



Research article

New water-based nanocapsules of poly(diallyldimethylammonium tetrafluoroborate)/ionic liquid for CO₂ capture

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ABSTRACT

Encapsulated ionic liquids as green solvents for CO₂ capture are reported in this work. We present a novel combination of water-based poly(ionic liquid) and imidazolium-based ionic liquids (Emim[X]). Poly(diallyldimethylammonium tetrafluoroborate)/Emim[X] capsules were developed for the first time using Nano Spray Dryer B-90. Capsules were characterized by FTIR, SEM/EDX, TEM, TGA, DSC, CO₂ sorption, and CO₂/N₂ selectivity. CO₂ sorption kinetic and recycling were also demonstrated. Comparing the capsules reported in this work, the combination of poly(diallyldimethylammonium tetrafluoroborate) and the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (P[DADMA]/BF₄) showed great potential for CO₂ capture and CO₂/N₂ separation, providing higher results (53.4 mg CO₂/g; CO₂/N₂ selectivity: 4.58).

1. Introduction

Combustion of fossil fuel and industrial processes are largely responsible for anthropogenic CO₂ emissions in the atmosphere. CO₂ capture and storage technologies are suggested as the easiest and most effective way to reduce CO₂ emissions at a large scale [1–3]. Current amine-based CO₂ capture systems, have some drawbacks such as high regeneration energy, equipment investment and corrosion [4].

The search for novel materials for CO₂ capture combining efficiency and safety, besides being sustainable processes is urgent. Despite water being considered safe, non-toxic, and environmentally friendly, it is not always compatible with the process systems. Green solvents are emerging as benign when compared to conventional solvents toxicity [5,6]. Ionic liquids (ILs) are classified as green solvents due to their low vapor pressure, non-flammability, and recyclability. Other properties such as tunability and high thermal stability also draw attention to this material [7,8]. Simulation studies showed that the energy consumption of the IL-based process can be 26% lower than the amine-based process [9]. However, high viscosity and low CO₂ sorption rate represent a challenge to its use [10–12]. Solvent encapsulation combines the advantages of liquid solvents and solid sorbents, overcoming the mass transfer limitation. Encapsulated ionic liquid has been proposed as a potential strategy for CO₂ capture, increasing the contact between the gas and liquid phases [13–16]. Encapsulated ionic liquid improved CO₂ sorption process, showing higher mass transfer rates when compared with neat ionic liquids [14,17–19]. Recently works present the combination of polymer shell (polysulfone [19,20], silicone [18,21,22],

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acrilates [22]) and ionic liquids using different encapsulation techniques as emulsification [19,20,23], UV [10,22], polymerization [23] and impregnation [13,14]. Studies also indicated that encapsulated ionic liquid can be successfully regenerated under mild conditions and used in consecutive CO₂ sorption/desorption cycles, without operation efficiency loss [13,16,18,21]. Knipe et al. presented ionic liquid encapsulation as a potential substitute for amines, since silicone capsules of [P₂₂₂₂][BnIm] and [P₂₂₂₈][2CNPr] performed similar or even better for CO₂ sorption than aqueous amines at low pressure and 25 °C [21].

Process criteria such as thermal stability, solvent regeneration, compatibility, and CO₂ permeability can be affected by shell material choice [22]. Poly(ionic liquid)s or polymerized ionic liquids (PILs) combine polymers (processability, film-forming properties, etc) and ILs properties (high thermal stability, affinity to CO₂, etc) emerging as high permeable membranes for CO₂ separation. Studies suggest that PILs are very selective for CO₂ separation from CO₂/N₂ mixture, showing better results for CO₂ separation when compared with ILs. CO₂ sorption capacity can be strongly affected by PIL cation, presenting better results with ammonium-based ones [24–27]. The use of water-based PILs to encapsulate IL contributes to the advance of scientific knowledge and technology for CO₂ capture, but also is in agreement with the green chemistry principles. It must be emphasized that the use of nanospray dryer allied to water as solvent in the encapsulation process offers a new platform to environmental benign syntheses, the use of alternative solvents and atom economy since the yield of the nanospray is higher compared to conventional spray dryer processes [28,29]. As far as we know, capsules combining water-based PILs as shell and ILs as core are a new approach for CO₂ capture.

Herein, we report the IL 1-Ethyl-3-methylimidazolium with different anions (Emim[X]) encapsulation, using as shell the water-based PIL poly(diallyldimethylammonium tetrafluoroborate). The encapsulation process using Nano Spray Dryer B-90 and water as solvent was also described. Yet, CO₂ sorption and CO₂/N₂ selectivity, process parameters, thermal stability and recyclability were also evaluated.

2. Experimental

2.1. Materials

Aqueous solution of poly(diallyldimethylammonium chloride), P[DADMA][Cl] (20 wt%, mw. 400,000–500,000), Lithium tetrafluoroborate salt (98%), 1-Ethyl-3-methylimidazolium methanesulfonate, Emim[MSO₃] (95%), 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, Emim[CF₃SO₃] (98%), were purchased from Merck. The chemicals were used without further purification. CO₂ (99.8%) and CO₂/N₂ (15.94%/balance) were purchased from White Martins.

First, the Poly(ionic liquid) poly(diallyldimethylammonium tetrafluoroborate) (P[DADMA][BF₄]), used as shell material, was obtained by anion exchange from Li[BF₄] and an aqueous solution of poly(diallyldimethylammonium chloride), P[DADMA][Cl], following literature procedures [30]. The ionic liquids 1-Ethyl-3-methylimidazolium bromide (Emim[Br]) and 1-Ethyl-3-methylimidazolium tetrafluoroborate (Emim[BF₄]), used as core, were synthesized as described in literature [31,32]. Proton Nuclear Magnetic Resonance (1H-NMR) (Varian spectrophotometer, VNMRs 300 MHz). Emim[Br]: H NMR δ 1.57 (t, 3H), 4.11 (s, 3H), 4.42 (q, 2H), 7.56 (s, 2H), 10.19 (s, 1H) Emim[BF₄]: 1H NMR 1.43 (t, 3H), 3.84 (s, 3H), 4.15 (q, 2H), 7.37 (s, 1H), 7.43 (s, 1H), 8.63 (s, 1H).

2.2. Ionic liquid encapsulation

Ionic liquid Emim[X] was encapsulated in P[DADMA][BF₄] by spray drying using a Nano Spray Dryer B-90 (BÜCHI Labortechnik AG, Flawil, Switzerland) equipment. The materials structure of encapsulated ionic liquids (ENILs) can be observed in Fig. 1.

For the encapsulation process, P[DADMA][BF₄] was dissolved in distilled water under mild heating. After complete dissolution, the ionic liquid was added and the solution was stirred until the complete homogenization. The solution was fed to the atomization system using a peristaltic pump. Mass proportion of P[DADMA][BF₄]:Emim[X] was 1:0.5. Nano Spray Dryer process parameters (Table 1) were previously tested and defined using distilled water in the equipment.

Yield was obtained using mass balance and encapsulation efficiency (EE) was calculated by equation (1) [33].

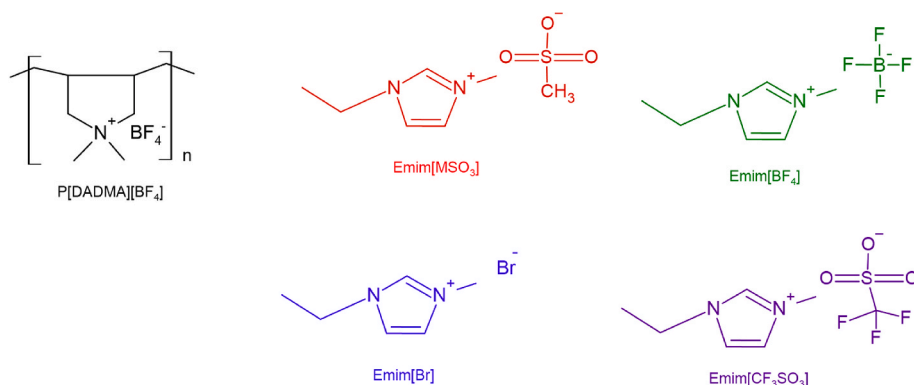


Fig. 1. Structure materials used to ENILs.

Table 1
Nano Spray Dryer process parameters.

Parameters	
Frequency (kHz)	110
Spray (%)	80
Pump (%)	36–46
Inlet Temperature (°C)	107
Spray mesh size	Small

$$EE (\%) = \frac{w_{IL-s}}{\left(\frac{w_{IL-e}}{Y}\right)} \times 100 \quad (1)$$

Where w_{IL-s} : IL mass fraction obtained by acetone extraction method [20]; w_{IL-e} : IL theoretical mass fraction; Y: Yield.

Aiming to compare results for both configurations – capsules and the pristine PIL (P[DADMA]-poly) – capsules were obtained (without IL - P[DADMA]-cap). Sample code and its components are shown in Table 2.

2.3. Encapsulated ionic liquids characterization

Scanning electron microscopy with field emission (SEM-FEG) using FEI Inspect F50 in the secondary electron mode (SE) was performed to evaluate particle morphology and size. Chemical composition was assessed by energy dispersion X-ray spectrometry (EDX). FTIR spectra were recorded on a PerkinElmer Spectrum100 spectrometer in UATR mode. Particle structure was assessed by transmission electron microscopy (TEM) (Model Tecnai G2 T20 FEI). Thermal stability was investigated by TGA (TA Instruments SDT-Q600), under nitrogen atmosphere with a temperature range from 25 to 700 °C and a heating rate of 20 °C/min. Differential scanning calorimetry - DSC (TA Instrument Q20) was performed from -90 °C to 100 °C at a heating rate of 5 °C/min under nitrogen atmosphere. IL encapsulated amount (% IL) was measured by the acetone extraction method (performed in triplicates) [20]. CO₂ sorption tests were performed using the well-known pressure decay technique [34,35]. CO₂/N₂ selectivity was performed using the same method coupled to gas chromatography (GC-2014ATFSP Shimadzu), detailed in previous works [36,37]. CO₂ sorption tests were performed at a range of equilibrium pressure (1–30 bar) and temperatures of 25 °C, 45 °C and 65 °C. CO₂/N₂ selectivity was measured at 45 °C and equilibrium pressure of ~27 bar. All tests were performed in triplicates. The stability was evaluated by ten CO₂ sorption/desorption cycles at 45 °C and 4.3 bar with desorption following each cycle by heating at 70 °C for 1 h.

2.4. Statistical analysis

Minitab 18 Statistical Software-ANOVA was used to carry out statistical analysis to assess tests standard deviation (performed in triplicate) and analyze the Tukey test with 95% reliability. Equal letters show statistical equivalence of the sample averages. Also, temperature and pressure parameters were optimized by analyzing the surface and contour graph.

3. Results and discussion

Nanospray dryer is one of the technologies that allow obtaining nanoparticles [38]. Yet, by selecting an adequate polymer to obtain the shell one can produce nanoparticles using water as solvent. Fig. 2 shows SEM in two magnifications (20.000x - Fig. 2A–E and 10.000x - Fig. 2A₁–E₁) proving the success of using this kind of technology to obtain green nanoparticles by combining water-based PILs as shell and ILs as core. Particles with spherical morphology were observed both in P[DADMA]-cap (Fig. 2A) and capsules having ionic liquid as core (Fig. 2B–E). Average diameters demonstrated nanometric sizes (Fig. 2A₁: ~665 nm (+266); Fig. 2B₁: ~695 nm (+190); Fig. 2C₁: ~678 nm (+222); Fig. 2D₁: ~718 nm (+260); e Fig. 2E₁: ~931 nm (+300)). EDX (Fig. S1) confirmed the presence of well-determined elements and uniform distribution of colors corresponding to C (red), F (green), S (blue), O (pink) and Br (yellow), confirming encapsulation and IL homogeneous distribution.

In terms of shape and construction, particles can be called capsules or spheres. For capsules, the confined liquid is surrounded by a well-defined polymer line, while for spheres, the core and shell are mixed [39]. Capsules can be observed in TEM images (Fig. 3) and it represents the typical behavior of all particles obtained in this work.

Table 2
Sample code.

Sample Code	Components
C	P[DADMA][BF ₄] capsules
P[DADMA]-poly	P[DADMA][BF ₄] polymer
P[DADMA]/MSO ₃	P[DADMA][BF ₄]/Emim[MSO ₃] capsules
P[DADMA]/BF ₄	P[DADMA][BF ₄]/Emim[BF ₄] capsules
P[DADMA]/Br	P[DADMA][BF ₄]/Emim[Br] capsules
P[DADMA]/CF ₃ SO ₃	P[DADMA][BF ₄]/Emim[CF ₃ SO ₃] capsules

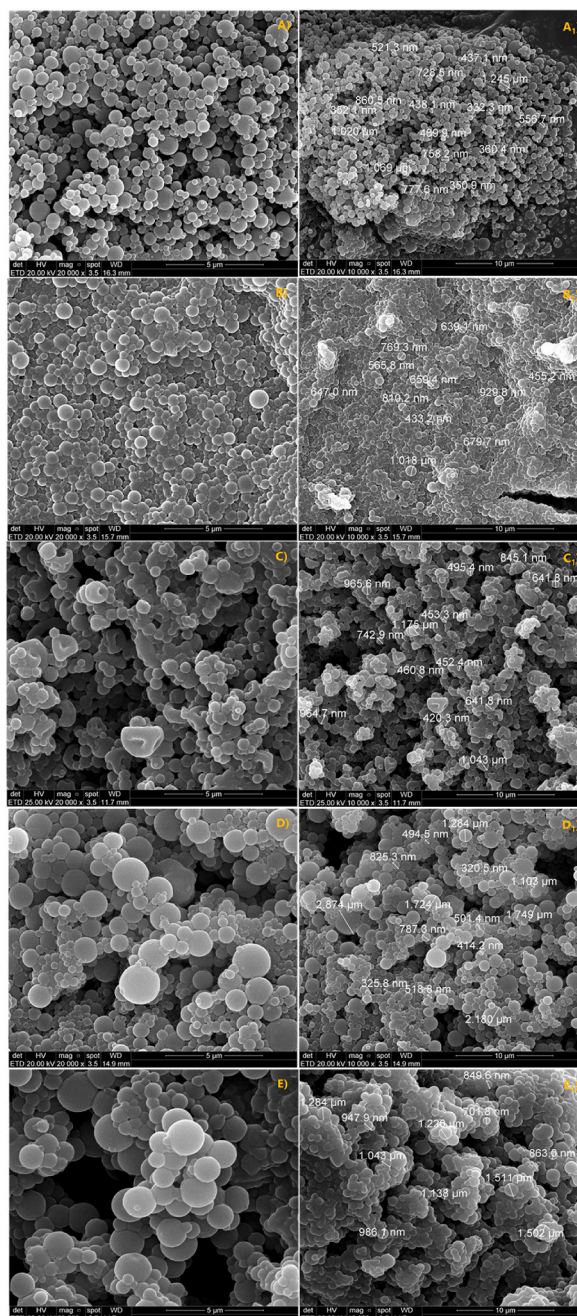


Fig. 2. SEM, 20.000x magnification and SEM with particle size(₁), 10.000x magnification: A) P[DADMA]-cap; B) P[DADMA]/MSO₃; C) P[DADMA]/BF₄; D) P[DADMA]/Br; E) P[DADMA]/CF₃SO₃.

FTIR also confirmed Emim[X] encapsulation within the P[DADMA][BF₄] shell. All samples showed characteristic peaks of (see Fig. S2) shell material - cation poly(diallyldimethylammonium: 3058 cm⁻¹ (C-H of N-CH₂), 2946–2869 cm⁻¹ (C-H of CH₃), 1482–1387 cm⁻¹ (C-H), 1286 cm⁻¹ (N-C); and tetrafluoroborate anion: 1037–897 cm⁻¹ (B-F) [30,40]. Characteristic peaks of ionic liquid were observed in encapsulated samples as cation [emim] [41]: 3170–3121 cm⁻¹ (C-H aromatic), 1570 cm⁻¹ (C=C aromatic), 1230 cm⁻¹ (C-N aromatic), 1170 cm⁻¹ (C-N aliphatic); and anions [42,43] [MSO₃]: 757 cm⁻¹ (C-S); [CF₃SO₃]: 1055 cm⁻¹ (S=O), 754–631 cm⁻¹ (C-F); [Br]: 617 cm⁻¹. Other bands indicate O-H deformations, referring to water.

Encapsulation yield range is directly affected by the encapsulation technique [38]. IL encapsulated amount also can be influenced by the preparation method [23]. Wang et al. [23] compared IL loading amounts obtained by three different encapsulation methods (sol-gel, suspension polymerization and solvent evaporation) and observed that the first two presented higher values. Classical spray

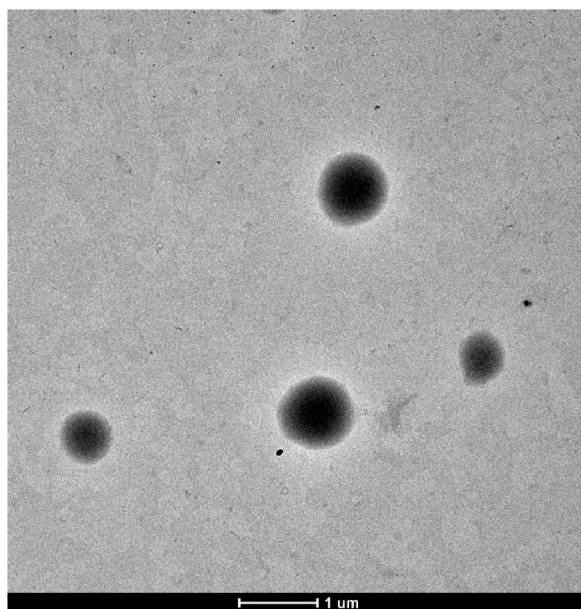


Fig. 3. TEM P[DADMA]/MSO₃.

dryer shows a maximum yield of 70% [28], while for the nanospray dryer the encapsulation yield achieved 82.9% (see Table 3).

TGA curves are presented in Fig. 4 (see Table S1 for more information). Without considering the moisture loss at the beginning of the test, the P[DADMA]-cap exhibited other two main degradation stages [40]. First, the T_{onset} was observed at, approximately, 336.2 °C, attributed to [BF₄]⁻ remotion and the loss of two methyl groups. The second $T_{\text{onset}2}$, at 486.6 °C, refers to the complete polymer degradation [44]. With IL encapsulation, except for P[DADMA]/Br, thermal stability was improved, indicating that the anion plays an important role on determining thermal stability [45]. Founds of residual weights were in agreement with % IL encapsulated (Table 3 and Table S1) [20]. Differential scanning calorimetry (DSC) (see Table S2) indicated PLI amorphous structure, ($T_g = -44.1$ °C), presenting no endothermic peak [46]. Similar thermal transition profiles for encapsulated IL and pristine IL support the presence of the IL core [47]. P[DADMA]/Br showed no peaks in the test temperature, despite similar behavior reported in literature it requires further investigation to be fully understood [48].

Fig. 5 demonstrates CO₂ sorption (at ~4.3 bar and 45 °C) and CO₂/N₂ selectivity results.

An increase in CO₂ solubility (P[DADMA]-poly: 35.65 (±0.42) mg/g; P[DADMA]-cap: 47.88 (±1.55) mg/g) and CO₂/N₂ selectivity (P[DADMA]-poly: 2.05 (±0.23); P[DADMA]-cap: 3.81 (±0.14)) is noticed when comparing two different configuration of poly(ionic liquid) in capsule (P[DADMA]-cap) and solid polymer (P[DADMA]-poly), suggesting capsule formation can increase the active surface area, improving gas contact [17,18]. IL encapsulation showed even better results, indicating a synergic interaction between shell material and the ionic liquid. CO₂ sorption best results were found for P[DADMA]/BF₄ (53.40 (±0.39) mg/g) and P[DADMA]/CF₃SO₃

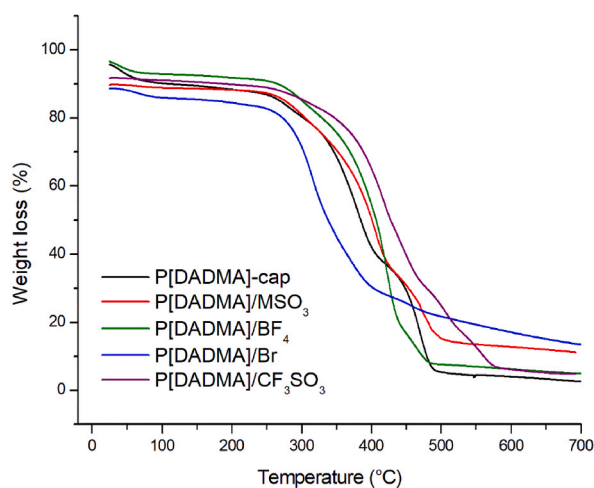
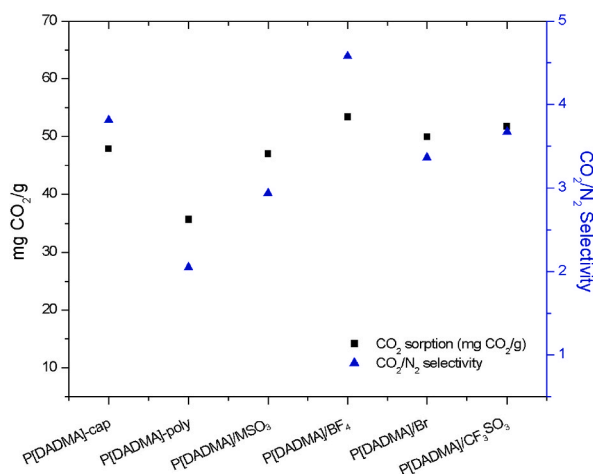


Fig. 4. Capsules TGA analysis.

Table 3

Process parameters: Yield (%), IL encapsulated amount (% IL) and encapsulation efficiency (EE).

Sample	Yield (%)	% IL	EE (%)
P[DADMA]-cap	74.4	–	–
P[DADMA]/MSO ₃	75.0	30.8 (+ 0.3)	69.2
P[DADMA]/BF ₄	72.0	31.4 (+ 0.4)	67.8
P[DADMA]/Br	82.9	27.0 (+ 1.4)	67.1
P[DADMA]/CF ₃ SO ₃	77.9	32.1 (+ 0.4)	75.1

**Fig. 5.** CO₂ sorption (mg CO₂/g) and CO₂/N₂ selectivity.

(51.76 (±0.26) mg/g), representing statistical equality (see Table S3). Ionic liquids with lower viscosity tend to favor CO₂ permeability and diffusivity (μ (mPa.s): Emim[BF₄] = 20.41 (40 °C) [49]; Emim[CF₃SO₃] = 23.86 (45 °C) [50]; Emim[MSO₃] = 69 (45 °C) [51]; Emim[Br] = solid (45 °C) [52]), also fluorinated anions present high CO₂ affinity [53,54]. These factors can be contributing for the obtained CO₂ sorption results. Higher CO₂/N₂ selectivity was evidenced by P[DADMA]/BF₄ (4.58 (±0.39)). ILs with smaller and symmetric anions tend to favor cavity creation and consequently a closer contact with CO₂, improving CO₂/N₂ selectivity [55–57], corroborating IL Emim[BF₄] best performance.

Emim[BF₄] encapsulation with poly(diallyldimethylammonium tetrafluoroborate) as shell appears as a potential option for CO₂ capture. The CO₂ sorption capacities of samples obtained in this work are higher compared with some results reported in the literature, under similar conditions (Table 4).

CO₂ sorption capacity of encapsulated ionic liquid tends to increase when compared with pristine ionic liquids. The encapsulation of Emim[BF₄] (P[DADMA]/BF₄) increased, approximately, four times the CO₂ solubility when compared with the CO₂ sorption capacity of the pristine IL Emim[BF₄] reported in literature [58] (compare 53 mg/g CO₂ at 45 °C and 4.3 bar to ~13 mg/g CO₂, at 40 °C and ~5 bar). CO₂ sorption kinetics can be drastically increased with encapsulation (see Fig. S3). Due to high viscosity, ILs take minutes or hours to achieve stability while encapsulated ionic liquid achieves this in seconds [17,20,37,59].

Response surface analysis for P[DADMA]/BF₄ was applied to determine the best conditions for CO₂ capture (Table S5; Fig. S4). Results showed CO₂ sorption capacity improvement with higher pressure and lower temperature (Fig. 6), typical behavior of physical absorption [60]. To achieve the highest CO₂ sorption, a higher pressure (30 bar) and temperature of around 25 °C will be needed.

Recycling tests are important in the development of new materials for CO₂ capture. P[DADMA]-cap and P[DADMA]/BF₄ were tested for ten cycles of CO₂ sorption/desorption and from Fig. 7 we can see the CO₂ sorption capacity of both are still the same, keeping the deviation stability (Table S6), suggesting P[DADMA]-cap and P[DADMA]/BF₄ were reversible for ten consecutive sorption/

Table 4CO₂ sorption (mg CO₂/g) comparison with different encapsulated ILs.

Shell	Ionic Liquid	Conditions (T, P and %IL)	mg CO ₂ /g	Ref.
PSF	Emim[TF ₂ N]	45 °C, 4 bar–37.5% (w)	44.2	[20]
PSF	Bmim[TF ₂ N]	45 °C, 4 bar–48% (w)	46.1	[19]
PVDF-HFP	Hmim[TF ₂ N]	23 °C, ~4.5 bar 20% (w)	~24.9	[17]
C _{cap}	Bmim[GLY]	45 °C, 5 bar 55% (w)	~50	[15]
C _{cap}	Bmim[PRO]	45 °C, 5 bar 55% (w)	~40	[15]
P[DADMA]/[BF ₄]	Emim[BF ₄]	45 °C, 4.3 bar ~31.4 (w)	53.4	This Work

PSF: Polysulfone; PVDF-HFP: Poly(vinylidene fluoride-co-hexafluoropropylene); C_{cap}: hollow carbon.

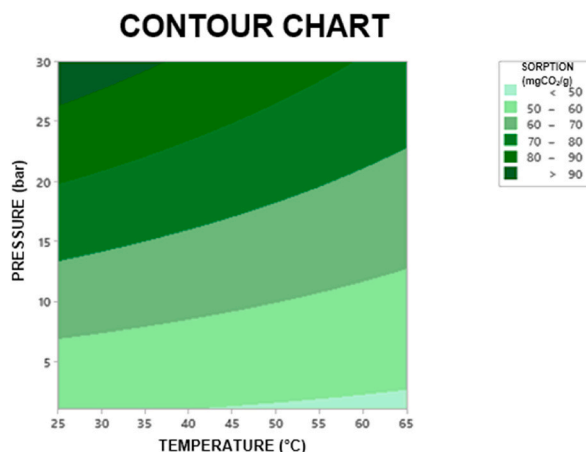


Fig. 6. Contour chart for P[DADMA]/BF₄ CO₂ sorption at different temperatures and pressures.

desorption cycles. Encapsulation of ionic liquids is suggested as an alternative to the leaching problem that occurs in some immobilization methods [13,16,18,21].

Aiming to confirm the stability of P[DADMA]/BF₄ capsule after ten cycles, SEM image and acetone extraction test were performed. From Fig. 8 we can see that the particles shape keep the same before (Fig. 8A) and after ten cycles (Fig. 8B). Capsules good stability was confirmed for both techniques as seen in Fig. 8 by the maintenance of capsules configuration and the encapsulated IL % content (30.9%).

4. Conclusions

Capsules of water-based poly(ionic liquid) P[DADMA][BF₄] and encapsulated ionic liquids Emim[X] were obtained for the first time using Nano Spray Dryer B-90. The combination of these promising materials for CO₂ capture promoted gains for CO₂ sorption, CO₂/N₂ selectivity, thermal stability and CO₂ sorption kinetic proving to be stable under use, emphasizing this as a potential alternative. P[DADMA]/BF₄ showed the best results for CO₂ capture. It must be emphasized that this new material for CO₂ capture is organic solvent-free in the encapsulation step helping also to create new options for the development of green processes.

Author contribution statement

Bárbara B. Polesso: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Rafael Duczinski: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Franciele L. Bernard: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Douglas J. Faria: Analyzed and interpreted the data; Wrote the paper.

Leonardo M. dos Santos: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sandra Einloft: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no competing interests.

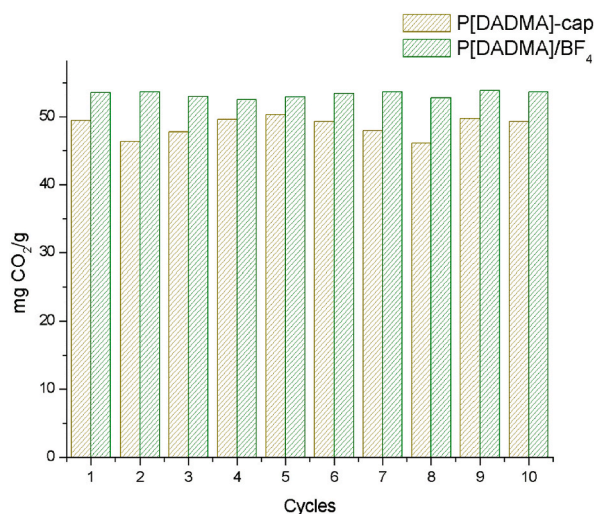


Fig. 7. Recycle test at ~ 4.3 bar and 45°C .

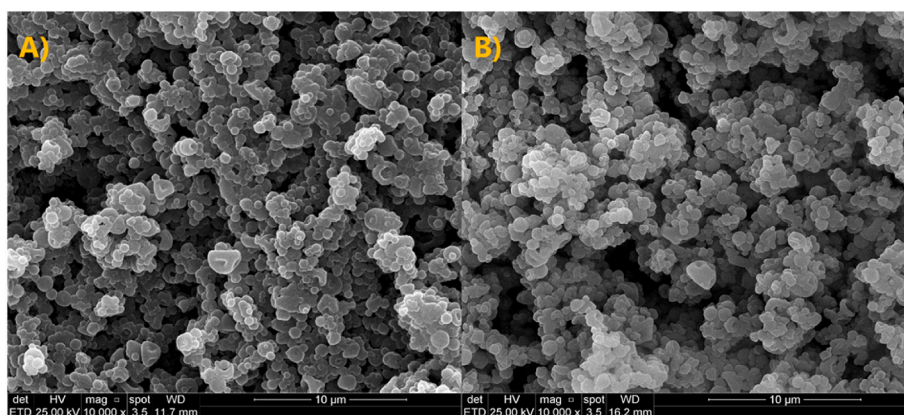


Fig. 8. P[DADMA]/BF₄ capsule stability. A) Before 10 cycles; B) After 10 cycles.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e13298>.

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