigma_i\) are the size and energy binary interaction parameters between species \(i\) and \(j\). These can either be set to one in pure predictive calculations or used to account for differences in the size and/or

| compound     | \(m\) (Å) | \(\sigma\) (Å) | \(\epsilon/k_B\) (K) | \(\epsilon_{\text{Hb}}/k_B\) (K) | \(\kappa_{\text{Hb}}\) (Å\(^3\)) | \(|Q|\) (10\(^{-40}\)C·m\(^2\)) | \(x_f\) | ref |
|--------------|-----------|---------------|----------------------|-------------------------------|-----------------------------|------------------------|-------|----|
| [DEEA][Ace]  | 6.401     | 3.445         | 268.35               | 3740                          | 515                         | 515                    | 515   | 58 |
| [DEEA][Prop] | 6.705     | 3.492         | 268.79               | 3740                          | 515                         | 515                    | 515   | 58 |
| [DEEA][But]  | 6.916     | 3.568         | 271.64               | 3740                          | 515                         | 515                    | 515   | 58 |
| [DEEA][Pent] | 7.100     | 3.634         | 275.68               | 3740                          | 515                         | 515                    | 515   | 58 |
| [DEEA][Hexa] | 7.319     | 3.689         | 280.58               | 3740                          | 515                         | 515                    | 515   | 58 |
| CO\(_2\)     | 1.571     | 3.166         | 166.50               | 14.68                         | 0.333                       | 57                     |       |     |
energy of the monomers composing the different compounds in the system, fitting to certain binary data.

3. RESULTS AND DISCUSSION

3.1. Physical Characterization of ENILs. The carbon submicroro_capsules were characterized using SEM and TEM, in order to analyze their mesoporous shell structure and hollow core. The analysis indicated that the carbon capsules have a high carbon content (w = ~90%) and a homogeneous morphology, with ~500 nm diameter and ~150 nm shell thickness (Figure 2).

To quantify the incorporation of PILs into the capsules, elemental analysis (EA) was used, and through the percentage of elemental N obtained in the final material (corresponding to the PIL), a linear regression reported previously46,49 was applied to confirm the adequate incorporation of PILs into C-cap (59−65% in mass), as reported in Table 3.

| Table 3. Characterization of C-cap and ENILs Prepared with Different Loads of ILs |
|-----------------|---|---|---|---|
| material       | % C | % H | % N | IL load (% w/w) |
| C-cap[DEEA][Ace] | 89.60 | 1.8 | 0.0 | 59.9 |
| [DEEA][But]    | 61.51 | 10.8 | 5.2 | 63.8 |
| [DEEA][Prop]   | 63.84 | 11.9 | 5.3 | 63.7 |
| [DEEA][Hexa]  | 66.79 | 13.2 | 5.6 | 65.2 |

The porous structure of the carbon capsules prepared in this work was evaluated using nitrogen adsorption−desorption isotherms at 77 K by BET analysis, as depicted in Figure S6 in the Supporting Information. BET analysis shows a complex porous structure (A_{BET} = 1721 m^2/g), resulting from the contributions of micro- and mesoporosity, which is clearly evident from the amount of nitrogen absorbed, in the whole pressure range, which is completely lost after incorporating the PIL.

3.2. CO2 Solubility. The CO2 solubility on the synthesized PILs was experimentally measured in the 303−343 K temperature range and pressures up to 0.8 MPa, using the isochoric method described in Figure S7. The experimental method employed is particularly suitable for the measurement of gas solubilities in ILs because the ILs’ negligible vapor pressure ensures that the gas remains as a pure gas and that changes in pressure are due to gas sorption. Recently, the use of this family of PILs has been suggested for CO₂ capture.35 Then, their thermophysical properties (density and viscosity), at atmospheric pressure, for different acid/base proportions were analyzed. However, despite the availability of some experimental data on CO₂ solubility in carboxylate-based PILs,46,59−63 there are no experimental data for gas−liquid equilibrium for carboxylate-based PILs based on the N,N-diethylethanolammo_nium cation, despite their promising potential for gas separation, which are reported here for the first time.

The experimental solubility data are reported in Table S1, in the Supporting Information, and depicted in Figure 3, along with the soft-SAFT modeling results (using the binary interaction parameters from Table 4). As depicted in Figure 3, the solubility data display the expected behavior, decreasing with the increasing temperature and increasing with the increasing pressure. Furthermore, the shape of the isotherms in the pressure range investigated resembles that of common physical absorbents.

Carvalho and Coutinho27 have reported that the behavior of CO₂ solutions in ILs and other low-volatility physical solvents deviates from the ideal behavior, which is usually small and dominated by entropic effects, mostly derived from the solute−solvent size and shape asymmetries responsible for important free-volume contributions. The CO₂ solubility in different PILs, at two different temperatures, is compared, in molality, in Figure 4. These data are also reported in Table S2, in the Supporting Information, for all the experimental isotherms.

As can be seen in Figure 4, the increase of the anions’ alkyl chain length does indeed lead to an increase of the CO₂ solubility. This is contrary to the behavior observed for aprotic ILs and most physical solvents, where, when expressed in molality, the pressure versus concentration phase diagrams are, within the experimental uncertainty, solvent independent, thus can be correlated as a single function of temperature. Such a correlation, proposed by Carvalho and Coutinho,27 is depicted in Figure 4, showing how the gas solubility in the synthesized PILs changes relatively to common physical absorbents. In particular, it can be observed that ILs with the shorter anions present lower solubility than expected for physical solvents, while those containing the larger anions show higher solubilities.

The striking result suggests the existence of a distinct sorption mechanism in these PILs than that exhibited in common physical absorbents. Thus, further studies are required for a better understanding of the sorption mechanism in PILs.

Analyzing the solubility data in terms of molality also provides a more quantitative engineering perspective regarding the mass of solvent required to remove a certain amount of CO₂ from the target streams. As such, based on the experimental values measured for the solubilities of the five PILs investigated, [DEEA][Hexa] exhibited the highest CO₂ absorption capacity, with a value of m_{CO2} = 0.524 mol CO₂·kg⁻¹IL at 0.45 MPa and 303 K.

The ability of the soft-SAFT EoS to effectively describe the solubility data is evaluated here. Clearly, binary mixtures of PILs with CO₂ are challenging systems to describe with any EoS due to the strong hydrogen bonds that characterize the ILs and the existence of a quadrupole moment in CO₂. For these reasons, as shown in Figure S8, in the Supporting Information, the prediction of the phase equilibrium data from the pure-component parameters alone (i.e., η_{ij} = ξ_{ij} = 1) presents a low accuracy, except for [DEEA][But].

Nevertheless, by using a state-independent binary interaction parameter (BIP) correcting the magnitude of the cross-dispersive interactions (ξ_{ij}), very close to unity, a good quantitative description of the experimental data is achieved, as depicted in Figure 3. The final BIP values, regressed from the experimental solubility data, are reported in Table 4, along with the deviations from the experimental solubility data, expressed in terms of percentage average absolute relative deviation (% AARD), estimated using eq 3.

\[
\text{% AARD}(x) = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{x_{i}^{\text{calc}} - x_{i}^{\exp}}{x_{i}^{\exp}} \right)
\]

The modeling results show no systematic deviations with either temperature or the anions’ chain length, although, as the chain length increased, the higher deviations move from the highest to the lowest temperatures. Nonetheless, considering the complexity of interactions present in these systems, average %
AARD values in the 2.5−7% interval are obtained, which are similar to those previously reported for simpler molecular solvents.

Furthermore, one can observe in Table 4 that the BIP values, correcting the magnitude of the cross interactions between the PIL and CO₂, increase with the increase of anion’s alkyl chain length. In fact, the ξ values applied are shown to increase linearly with the PIL’s molecular weight, according to the following expression

\[
\xi_{\text{PIL-CO}_2} = 0.001903 M_{\text{PIL}} \left( \frac{g}{\text{mol}} \right) + 0.6028;
\]

\[R^2 = 0.9989\]
This not only allows the prediction of the solubility in PILs with longer anions, without further experiments, but also suggests an increase in the magnitude of the anion—CO2 interactions with increasing chain length of the anion.

Although soft-SAFT can successfully predict such an effect using only the pure-component parameters (see Figure S9, in the Supporting Information), the need for a BIP to obtain a quantitative agreement with the experimental data is expected; the main reason being the use of constant association parameters in the carboxylate-based PIL model developed in our previous work.\(^6\)\(^8\) Although such a simplification is necessary given the constrained parameterization of ILs in EoS models (i.e., vapor pressures, vaporization enthalpies, and other data commonly used for parameterization are not measurable for ILs), the resulting association parameters typically represent the average behavior of the homologous series of compounds being parameterized and not the value that best represents each IL. Therefore, the association parameters, reported in Table 2, tend to underestimate/overestimate the cation—anion interactions for the shortest/largest ILs and, consequently, to overestimate/underestimate their interactions with the gas molecules. This is the reason behind the excellent results obtained for the intermediate chain lengths, namely [DEEA][But] and [DEEA]-[Pent] that are accurately described with a BIP very close to unity, or even considering the model predictions from the pure-component parameters alone, shown in Figure S8 of the Supporting Information. Such results suggest that an increase in the CO2 solubility with an increase of the anion’s alkyl chain length may be partially due to the decreased cation—anion interaction and the consequent increase of the free volume between the ion pairs. This should thus be the object of further studies aiming at a better understanding of the sorption mechanism in PILs. Moreover, the fact that the model is able to successfully describe the experimental solubility data without accounting for any reaction is yet another indication, along with the shape of the isotherms, that chemisorption is not present in these PILs, at the CO2 partial pressures evaluated.

After the solubility measurements in the neat PILs, all the PILs were incorporated in carbonaceous submicrocapsules, aiming to improve the absorption kinetics. These ENIL materials are a powdered solid with an IL mass content around \(\sim 62\%\), characterized by a high surface area (due to the small particle size), and a higher thermal stability than the neat PILs.

Figure 5 depicts the CO2 sorption isotherms of the neat and the encapsulated PILs at two fixed temperatures (303 and 343 K) and pressures up to 0.8 MPa. The experimental solubility data of ENILs are reported for all the isotherms in Table S3, in the Supporting Information. The results obtained show that, as expected, the absorption capacity of the PILs remains unaltered after immobilization into the capsules, in good agreement with previous reports for other ENILs.\(^1\(^8\),\(^4\(^5\),\(^4\(^8\),\(^6\)\(^2\) These results suggest that the approach of using microsolid droplets of ILs allows overcoming some of the limitations of using ILs in absorption columns.

3.3. Henry’s Law Constant. Henry’s law, expressed in eq 5, is frequently used to describe the solubility of gases in liquids, where the amount of gas dissolved in a liquid is directly proportional to its partial pressure, at constant temperature. The proportionality constant, Henry’s law constant, \(K_H\), can be obtained from eq 6, valid in the diluted region limit:\(^6\(^3\),\(^6\(^6\)

\[
p = K_H x_{CO_2}
\]

\[
K_H = \lim_{x_{CO_2} \to 0} \frac{\int_{CO_2}^L}{x_{CO_2}} \approx \frac{p_{CO_2}}{x_{CO_2}}
\]

In eqs 5 and 6, \(x_{CO_2}\) is the mole fraction of the gas dissolved in the liquid phase, \(f_{CO_2}^L\) is the fugacity of CO2 in the liquid phase, and \(p_{CO_2}\) represents the partial pressure of CO2 in the gas phase.

**Table 4. Temperature-Independent Energy Binary Interaction Parameters Used in the Soft-SAFT Calculations and Percentage Average Absolute Relative Deviations (% AARD) from the Experimental Data**

<table>
<thead>
<tr>
<th>PIL</th>
<th>(\xi_{PIL-CO_2}) 303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
<th>343 K</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEEA][Ace]</td>
<td>0.940</td>
<td>9.47</td>
<td>6.75</td>
<td>3.31</td>
<td>4.22</td>
<td>10.63</td>
</tr>
<tr>
<td>[DEEA][Prop]</td>
<td>0.965</td>
<td>3.57</td>
<td>2.82</td>
<td>3.26</td>
<td>6.22</td>
<td>10.44</td>
</tr>
<tr>
<td>[DEEA][But]</td>
<td>0.996</td>
<td>1.74</td>
<td>1.15</td>
<td>1.18</td>
<td>3.42</td>
<td>5.15</td>
</tr>
<tr>
<td>[DEEA][Pent]</td>
<td>1.020</td>
<td>6.12</td>
<td>2.86</td>
<td>1.47</td>
<td>1.68</td>
<td>2.35</td>
</tr>
<tr>
<td>[DEEA][Hexa]</td>
<td>1.046</td>
<td>8.75</td>
<td>7.04</td>
<td>5.93</td>
<td>4.69</td>
<td>2.93</td>
</tr>
</tbody>
</table>

**Figure 4.** \(p\)~\(Tm_{CO_2}\) phase diagrams for the studied systems, at 303 and 343 K. Symbols represent the experimental data measured in this work and the solid lines the correlation proposed by Carvalho and Coutinho\(^2\)\(^7\) for the CO2 solubility in low-volatility physical solvents.
phase, and as the gas phase is pure, the pressure of CO$_2$ is equal to the total pressure $p$.

Henry’s constant for CO$_2$ in the investigated PILs was determined from the experimental solubility data using a fitting of the experimental data to eq 5. Such calculations assume that the experimental equilibrium pressure increases linearly with the solubility of the gas in the liquid ($R^2 > 0.99455$) and thus the $K_H$ values are obtained from the limiting slope as the solubility approaches zero. The values obtained for Henry’s constant are shown in Table 5 and depicted in Figure 6, along with the values calculated with the soft-SAFT EoS, applying eq 6, using the parameters reported in Tables 2 and 4.

According to Table 5, and in agreement with the solubility trends previously discussed, the $H_{CO2}$ values decrease with the increasing chain length of the anion, resulting in a higher solubility under the same ($T$, $p$) conditions. Also, in agreement with the solubility behavior, the values are found to increase with increasing temperature. The $K_H$ values obtained are of the same order as those previously reported for carboxylate-based PILs with different ammonium cations.$^{46, 59-63}$

### 3.4. Role of Encapsulation in Separation Kinetics.

Due to the high viscosity exhibited by most ILs, their industrial application in typical absorption columns is commonly unfeasible, leading to unrealistically large columns.$^{67}$ Aiming at improving the mass transfer during the separation phenomena, the effect of encapsulation of the investigated PILs on the kinetics of absorption was evaluated.$^{68, 69}$

Figure 7 compares the CO$_2$ kinetic sorption curves recorded for both neat and encapsulated [DEEA][Pent] at 333 K and a CO$_2$ pressure of 0.4 MPa, using a similar sorbent sample mass, while the results obtained for the remaining PILs are depicted in Figure S10 of the Supporting Information. As shown in Figure 7, 8 h were required for the PIL system to attain its equilibrium, suggesting a slow mass and heat transfer that would eventually result in large separation units characterized by high capital and operational costs, due to high viscosity of the solvents.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Pressure–composition diagram of the binary systems’ neat and encapsulated PILs studied in this work at two fixed temperatures. The empty markers correspond to ENILs and full markers the neat PILs.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Henry’s constant of the studied systems as a function of temperature. Symbols represent Henry’s constant obtained from the experimental data, while the dashed lines represent those calculated using the soft-SAFT EoS.

### Table 5. Henry’s Law Constant as a Function of Temperature for PILs + CO$_2$

<table>
<thead>
<tr>
<th>PIL</th>
<th>$303$ K</th>
<th>$313$ K</th>
<th>$323$ K</th>
<th>$333$ K</th>
<th>$343$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEEA][Ace]</td>
<td>$15.19 \pm 0.42$</td>
<td>$16.82 \pm 0.32$</td>
<td>$18.80 \pm 0.24$</td>
<td>$21.50 \pm 0.15$</td>
<td>$24.33 \pm 0.13$</td>
</tr>
<tr>
<td>[DEEA][Prop]</td>
<td>$10.31 \pm 0.06$</td>
<td>$11.55 \pm 0.06$</td>
<td>$13.03 \pm 0.03$</td>
<td>$14.69 \pm 0.07$</td>
<td>$16.72 \pm 0.12$</td>
</tr>
<tr>
<td>[DEEA][But]</td>
<td>$6.97 \pm 0.06$</td>
<td>$7.80 \pm 0.07$</td>
<td>$8.71 \pm 0.09$</td>
<td>$9.62 \pm 0.22$</td>
<td>$10.68 \pm 0.33$</td>
</tr>
<tr>
<td>[DEEA][Pent]</td>
<td>$5.28 \pm 0.09$</td>
<td>$5.78 \pm 0.07$</td>
<td>$6.36 \pm 0.05$</td>
<td>$7.06 \pm 0.01$</td>
<td>$7.80 \pm 0.02$</td>
</tr>
<tr>
<td>[DEEA][Hexa]</td>
<td>$3.87 \pm 0.11$</td>
<td>$4.31 \pm 0.11$</td>
<td>$4.76 \pm 0.10$</td>
<td>$5.44 \pm 0.10$</td>
<td>$6.10 \pm 0.09$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PIL</th>
<th>$303$ K</th>
<th>$313$ K</th>
<th>$323$ K</th>
<th>$333$ K</th>
<th>$343$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEEA][Ace]</td>
<td>$14.40 \pm 0.02$</td>
<td>$16.20 \pm 0.02$</td>
<td>$18.31 \pm 0.03$</td>
<td>$21.78 \pm 0.03$</td>
<td>$24.79 \pm 0.04$</td>
</tr>
<tr>
<td>[DEEA][Prop]</td>
<td>$10.58 \pm 0.01$</td>
<td>$11.96 \pm 0.01$</td>
<td>$13.35 \pm 0.02$</td>
<td>$14.73 \pm 0.02$</td>
<td>$16.09 \pm 0.02$</td>
</tr>
<tr>
<td>[DEEA][But]</td>
<td>$6.90 \pm 0.01$</td>
<td>$7.93 \pm 0.02$</td>
<td>$8.99 \pm 0.02$</td>
<td>$10.06 \pm 0.02$</td>
<td>$11.14 \pm 0.02$</td>
</tr>
<tr>
<td>[DEEA][Pent]</td>
<td>$4.85 \pm 0.01$</td>
<td>$5.64 \pm 0.01$</td>
<td>$6.46 \pm 0.01$</td>
<td>$7.32 \pm 0.02$</td>
<td>$8.18 \pm 0.02$</td>
</tr>
<tr>
<td>[DEEA][Hexa]</td>
<td>$3.79 \pm 0.01$</td>
<td>$4.20 \pm 0.01$</td>
<td>$4.69 \pm 0.01$</td>
<td>$5.41 \pm 0.02$</td>
<td>$6.08 \pm 0.02$</td>
</tr>
</tbody>
</table>

*Standard deviation.

---

https://doi.org/10.1021/acs.iecr.1c04335
Ind. Eng. Chem. Res. XXXX, XXXX, XXX--XXX
PILs in CO2 separation technologies is often dependent on an equilibration from 8 to 0.5 h under the same conditions due to the rate being remarkably increased, reducing the time required for diffusion.

[DEEA][Pent] as a function of time at 333 K and 0.4 MPa.

Conversely, through encapsulation of the PIL, the CO2 sorption rate is remarkably increased, reducing the time required for equilibration from 8 to 0.5 h under the same conditions due to the exponential increase of the available area for mass transfer.

3.5. Process Reversibility. A viable industrial application of PILs in CO2 separation technologies is often dependent on a simple regeneration step with low energy demand. Therefore, the sorption capacity of the studied ENILs was further evaluated during sorption–desorption cycles. The desorption cycles were carried out at 343 K for 2 h and at 1 Pa, while the absorption steps were performed with an initial gas pressure of 0.5 MPa. As depicted in Figure 8, for the four cycles evaluated, the ENIL is completely regenerated showing no loss in the IL solubility capacity. The low deviations observed are related to the experimental uncertainty, especially in terms of the system’s initial pressure. Hence, the ENILs investigated in this work show a good stability and recyclability, being able to uphold kinetic performance and sorption capacity during successive separation cycles, which is in concordance with previous studies.

Although ENILs result in improved mechanical integrity and allow solving some of the issues of their neat counterparts, specifically their viscosity and slow gas diffusivity, the current technology state, for their application, is still immature, delaying its scale-up and consequent industrial application. One possible approach is their incorporation in a membrane support. The immobilization of absorbents on a membrane for achieving a new hybrid hollow fiber membrane was recently proposed by us. The resulting membranes showed improved permeation and selectivity compared to the conventional polymeric membranes. This improvement is due to the kinetic diameter, low specific volume, and more interactions between water vapor and the IL polar groups. The incorporation of this type of absorbents on a membrane suggests thus that this hybrid material is efficient for the proposed separation with potential for gas separations.

4. CONCLUSIONS

In this work, the potential of ENILs as adsorbents for CO2 separation was extensively evaluated. In a first step, the gas solubility in five different neat carboxylate-based PILs, namely [DEEA][Ace], [DEEA][Prop], [DEEA][But], [DEEA][Pent], and [DEEA][Hexa], was experimentally measured, in the 303–343 K temperature range and partial CO2 pressures up to 0.8 MPa, in order to assess the sorption capacity of the selected compounds.

Contrarily to what is observed in aprotic ILs and other low-volatile solvents, the solubility data obtained in this work, even when expressed in molality, show a marked increase in the solubility with an increase of the anion chain length. This striking result suggests that PILs exhibit a sorption mechanism distinct from the one commonly observed in physical absorbents, where differences in solubility are mostly related to entropic effects due to solvent–solute size/shape asymmetries. Therefore, additional studies should be carried out aiming at a better understanding of the underlying sorption mechanism of CO2 in PILs.

The experimental data were also successfully described using a molecular-based EoS that was further used to rationalize the magnitude of interactions between the solvent and the gas and to predict the corresponding Henry’s constants.

Afterward, considering that the high viscosity of PILs hinders their large-scale industrial application due to the reduced mass transfer coefficients, the selected PILs were encapsulated in hollow carbon submicrocapsules. The ENIL materials were extensively characterized and shown to retain their sorption capacity presenting the same solubility as their neat counterparts, while considerably increasing the gas sorption rate. The thermal stability and regeneration of these materials after successive sorption–desorption cycles were also successfully demonstrated.

The high sorption capacity, improved separation kinetics, and easy regeneration of the adsorbent under mild conditions show the potential for implementation of these materials in new gas separation technologies, such as their application in gas–liquid membrane contactors to improve the separation selectivity and mass transfer driving force across the membranes, which will be the object of a future work.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c04335.

Synthesis and characterization of the ILs; BET analysis; solubility measurement setup; solubility data; soft-SAFT modeling results; and graphical representation of sorption kinetics (PDF)
AUTHOR INFORMATION

Corresponding Author
Pedro J. Carvalho — CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0002-1943-0006; Email: quijorge@ua.pt

Authors
Liliana P. Silva — CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0002-6636-1920
Emanuel A. Crespo — CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0003-2137-0564
Mônia A. R. Martins — CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0003-0748-1612
Paula C. Barbosa — CICECO—Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0002-6185-5825
Ramesh L. Gardas — Department of Chemistry, Indian Institute of Technology Madras, 600 036 Chennai, India; orcid.org/0000-0002-6185-5825
Lourdes F. Vega — Research and Innovation Center on CO2 and H2 (RICH Center) and Chemical Engineering Department, Khalifa University of Science and Technology, 127788 Abu Dhabi, United Arab Emirates; orcid.org/0000-0002-7609-4184
João A. P. Coutinho — CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; orcid.org/0000-0002-3841-743X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.1c04335

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was developed within the scope of the project CICECO—Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). This work was also developed within the scope of the Indo-Portuguese Program for Cooperation in Science & Technology DST/INT/Portugal/P-01/2017, financed by FCT and the Government of India. L. P. Silva and E. A. Crespo acknowledge FCT for their Ph.D. Grants SFRH/BD/135976/2018 and SFRH/BD/130870/2017, respectively. P. J. Carvalho acknowledges FCT for his contract under the Investigator FCT 2015 contract number IF/00758/2014. The research contract of P. B. is funded by national funds (OE), through FCT—Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of article 23, of the Decrease-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

REFERENCES

myths about the CO2 solubility in ionic liquids.

2014
Thermodyn.
2016
6312.

Thermophysical Properties of Two Ammonium-Based Protic Ionic capture.


