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Synthesis and gas separation properties of poly(ionic liquid)-ionic liquid composite membranes containing a copper salt

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Abstract

Composite poly(ionic liquid)-ionic liquid membranes containing copper (I) chloride (CuCl) have been successfully fabricated via photopolymerization of an IL monomer, 1-vinyl-3-butylimidazolium bistriflimide ($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$), in the presence of CuCl and a non-polymerizable IL, 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}][\text{Cl}]$), forming the chlorocuprate anion ($[\text{CuCl}_2]^-$) in situ. The influence of the metal salt content on the gas separation performance of the composite membranes was assessed. Results showed that increasing the content of non-polymerizable IL enhanced the permeabilities of CO_2 , H_2 , N_2 and CO relative to those obtained in the pristine poly($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$); whereas the addition of CuCl induced a general reduction of gas diffusivity. On the whole, and enhancement of both gas permeability and ideal gas pair selectivity were observed for CO_2/N_2 and H_2/N_2 separations in the Cu-containing composite membranes with respect to the neat poly($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$).

Keywords

Polymer, ionic liquid, membrane, copper (I) chloride, gas separation

1. Introduction

The well-known properties of ionic liquids (ILs), namely extremely low vapor pressure and high thermal stability, together with the vast matrix of possible cation/anion combinations as well as the high affinity towards targeted compounds have boosted their application as gas separation agents in absorption [1] and membrane processes [2,3] over the past decade. Although this field has been in development since 2002 [4] employing ILs as supported ionic liquid membranes (SILMs), recent reviews continue to highlight the mechanical stability of SILMs as a recurrent concern among researchers [5,6]. Despite avoiding the risk of failure due to solvent evaporation from the support, ILs can still be expelled from the membrane pores at relatively low transmembrane pressure differentials exceeding the capillary forces that hold the IL within the support and therefore, pressure differentials applied to SILMs rarely exceed 200 kPa.

Current approaches to face the stability drawbacks inherent to SILMs focus on: (i) the gelation of the IL phase, (ii) the preparation of composite polymer-IL membranes and (iii) the synthesis of polymerizable ILs (poly(ILs)) and preparation of poly(IL)-IL composite films. To a lesser extent, gelled membranes have been prepared by combining ILs with small loadings, typically within 2%, of a gelator, e.g., gelatine, oligomeric electrolytes, saturated fatty acids and aspartame-based cyclo(dipeptide)s [7-16]. Although these membranes became mechanically stable at moderate pressures, the gas permeability decreased between 10-50% compared to conventional SILMs and the thermal stability was limited by the gelation temperature, that is, the temperature above which the gel becomes a fluid.

A more extended approach to the stabilization of IL-based membranes has been the development of composite films by blending ILs with common polymers such as

polyimides, poly(vinylidene fluoride) and copolymers like poly(vinylidene fluoride-hexafluoropropylene) or polyether block amides [17-28]. These membranes are easily prepared by solution casting of a mixture containing the IL, the polymer and a proper solvent in which the IL and polymer are mutually miscible. After evaporation of the solvent, the IL phase is embedded within the polymer matrix, which prevents the expelling of the IL at high pressure differences. The permeability of light gases through polymer-IL films increased, with respect to that of the neat polymer, with increasing IL content owing to the faster gas diffusion in ILs than in polymers; yet this happened at the expense of slightly decreasing the selectivity, except for CO₂/H₂ separation, and worsening the mechanical and thermal stabilities due to the fact that both the Young's modulus and melting temperature of the composites also decreased. The observed gas transport behavior through these composite membranes presumably indicates that while diffusivity differences promote the gas separation at low IL content, it is the solubility selectivity that dominates at high IL content, as also occurs in SILMs.

Another approach to face the stability drawbacks attributed to SILMs relies on tethering polymerizable functional groups to the cation or anion of ILs and subsequent polymerization of these IL monomers to form self-supported polymerized ionic liquids (poly(ILs)) [29]. Despite the wide number of poly(IL)-based membranes synthesized varying the polymerizable groups (vinyl, styrene, acrylate) as well as the length and chemical composition of the pendant groups, these poly(ILs) commonly reported substantially lower permeabilities of 1-2 orders of magnitude less than their analogous non-polymerizable ILs [30-37]. In light of these facts, the synthesis of composite membranes by blending poly(ILs) with "free" non-polymerizable ILs seems to be the most promising strategy to obtain membranes that preserve the mechanical and thermal stability of common polymers [38] while providing high permeation rates and

separation factors close to those obtained with SILMs, which are attractive for industrial purposes. Although these poly(IL)-IL composites are analogous to the composites of ILs with conventional polymers previously mentioned, in the poly(IL)-IL composites, additional Coulombic attractions provide strong ion-ion interactions between the charged polymer and the IL phase. This allows forming stable blends with high free IL content. Simultaneously, the IL serves as non-volatile plasticizer of the rigid poly(IL) matrix, thus enhancing the diffusivity of the gas species and, although most of the initial results did not meet the expected performance, there are certain combinations that provide separation efficiencies very close or even above the Robeson upper-bound plots in terms of permeability of target species and selectivity over other compounds [39-47]. In addition, recent works have reported that supported thin-film (nano layers) of poly(IL)-IL composites exhibit excellent CO₂ permeation rates together with acceptable CO₂/N₂ selectivities [48], thus indicating that there is still a lot of room for improvement in the development of this type of membranes.

In previous works, we aimed at enhancing the transport of carbon monoxide (CO) through SILMs that contained dissolved CuCl in [C₆mim][Cl] [49]. In that system, chlorocuprate(I) anions ([CuCl₂]⁻) with improved stability against oxidation and disproportion were formed due to the use of chloride ions as stabilizing ligands for the cuprous ion, which otherwise is readily oxidized to the cupric state [50]. These chlorocomplexes have the ability to selectively and reversibly bind CO molecules, hence greatly increasing the solubility of CO [51,52], which we believe can be employed to design facilitated-transport membranes.

Therefore, in this work, the effect of the incorporation of this metal salt into poly(IL)-IL composites is explored as a means to improve the gas separation performance and the membrane stability of previously studied SILMs. To that end, three-component

composite membranes (poly(IL)/IL/salt) were prepared and the permeation properties of the light gases CO₂, H₂, CO and N₂ were assessed.

2. Experimental

2.1. Materials

The synthesis of Cu(I)-based poly(IL)-IL composites requires the combination of an IL-based monomer that contains a polymerizable functional group and a compatible non-polymerizable IL. The IL monomer 1-butyl-3-vinylimidazolium bistriflimide, [C₄vim][Tf₂N], which has already been employed in other works [34,41], was used here to fabricate the polymer matrix. On the other hand, two different ILs were initially selected as non-polymerizable ILs: [C₄mim][Cl], which easily dissolves CuCl; and [C₂mim][Tf₂N], which contains an anion in common with the IL monomer, so as to increase the chemical compatibility, and is much less viscous than [C₄mim][Cl] which helps facilitate mixing. The general structures of the IL monomer and non-polymerizable ILs are depicted in Figure 1.

In this work, [C₄mim][Cl] and [C₂mim][Tf₂N] were synthesized following classical literature procedures [53,54], whereas the IL-based monomer [C₄vim][Tf₂N] was prepared as follows: 1-chlorobutane (220 mmol) was dissolved dropwise in 1-vinylimidazole (110 mmol) in a 100-mL pressure tube. Acetonitrile (20 mL) was then added, the tube sealed, and the solution heated while under stirring for 48 h at 80°C. After this time, the alkylation reaction was stopped and the mixture poured in Et₂O (300 mL) and placed in a freezer overnight to obtain crude [C₄vim][Cl] by precipitation. To proceed with the anion-exchange reaction, the diethyl ether phase was decanted and the product dissolved in deionized H₂O (125 mL) in a 250 mL round-bottom flask. The

aqueous phase was washed with 3 x 100 mL of EtOAc. Then, lithium bistriflimide (120 mmol), was added and the mixture stirred for 3 h at room temperature ($\sim 22^{\circ}\text{C}$). An oily precipitate was formed which was assumed to be the $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$ product. The aqueous phase was decanted and the precipitate was dissolved in 150 mL CH_2Cl_2 . The organic phase was washed with 5 x 75 mL deionized H_2O , with AgNO_3 used to confirm the absence of Cl^- in the final two washings. Afterwards, the organic phase was dried over anhydrous MgSO_4 and the filtrate reduced in a rotary evaporator. Finally, the product was further dried under vacuum at 313 K while stirring overnight and obtained as a clear, colorless liquid. ^1H NMR were consistent with published values [43].

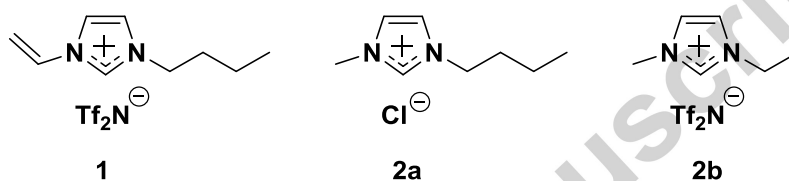


Figure 1. Structures of (1) IL-based monomer $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$ and non-polymerizable ILs: (2a) $[\text{C}_4\text{mim}][\text{Cl}]$ and (2b) $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$.

2.2. Membrane preparation and characterization

In this work, the composite poly(IL)-IL membranes were prepared combining in several molar ratios the IL-based monomer (1), a non-polymerizable IL (2a or 2b) and the copper(I) salt CuCl . Both of the non-polymerizable ILs considered in this work were soluble in the IL monomer $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$; however, CuCl could not be solubilized in the binary mixture of $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$ and $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ and a particulate suspension was obtained instead, thus indicating that an excess of Cl^- anions was required to form the $[\text{CuCl}_2]^-$ complexes and obtain an homogeneous IL solution. Therefore, composite poly(IL)-IL membranes were only fabricated blending $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$, $[\text{C}_4\text{mim}][\text{Cl}]$ and CuCl . Mixing these three ionic substances yielded a red-colored solution thus indicating

that some favorable interactions were taking place. To obtain a poly(IL)-IL composite film, the photoinitiator 2-hydroxy-2-methylpropiophenone (1 wt %) was dissolved in the ternary solution of 1 + 2a + CuCl and the photoinitiator was then homogenized by employing a vibrating mixer. Afterwards, the solution was poured on a piece of microporous nylon membrane (0.45 μm pore size, 0.8 porosity, Nylaflo, Pall) that had been placed on top of a quartz plate treated with a hydrophobic monolayer. An identical quartz plate was then positioned on top and the whole assembly was placed under a 254 nm UV lamp (UV crosslinker, VWR) for 3 h until complete polymerization as verified by FT-IR (Spectrum 2, Perkin Elmer). Finally, the membrane was punched to a 47 mm diameter disc using a steel die with a final thickness of ~ 150 μm . Portions of self-supported poly(IL)-IL composites (without support) were collected for characterization with FT-IR.

2.3. Gas permeability and diffusivity measurements

The gas permeation properties through the composite membranes were determined employing a time-lag apparatus. Details on the experimental set-up and measurement procedure can be found in previous works [30]. The permeability of the single gases N_2 , CO_2 , H_2 and of a binary N_2/CO mixture (90/10 vol %) were measured at room-temperature (295 K) and replicated at least three times. A typical plot of the permeate volume profile obtained in these experiments is shown in Figure 2. The permeability of one single gas (ρ_i) through the composite membranes was then obtained from the steady-state flux (J_i), which is proportional to the permeate pressure increase with time, that is, the slope of the steady-state portion of Figure 2 $\left(\frac{\Delta P_p}{\Delta t} \right)_{ss}$.

$$\phi_i = J_i \cdot \frac{\delta}{\Delta P_i} = \frac{V_p}{A \cdot R \cdot T \cdot \phi} \cdot \left(\frac{\Delta P_p}{\Delta t} \right)_{ss} \cdot \left(\frac{\delta}{\Delta P_i} \right) \quad (1)$$

where V_p is the permeate chamber volume, A is the membrane area, T is the temperature, ΔP_i is the pressure difference between the feed and permeate chambers, and ϕ and Δz the porosity and thickness of the support employed, respectively.

On the other hand, with this technique it is also possible to obtain the gas diffusivity (D_i) through the membrane by extrapolating the slope of the steady-state flux towards the time axis. The intercept is known as the time-lag (θ) of the gas and is related to the gas diffusivity and the membrane thickness according to Eq. (2).

$$D_i = \frac{\Delta z^2}{6\theta} \quad (2)$$

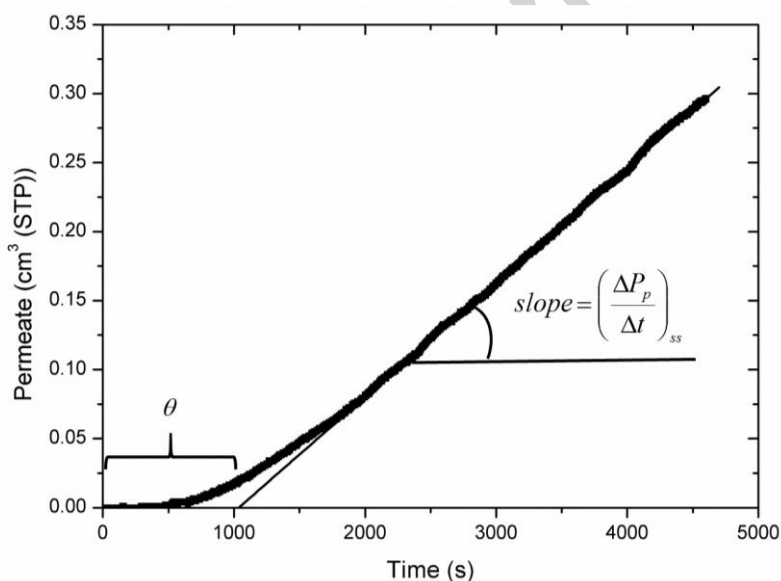


Figure 2. Permeate volume data of CO₂ through a PIL-IL composite membrane (75 mol % [C₄vim][Tf₂N] - 25 mol % [C₄mim][Cl]) and determination of gas permeation properties employing the time-lag technique.

Then the solubility coefficient (S_i) can be directly obtained from the relationship given by

$$\phi_i = S_i \cdot D_i \quad (3)$$

Therefore, the ability to separate two different gases, known as membrane selectivity (α_{ij}), is defined as the ratio of the individual gas permeabilities, hence it can also be expressed as the product of the ratio of diffusion coefficients (diffusivity selectivity) times the ratio of solubility coefficients (solubility selectivity).

$$\alpha_{ij} = \frac{\phi_i}{\phi_j} = \left(\frac{D_i}{D_j} \right) \cdot \left(\frac{S_i}{S_j} \right) \quad (4)$$

3. Results and discussion

3.1 Membrane characterization

So far, the direct synthesis of metal-containing PIL-IL composite membranes by UV-photopolymerization has not been reported. Only Ag^+ -containing PIL-IL membranes that provided selective transport of ethylene over ethane have been obtained by Tomé et al. [55], but in that case, they blended a silver salt dissolved in a non-polymerizable IL with an already polymerized IL dissolved in acetone and then, cast the membrane.

For this reason, in this work, the membrane compositions that would yield mechanically stable films was completely unknown beforehand and more than 20 different PIL-IL composite films were initially fabricated combining the IL-based monomer (1), the non-polymerizable IL (2a) and CuCl salt in several proportions. It was found that the IL-based polymer, poly($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$), was brittle whereas PIL-IL membranes containing $[\text{C}_4\text{mim}][\text{Cl}]$ were rubbery-like due to the presence of free IL that acted as a plasticizer

of the polymer matrix. Moreover, it was determined that the ratio of [C₄mim][Cl] to CuCl has to be around 4-5 in order to obtain self-supported Cu(I)-based membranes; otherwise, either a sticky gel was obtained or the membrane formed was too brittle to handle. The lower content of IL-based monomer with which stable membranes could be fabricated was 50 mol %. Among these membranes, five were selected to perform the gas permeability measurements, whose composition is listed in Table 1. Membrane 1 was pure poly([C₄vim][Tf₂N]), membranes 2 and 3 combined the IL-based monomer with up to 25 mol % of free [C₄mim][Cl] and membranes 4 and 5 also contained CuCl in different proportions.

Table 1. Composition of PIL-IL composite membranes.

PIL-IL membrane	Composition (mol %)		
	[C ₄ vim][Tf ₂ N]	[C ₄ mim][Cl]	CuCl
1	100	0	0
2	90	10	0
3	75	25	0
4	70	25	5
5	60	32	8

The composite PIL-IL membranes were analyzed with FTIR spectroscopy in order to evaluate the degree of polymerization, i.e., the vinyl group conversion. The FTIR spectra before UV-polymerization and that of the resulting membrane are shown in Figure 3. The characteristic peaks of the vinyl group, which can be observed at IR wavenumbers of 916 and 958 cm⁻¹ (CH₂ and CH wag) and 1659 cm⁻¹ (C=C stretching) [44], completely disappeared after polymerization hence indicating a high degree of monomer conversion (>95%) after 3 h. This was observed for all the membranes synthesized regardless of the IL-based monomer concentration.

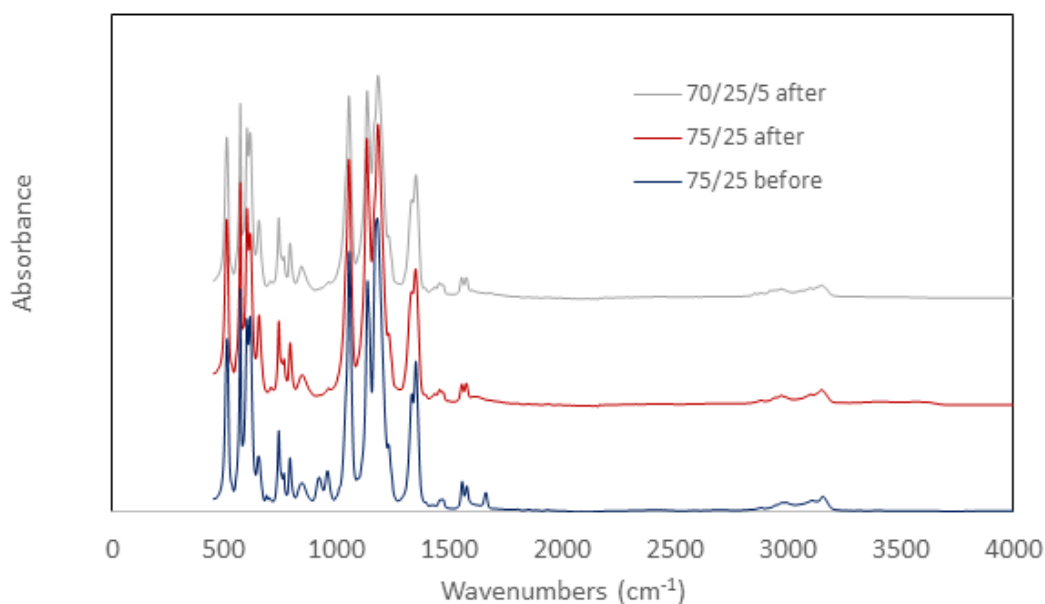


Figure 3. FT-IR spectra of IL-monomer + non-polymerizable IL (without CuCl and with 5 mol % CuCl) before and after polymerization.

3.2. Gas transport properties through composite films

3.2.1. Poly([C₄vim][Tf₂N])- [C₄mim][Cl]

The gas permeation properties of PIL-IL membranes without copper salt are discussed first. The experimental permeability, diffusivity and solubility coefficients obtained from these membranes are presented in Table 2. The neat poly([C₄vim][Tf₂N]), membrane 1, exhibited low gas permeabilities, particularly, if they are compared to other PIL membranes with the same alkyl chain length but different polymerizable functional groups. For instance, the CO₂ permeability was just 5.2 barrer in the vinyl-based poly(IL), while Bara et al. [30] found permeabilities of 20 and 22 in the styrene- and acrylate-functionalized analogous polymers, respectively. In any case, these low permeability values are typical for many poly(IL) membranes [31-33,36,44,46,56]. In

fact, the CO₂ permeability obtained through poly([C₄vim][Tf₂N]) is consistent with the result found by Carlisle et al. [34], e.g., CO₂ permeability of 4.8 barrer through poly([C₁vim][Tf₂N]), which is another vinylimidazolium-based polymer with a shorter alkyl chain than the one used in this work. Results of H₂ permeability are also in accordance with the scarce number of works that report permeability data for this gas, for instance, Bhavsar et al. [33] reported H₂ permeabilities that ranged between 1.4 and 18.3 barrer through several PIL membranes. These results can be attributed to the formation of a rigid polymer matrix in which gas diffusion is restricted as can be inferred from the rather low diffusion coefficients, e.g., 0.22 and 7.8 x 10⁻⁸ cm² s⁻¹ for CO₂ and H₂, respectively. Regarding the N₂ permeability, it was one order lower than that of CO₂ and H₂ and identical to the permeability of the N₂/CO mixture indicating that both N₂ and CO possess very low permeabilities owing to their minimal solubilities. Unfortunately, determining the time-lag of the gases with very low permeation rates could not be done without high uncertainty, thus diffusivity and solubility data for CO and N₂ are not reported here. On the other hand, the gas permeation after inclusion of a non-polymerizable IL within the polymer matrix was assessed through the poly([C₄vim][Tf₂N])-[C₄mim][Cl] (membranes 2 and 3). As expected, the permeability of all gases increased with the presence of [C₄mim][Cl] due to the faster gas diffusivity through the non-polymerized IL phase than through the PIL matrix.

Table 2. Gas permeation properties through poly([C₄vim][Tf₂N])- [C₄mim][Cl] composite membranes at 293 K.

Membrane	Gas	P (barrer)	D ¹ (x 10 ⁷ cm ² s ⁻¹)	S (cm ³ cm ⁻³ MPa ⁻¹)
1	N ₂	0.3	N/A	N/A
	CO ₂	5.2	0.22	18.1
	H ₂	4.9	7.8	0.48
	N ₂ /CO	0.3	N/A	N/A
2	N ₂	0.3	N/A	N/A
	CO ₂	7.2	0.37	14.5
	H ₂	5.4	12.4	0.33
	N ₂ /CO	0.3	N/A	N/A
3	N ₂	0.9	N/A	N/A
	CO ₂	26.7	0.91	22.0
	H ₂	9.9	21.6	0.35
	N ₂ /CO	1.0	N/A	N/A

¹N/A: time-lag could not be accurately determined due to very slow permeation rate.

3.2.2. Copper(I)-containing poly([C₄vim][Tf₂N])- [C₄mim][Cl]

Let us now consider the effect of copper(I) chloride salt addition on the gas transport properties through the composite membranes 4 and 5 which are collected in Table 3, together with the results of membrane 3 for comparison purposes. The comparison of membranes 3 and 4, which contain the same amount of free [C₄mim][Cl], reveals that gas permeability significantly decreased after addition of 5 mol% CuCl, e.g., H₂ permeability decreased from 9.9 to 5.7 barrer. These results can be attributed to an inhibition of gas diffusion, which was reduced from 21.6 to 5.3 x 10⁻⁷ cm² s⁻¹. This trend, however, is not surprising as it had already been observed by Tomé et al. [54] in the previously mentioned Ag⁺-containing membranes. In that work, the observed general reduction of gas diffusivity upon increasing concentration of silver salt was attributed to an increased packing efficiency, and consequently reduced fractional free volume, owing to strong interactions between the silver salt and the IL.

On the other hand, the CO₂ and H₂ gas diffusivities in membrane 5, which contains 8 mol % of CuCl, were higher than in membrane 4 due to the higher content of non-polymerizable IL; however, a reduction of the gas solubilities was observed. In addition, it was expected that permeation rates of the N₂/CO mixture (90/10 vol %) through membranes 4 and 5 would be higher than that of pure N₂ owing to the synergistic effect of a carrier-mediated transport available for CO molecules. Although this transport mechanism has already been reported for SILMs with similar IL composition [49,55], in which the [CuCl₂]⁻ species reversibly and selectively react with CO, there was no evidence of CO facilitated-transport through the membranes prepared in this work, as can be observed from the almost identical permeability values of N₂ and N₂/CO mixture through the Cu(I)-containing poly(IL)-IL composites. This may be due to the lack of mobility of the active species in the poly(IL)-IL composite compared to the SILM configuration.

Table 3. Gas permeation properties of copper(I)-containing poly([C₄vim][Tf₂N])- [C₄mim][Cl] composite membranes at 293 K.

Membrane	Gas	P (barrer)	D ¹ (x 10 ⁷ cm ² s ⁻¹)	S (cm ³ cm ⁻³ MPa ⁻¹)
3	N ₂	0.9	N/A	N/A
	CO ₂	26.7	0.91	22.0
	H ₂	9.9	21.6	0.35
	N ₂ /CO	1.0	N/A	N/A
4	N ₂	0.3	N/A	N/A
	CO ₂	11.2	0.55	15.6
	H ₂	5.7	5.3	0.81
	N ₂ /CO	0.3	N/A	N/A
5	N ₂	0.3	N/A	N/A
	CO ₂	8.4	1.3	5.03
	H ₂	7.0	16.3	0.33
	N ₂ /CO	0.3	N/A	N/A

¹N/A: time-lag could not be accurately determined due to very slow permeation rate.

In respect of the resulting ideal gas selectivities of CO₂ and H₂ towards N₂ through the composite membranes assessed, it is interesting to observe their evolution plotted in

Figure 4 as a function of the poly(IL)-IL membrane composition. The CO_2/N_2 and H_2/N_2 ideal selectivities through the neat poly($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$) were 19.5 and 18.5, respectively, at 293 K. After addition of $[\text{C}_4\text{mim}][\text{Cl}]$, the selectivities of CO_2 and H_2 towards N_2 were affected in distinct manner in membranes 2 and 3: CO_2/N_2 selectivity increased, most likely owing to the preferential solubility of CO_2 over that of N_2 into ILs [58]; on the contrary, H_2/N_2 selectivity diminished probably due to a slightly higher solubility in ILs of N_2 over that of H_2 , what can be related to its more condensable character [59,60]. This is not surprising as comparable trends have already been described for CO_2/N_2 and H_2/N_2 selectivities upon increasing the free IL content in composite membranes based on polymer-IL blends [17,26].

In contrast, in membranes 4 and 5, both CO_2/N_2 and H_2/N_2 ideal selectivities increased with the content of CuCl , yet this increase was more significant in the case of H_2/N_2 selectivity. This trend may be attributed to how these membranes are affected by the trade-off between permeability and selectivity upon the simultaneous increase of CuCl and non-polymerizable IL content. Let us first consider CO_2/N_2 separation, in this case a similar reduction of the mobility of both gases is expected owing to their similar molecular size (the kinetic diameters of CO_2 and N_2 are 3.3 and 3.64 Å, respectively); however, the solubility of CO_2 will be favored over that of N_2 in membrane 5, in which the content of non-polymerizable IL was increased with respect to membrane 4 from 25 to 32 mol %, hence the enhancement of CO_2/N_2 selectivity. With respect to H_2/N_2 separation, both H_2 and N_2 are just slightly soluble in ILs and therefore, their solubility would be similarly affected by increasing content of free IL. However, it is expected that increasing the content of CuCl from 5 to 8 mol % affects more negatively N_2 diffusivity than that of H_2 , which has a smaller kinetic diameter (2.89 Å). This would

also explain the improvement of H_2/N_2 selectivity in membrane 5 with respect to membrane 4.

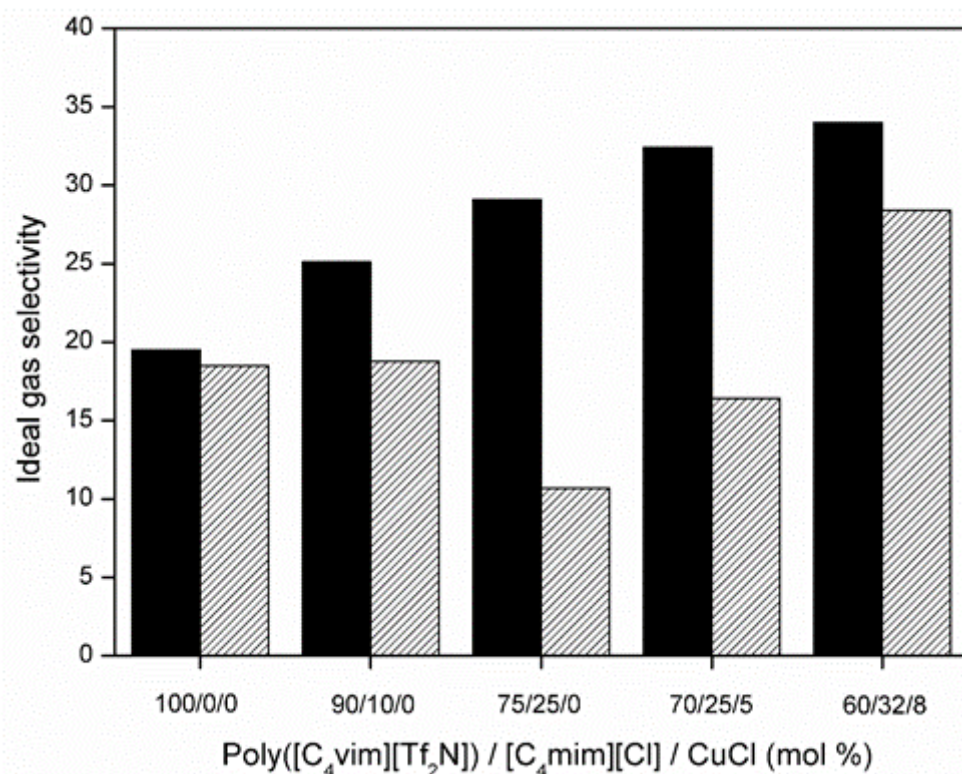


Figure 4. Influence of poly(IL)-IL membrane composition on the ideal CO_2/N_2 (solid bar) and H_2/N_2 (striped bar) selectivity depending on the relative content of polymerized IL, non-polymerizable IL and CuCl.

4. Conclusions

In this work, composite poly(IL)-IL membranes containing CuCl (as $[CuCl_2]^-$) in various proportions have been successfully obtained by radical photopolymerization for the first time. Their gas permeation properties were assessed with respect to CO_2 , H_2 , N_2 and CO. On the whole, although the expected performance of the fabricated poly(IL)-IL composite membranes with respect to the facilitated-transport of CO was not observed after combination of the pristine poly($[C_4vim][Tf_2N]$) with an IL that dissolves CuCl, we have shown that the performance of the membranes fabricated can be altered to form

more permeable and more selective membranes, what would be particularly beneficial for size-sieving-based gas separations such as H₂/N₂. Membranes containing 8 mol % CuCl and 32 mol % of non-polymerizable [C₄mim][Cl] reported better CO₂ and H₂ permeabilities than the original poly([C₄vim][Tf₂N]) along with significantly higher CO₂/N₂ and H₂/N₂ ideal gas selectivities, proving that applying this approach to a more suitable selection of PIL-ILs could result in the development of high-performance membranes with fascinating physical and chemical properties. This may be achieved by synthesizing composite membranes with novel PILs, which already outperform the membranes prepared in this work, and employing less viscous non-polymerizable ILs combined with a compatible metal salt. In addition, this metal-based composite membranes may prove useful in other catalytic applications in which reaction and separation takes place simultaneously [61].

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Highlights

- Poly(IL)-IL composites containing Cu^+ (as CuCl_2^-) fabricated via photopolymerization
- Presence of Cu^+ did not promote facilitated transport of carbon monoxide
- Design approach could enable new poly(IL) materials with other transition metals