Polymeric ionic liquid-based membranes: influence of polycation variation on gas transport and CO₂ selectivity properties

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Abstract

This work evaluates the CO₂, CH₄ and N₂ permeation properties of five novel composite membranes based on polymeric ionic liquids (PILs) having different cation pendant units, namely imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium, combined with the same counter-anion ([NTf₂]⁻). The results show that the CO₂ permeability in the composite membranes is related to their respective CO₂ diffusivities, which are dependent on the PIL polycation nature. The composite membranes of the PILs containing different polycations and 10 wt% of free ionic liquid (IL) with similar structures to each PIL monomeric unit have CO₂ permeabilities between 3.66 and 20.4 Barrer, while they exhibit permselectivities ranging from 28.3 to 43.0 for CO₂/CH₄ and from 25.8 to 34.7 for CO₂/N₂. The best CO₂ permselectivities were obtained when tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) are used rather than imidazolium or pyridinium. Also, the results of this work indicate that the polycation backbones of PILs can also play a significant role in the design of PIL – IL membranes with the finest gas permeation properties and improved CO₂ separation performances.

Keywords: Polymeric ionic liquids, ionic liquids, composite membranes, gas transport, CO₂/CH₄ and CO₂/N₂ separation.

1. Introduction

The efficient separation of carbon dioxide from other light gases is a key chemical engineering and environmental challenge which has been extensively researched in recent years [1]. In particular, CO₂/CH₄ separation is of paramount importance in natural gas purification since CO₂ is a contaminant that not only reduces the heating value of methane gas as a fuel source but also causes corrosion in pipelines [2]. Additionally, the imminent climate change issues and environmental risks, due to increasing concentrations of anthropogenic CO₂, have recently highlighted the importance of carbon dioxide recovery from flue gas (CO₂/N₂ separation) produced by combustion of fossil fuels in electric power plants [3].

Different technologies, including absorption with amines, pressure swing adsorption using porous solids, cryogenic separation and membranes, have been proposed for CO₂ separation [4]. Although amines have advantages such as high reactivity and good absorption capacity allowing for highly efficient separation of CO₂ from the stream, the use of amines is of environmental and economical concern owing to their corrosive nature, volatility, and in some cases toxicity [5]. Besides cryogenic distillation and pressure swing adsorption processes which require high amounts of energy and equipment costs, gas membrane separation technology present several advantages such as low energy consumption and operating costs, easy scale-up and incorporation into existing processes, and small foot print [6, 7]. The major challenge in membrane operation, other than long operation term under different environmental conditions, is the need of having membranes with simultaneously high CO₂ permeability and selectivity. Thus, industrial and academic research has been undertaken and currently the goal is to design novel materials with improved CO₂ separation performances in order to make membrane-based processes more competitive.

1 A quite recent approach for CO₂ separation makes use of ionic liquids (ILs), a class
2 of materials that offer a unique set of properties such as negligible vapour pressure, high
3 thermal stability, low flammability, and high CO₂ solubility and selectivity over other
4 light gases. As a chemical platform, their most attractive feature within the CO₂
5 separation context is perhaps the easy tailoring of their physical/chemical properties as
6 well as their CO₂ affinity [8-10]. Many researchers have exploited these properties
7 using supported ionic liquid membrane (SILM) configurations [11-17], in which the
8 desired IL is immobilized into the pores of an inert polymer membrane by capillary
9 forces. Nevertheless, SILMs stability is still an open issue and their operation and long-
10 term stability is only possible at pressures up to 400 kPa due to the risk of IL draining
11 from the support pores [18]. In order to circumvent this drawback, different approaches
12 have been explored to prepare CO₂ separation membranes using ILs. For instance,
13 polymer/IL composite membranes have been developed by blending ILs with
14 poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [19, 20]. These
15 membranes have shown good mechanical strength and favorable gas transport
16 properties, but a limiting working pressure was also observed. Since the IL is entrapped
17 in the tight spaces between the polymer chains, there are no chemical bonds tethering
18 the IL to the polymer, and consequently high pressure differentials compress the
19 membrane and cast out the IL. Alternatively and considering that ILs present a unique
20 platform for monomer design, the most promising way to take advantage of ILs for CO₂
21 separation, and simultaneously overcome the inherent disadvantages of the previous
22 approaches, is to polymerize IL monomers and prepare polymeric ionic liquid-based
23 membranes [21].

24 Polymeric ionic liquids or poly(ionic liquid)s (PILs) are a new generation of
25 functional materials that comprise IL species connected through a polymeric backbone

generating a macromolecular architecture [22]. The potential of PILs as CO₂ separation membranes was initially addressed in 2006 by Noble's group [23]. Neat PIL membranes with functionalized imidazolium cation units containing substituent groups such as *n*-alkyl [24], oligo(ethylene glycol) or alkyl-terminated nitrile [25], were fabricated by photo-initiated chain-addition polymerization and their gas permeation properties were studied. Whilst these membranes demonstrated good CO₂/CH₄ and CO₂/N₂ permselectivities, their CO₂ permeabilities and diffusivities were significantly lower than those observed in analogous SILMs [26]. Consequently, different strategies have been investigated to design PIL-based membranes with improved CO₂ permeability and selectivity, including the blending of free ILs with PILs to form homogeneous PIL – IL composites [27-36], the synthesis of PIL copolymers to control segmental motion and chain packing for increasing gas permeability and mechanical stability of the membranes [37-39], and the incorporation of zeolites into PILs to prepare PIL – IL – zeolite mixed matrix membranes [40, 41]. Despite all the progresses and considering that the PIL-based CO₂ separation membranes tested so far comprise imidazolium-based PILs as polymer matrices [24, 25, 27-34, 38, 39], with the exception of our recent studies where PIL with pyrrolidinium polycations were used [35-37], additional research is still required to complete understand the relationships between PIL chemical structures and gas permeation properties. Although valuable clues regarding the role of specific structural variations on the imidazolium cationic moieties of the polymeric backbone [23-25, 30, 33, 34], or the influence of using different anions [32, 37, 42], can be gathered from literature, the gas permeation properties of PIL-based membranes having different cation functionalities attached to their polycation backbones have not yet been studied.

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In the present work, five novel membranes based on PILs containing the most important ionic liquid cations (imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium) and the bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻) as counter-anion, were prepared by the solvent casting method and gas permeation experiments using CO₂, CH₄ and N₂ were performed in order to fully explore the influence of polycation functionality in the CO₂ separation performance of PIL-based membranes for natural gas purification and flue gas separation. The PILs used herein (Fig. 1) were prepared in general via synthetic routes that consist on conventional free radical polymerization of the different prepared monomers with a thermal initiator followed by simple anion exchange reactions of the halides. The [NTf₂]⁻ was selected as the PILs counter-anion due, not only to its inherent CO₂-philic behavior and high thermal stability, but also to its relatively high commercial availability.

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2. Experimental section

2.1. Materials

Bromoethane (≥ 99%), 2-bromoethanol (95%), 1-vinylimidazole (≥ 99%), 4-vinylpyridine (95%), poly(diallyldimethylammonium) chloride solution (average Mw 400,000-500,000, 20 wt% in water), 2-(methacryloyloxy)ethyl trimethylammonium chloride solution (80 wt% in water), 2-(dimethylamino)ethyl methacrylate (98%), 2,2'-azobis (2-methylpropionamidine) dihydrochloride (AIBA, 97%), methanol (99.8%), acetonitrile (99.8%), acetone (99.8%) and ethyl acetate (99.8%) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide salt (LiNTf₂, 99%) was supplied by IoLiTec GmbH. All the chemicals utilized as starting materials in the synthesis of monomers and polymers were used as received without further purification. The water was double distilled, passed through a reverse osmosis system and further

1 treated with a Milli-Q plus 185 water purification equipment. Carbon dioxide (CO₂),
2 methane (CH₄) and nitrogen (N₂) were supplied by Air Liquide and were of at least
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4 99.99% purity.
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7 IoLiTec GmbH provided the 1-ethyl-3-methylimidazolium
8 bis(trifluoromethylsulfonyl)imide ([C₂mim][NTf₂]) (99 wt% pure), 1-ethyl-3-
9 methylpyridinium bis(trifluoromethylsulfonyl)imide ([C₂mpy][NTf₂]) (99 wt% pure), 1-
10 butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][NTf₂]) (99
11 wt% pure) and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide
12 ([N₄₁₁₁][NTf₂]) (99 wt% pure).
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21 Also called as ethylcholinium bistriflamide, *N*-ethyl-*N,N*-dimethyl-*N*-(2-
22 hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([N_{1122OH}][NTf₂]) (purity of
23 99%) was synthesized in our lab according to previously described synthetic routes
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31 In order to reduce the water and other volatile substances content, all the ionic liquid
32 samples were dried under vacuum and subject to vigorous stirring at ≈ 333 K for at least
33 2 days immediately prior to use. No further purification of the purchased ionic liquids
34 was carried out, but their purities were further evaluated by ¹H and ¹³C RMN analysis
35 and were found to be in accordance with the levels given by the supplier.
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46 2.2. Synthesis of polymeric ionic liquids

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48 Five polymeric ionic liquids (PILs) (Fig. 1) containing different polycations, namely
49 imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium pendant units, and
50 the [NTf₂]⁻ as counter-anion, were synthesized according to established literature
51 procedures [44-47]. As it can be seen in Fig. 2, depending on the target PIL different
52 reaction schemes were used. Overall, polymerizable ionic liquid-based monomers
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1 containing the desired cation units combined with halide anions were synthesized and
2 conventional free radical polymerization followed by simple anion exchange reaction
3 were carried out in order to prepare the different polycations having the $[\text{NTf}_2]^-$ as
4 counter-anion. The chemical structures of the prepared PILs were confirmed by ^1H - and
5 ^{13}C -NMR analysis.
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14 2.2.1. *Poly([ViEtIm][NTf₂])* (Fig. 2(a)). The monomer 1-vinyl-3-ethyl-imidazolium
15 bromide was prepared by mixing 10 g of 1-vinylimidazole (0.1062 mol), previously
16 distilled, with 17.4 g of bromoethane (0.1593 mol). The mixture was then allowed to
17 react at 318 K, in an oil bath for 16 hours with constant and vigorous stirring. After
18 cooling down at 268 K overnight, the resulting white precipitate was washed several
19 times with ethyl acetate, filtered and dissolved in methanol, which was then removed in
20 a rotary evaporator. The product was dried in a vacuum oven at room temperature until
21 constant weight was attained (yield: 76 %) and its purity was confirmed by ^1H -NMR.
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34 Poly([ViEtIm][Br]) was then synthesized by conventional free radical polymerization
35 in water. In a typical procedure, 15 g (0.0739 mol) of the prepared 1-vinyl-3-ethyl-
36 imidazolium bromide were dissolved in 150 mL of distilled water in a round bottom
37 flask. Then, an aqueous solution of the thermal radical initiator (0.075 g of AIBA and 2
38 mL of water) was added dropwise to the polymer solution and all the reactants were
39 mixed by vigorous stirring and purged with dry nitrogen for 30 min, before the sealed
40 flask was immersed in an oil bath at 338 K and kept for 3 hours. The amount of the
41 AIBA initiator was 0.5 wt% of the monomer used. After cooling down to room
42 temperature, the resulting aqueous solution was slowly dropwise added to an excess
43 amount of acetone in order to precipitate the polymer, which was then filtered and dried
44 under vacuum at 338 K until constant weight was attained (yield: 90 %).
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To prepare the poly([ViEtIm][NTf₂]), a simple anion exchange method was used, according to a procedure previously reported [44]. Briefly, the poly([ViEtIm][Br]) (8 g, 0.0394 mol) was dissolved in water (150 mL) and mixed by stirring for 30 min with an excess of an aqueous solution of LiNTf₂ (13.57 g, 0.0473 mol). Immediately after mixing, the formed polymer became hydrophobic and precipitated in the aqueous media as a result of the anion exchange reaction. The obtained yellow solid was washed with an excess amount of water, filtered and dried in a vacuum oven at 338 K until constant weight was attained (yield: 87 %).

2.2.2. *Poly([ViEtPy][NTf₂])* (Fig. 2(b)). First, the bromoethane (15.5 g, 0.1427 mol) was added dropwise under vigorous stirring to 10 g of 4-vinylpyridine (0.0951 mol) in a 100 mL one neck round bottom flask. The mixture was stirring at room temperature for 24 hours. The resulting red-pink solid was washed with ethyl acetate, filtered and dried (yield: 57 %). As expected for this case, instead of pyridinium monomer quaternary salt, the poly([ViEtPy][Br]) was formed [45]. The poly([ViEtPy][NTf₂]) was obtained following the same procedure used for poly([ViEtIm][NTf₂]). The obtained orange solid product was washed with water, filtered and dried (yield: 93 %).

2.2.3. *Poly([Pyr₁₁][NTf₂])* (Fig. 2(c)). This PIL, containing pyrrolidinium cation pendant units, was synthesized solely by carrying out the anion exchange reaction directly into the commercially available poly(diallyldimethylammonium) chloride, according to a procedure described elsewhere [46]. The obtained white solid poly([Pyr₁₁][NTf₂]) was washed with water, filtered and dried (yield: 95 %).

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2.2.4. *Poly([EMTMA][NTf₂])* (Fig. 2(d)). Initially, 20 g of the commercially available 2-(methacryloyloxy)ethyl trimethylammonium chloride solution (80 wt% in water) was diluted with 200 mL of distilled water and then 0.075 g of the thermal initiator AIBA were added. The free radical polymerization reaction was carried out at 338 K for 3 hours under nitrogen atmosphere. After that, the resulting poly([EMTMA][Cl]) was quantitatively obtained by evaporating the water. Poly([EMTMA][NTf₂]) was synthesized using the same anion exchange method described in detail for the preparation of poly([ViEtIm][NTf₂]) and a yield of 88 % was achieved.

2.2.5. *Poly([EMCh][NTf₂])* (Fig. 2(e)). In this case, the halide forms of both the monomer and the polymer, containing cholinium cation pendant units, were prepared via similar procedures to those previously reported [47]. First, 10 g (0.0636 mol) of 2-(dimethylamino)ethyl methacrylate were mixed with 11.92 g of 2-bromoethanol at 318 K for 24 hours. The resulting product was washed five times with an excess of ethyl acetate and dried under vacuum at room temperature to give the white solid cholinium ethyl methacrylate bromide (yield: 89 %). Afterwards, the prepared monomer was polymerized by free radical polymerization in water, which was carried out in sealed round bottom flask under nitrogen atmosphere at 338 K for 3 hours. The resulting aqueous polymer solution was added dropwise to an excess amount of acetone in order to precipitate the poly([EMCh][Br]), which was then filtered and dried in a vacuum oven at 318 K until constant weight was attained (yield: 85 %). As it is shown in Fig. 2, the same straightforward anion exchange procedure used for the other polycations was also successfully implemented to prepare the poly([EMCh][NTf₂]) (yield: 81 %).

2.3. Membranes preparation

Composite membranes based on the synthesized PILs (Fig. 1) with free ionic liquids (Fig. 3), containing the same anion and structural similar cations to the monomeric of the respective PIL, were prepared by solvent casting method. Initially, 6 (w/v)% solutions of each PIL in appropriate solvents were prepared and the corresponding ionic liquids were added in order to obtain solutions with 10 wt% of free IL to the polymer matrix. The solutions were magnetically stirred for 8 hours. Afterwards, transparent and free standing membranes were obtained by casting each solution into poly(tetrafluoroethylene) plates. The experimental conditions of the casting process used to prepare the different composite membranes are presented in Table 1. All solvents were slowly evaporated in a saturated solvent environment in order to obtain dense homogeneous membranes. Finally, all the composites were dried in an oven (338 K) until constant weight was attained. Membrane thicknesses (145– 190 μm) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample.

Porous hydrophobic poly(vinylidene fluoride) (PVDF) membranes provided by Millipore Corporation (USA), with a pore size of 0.22 μm and average thickness of 125 μm , were used to prepare SILM configurations of the pure ionic liquids according to our previously reported procedure [13]. The thickness of the SILMs was assumed to be equivalent to the membrane filter thickness.

2.4. Single gas permeation experiments

Single gas permeabilities and diffusivities through the prepared membranes were measured using a time-lag apparatus. Details on the construction and operation of this experimental setup are entirely described elsewhere [35]. All the membranes were

degassed under vacuum inside the permeation cell during 12 hours before testing, in order to remove entrained gases and traces of water. The single CO₂, CH₄ and N₂ permeation experiments were conducted at 293 K with an upstream pressure of 100 kPa (feed) and initial vacuum (< 0.1 kPa) as the initial downstream pressure (permeate). At least three separate experiments of each gas on a single membrane sample were carried out. No residual ionic liquid was found inside the permeation cell at the end of the experiments and, likewise, the membranes mass remained constant throughout the experiment.

Gas transport through the prepared composite membranes was assumed to follow a solution-diffusion mass transfer mechanism where the permeability (P) is related to solubility (S) and diffusivity (D) as follows [48]:

$$P = D \times S \quad (1)$$

Assuming a homogeneous membrane and ideal gas behaviour, the permeate flux of each gas (J_i) was determined using the following equation [49]:

$$J_i = \frac{V^p \Delta p_d}{A t R T} \quad (2)$$

where V^p is the permeate volume, Δp_d is the variation of downstream pressure, A is the effective membrane surface area, t is the experimental time, R is the Ideal Gas Law constant and T is the absolute temperature. The ideal (i.e. single gas) permeability (P_i) was then calculated from the pressure driving force (Δp_i) and membrane thickness (ℓ) according to Eq. (3).

$$P_i = \frac{J_i}{\Delta p_i / \ell} \quad (3)$$

The permeate diffusivity (D_i) was calculated from the membrane thickness (ℓ) and the time-lag parameter (θ) as shown in Eq. (4) [50].

$$D_i = \frac{\ell^2}{6\theta} \quad (4)$$

After knowing both P_i and D_i , it was also possible to calculate gas solubility (S_i) using the relationship shown in Eq. (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie i to the permeability of the less permeable specie j . As shown in Eq. (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j} \right) \times \left(\frac{S_i}{S_j} \right) \quad (5)$$

3. Results and discussion

On the contrary to the pyrrolidinium-PIL with the $[\text{NTf}_2]^-$ as counter-anion [35, 51], the other PILs synthesized in the present work, having different polycations and the same counter-anion, cannot be tested as pure PIL gas separation membranes as they are unable to be processed into a mechanically stable flat form membrane using the solvent casting method, due to their brittle nature. In order to measure the CO_2 , CH_4 and N_2 permeation properties and evaluate the influence of the polycation functionality on the CO_2 separation performance, composite membranes of the synthesized PILs (Fig. 1) with 10 wt% of free ILs (Fig. 3) were successfully prepared (Table 1). The ILs were chosen due to their structural similarity to the monomeric unit of the respective PIL. In particular, $[\text{C}_4\text{mpyr}][\text{NTf}_2]$, $[\text{N}_{4111}][\text{NTf}_2]$ and $[\text{N}_{1122(\text{OH})}][\text{NTf}_2]$ were used since similar ILs with smaller chains in the cation are solid at room temperature. The exact amount of 10 wt% of free IL was selected because it corresponds to the minimum amount of the plasticizer component (IL) necessary to obtain mechanical stable membranes, which do

not break during the gas permeation measurements. Generally, the presence of free IL enables an increase in the CO₂ permeability of PIL-based membranes with little, if no, sacrifice of their CO₂ permselectivities [27-29]. All the prepared composite membranes were homogeneous and exhibited no evidence of phase separation even after several months of storage under ambient conditions.

3.1. Gas permeability, diffusivity and solubility

The measured gas permeability and diffusivity values in the composite membranes containing the PILs with different polycations and 10 wt% of free IL are presented in Fig. 4 and Fig. 5, respectively, while the gas solubility values calculated using Eq. (1) are shown in Fig. 6. It should be pointed out that even though imidazolium-PILs have been extensively used as polymer matrices to prepare CO₂ separation membranes [24, 25, 27-34, 38, 39], the gas permeation properties of PIL-based membranes containing pyridinium, ammonium and cholinium cations in the polymer backbone are reported here for the first time. Concerning the pyrrolidinium-PIL, a comparison of CO₂, CH₄ and N₂ permeabilities measured in this work with values previously determined by us for similar membranes is shown in Table 2. Although an exact comparison of these results cannot be made due to the different IL content used in the present work (10 wt%), the permeability values of the three gases in the PIL pyrrolidinium – 10 IL are between those reported for the pure PIL and the composite membrane containing 20 wt% of the same free IL ([C₄mpyr][NTf₂]). This is in agreement to what has been observed by different authors [19, 33, 35, 51], where the gas permeability values increase with the amount of free IL incorporated into the PIL membranes.

The results presented in Fig. 4 show that the composite membranes containing distinct PILs and 10 wt% of free IL possess gas permeabilities that are substantially

different than those of PIL imidazolium – 10 IL. The highest gas permeabilities were obtained for PIL pyridinium-based membrane, whilst the PIL cholinium exhibited the lowest gas permeabilities. In fact, the relative gas permeability enhancement or reduction is clearly dependent on the polycation backbone (Fig. 4). For example, the obtained CO₂, CH₄ and N₂ permeabilities of PIL pyridinium – 10 IL were 20.4, 0.81 and 1.01 Barrer, respectively, which are about 1.3 times higher than those achieved with PIL imidazolium. In contrast, the PIL pyrrolidinium – 10 IL presented a CO₂ permeability of 11.5 Barrer, which is roughly 1.3 times smaller than that of PIL imidazolium (14.9 Barrer). Moreover, the gas permeability reductions between PIL imidazolium – 10 IL and PIL cholinium – 10IL, in which the CO₂, CH₄ and N₂ permeabilities decreased by 303%, 556% and 473%, are larger than those between PIL imidazolium – 10 IL and PIL ammonium – 10 IL, where permeability reductions of only 59%, 97% and 70% occurred, respectively. Although PIL cholinium has a bulkier tetra-alkyl ammonium pendant unit connected to the poly(methyl methacrylate) backbone than that of analogous PIL ammonium, the presence of the hydroxyl group seems to increase linear chain packing, certainly through hydrogen bond interactions, contributing to a more polymer packed membrane with higher resistance to gas diffusion.

We also noticed that diffusivity is the primary factor differentiating the gas permeabilities among the composite membranes comprising the PILs with different polycations. For instance, the CO₂ and N₂ permeabilities (Fig. 4) are related with their respective gas diffusivities (Fig. 5), both following the order of the polycation backbone variation as: PIL pyridinium > PIL imidazolium ≥ PIL pyrrolidinium > PIL ammonium > PIL cholinium. The obtained results clearly show that PILs with pyridinium or imidazolium polycations exhibited higher CO₂ permeabilities and diffusivities compared to those having tetra-alkyl ammonium pendant units. Conversely, the

opposite behavior occurs in CO₂ solubility. As it can be seen from Fig. 6, tetra-alkyl ammonium-based PIL, namely pyrrolidinium, ammonium and cholinium, possess higher CO₂ solubility than imidazolium- and pyridinium-based PILs, which can be caused by their localized charge density that results in stronger interactions with CO₂ and consequently contributes for lower CO₂ permeabilities and diffusivities. These findings also suggest that the CO₂ solubility in the prepared composite membranes can be improved by increasing the polycation polarity.

Overall, our results demonstrate that the type of polycation influences the gas transport properties. Depending on the chemical structure of the polycation, the PIL chains interact and pack differently and thus PIL – IL composite membranes with different gas permeabilities, diffusivities and solubilities can be obtained.

3.2. CO₂ separation performance

The measured CO₂ permeabilities and both the CO₂/CH₄ and CO₂/N₂ permselectivities of all the studied composite membrane are summarized in Table 3. These results are also plotted on the so-called Robeson plots [52], where the comparison of CO₂/CH₄ and CO₂/N₂ separation performances between the results obtained in this work and the previously published data for other PIL-based membranes can be evaluated, respectively, in Fig. 7(a) and Fig. 7(b).

In contrast to what has been observed for PIL – IL membranes with IL contents higher than 20 wt% [25, 28-30, 33, 35, 37], and also for SILMs [13, 15, 17, 26], the Robeson plots indicate that CO₂/CH₄ (Fig. 7(a)) is a more favorable separation than CO₂/N₂ (Fig. 7(b)) for the composite membranes herein prepared. With the exception of PIL pyrrolidinium – 10 IL, that presents similar permselectivities values for both separations, the CO₂/CH₄ permselectivity is always higher than the CO₂/N₂

permselectivity (Table 3) since the N_2 permeability is greater than that of CH_4 in the prepared composite membranes. Nevertheless, these results are in agreement with previous studies on pure PIL membranes [35, 53]. It means that, in the case of PIL – IL membranes blended with only 10 wt% of free IL, the polymer matrix has great influence on their permselectivity properties. Looking at the results presented in Table 3, the composite membranes comprising the different PILs have indeed intrinsically superior CO_2/CH_4 permselectivities, whereas the CO_2/N_2 values are smaller than those of their ionic liquid analogues in SILM configurations.

Fig. 7 shows that the CO_2 separation performances of the prepared composite membranes with 10 wt% of free IL are below the CO_2/CH_4 and CO_2/N_2 upper bounds, close to available literature data for the neat PIL membranes. However, it can also be observed that the use of PILs possessing different polycation backbones impacts the CO_2/CH_4 and CO_2/N_2 separation performance of the composite membranes. For example, the use of PIL pyridinium increases the CO_2 permeability without affecting CO_2/CH_4 permselectivity, but it also decreases the CO_2/N_2 permselectivity of the PIL pyridinium – 10 IL compared to PIL imidazolium – 10 IL. On the other hand, the presence of tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) decreases the CO_2 permeability of the composite, whereas they promote improved CO_2/CH_4 and CO_2/N_2 permselectivities (Table 3) compared to those of the composite membrane comprising the PIL imidazolium. Even though PIL cholinium promotes the lowest gas permeabilities (Fig. 4) and diffusivities (Fig. 5), remarkable CO_2/CH_4 and CO_2/N_2 permselectivities of 43.0 and 34.7, respectively, can be achieved using this PIL as polymer matrix. This behavior is in accordance with the well known trade-off between flux and selectivity, which means that improvements in polymeric membrane permselectivities are generally associated to a reduction of their gas

permeabilities. Taking into account that the diffusivity selectivities of all the studied membranes are between 0.4 and 1.9, the membranes of tetra-alkyl ammonium-based PILs are intrinsically more CO₂ permselective probably due to their high CO₂/CH₄ (29.4 – 71.6) and CO₂/N₂ (52 – 59) solubility selectivities compared to those (CO₂/CH₄ 13.4 – 18.3, CO₂/N₂ 28.4 – 39.0) obtained when PIL imidazolium or PIL pyridinium are used.

All the above mentioned evidences contribute to understand the behavior and show the influence of polycation variation on the CO₂ separation performance of these materials. It is clear that the structure of the polycation functionality can play an important role in the gas transport properties through PIL – IL membranes.

4. Conclusions

Five polymeric ionic liquids containing different polycations and the [NTf₂]⁻ as counter-anion were synthesized by suitable reaction schemes. Since the nature of the pure PILs was very brittle and their films easily broke, composite membranes with 10 wt% of free ionic liquids having similar chemical structures to each PIL monomeric unit were prepared and their single CO₂, CH₄ and N₂ permeation properties were measured.

The results showed that the membranes based on the tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) generally have lower gas permeabilities and diffusivities, whereas they present higher CO₂/CH₄ and CO₂/N₂ permselectivities than those of membranes containing PIL imidazolium and pyridinium. The gas permeabilities, diffusivities and solubilities in the composite membranes were found to be dependent on the PIL polycation backbone. Moreover, the Robeson plots showed that CO₂/CH₄ is more favorable separation for the prepared composite membranes, but their performance is still below the upper bounds (from 2008) for both

1 separations CO₂/CH₄ and CO₂/N₂. Overall, the results of this work not only point out
2 that the PIL polycation nature can influence the CO₂ separation in PIL – IL composite
3 membranes, but also reaffirm that to better understand and thus improve the gas
4 transport through these type of membranes it is necessary to further explore the
5 available high diversity of chemical structures that are inherent to PILs.
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12 Even though it is evident that the PIL polycation variation alone cannot promote the
13 large improvement in gas permeability required for these membranes to be
14 technologically competitive, the knowledge gained from this work, particularly
15 regarding the relationships between PIL structure and gas transport properties, is
16 undoubtedly important for the development of PIL-based membranes with superior CO₂
17 separation performances.
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Table 1 Composition and experimental conditions of the procedure used to prepare each membrane studied.

Membrane sample	Polymer (PIL)	10 wt % of Ionic Liquid (IL)	Solvent	T (K)	Evaporation time (days)
PIL imidazolium – 10 IL	Poly([ViEtIm][NTf ₂])	[C ₂ mim][NTf ₂]	Acetonitrile	303	3
PIL pyridinium – 10 IL	Poly([ViEtPy][NTf ₂])	[C ₂ py][NTf ₂]	Acetonitrile	303	3
PIL pyrrolidinium – 10 IL	Poly([Pyr ₁₁][NTf ₂])	[pyr ₁₄][NTf ₂]	Acetone	298	2
PIL ammonium – 10 IL	Poly([EMTMA][NTf ₂])	[N ₄₁₁₁][NTf ₂]	Acetonitrile	303	3
PIL cholinium – 10 IL	Poly([EMCh][NTf ₂])	[N _{1122(OH)}][NTf ₂]	Acetonitrile	303	3

Table 2 Comparison of CO₂, CH₄ and N₂ permeabilities (P)^a measured in this work with the values previously determined using the same experimental conditions (20 °C with a trans-membrane pressure differential of 100 kPa) for pyrrolidinium-based PILs.^b

Membrane	P CO ₂	P CH ₄	P N ₂
Pure PIL pyrrolidinium ^c	5.09 ± 0.03	0.18 ± 0.01	0.23 ± 0.01
PIL pyrrolidinium – 10 IL	11.5 ± 0.09	0.41 ± 0.01	0.40 ± 0.01
PIL pyrrolidinium – 20 IL ^c	25 ± 0.16	0.98 ± 0.03	0.78 ± 0.01

^a Barrer (1 Barrer = 10⁻¹⁰ cm³(STP)cm cm⁻² s⁻¹ cmHg⁻¹)

^b The listed uncertainties represent the standard deviations, based on three experiments.

^c Values taken from Tomé *et al.* [35].

Table 3 Single CO₂ permeability (P)^a measured at 20 °C and ideal permselectivities (α) of the membranes studied.^b

Membrane sample	P CO ₂	α CO ₂ /CH ₄	α CO ₂ /N ₂
PIL imidazolium – 10 IL	14.9 ± 0.12	25.1 ± 1.0	23.7 ± 0.5
PIL pyridinium – 10 IL	20.4 ± 0.07	25.1 ± 0.3	20.1 ± 0.8
PIL pyrrolidinium – 10 IL	11.5 ± 0.09	28.3 ± 1.0	28.9 ± 0.8
PIL ammonium – 10 IL	9.44 ± 0.13	31.5 ± 4.4	25.8 ± 2.9
PIL cholinium – 10 IL	3.66 ± 0.01	43.0 ± 1.1	34.7 ± 0.9
SILM [C ₂ mim][NTf ₂] ^c	589 ± 1.0	18.1 ± 0.3	35.5 ± 0.3
SILM [C ₂ mpy][NTf ₂]	536 ± 3.3	17.6 ± 0.2	31.9 ± 0.6
SILM [C ₄ mpyr][NTf ₂] ^d	340 ± 0.7	14.0 ± 0.1	28.4 ± 0.3
SILM [N ₄₁₁₁][NTf ₂]	333 ± 0.4	15.4 ± 0.1	27.2 ± 0.3
SILM [N _{1122OH}][NTf ₂]	84 ± 0.2	21.8 ± 0.1	37.4 ± 0.3

^a Barrer (1 Barrer = 10⁻¹⁰ cm³(STP)cm cm⁻² s⁻¹ cmHg⁻¹)

^b The listed uncertainties represent the standard deviations, based on three experiments.

^c Values taken from Tomé *et al.*[13].

^d Values taken from Tomé *et al.*[35].

Fig. 1 Chemical structures of the prepared polymeric ionic liquids (PILs): (a) poly([ViEtIm][NTf₂]), (b) poly([ViEtPy][NTf₂]), (c) poly([Pyr₁₁][NTf₂]) (d) poly([EMTMA][NTf₂]), (e) poly([EMCh][NTf₂]).

Fig. 2 Schemes illustrating the synthesis of the polymeric ionic liquids containing different polycation functionalities (a) imidazolium, (b) pyridinium, (c) pyrrolidinium, (d) ammonium and (e) cholinium, combined with the NTf₂ as counter-anion.

Fig. 3 Chemical structures and short names of the ionic liquids used to prepare the composite membranes.

Fig. 4 Gas permeabilities ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP})\text{cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) through the prepared composite membranes at 20°C . Error bars represent standard deviations based on three experimental replicas.

Fig. 5 Gas diffusivities through the prepared composite membranes at 20 °C. Error bars represent standard deviations based on three experimental replicas.

Fig. 6 Gas solubilities in the prepared composite membranes, calculated using Eq. (1).

Fig. 7 CO₂ separation performance of the studied composite membranes plotted on (a) CO₂/CH₄ and (b) CO₂/N₂ Robeson plots. The experimental error is within the data points. Data are plotted on a log-log scale and the upper bound for each gas pair is adapted from Robeson [52]. For comparison, also plotted in (a) and (b) are literature data previously reported for (□) other PIL – IL membranes [27-32, 34, 35, 37, 38], and (○) neat PIL membranes [25, 30, 32, 34, 35, 42, 53].