Exploring the effect of fluorinated anions on the CO₂/N₂ separation of supported ionic liquid membranes†

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The CO₂ and N₂ permeation properties of ionic liquids (ILs) based on the 1-ethyl-3-methylimidazolium cation ([C₂mim]⁺) and different fluorinated anions, namely 2,2,2-trifluoromethylsulfonyl-N-cyanoamide ([TFSAM]⁻), bis(fluorosulfonyl) imide ([FSI]⁻), nonafluorobutanesulfonate ([C₉F₈SO₃]⁻), trifluoromethyl(trifluorophosphate) ([FAP]⁻), and bis(pentafluoroethylsulfonyl)imide ([BETI]⁻) anions, were measured using supported ionic liquid membranes (SILMs). The results show that pure ILs containing [TFSAM]⁻ and [FSI]⁻ anions present the highest CO₂ permeabilities, 753 and 843 Barrer, as well as the greatest CO₂/N₂ permselectivities of 43.9 and 46.1, respectively, with CO₂/N₂ separation performances on top of or above the Robeson 2008 upper bound. The re-design of the [TFSAM]⁻ anion by structural unfolding was investigated through the use of IL mixtures. The gas transport and CO₂/N₂ separation properties through a pure [C₂mim][TFSAM] SILM are compared to those of two different binary IL mixtures containing fluorinated and cyano-functionalized groups in the anions. Although the use of IL mixtures is a promising strategy to tailor gas permeation through SILMs, the pure [C₂mim][TFSAM] SILM displays higher CO₂ permeability, diffusivity and solubility than the selected IL mixtures. Nevertheless, both the prepared mixtures present CO₂ separation performances that are on top of or above the Robeson plot.

Introduction

The development of supported ionic liquid membranes (SILMs) for CO₂ separation has been widely investigated in recent years mainly due to their easy preparation and versatility.1–3 In contrast to traditional liquid membranes, which are produced by impregnating a porous membrane support with common organic solvents,4 SILMs use ionic liquids (ILs) and thus benefit from negligible displacement of the liquid phase from the membrane pores through evaporation,5,6 due to the low volatility of ILs.7 It should also be emphasized that within the CO₂ separation context, the most important features of ILs are their high CO₂ affinity over light gases8–10 and their inherent designer nature that enables the tailoring of IL properties by proper selection of cations and/or anions or via the addition of specific functional groups.

Numerous works have investigated the effect of IL chemical structure on the gas permeation properties of SILMs. A broad diversity of cations, such as imidazolium,11 triazolium,12 thiazolium,13 pyridinium,14 polyanion,15 ammonium,16 and phosphonium,17 combined with halogens, sulfonates, carboxylates, fluorinated or cyano-functionalized anions, have been studied. Other works, mostly focusing on imidazolium-based ILs, have also explored the effect of alkyl,18 fluoroalkyl,19 etoxyalkyl,20 and aminoalkyl21-functionalized cations. Since IL anions have a stronger influence on the CO₂ separation performance of SILMs than IL cations,1 they deserved from the start a closer look. The first studies on SILMs made use of fluorinated anions such as bis(trifluoromethylsulfonyl)imide [NTf₂]⁻, tetrafluoroborate [BF₄]⁻, and hexafluorophosphate [PF₆]⁻ and enabled drawing conclusions about the CO₂-phylic behaviour and high CO₂ permeabilities of these anions.22 More recently, low viscous ILs with cyano-functionalized anions, such as tricyanomethanide [C(CN)₃]⁻ and tetracyanoborate [B(CN)₄]⁻,23–25 have been recognized as better candidates for the development of improved SILMs, because of their superior CO₂ permeabilities and permselectivities when compared to the most used [NTf₂]⁻ anion. Task-specific ILs bearing amine groups, such as those containing amino acid...
anions,26–28 have also been proposed to prepare SILMs, since amine groups can chemically bond CO₂ and act as carriers for CO₂ facilitated transport through SILMs at low pressures. However, the high viscosity of these task-specific ILs is undoubtedly a key limitation, as CO₂ diffusion is strongly compromised.

In an effort to improve the CO₂ permeability and permselectivity properties of SILMs, our recent studies explored the use of IL mixtures by fixing the [C₂mim]⁺ cation and researching on different anion chemical structures. Initially, SILMs based on IL mixtures combining anions with different CO₂ solubility behaviours were investigated: thiocyanate ([SCN]⁻), dicyanamide ([N(CN)₂]⁻) and bis(trifluoromethylsulfonylimide) ([NTf₂]⁻) that present physical solubility; acetate ([Ac]⁻) and lactate ([Lac]⁻), which additionally have chemical solubility.29 Afterwards, we focused on IL mixtures based on sulfate ([CH₃SO₄]⁻) and cyano-functionalized anions ([SCN]⁻, [N(CN)₂]⁻, [C(CN)₃]⁻ and [B(CN)₄]⁻).30 Moreover, we studied IL mixtures containing [C(CN)₃]⁻ and different amino acid anions, so that one IL component maintains the low viscosity, while the other provides the desired chemical characteristics for the active transport of CO₂.31 The overall results of these studies showed that mixing anions with specific chemical features allows variations in IL viscosity and molar volume that significantly impact the gas transport through SILMs, and thus tailored permeabilities and permselectivities can be achieved.29–31

In the present work, the gas permeation properties and CO₂/N₂ separation performance of SILMs prepared with pure ILs bearing the [C₂mim]⁺ cation and different less conventional fluorinated anions, namely [TFSAM]⁻, [FSI]⁻, [C₂F₅SO₃]⁻, [FAP]⁻ and [BETI]⁻, were evaluated and the effect of the fluorinated moieties in the IL anion was discussed. Despite the fact that several SILMs with common fluorinated anions have already been reported,1–3 the gas permeation properties of SILMs containing fluorinated anions, such as those selected herein, have still not been properly studied and discussed. Only three studies have reported SILMs that made use of [C₂F₅SO₃]⁻, [FAP]⁻ and [BETI]⁻ anions. Pereiro et al.32 conducted single gas permeation experiments through a [C₂C₁py][C₂F₅SO₃] SILM, at 294 K and 75 kPa, using CO₂, N₂, O₂, hydrocarbon gases (CH₄, C₂H₆, C₃H₈, C₄H₁₀) and perfluorocarbon gases (CF₃, C₂F₆, C₃F₈). Scovazzo et al.33 determined ideal/mixed CO₂/CH₄ and CO₂/N₂ permselectivities in a [C₂mim][BETI] SILM at 303 K and 200 kPa, while Althuluth et al.33 reported ideal/mixed CO₂/CH₄ permselectivities in a [C₂mim][FAP] SILM at 313 K and 700 kPa. Nevertheless, the obtained results cannot be directly compared due to the different measurement conditions, as well as the use of diverse IL cation structures.

Additionally, this work investigates the impact on gas transport through SILMs of using a pure IL versus a structurally similar IL mixture as the liquid phase. Inspired by the fact that the [TFSAM]⁻ anion has an unusual asymmetric chemical structure, which combines both fluorinated and cyano functionalities, the re-design of the chemical structure of a pure [C₂mim][TFSAM] IL through the use of IL mixtures is explored. For that purpose, different pairs of ILs, based on the [C₂mim]⁺ cation and anions containing fluorinated or cyano functionalities, were selected and their gas permeation properties were compared to those of the pure [C₂mim][TFSAM] SILM. One of the IL mixtures contains [NTf₂]⁻ and [N(CN)₂]⁻ anions, whose gas permeation properties were previously determined,29 whereas the other IL mixture is based on [OTf]⁻ and [SCN]⁻ anions and its gas transport properties are reported here for the first time.

Results and discussion

Gas permeation through SILMs having fluorinated anions

The structures of the pure ILs bearing fluorinated anions are depicted in Fig. 1.

The water content (wt%), molar mass (M), viscosity (η), density (ρ) and molar volume (V_m) values of the pure ILs used as liquid phases in the studied SILMs are summarized in Table 1. The thermophysical properties of the conventional [C₂mim][NTf₂] IL are also included for comparison.29 From Table 1, it can be observed that the IL containing the [C₂F₅SO₃]⁻ anion shows the highest viscosity, while [C₂mim][FSI] presents the lowest viscosity. The IL viscosity values can be organized following the IL anion order: [C₂F₅SO₃]⁻ > [BETI]⁻ > [FAP]⁻ > [NTf₂]⁻ > [TFSAM]⁻ > [FSI]⁻. A slightly different trend was observed for molar volumes, with the IL comprising the [FAP]⁻ anion showing the highest molar volume, while [C₂mim][FSI] exhibiting the lowest molar volume. These data will be used subsequently in the understanding of the gas permeation results.

The experimental gas permeability (P) values obtained through the prepared SILMs having ILs with fluorinated anions, measured at 293 K with a trans-membrane pressure differential of 100 kPa, are shown in Table 2. To the best of our knowledge, the CO₂/N₂ separation properties of [C₂mim][TFSAM], [C₂mim][FSI], [C₂mim][FAP], [C₂mim][BETI] and [C₂mim][C₂F₅SO₃] SILMs are reported here for the first time, while those of the [C₂mim][NTf₂] SILM were previously determined using the same experimental conditions.29 It is important to mention that in order to attain stable SILMs, both hydrophilic and hydrophobic supports were used according to the hydrophobicity of ILs, and the results are compared in this section, irrespective of the support used.

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Fig. 1 Chemical structures of the pure ionic liquids (ILs) used in this work to prepare SILMs.
were taken from Tome et al. The density and viscosity values of [C2mim][FAP] were taken from Neves et al.

From Table 2, the same trend in gas permeability is valid for all the studied SILMs: \( \text{PCO}_2 > \text{PN}_2 \), as expected. Regarding the influence of the fluorinated-based anions, SILMs having the [FSI]-, [TFSAM]- and [FAP]- anions present higher CO2 permeabilities of 843, 753 and 624 Barrer, respectively, than the SILM containing the [NTf2]- anion, which is well-known for its high CO2 permeability (589 Barrer). It should be noted that in spite of the similar structures of [NTf2]- and [FSI]- anions, in which the difference consists in two extra \( \text{CF} \) groups in the [NTf2]- anion structure (Fig. 1), the CO2 permeability through the [C2mim][FSI] SILM is \( \sim 1.5 \) times higher than that through the [C2mim][NTf2] SILM. Generally, CO2 permeabilities through the studied SILMs are found to decrease in the following IL anion order: [FSI]- > [TFSAM]- > [FAP]- > [NTf2]- > [BETI]- > [C4F9SO3]- (Table 2). Considering the IL anion viscosity trend, obtained at 293 K (Table 1), [FSI]- < [TFSAM]- < [NTf2]- < [BETI]- < [C4F9SO3]- (Table 2). It can be concluded that these experimental data are in agreement with the general trend usually observed in the literature, where ILs with high viscosities yield SILMs with low gas permeabilities. However, [C2mim][FAP] is the only exception since it presents a different behaviour (Table 2): despite its high viscosity (76.4 mPa s), it also exhibits high CO2 permeability (624 Barrer), higher than those of the [C2mim][NTf2] IL (39.1 mPa s and 589 Barrer). Notice that the [FAP]- anion has the most different chemical structure among all the IL anions studied in this work, consisting of a phosphorus atom surrounded by fluorine atoms, without sulfonil functional groups (Fig. 1). Moreover, taking a closer look at the gas permeabilities obtained through SILMs immobilized with the remaining ILs, it can be seen that higher CO2 permeabilities are achieved for ILs with anions bearing a smaller number of fluorine elements, such as [TFSAM]- and [FSI]- anions (Table 2).

Table 2 Gas permeabilities \( (P) \) through the prepared SILMs of pure ILs

| SILM sample   | \( P (\text{CO}_2) \) | \( P (\text{N}_2) \) | \( \frac{P (\text{CO}_2)}{P (\text{N}_2)} \) |
|---------------|---------------------|---------------------|-----------------------------------|
| [C2mim][TFSAM]| 753 ± 0.2           | 17 ± 0.1            | 43.9 ± 0.1                        |
| [C2mim][FSI]  | 843 ± 0.5           | 18 ± 0.2            | 46.1 ± 0.5                        |
| [C2mim][NTf2] | 589 ± 0.10          | 17 ± 0.1            | 35.5 ± 0.3                        |
| [C2mim][FAP]  | 624 ± 0.4           | 24 ± 0.1            | 26.0 ± 0.1                        |
| [C2mim][BETI] | 437 ± 1.9           | 18 ± 0.1            | 24.8 ± 0.2                        |
| [C2mim][C4F9SO3]| 32 ± 0.2           | 62 ± 0.1            | 5.5 ± 0.1                         |

\( a \) Barrer \( = 10^{-10} \text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1} \). \( b \) The listed uncertainties represent the standard deviations, based on three experiments. \( c \) Values taken from Tome et al.

In agreement to what was previously observed in the literature for other SILMs, the \( \text{CO}_2 \) diffusivity through SILMs having fluorinated anions decreases as the IL viscosity increases. The SILMs with the lowest \( \text{CO}_2 \) diffusivities are [C2mim][C4F9SO3] (55 \( \times 10^{-12} \text{m}^2 \text{s}^{-1} \)) and [C2mim][BETI] (167 \( \times 10^{-12} \text{m}^2 \text{s}^{-1} \)), which also have the lowest \( \text{CO}_2 \) permeabilities (437 and 32 Barrer), depicting the highest viscosities (109.7 and 85.5 mPa s). Similarly to what is mentioned above for \( \text{CO}_2 \) permeabilities, again a deviant behaviour can be observed for the [C2mim][FAP] SILM, since its \( \text{CO}_2 \) diffusivity is in between those of [C2mim][NTf2] and [C2mim][TFSAM] (Table 3), but its viscosity values (76.4 mPa s) are higher than those of [C2mim][NTf2] (39.1 mPa s) and [C2mim][TFSAM] (23.7 mPa s) (Fig. 2).

The gas solubility \( (S) \) values calculated using Eqn 1 are listed in Table 4. It can be seen that the [C2mim][C4F9SO3] SILM presents the lowest \( \text{CO}_2 \) solubility \( (4 \times 10^{-6} \text{m}^3 \text{m}^{-3} \text{Pa}^{-1}) \), while the previously reported [C2mim][NTf2] SILM has the highest \( \text{CO}_2 \) solubility \( (26 \times 10^{-6} \text{m}^3 \text{m}^{-3} \text{Pa}^{-1}) \). The \( \text{CO}_2 \) solubility values of the remaining studied SILMs having different fluorinated anions are very similar (ranging from 20 \( \times 10^{-6} \).

Table 3 Gas diffusivity \( (D) \) through the prepared SILMs of pure ILs

| SILM sample   | \( D (\text{CO}_2) \) | \( D (\text{N}_2) \) |
|---------------|---------------------|---------------------|
| [C2mim][TFSAM]| 258 ± 1.1           | 291 ± 4.5           |
| [C2mim][FSI]  | 315 ± 4.4           | 353 ± 7.5           |
| [C2mim][NTf2]| 172 ± 1.7           | 203 ± 2.5           |
| [C2mim][FAP]  | 214 ± 1.9           | 326 ± 0.2           |
| [C2mim][BETI] | 167 ± 2.1           | 216 ± 2.4           |
| [C2mim][C4F9SO3]| 55 ± 1.2           | 88 ± 2.0            |

\( a \) The gas diffusivity values through the [C2mim][NTf2] SILM were taken from Tome et al.
to $2.2 \times 10^{-6} \text{m}^3 \text{s}^{-1} \text{Pa}^{-1}$) and can be ordered as follows: $[\text{TFSAM}]^+ \approx [\text{FAP}]^- > [\text{FSI}]^- \approx [\text{BETI}]^-$. Regarding the $\text{N}_2$ solubility, its values are always significantly lower (between 0.39 to $10^{-6}$ and 0.61 to $10^{-6} \text{m}^3 \text{s}^{-1} \text{Pa}^{-1}$) than those of $\text{CO}_2$ for all the SILMs studied.

Over the past few years, a number of correlations have been proposed with the intention of understanding the relationships between $\text{CO}_2$ solubility and the intrinsic properties of ILs.\textsuperscript{42-44} The proposed models showed that $\text{CO}_2$ solubility increases with increasing IL molecular weight, molar volume and free volume.\textsuperscript{10} Taking into consideration the gas solubility results obtained in this work (Table 4), as well as the range of molar volumes (from 201.2 up to 325.6 cm$^3$ mol$^{-1}$) and molecular weights (from 284.3 up to 556.2 g mol$^{-1}$) of the ILs used, divergences from the abovementioned trends can be found for the studied SILMs having fluorinated anions. For example, the $[\text{C}_2\text{mim}][\text{NTf}_2]$ SILM shows the highest $\text{CO}_2$ solubility ($2.6 \times 10^{-6} \text{m}^3 \text{s}^{-1} \text{Pa}^{-1}$), but it does not have the highest IL molar volume and molecular weight (Table 1). Likewise, the lowest $\text{CO}_2$ solubility ($4 \times 10^{-6} \text{m}^3 \text{s}^{-1} \text{Pa}^{-1}$) belongs to the $[\text{C}_2\text{mim}][\text{F} \text{SO}_3]$ SILM, although it does not present the lowest IL molar volume and molecular weight (Table 1). The effect of fluorination, either in the IL cation or anion, on $\text{CO}_2$ solubility has been studied by different researchers.\textsuperscript{19,45-47} Tagiuri \textit{et al.}\textsuperscript{48} explored the effect of cation on the $\text{CO}_2$ solubility of three different ILs combining the $[\text{FSI}]^-$ anion. Moreover, Kroon \textit{et al.}\textsuperscript{49} determined the $\text{CO}_2$ solubility in the $[\text{C}_2\text{mim}][\text{FAP}]$ IL by measuring the bubble point pressure of the binary mixture of $[\text{C}_2\text{mim}][\text{FAP}] + \text{CO}_2$. The results showed that the $\text{CO}_2$ solubility in $[\text{C}_2\text{mim}][\text{FAP}]$ is higher when compared to that of ILs having the same cation combined with other fluorinated anions such as $[\text{NTf}_2]^-$, $[\text{BF}_4]^{-}$ and $[\text{PF}_6]^{-}$, due to the fact that $[\text{FAP}]^-$ has a large size and it is highly fluorinated. Although it has been recognized that introducing fluorination into the cation and/or anion can effectively improve $\text{CO}_2$ solubility,\textsuperscript{46} it was recently reported after critical analysis that no special effect of the fluorination upon the $\text{CO}_2$ solubility has been observed for both perfluorocarbon and heavily fluorinated ILs.\textsuperscript{29} In fact, the introduction of fluorination into the anions of the ILs studied in this work does not significantly affect the obtained gas solubility values (Table 4), except for the case of the $[\text{C}_2\text{mim}][\text{F} \text{SO}_3]$ IL that displays a very low $\text{CO}_2$ solubility.

### Table 4: Gas solubility ($S$) values through the prepared SILMs of pure ILs

| SILM sample | $S$ ($\text{CO}_2$) ($\times 10^6$) (m$^3$ STP$^{-1}$ m$^{-3}$ Pa$^{-1}$) | $S$ ($\text{N}_2$) ($\times 10^6$) (m$^3$ STP$^{-1}$ m$^{-3}$ Pa$^{-1}$) |
|-------------|---------------------------------|---------------------------------|
| $[\text{C}_2\text{mim}][\text{TFSAM}]$ | 22 ± 0.09 | 0.44 ± 0.01 |
| $[\text{C}_2\text{mim}][\text{FAP}]$ | 20 ± 0.29 | 0.39 ± 0.01 |
| $[\text{C}_2\text{mim}][\text{NTf}_2]^-$ | 26 ± 0.28 | 0.61 ± 0.01 |
| $[\text{C}_2\text{mim}][\text{F} \text{SO}_3]$ | 22 ± 0.21 | 0.55 ± 0.001 |
| $[\text{C}_2\text{mim}][\text{BETI}]$ | 20 ± 0.17 | 0.61 ± 0.01 |
| $[\text{C}_2\text{mim}][\text{C}_6\text{F}_5\text{SO}_3]$ | 4 ± 0.07 | 0.49 ± 0.002 |

[a] The gas solubility values through the $[\text{C}_2\text{mim}][\text{NTf}_2]$ SILM were taken from Tome et al.\textsuperscript{29}

pressures of the binary mixture of $[\text{C}_2\text{mim}][\text{FAP}] + \text{CO}_2$. The results showed that the $\text{CO}_2$ solubility in $[\text{C}_2\text{mim}][\text{FAP}]$ is higher when compared to that of ILs having the same cation combined with other fluorinated anions such as $[\text{NTf}_2]^-$, $[\text{BF}_4]^{-}$ and $[\text{PF}_6]^{-}$, due to the fact that $[\text{FAP}]^-$ has a large size and it is highly fluorinated. Although it has been recognized that introducing fluorination into the cation and/or anion can effectively improve $\text{CO}_2$ solubility,\textsuperscript{46} it was recently reported after critical analysis that no special effect of the fluorination upon the $\text{CO}_2$ solubility has been observed for both perfluorocarbon and heavily fluorinated ILs.\textsuperscript{29} In fact, the introduction of fluorination into the anions of the ILs studied in this work does not significantly affect the obtained gas solubility values (Table 4), except for the case of the $[\text{C}_2\text{mim}][\text{F} \text{SO}_3]$ IL that displays a very low $\text{CO}_2$ solubility.

### Re-designing the [TFSAM]$^-$ anion by structural unfolding:

**Effect on gas permeation**

Taking into account that the $[\text{TFSAM}]^-$ anion has an unconventional and asymmetric chemical structure, combining both fluorinated and cyano functionalities, which have both been recognized to be responsible for high $\text{CO}_2$ separation performance, we explore here the effect of structural unfolding of the pure $[\text{C}_2\text{mim}][\text{TFSAM}]$ IL on gas permeation properties of SILMs using IL mixtures. Thus, two equimolar IL mixtures were used for this purpose: $[\text{C}_2\text{mim}][\text{SCN}][\text{OTf}]$ (Fig. 3), which is studied here for the first time, and $[\text{C}_2\text{mim}][\text{N} \text{(CN)}_2][\text{NTf}_2]$, whose gas permeation and thermophysical properties were previously determined by us.\textsuperscript{29} Both these mixtures have IL anions that show structural similarities to the $[\text{TFSAM}]^-$ anion (Fig. 3). The composition description, water content (wt%), molar mass ($M$), viscosity ($\eta$), density ($\rho$) and molar volume ($V_m$) values of the pure ILs, $[\text{C}_2\text{mim}][\text{TFSAM}]$, $[\text{C}_2\text{mim}][\text{SCN}]$, $[\text{C}_2\text{mim}][\text{OTf}]$, $[\text{C}_2\text{mim}][\text{N} \text{(CN)}_2][\text{NTf}_2]$, and the selected IL mixtures are listed in Table S, while their gas permeability, diffusivity and solubility values are depicted in Fig. 4(a)-(c), respectively.

![Fig. 3](image-url)  
**Fig. 3** Chemical structures of the pure IL and IL mixtures studied in this work.
Tome´[C2mim][SCN] did not significantly affect CO2 permeability but decreases with the increase in IL viscosity. 4,21–23 SILMs not only show the highest gas permeabilities (843 and 220.3 cm3 mol−1) but also have the largest CO2/N2 permselectivities (43.9 and 46.1, respectively). In contrast, the lowest gas permeabilities and CO2/N2 permselectivity belong to the [C2mim][C4F9SO3] SILM. The CO2/N2 permselectivities of the pure SILMs decrease as the fluorinated chain increases in the IL anion: [FSI]− > [TFSAM]− > [NTf2]− > [BETI]−, the [C2mim][FAP] and [C2mim][C4F9SO3] SILMs being the only exceptions.

Concerning the effect of the structural unfolding of the [TFSAM] anion, and as previously discussed, the pure [C2mim][TFSAM] SILM presents higher gas permeabilities compared to its structurally similar IL mixtures (Table 6). Nevertheless, the greatest CO2/N2 separation performance (753 Barrer, respectively), but also have the largest CO2/N2 permselectivities (43.9 and 46.1, respectively). In contrast, the lowest gas permeabilities and CO2/N2 permselectivity belong to the [C2mim][C4F9SO3] SILM. The CO2/N2 permselectivities of the pure SILMs decrease as the fluorinated chain increases in the IL anion: [FSI]− > [TFSAM]− > [NTf2]− > [BETI]−, the [C2mim][FAP] and [C2mim][C4F9SO3] SILMs being the only exceptions.

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permeability (57.6) was achieved for the SILM containing the [C2mim][SCN][OTf] IL mixture.

With the purpose of comparing the performance results obtained in this work to those reported in the literature for other SILMs, Fig. 5 displays the Robeson plot for CO2/N2 separation, where the CO2/N2 permselectivity is plotted against CO2 permeability and the solid black line represents the empirical 2008 upper bound for this gas pair.51 It can be seen that among the SILMs immobilized with the pure IL having fluorinated anions, both the [C2mim][TFSAM] and [C2mim][FSI] SILMs fall or exceed the Robeson 2008 upper bound, meaning that these two ILs are the most promising candidates for CO2/N2 separation processes. Comparing the results of the pure [C2mim][TFSAM] SILM with those of selected IL mixtures, Fig. 5 clearly shows that the CO2/N2 separation performance of the SILM immobilized with the [C2mim][SCN][OTf] IL mixture surpasses the upper bound, primarily due to its higher CO2/N2 permselectivity (57.6). On the other hand, the CO2/N2 separation efficiency of the [C2mim][N(CN)2][NTf2] SILM is on top of the upper bound, since it presents lower permselectivity (41.8), despite its high CO2 permeability (589 Barrer) in comparison to that of the [C2mim][SCN][OTf] SILM (428 Barrer). Actually, it is the [C2mim][N(CN)2][NTf2] SILM that discloses the most similar CO2/N2 separation performance results to the pure synthesized [C2mim][TFSAM] IL (Fig. 5).

Experimental

Materials

Lithium bis[pentafluoroethylsulfonyl]imide ([LiCF2CF2SO2]2N, LiBETI, 98%, Chameleon Reagent) and lithium nonafluoro-1-butanesulfonate ([LiC4F9SO3]−, > 95%, TCI Chemicals) were used without purification. Reagent-grade dichloromethane, acetonitrile, hexane and ethyl acetate were obtained from Aldrich or Merck and were dried by vacuum distillation over P2O5. N-Methylimidazole (98%, Aldrich) and bromoethane (98%, Acros) were distilled under an inert atmosphere over CaH2.

1-Ethyl-3-methylimidazolium bis[fluorosulfonyl]imide ([C2mim][FSI], 99.5 wt%, Solvionic), 1-ethyl-3-methylimidazolium tris(pentafluoro-ethyl)trifluorophosphate ([C2mim][FAP], 98 wt%, Merck), 1-ethyl-3-methylimidazolium thiocyanate ([C2mim][SCN], > 98 wt%, IoLiTec) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C2mim][OTf], ≥ 98 wt%, Aldrich) were obtained from the specified suppliers. To reduce the content of water and other volatile substances, the pure ILs were dried at approximately 1 Pa and 318 K for at least 4 days.

II. synthesis and characterization

1-Ethyl-3-methylimidazolium bromide ([C2mim][Br]). [C2mim][Br] was synthesized by the reaction between N-methylimidazole and an excess of bromoethane following the method used in a previous work.34 Spectroscopic data of the target compound were in accordance with those reported in the literature.

1-Ethyl-3-methylimidazolium 2,2,2-trifluoromethylsulfonyl-N-cyanoamide ([C2mim][TFSAM]). [C2mim][TFSAM] was prepared by ion exchange between [C2mim][Br] and KTFSAM, in an aqueous medium in accordance with a described procedure.35 Yield: 85%; anal. calcd for C8H11N4F3SO2 (284.26), %: N, 19.71%; C, 33.80%; H, 3.90%; Found, %: N, 19.68%; C, 33.78%; H, 3.99%; 1H NMR (300 MHz, DMSO-d6): 9.08 (s, 1H, 2H (Im)), 7.72 (s, 1H, H4 (Im)), 7.64 (s, 1H, H5 (Im)), 4.22–4.15 (m, 2H, CH2CH3), 3.84 (s, 3H, CH3), 1.42 (t, 3H, CH2CH3, JHH = 7.5 Hz); 13C NMR (100.6 MHz, DMSO-d6): 136.1, 125.0–115.4 (q, JCF = 325 Hz), 123.4, 121.8, 44.1, 35.5, 14.8; 19F NMR (282.4 MHz, DMSO-d6): −77.8; IR (KBr pellet): 3158 (m, νC=O), 3117 (m, νC–N), 2192 (vs, νC=CH), 1573 (m), 1468 (w), 1333 (vs, νasSO2), 1236 (s), 1217 (vs, νCF), 1170 (vs, νSO2), 1119 (s, νC==O), 832 (s), 752 (w), 639 (m), 595 (s), 479 (m) cm−1.

1-Ethyl-3-methylimidazolium nonafluorobutanesulfonate ([C2mim][C6F5SO3]). Lithium nonafluoro-1-butanesulfonate (8.00 g, 0.026 mol) was dissolved in 20 mL of distilled water and added dropwise to a solution of [C2mim][Br] (3.84 g, 0.020 mol) in 15 mL of H2O at ambient temperature. The solution was stirred for 2 h at room temperature and then [C2mim][C6F5SO3] was extracted...
with dichloromethane (4 × 40 mL). The combined CH₂Cl₂ solution was washed with a small amount of water and dried over anhydrous MgSO₄. The magnesium sulfate was filtered off and dichloromethane was stripped off under reduced pressure. The product was obtained as slightly yellow transparent fluid oil, which was finally dried at 323 K and 100 Pa for 12 h using a special flask filled with P₂O₅ and introduced into the vacuum line. Yield: 5.61 g (68%); anal. calc. for C₉H₁₉N₂F₉SO₃ (410.26), %: C, 29.28%; H, 2.70%; F, 41.68%; Found, %: C, 28.99%; H, 2.83%; F, 41.39%; [1H NMR (300 MHz, DMSO-d₆): 9.09 (s, 1H, H₁ H₂ (Im)), 7.77 (s, 1H, H₄ (Im)), 7.68 (s, 1H, H₅ (Im)), 4.22–4.17 (m, 2H, CH₂CH₃), 3.85 (s, 3H, CH₃), 1.43–1.39 (m, 3H, CH₂CH₃), 13C NMR (100.6 MHz, DMSO-d₆): 136.2, 123.5, 121.9, 117.1 (qt, –CF₂–, 1/2C₀ = 33 Hz), 110.4 (tp, –CF₂–, 1/2C₀ = 36 Hz), 109.8 (qq, –CF₂–, 1/2C₀ = 38 Hz), 44.1, 35.6, 14.9; 19F NMR (282.4 MHz, DMSO-d₆): –80.8, –114.9, –121.6, –125.9; IR (KBr pellet): 3156 (s, νC=H), 3117 (s, νC–H), 2993 (m, 2H, CH₂CH₃), 1574 (s), 1542 (w), 1432 (w), 1393 (w), 1353 (s), 1261 (vs ν νS=O), 1236 (vs), 1214 (vs ν C=O), 1170 (vs ν νS=O), 1134 (s, ν νC=O), 1057 (vs), 1119 (m), 1006 (m), 988 (w), 870 (m), 845 (m), 802 (m), 736 (m), 699 (m), 679 (w), 656 (s), 620 (s), 596 (m), 564 (m), 532 (w) cm⁻¹.

1-Ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide ([C₂mim][BF₄]). The procedure previously described for [C₂mim][CF₃SO₃] was also used for the synthesis of [C₂mim][BF₄]. After purification and drying, [C₂mim][BF₄] was obtained as colorless transparent liquid. Yield: 59.6% (28.5 g, 94.6 mmol, 32.6 mmol 1-Ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide ([C₂mim][BF₄]) was prepared using an analytical high precision balance with an uncertainty of ±10⁻⁵ g by syringing known masses of the IL components into a glass vial. Good mixing was ensured by magnetic stirring for 30 min at 298 K. Then, the IL mixture of [C₂mim][BF₄] was dried at roughly 1 Pa and 318 K for at least 4 days immediately prior to use. The water contents of all IL samples were determined by Karl Fischer titration using an 831 KF Coulometer (Metrohm).

Density and viscosity determination. The density and viscosity measurements of the pure ILs and the [C₄mim][SCN]OTf IL mixture were performed at 293 K and atmospheric pressure using an SVM 3000 Anton Paar rotation Stabinger viscometer-densimeter, where the standard uncertainty for the temperature was 0.02 K. The repeatability of density and dynamic viscosity of this equipment was 0.0005 g cm⁻³ and 0.35%, respectively. Measurements of each sample were performed in triplicate to ensure accuracy and the reported results are average values. The highest relative standard uncertainty registered for the density and dynamic viscosity measurements was 1 × 10⁻⁴ and 0.03, respectively.

Gas permeation measurements. Porous hydrophobic poly(vinylidene fluoride) (PVDF) membranes supplied by Millipore Corporation (USA), with a pore size of 0.22 μm and an average thickness of 125 μm, were used to support [C₂mim][FSI], [C₄mim][BF₄] and [C₂mim][BF₄]. Since the impregnation of the remaining IL samples into hydrophobic PVDF resulted in unstable SILMs, the other IL samples were supported on porous hydrophilic poly(tetrafluoroethylene) (PTFE) membranes acquired from Merck Millipore, with a pore size of 0.2 μm and an average thickness of 65 μm. All the SILM configurations were prepared by the vacuum method.²⁹

Ideal gas permeabilities and diffusivities through the prepared SILMs were measured using a time-lag apparatus.³⁶ First, each SILM was degassed under vacuum inside the permeation cell for 12 h. Then, CO₂ and N₂ permeation experiments were carried out at 293 K with a trans-membrane pressure differential of 100 kPa. All the permeation data were measured at least in triplicate on a single SILM sample. The highest relative standard uncertainty registered for gas permeability measurements was 0.03. The permeation cell and lines were evacuated until the pressure was below 0.1 kPa before each run. No residual IL was found inside the permeation cell at the end of the experiments. The thickness of the SILMs was assumed to be equivalent to the membrane filter thickness.

Gas transport through the prepared SILMs was assumed to follow a solution–diffusion mass transfer mechanism,³⁷ where the permeability (P) is related to diffusivity (D) and solubility (S) as follows:

\[ P = D \times S \quad (1) \]

The permeate flux of each gas (Jₗ) was determined experimentally using eqn (2),³⁸ 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 gas constant and \( T \) is the temperature.

\[ J_l = \frac{V_p \Delta P_d}{A t R T} \quad (2) \]

Ideal gas permeability (Pᵢ) was then determined from the steady-state gas flux (Jᵢ), the membrane thickness (ℓ) and the trans-membrane pressure difference (ΔPᵢ), as shown in eqn (3).³⁸

\[ P_i = \frac{J_i}{\Delta P_i/\ell} \quad (3) \]
Gas diffusivity \( (D_i) \) was determined according to eqn (4). The time-lag parameter \( (\theta) \) was calculated by extrapolating the slope of the linear portion of the \( p_0 \) vs. \( t \) curve back to the time axis, where the intercept was equal to \( \theta \).

\[
D_i = \frac{\ell^2}{6\theta}
\]

After \( P_i \) and \( D_i \) were known, the gas solubility \( (S_i) \) was calculated using the relationship shown in eqn (1). The ideal permeability selectivity (or permselectivity), \( z_{ij} \), was obtained by dividing the permeability of the more permeable species \( i \) to the permeability of the less permeable species \( j \). The permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity:

\[
z_{ij} = \frac{P_i}{P_j} = \left( \frac{D_i}{D_j} \right) \times \left( \frac{S_i}{S_j} \right)
\]

**Conclusions**

In this work, ILs containing a common cation ([C$_2$mim]$^+$) and different fluorinated anions ([TFSAM]$^-$, [FSI]$^-$, [CF$_3$SO$_3$]$^-$, [BETI]$^-$, [FAP]$^-$) were synthesized and used as liquid phases to prepare SILMs for flue gas separation (CO$_2$/N$_2$). The single CO$_2$ and N$_2$ permeation properties through the prepared SILMs were determined. The viscosity and density of the IL phases were also evaluated. The results showed that CO$_2$ permeabilities and diffusivities through the studied SILMs follow the same fluorinated anion order: [FSI]$^-$ > [TFSAM]$^-$ > [FAP]$^-$ > [NTf$_2$]$^-$ > [BETI]$^-$ > [CF$_3$SO$_3$]$^-$, which is inversely related to IL viscosity, with the only outlier being [C$_2$mim][FAP]. Conversely, the introduction of fluorination in the IL anions did not significantly affect gas solubility, except for the case of the [C$_2$mim][CF$_3$SO$_3$] SILM displaying a very low CO$_2$ solubility. Among the pure SILMs, it is worth noting that the best separation performances were achieved for [C$_2$mim][TFSAM] and [C$_2$mim][FSI] SILMs that fall on top of or surpassed the Rosbben 2008 upper bound, with CO$_2$ permeabilities of 753 and 843 Barrer and CO$_2$/N$_2$ permselectivities of 43.9 and 46.1, respectively.

Furthermore, the effect of structural unfolding of the [TFSAM]$^-$ anion on gas permeation properties of SILMs was investigated using IL mixtures comprising both fluorinated and cyan functional groups in the anions. The pure [C$_2$mim][TFSAM] IL provided a membrane with improved CO$_2$ permeabilities, diffusivities and solubilities compared to those of the SILMs based on the selected [C$_2$mim][SCN][OTf] and [C$_2$mim][N(CN)$_2$][NTf$_2$] IL mixtures. Overall, and despite the fact that the [C$_2$mim][SCN][OTf] SILM revealed better CO$_2$/N$_2$ separation performance essentially due to its higher CO$_2$/N$_2$ permselectivity (57.6), the [C$_2$mim][N(CN)$_2$][NTf$_2$] IL mixture disclosed the most similar results to the pure synthesized [C$_2$mim][TFSAM] IL, not only in terms of thermophysical properties, but also regarding gas transport and CO$_2$/N$_2$ separation performance.

**Conflicts of interest**

There are no conflicts to declare.

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