



Solubility of carbon dioxide in encapsulated ionic liquids

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ARTICLE INFO

Keywords:

Gas treatment
Carbon dioxide capture
Encapsulated ionic liquids
Templated carbon

ABSTRACT

Ionic liquids (ILs) have been object of extensive research during the last years due to their potential for industrial application with special interest on carbon dioxide (CO₂) capture. Nonetheless, ILs transport properties have stand out as the major drawback for their use on absorption applications. This work proposes ionic liquids encapsulated (ENILs) into carbonaceous submicrocapsules, as a novel material for CO₂ capture. This innovative material takes advantage of the ILs gas-absorbing properties and cost-effectiveness while circumventing the IL viscosity by increasing the surface contact area with respect to the bulk fluid. The ENILs prepared using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂C₁im][NTf₂]) and N-methyl-2-hydroxyethylammonium pentanoate (m-HEAP), were characterized by SEM, TEM, elemental analysis, TGA and BET to assess their morphology, chemical composition, porous structure and thermal stability. The absorption of CO₂ on these materials was studied up to 0.6 MPa and 353 K. Desorption of CO₂ from the exhausted ENILs was evaluated, at mild conditions, evidencing the ENILs as suitable separating agents for CO₂ capture, with high sorption capacity and fast and complete regeneration, and feasible alternatives to bulk IL absorption.

1. Introduction

CO₂ is regarded as the most significant anthropogenic greenhouse gas, with its global atmospheric concentration increasing mainly as a result of fossil fuel combustion, in particular power plant emissions [1]. One of the most promising near-term methodologies for mitigating the global warming effects caused by greenhouse gases consists of direct CO₂ capture at power plants [2]. Conventional CO₂ post-combustion capture technologies are based on amine absorption processes, which arise several concerns such as their corrosive nature and volatility, leading to high operational cost and environmental impact [3–5]. Therefore, it is critical to develop innovative and cost-effective technologies capable of efficiently capture CO₂, overcoming the problems related to commercially available systems. Ionic liquids (ILs) are being explored for CO₂ capture due to their unique properties, such as high solvating capacity for different compounds, tunability, low vapor pressure, wide liquid temperature range, high thermal stability, non-flammability, etc. [6–8]. However, after binding to CO₂, many ILs undergo a strong increase in viscosity and this high viscosity limits the use of ILs in liquid absorbers and is a major drawback to industrial application of ILs [9,10]. The modification of ILs is essential before these agents can be used in a CO₂ capture/separation processes [11–14]. In this way, the supported ionic liquids phase (SILP) have been proposed

as a practical result to overcome the mass transfer limitations of ILs in gas-liquid separation processes [15]. However, the relatively low amount of IL that can be placed on these materials may limit their applications in chemical reactions and separation processes.

In this context, the ENIL concept appears as an interesting option [16,17]. ENIL consists of hollow carbonaceous submicrocapsules (C_{cap}) that confine the ILs [18–20]. The preparation of ENILs is favored by the high affinity found between ILs and activated carbon [21,22]. This new material is characterized by a high proportion of IL (80 % in weight) and capsule sizes ranging from 700 to 1000 nm. Therefore, the ENIL concept implies a shift from continuous to discrete IL phase with sub-micron size units. Due to their unique structure, ENILs drastically increase the specific contact area with respect to the neat ILs, enhancing the rate of mass transfer while maintaining the solvation capability of the ILs [15]. Moreover, ENILs show an additional advantage of high versatility, since they can be prepared at different loads (up to 80% w/w) using ILs with optimized properties for a specific application. Additional efforts to develop new sorbents based on ILs have also been actively investigated in the past decades, with researchers looking for ILs modifications, like anion-functionalized task-specific ionic liquids (AAILs) [23,24], reversible ILs [25], aprotic heterocyclic anion based IL (AHA-IL) [26] or carboxylate anion-based ILs [27], with enhanced CO₂ absorption capability. These previous works evidence common

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characteristics for IL-based systems promoting CO₂ absorption, such as high uptake capacity but low mass transfer rate, due to the high viscosity of the IL and difficulties in solvent regeneration.

This work aims at evaluating the applicability of ENILs as separating agents for the purification of gas streams contaminated with CO₂. The ENILs used have been designed to provide high CO₂ sorption capacities, high mass transfer rates, high thermal stability and easy and low energy demanding regeneration. Hollow carbon submicrospheres with a thick porous wall were synthesized, by templating method, in order to increase their mechanical strength [19]. The ENILs were prepared introducing in the microcapsules high loads (70–80% w/w) of two ILs that present outstanding CO₂ sorption capacity, relatively favorable CO₂ diffusion coefficients and high selectivity [25,26,28,32,33]: namely, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C₂C₁im][NTf₂]) and a protic IL, N-methyl-2-hydroxyethylammonium pentanoate (m-HEAP). The carbon submicrocapsules and ENILs were characterized by several techniques, including scanning and transmission electron microscopy (SEM and TEM), elemental analysis (EA), N₂ adsorption–desorption at –196 °C, and thermogravimetric analysis (TGA). Sorption experiments were carried out using ENILs as separating agent at (308, 323, 338 and 353) K, for pressures up to 0.7 MPa and CO₂ mole fractions up to 0.3. The influence of the chemical nature and the load of IL in the ENILs was analyzed at different operating conditions. The regeneration of the exhausted ENIL beds was assessed by desorption experiment performed at 1 Pa, 353 K for 2 h.

2. Materials and methods

2.1. Materials

The synthesis of carbon submicrocapsules (C_{cap}) was carried out using phenol (99%), paraformaldehyde (96%), aluminum trichloride (95–100%), ammonia (25%), absolute ethanol (99.9%), hydrofluoric acid (48%) and sodium hydroxide (98%), provided by Panreac, and tetraethylorthosilicate (98%) (TEOS) and octadecyltrimethoxysilane (90%) (C18TMS) purchased from Sigma–Aldrich.

The ILs 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C₂C₁im][NTf₂]) was supplied by Iolitec with 99% purity. The protic IL, N-methyl-2-hydroxyethylammonium pentanoate (m-HEAP or [N₁(2OH)_{HH}][Pe]) was prepared from stoichiometric quantities of the 2-methylaminoethanol with pentanoic acid using the methodology described in detail by Talavera-Prieto et al. [29] with a final mass fraction purity, determined by ¹H NMR, higher than 98%. The final water content was determined with a Metrohm 831 Karl Fisher coulometer. The two ILs were used without previous purification. To prevent hydration of the ILs were kept in their original tightly closed bottles in a desiccator before using. The sorption experiments were carried out using CO₂ (purity > 99.99%) supplied by Air Liquide Portugal.

The studied ILs were selected due to their anion basicity, high CO₂ solubilities (low Henry constants) and high selectivities [28,30]. As reported before, shorter imidazolium alkyl chain length and oxygenation of the cation (methylsulfonate or propionate) allows higher CO₂/CH₄ and CO₂/H₂ selectivities [28,31].

2.2. Preparation of ENILs

The thick wall carbon submicrocapsules (C_{cap}) were synthesized following the template method described in detailed in previous works [18,19]. The thick wall C_{cap} were selected, over the single wall, aiming to achieve higher mechanical resistance and porosity. The C_{cap} were filled by successive impregnation steps using 1 mL of IL-acetone solution and 100 mg of support [20]. The number of impregnation steps and the concentration of IL in the acetone solution were adjusted to obtain ENILs with different IL loadings. To ensure a homogeneous penetration, into the pores, the of the IL solution was added dropwise over the C_{cap},

followed by vacuum evacuation, to remove the solvent, at 333 K and 10 mbar over 2 h. The procedure followed allowed to impregnate 80% 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}. Acetone was used as solvent due to its high impregnation in the carbon material (contact angles were not possible to be measured due to essentially complete wettability).

Elemental analysis (EA) was used to validate by direct measurements of the IL impregnation. The IL impregnation percentage was derived from the linear relationship, proposed in a previous publication [15], using the percentage of elemental nitrogen, in the supported-IL materials and the weight percentage of imidazolium-based IL, supported on porous carbons. All the ENILs prepared had the resemblance and behavior of a powdered material, allowing one to infer that all the IL was encapsulated. The ENILs were stored at 363 K during 24 h prior to their use.

2.3. Characterization of ENILs

The morphology and microstructure of C_{cap} and ENILs were studied by scanning and transmission electron microscopy (SEM and TEM). SEM micrographs were obtained using a FEG-SEM Hitachi S4100 microscope operating at 25 kV. TEM analyses were performed by means of a Hitachi SU-70 microscope operating at 15 kV. Elemental analyses (EA) of C_{cap} and ENILs were carried out in a LECO CHNS-932 analyzer to obtain C, H and N content. The porous structure was characterized by means of nitrogen adsorption–desorption isotherms at –196 °C using a Quantachrome apparatus. Before adsorption–desorption experiments, samples were degassed at 423 K under vacuum for 6 h. The BET equation was applied to determine the total surface area (A_{BET}) and the external or non-micropore area (A_e) was obtained using the *t*-method. The Dubinin–Radushkevich equation was applied for micropore volume estimation. The difference between the volume of N₂ adsorbed (as liquid) at 0.95 relative pressure and the micropore volume was taken as the mesopore volume, and the DFT method was used to obtain the pore size distribution. Thermogravimetric analyses (TGA) of ILs and ENILs were conducted in a Setaram SETSYS thermobalance under nitrogen atmosphere. A dynamic method was used with a temperature range from (308–1073) K at a heating rate of 10 °C min^{–1} under a nitrogen flow of 200 ml min^{–1}. The accuracy of temperature and mass measurements was 0.1 K and 10^{–3} mg, respectively. Aluminum 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. T_{DTG} (°C) was assigned to IL decomposition in the solid supports from the DTG curve.

2.4. Solubility measurements

The CO₂ capture was evaluated using a constant temperature–volume equilibrium cell made of stainless steel. The isochoric equilibrium cell consists of a fixed volume cell connected to a gas line. 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 allows to control the gas addition. The experimental setup, with the exception of 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 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 line up to the desired pressure from an ultra-lightweight composite cylinder by means of a flexible pressure capillary, and its mass measured with the high weight/high precision balance. The

amount of gas (number of moles) present in the gas line is calculated by the mass of gas that flows into the cell and validated using the ideal gas law 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 line with the measuring cell is open, allowing the gas to get in contact with the ENIL. The pressure decay is then monitored and logged, until a 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 initially added. The temperature is then decreased to a new set point allowing for additional gas to dissolve in the ENIL. Once the new equilibrium is reached the number of moles adsorbed into the ENIL is again calculated. This process is repeated for all the defined temperatures.

For the sorption/desorption cycles the system is degassed at 1 Pa, 353 K and 2 h and the solubility measurements repeated for 4 cycles with the sorption step set for an initial pressure of 0.55 MPa.

3. Results and discussion

3.1. ENILs characterization

The C_{cap} were studied by SEM and as depicted in Fig. 1A and B a regular spherical morphology, with a mean diameter of 900 nm, was obtained. A wall thickness ca. 120 nm was determined from TEM image (Fig. 1C and D). On TEM micrographs, Fig. 1D, the second shell formation, that confers higher porosity and resistance to the carbon sub-microcapsules, can be observed.

Adsorption–desorption isotherms of N_2 at 77 K were used to analyze the porous structure of C_{cap} and ENILs. The results of the BET analysis are reported in Table 1. C_{cap} showed a highly developed porous structure ($A_{BET} = 1834 \text{ m}^2 \text{ g}^{-1}$), with contributions of micro- and mesoporosity, as indicated by the high amount of nitrogen adsorbed in the whole relative pressure range. Fig. 2 shows the isotherms comparison between the double shell C_{cap} , synthesized in this work, and that reported in a previous work, for the single shell C_{cap} [20]. As expected, an increment in the BET surface is present due to the development of the core-shell structure.

The most efficient procedure to determine the amount of IL confined

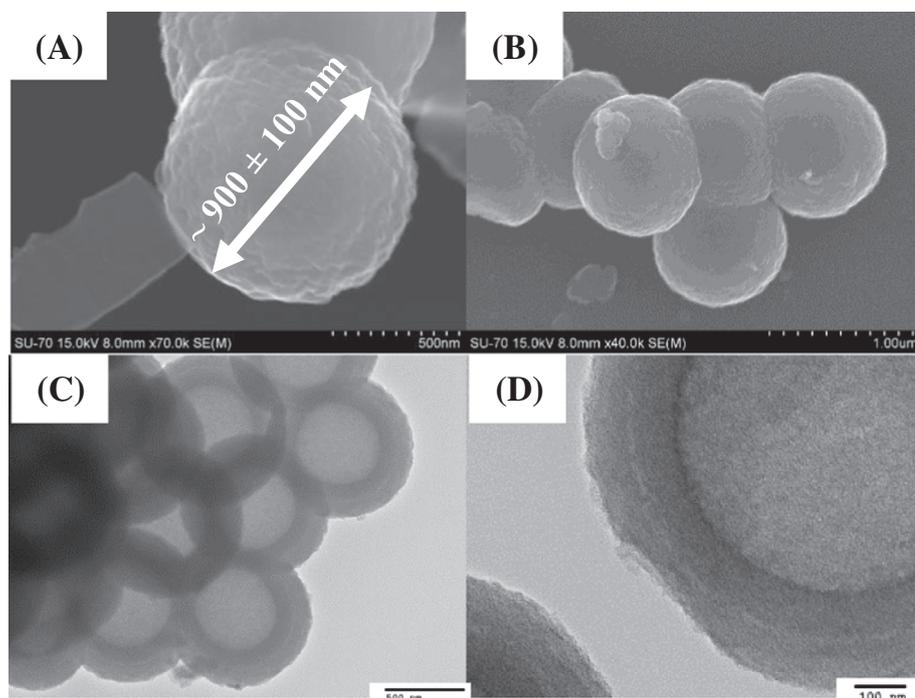


Fig. 1. SEM (A, B) and TEM (C, D) images of C_{cap} used for the ENIL preparation.

Table 1
Characterization of the C_{cap} and ENILs prepared with different load of IL.

Material	EA				Textural properties				Thermal stability T_{DTG} (°C)
	%C	%H	%N	IL load (%, w/ w)	A_{BET} ($\text{m}^2 \text{ g}^{-1}$)	A_s	V_{microp} ($\text{cm}^3 \text{ g}^{-1}$)	V_{mesop}	
C_{cap}	86.1	0.51	0.0	–	1834	1786	0.03	1.57	–
$[C_2C_1im]$	39.6	2.48	8.65	80.5	–	–	–	–	448 (475)
$[NTf_2]$	–	–	–	–	–	–	–	–	–
m-HEAP	59.7	7.18	5.37	67.9	–	–	–	–	140 (205)

inside the carbon capsules is through elemental analysis (EA). This procedure, detailed in a previous publication [15], determines the load of IL on the active carbon (AC) capsules by a linear regression between the percentage of elemental nitrogen, obtained by EA, and the weight percentage of IL incorporated on the support.

The results reported in Table 1 shows that, while for the two imidazolium-based ILs the targeted amount of 80% of impregnation is closely to that obtained experimentally, for the protic IL, this amount is much lower. This lower amount of IL in the AC capsules seems to be related to its hydrophilic character and increased amount of water, compared to the other ILs, present during the impregnation procedure that allowed less IL to be retained inside the AC capsules.

The thermal stability of the ENIL is also an important factor to be considered if aiming for a process application. Fig. 3 depicts the TGA curves of the two neat ILs and the respective ENIL materials. As depicted in Fig. 3A, $[C_2C_1im][NTf_2]$ starts to decompose at around 613 K and finished decomposing at 733 K. The respective ENIL exhibits a weight loss with a similar pattern to the neat IL, however the peak appears a somewhat lower temperatures, denoting worse thermal stability due to the encapsulation. The m-HEAP-based ENIL showed the lowest thermal stability, with the decomposition starting around 453 K and presenting two peaks, provable due to the decomposition of cation and anion.

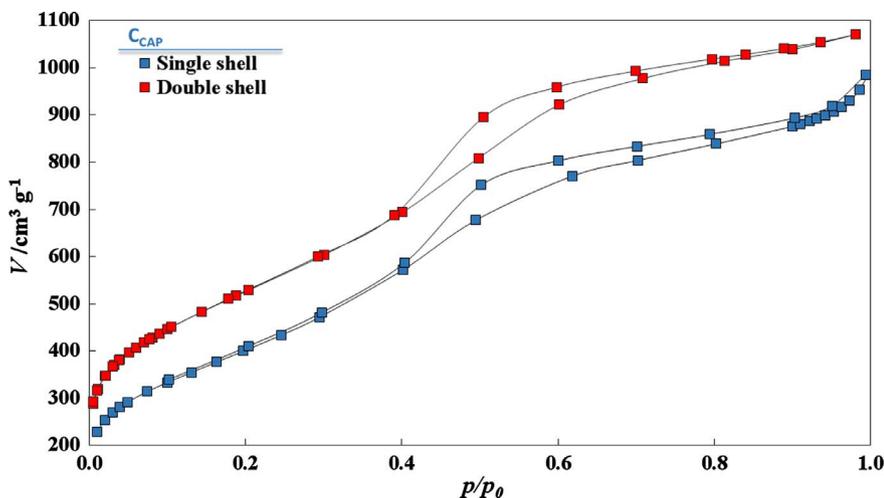


Fig. 2. Nitrogen adsorption-desorption isotherms, at 77 K, for C_{cap} with single (reported in reference [19]) and double shell.

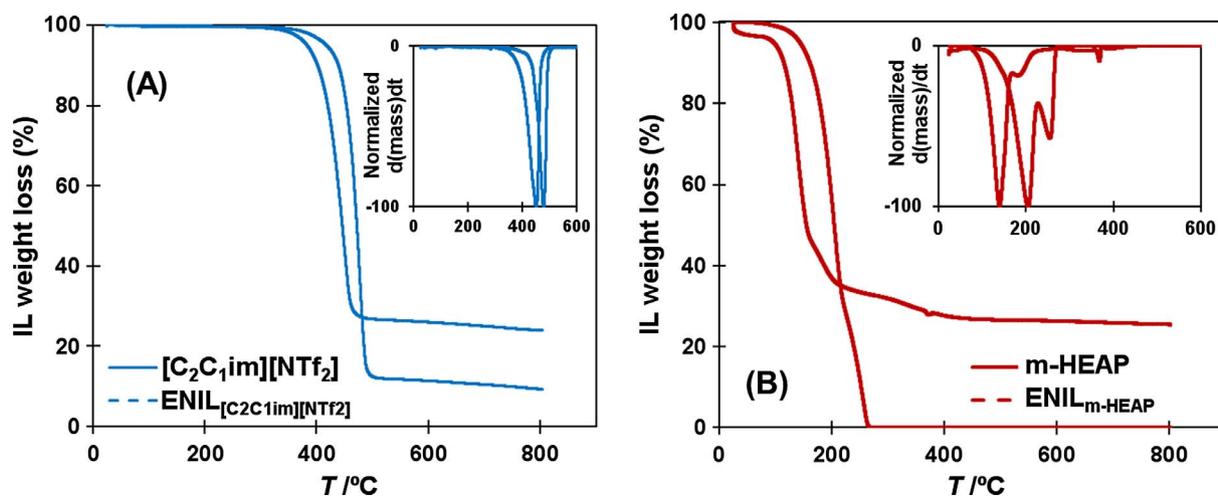


Fig. 3. Dynamic thermogravimetric curve (TGA) and normalized derivative thermogravimetric curve (DTG) of neat $[C_2C_1im][NTf_2]$ and ENIL prepared with $[C_2C_1im][NTf_2]$ (A) and m-HEAP(B) (using nitrogen atmosphere and 10 K min^{-1}).

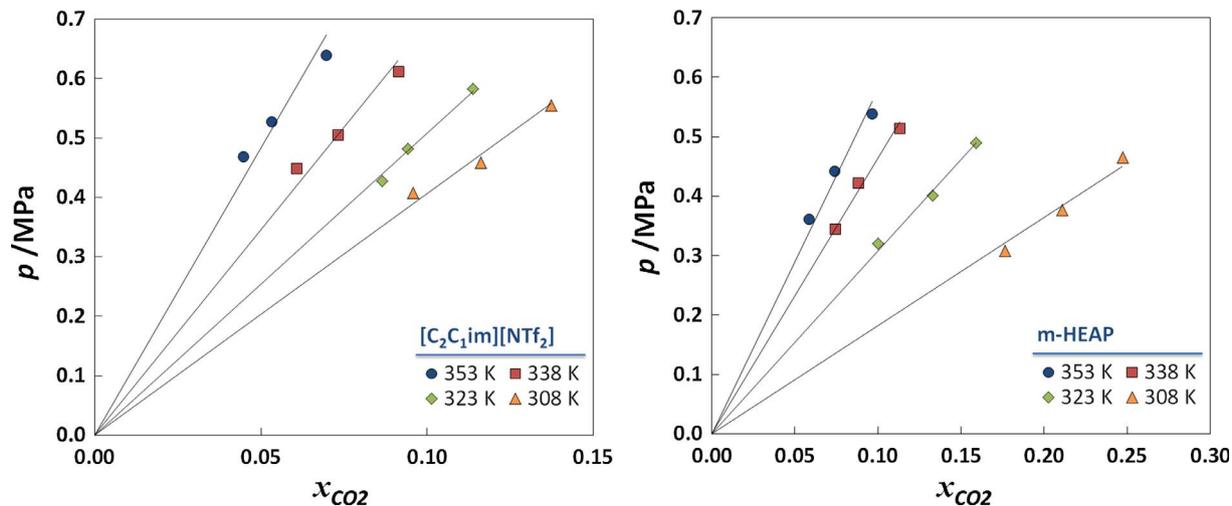


Fig. 4. Pressure-composition diagram of the binary systems $CO_2 + [C_2C_1im][NTf_2]$ and $CO_2 + m\text{-HEAP}$. The lines are guides for the eyes.

3.2. CO_2 solubilities

The sorption isotherms of CO_2 in ENIL were determined at four temperatures (308, 323, 338 and 353) K, as depicted in Fig. 4, with the CO_2 mole fractions calculated based on the moles of IL encapsulated.

It is noticeable in Fig. 5, that the CO_2 equilibrium pressures reported for the ENILs prepared with the $[C_2C_1im][NTf_2]$ present the same behavior expected to those reported for the neat IL [34–38]. Furthermore, the equilibrium pressures reported for $[C_2C_1im][NTf_2]$ ENILs are within those extrapolated using the reported Henry’s constants. These results

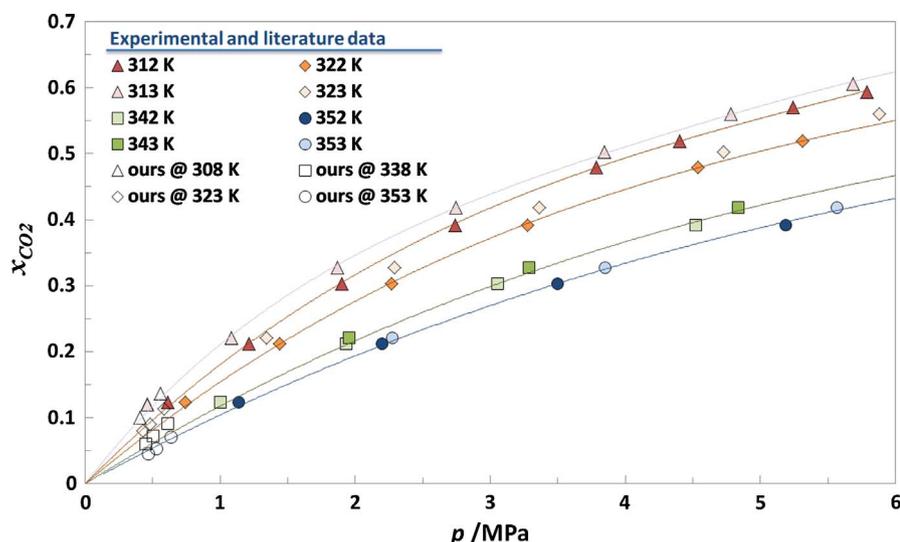


Fig. 5. Vapor-liquid equilibrium data for the binary system $\text{CO}_2 + [\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$. The solid symbols represent the data gathered from the literature [34–36], the empty symbols the experimental data and the solid lines guides for the eyes.

Table 2
Operating condition of the CO_2 capture experiments and Henry constant obtained from them.

T/K	H_{12}/MPa [$\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$	H_{12}/MPa m-HEAP	H_{12}/MPa m-HEAP	H_{12}/MPa m-HEAP
308	4.07	0.997	1.82	0.996
323	5.08	0.999	3.08	0.998
338	6.90	0.995	4.64	0.998
353	9.67	0.989	5.80	0.994

$$H_{i,L}(T,p) = \lim_{x_i \rightarrow 0} \frac{f_i^L}{x_i} \quad (1)$$

where $H_{i,L}(T, p)$ is the Henry's constant, x_i the mole fraction of gas i dissolved in the liquid, and f_i^L the fugacity of the gas in the liquid phase (L). In this work, the Henry's constants were estimated by fitting a polynomial equation to the experimental data and calculating the limiting slope as the solubility approaches zero. The Henry's constants for the studied systems are reported in Table 2.

3.3. Process reversibility

In order to assure a successful industrial application one must ensure an easy and low energy demanding regeneration [39]. Thus, sorption capability of an ENIL, prepared with the m-HEAP, was evaluated during four cycles of sorption-desorption. The desorption cycles were performed after each sorption cycle at 1 Pa, 353 K during 2 h, while the sorption was performed with an initial pressure of (0.55 ± 0.05) MPa. As depicted in Fig. 6, the regeneration of the ENIL was successful with the solubility, after four successive regeneration cycles, virtually constant, with the deviations observed related to the experimental uncertainty but mainly related to different starting pressures.

4. Conclusions

Encapsulated ionic liquids (ENILs) were designed for CO_2 capture from gaseous effluents and their performance evaluated by means of a controlled pressure cell. The confinement of specific ILs into the carbon submicrocapsules resulted in ENILs with high CO_2 capture capacities and thermal stabilities, very close to those of neat ILs. The incorporation of the ILs into the carbon submicrocapsules void spaces increased the efficiency respect the neat IL, due to an 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_2 capture-desorption cycles, without loss of operation efficiency. These results present ENILs as new separating agents with promising characteristics for future industrial application.

Acknowledgements

This work was developed in the scope of the project CICECO – Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership

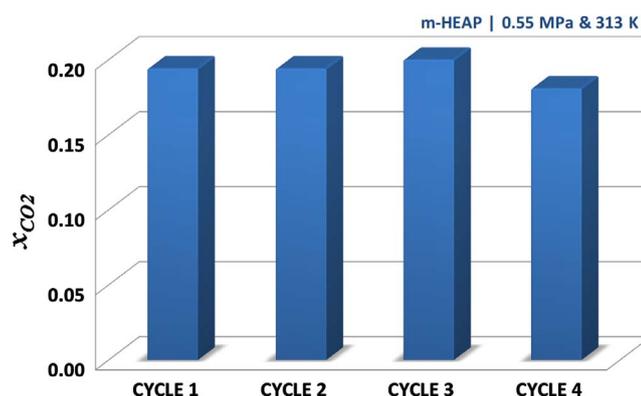


Fig. 6. m-HEAP ENIL CO_2 sorption (313 K and 0.55 MPa) and desorption (313 K and 1 Pa) cycles.

indicate that the IL maintains its high CO_2 absorption capacity even when encapsulated, allowing one to use this approach of microsolid droplets of IL, as a separation mechanism capable of overcoming the problems of using ILs in absorption columns.

To our knowledge, pressure-temperature-composition phase equilibria for the binary system $\text{CO}_2 + \text{m-HEAP}$ is here reported for first time. As depicted in Fig. 4, m-HEAP presents the highest CO_2 solubility at the lowest temperature, however, this IL is highly affected by the temperature, showing, in contrast, the lowest uptake at 353 K. Nonetheless, the m-HEAP stands still as the IL with the highest potential for CO_2 capture if one takes into consideration the low CH_4 solubilities with strong positive deviations from ideality, that result from positive deviations in the residual (enthalpic) term, and therefore one of the highest selectivities reported [28].

The Henry's law relates the amount of a gas dissolved in a liquid, at a constant temperature, to the fugacity of that gas in equilibrium with that liquid and can be described as:

Agreement. P.J. Carvalho acknowledges FCT for a contract under the Investigador FCT 2015 (contract number IF/00758/2015) and J. Lemus for the postdoctoral grant (SFRH/BPD/110550/2015).

References

- [1] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program, *Int. J. Greenh. Gas Con.* 2 (2008) 9–20.
- [2] H.J. Herzog, What future for carbon capture and sequestration? *Environ. Sci. Technol.* 35 (2001) 148A–153A.
- [3] R.E. Baltus, R.M. Counce, B.H. Culbertson, H. Luo, D.W. DePaoli, S. Dai, D.C. Duckworth, Examination of the potential of ionic liquids for gas separations, *Sep. Sci. Technol.* 40 (2005) 525–541.
- [4] A.A. Olajire, CO₂ capture and separation technologies for end-of-pipe applications – a review, *Energy* 35 (2010) 2610–2628.
- [5] Z. Ziobrowski, R. Krupiczka, A. Rotkegel, Carbon dioxide absorption in a packed column using imidazolium based ionic liquids and MEA solution, *Int. J. Greenh. Gas Control.* 47 (2016) 8–16.
- [6] S. Kasahara, E. Kamio, A. Otani, H. Matsuyama, Fundamental investigation of the factors controlling the CO₂ permeability of facilitated transport membranes containing amine-functionalized task-specific ionic liquids, *Ind. Eng. Chem. Res.* 53 (2014) 2422–2431.
- [7] A. Otani, Y. Zhang, T. Matsuki, E. Kamio, H. Matsuyama, E.J. Maginn, Molecular design of high CO₂ reactivity and low viscosity ionic liquids for CO₂ separative facilitated transport membranes, *Ind. Eng. Chem. Res.* 55 (2016) 2821–2830.
- [8] B.E. Gurkan, J.C. de la Fuente, E.M. Mindrup, L.E. Ficke, B.F. Goodrich, E.A. Price, W.F. Schneider, J.F. Brennecke, Equimolar CO₂ absorption by anion-functionalized ionic liquids, *J. Am. Chem. Soc.* 132 (2010) 2116–2117.
- [9] J. Huang, T. Rütger, Why are ionic liquids attractive for CO₂ absorption? An overview, *Aust. J. Chem.* 62 (2009) 298.
- [10] C. Wu, T.P. Senftle, W.F. Schneider, First-principles-guided design of ionic liquids for CO₂ capture, *Phys. Chem. Chem. Phys.* 14 (2012) 13163–13170.
- [11] J.F. Brennecke, B.E. Gurkan, Ionic liquids for CO₂ capture and emission reduction, *J. Phys. Chem. Lett.* 1 (2010) 3459–3464.
- [12] H. Tang, C. Wu, Reactivity of azole anions with CO₂ from the DFT perspective, *ChemSusChem* 6 (2013) 1050–1056.
- [13] P.J. Carvalho, K.A. Kurnia, J.A.P. Coutinho, Dispelling some myths about the CO₂ solubility in ionic liquids, *Phys. Chem. Chem. Phys.* 18 (2016) 14757–14771.
- [14] J. de Riva, J. Suarez-Reyes, D. Moreno, I. Diaz, V. Ferro, J. Palomar, Ionic liquids for post-combustion CO₂ capture by physical absorption: thermodynamic, kinetic and process analysis, *Int. J. Greenh. Gas Control* 61 (2017) 61–70.
- [15] J. Lemus, J. Palomar, M.A. Gilarranz, J.J. Rodriguez, Characterization of Supported Ionic Liquid Phase (SILP) materials prepared from different supports, *Adsorption* 17 (2011) 561–571.
- [16] J. Palomar, J. Lemus, N. Alonso-Morales, J. Bedia, M.A. Gilarranz, J.J. Rodriguez, Encapsulated ionic liquids (ENILs): from continuous to discrete liquid phase, *Chem. Commun. (Camb)*. 48 (2012) 10046–10048.
- [17] J. Lemus, J. Bedia, C. Moya, N. Alonso-Morales, M.A. Gilarranz, J. Palomar, J.J. Rodriguez, Ammonia capture from the gas phase by encapsulated ionic liquids (ENILs), *RSC Adv.* 6 (2016) 61650–61660.
- [18] S.B. Yoon, K. Sohn, J.Y. Kim, C.H. Shin, J.S. Yu, T. Hyeon, Fabrication of carbon capsules with hollow macroporous core/mesoporous shell structures, *Adv. Mater.* 14 (2002) 19–21.
- [19] P. Valle-Vigón, M. Sevilla, A.B. Fuertes, Synthesis of uniform mesoporous carbon capsules by carbonization of organosilica nanospheres, *Chem. Mater.* 22 (2010) 2526–2533.
- [20] N. Alonso-Morales, M.A. Gilarranz, J. Palomar, J. Lemus, F. Heras, J.J. Rodriguez, Preparation of hollow submicrocapsules with a mesoporous carbon shell, *Carbon N. Y.* 59 (2013) 430–438.
- [21] J. Palomar, J. Lemus, M.A. Gilarranz, J.J. Rodriguez, Adsorption of ionic liquids from aqueous effluents by activated carbon, *Carbon N. Y.* 47 (2009) 1846–1856.
- [22] J. Lemus, J. Palomar, F. Heras, M.A. Gilarranz, J.J. Rodriguez, Developing criteria for the recovery of ionic liquids from aqueous phase by adsorption with activated carbon, *Sep. Purif. Technol.* 97 (2012) 11–19.
- [23] K.E. Gutowski, E.J. Maginn, Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO₂ from molecular simulation, *J. Am. Chem. Soc.* 130 (2008) 14690–14704.
- [24] S. Sarmad, J.-P. Mikkola, X. Ji, Carbon dioxide capture with ionic liquids and deep eutectic solvents: a new generation of sorbents, *ChemSusChem* 10 (2017) 324–352.
- [25] C. Wang, H. Luo, X. Luo, H. Li, S. Dai, Equimolar CO₂ capture by imidazolium-based ionic liquids and superbase systems, *Green Chem.* 12 (2010) 2019.
- [26] F.F. Chen, K. Huang, Y. Zhou, Z.Q. Tian, X. Zhu, D.J. Tao, D.E. Jiang, S. Dai, Multimolar absorption of CO₂ by the activation of carboxylate groups in amino acid ionic liquids, *Angew. Chemie - Int. Ed.* 55 (2016) 7166–7170.
- [27] A. Yokozeki, M.B. Shiflett, C.P. Junk, L.M. Grieco, T. Foo, Physical and chemical absorptions of carbon dioxide in room-temperature ionic liquids, *J. Phys. Chem. B.* 112 (2008) 16654–16663.
- [28] P.J. Carvalho, J.A.P. Coutinho, The polarity effect upon the methane solubility in ionic liquids: a contribution for the design of ionic liquids for enhanced CO₂/CH₄ and H₂S/CH₄ selectivities, *Energy Environ. Sci.* 4 (2011) 4614–4619.
- [29] N.M.C. Talavera-Prieto, A.G.M. Ferreira, P.N. Simões, P.J. Carvalho, S. Mattedi, J.A.P. Coutinho, Thermophysical characterization of N-methyl-2-hydroxyethylammonium carboxylate ionic liquids, *J. Chem. Thermodyn.* 68 (2014) 221–234.
- [30] M.L.S. Batista, C.M.S.S. Neves, P.J. Carvalho, R. Gani, J.A.P. Coutinho, Chameleonic behavior of ionic liquids and its impact on the estimation of solubility parameters, *J. Phys. Chem. B.* 115 (2011) 12879–12888.
- [31] V. Sanz, R. Alcalde, M. Atilhan, S. Aparicio, Insights from quantum chemistry into piperazine-based ionic liquids and their behavior with regard to CO₂, *J. Mol. Model.* 20 (2014).
- [32] S. Azizi, A. Kargari, T. Kaghazchi, Experimental and theoretical investigation of molecular diffusion coefficient of propylene in NMP, *Chem. Eng. Res. Des.* 92 (2014) 1201–1209.
- [33] C.R. Wilke, P. Chang, Correlation of diffusion coefficients in dilute solutions, *AIChE J.* 1 (1955) 264–270.
- [34] A.M. Schilderman, S. Raeissi, C.J. Peters, Solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, *Fluid Phase Equilib.* 260 (2007) 19–22.
- [35] E. Shin, B. Lee, J.S. Lim, High-pressure solubilities of carbon dioxide in ionic liquids: 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, *J. Supercrit. Fluids.* 45 (2008) 282–292.
- [36] P.J. Carvalho, V.H. Álvarez, I.M. Marrucho, M. Aznar, J.A.P. Coutinho, High pressure phase behavior of carbon dioxide in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium dicyanamide ionic liquids, *J. Supercrit. Fluids.* 50 (2009) 105–111.
- [37] K. Kortenbruck, B. Pohrer, E. Schluucker, F. Friedel, I. Ivanovic-Burmazovic, Determination of the diffusion coefficient of CO₂ in the ionic liquid EMIM NTf₂ using online FTIR measurements, *J. Chem. Thermodyn.* 47 (2012) 76–80.
- [38] D. Camper, C. Becker, C. Koval, R. Noble, Diffusion and solubility measurements in room temperature ionic liquids, *Ind. Eng. Chem. Res.* 45 (2006) 445–450.
- [39] J. Balth, N. Deubler, T. Hirth, T. Schiestel, Chemisorption of carbon dioxide in imidazolium based ionic liquids with carboxylic anions, *Chem. Eng. J.* 181–182 (2012) 152–158.