



# Effect of feed pressure and long-term separation performance of Pebax-ionic liquid membranes for the recovery of difluoromethane (R32) from refrigerant mixture R410A

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## ABSTRACT

The R410A refrigerant blend (GWP = 2088), a near azeotropic and equimass mixture of difluoromethane (R32, GWP = 675) and pentafluoroethane (R125, GWP = 3500), has been included in the HFC phase down road map established worldwide. In this context, the recovery of value-added R32 from R410A using membrane technology would be a breakthrough in the refrigeration and air conditioning sector, given that conventional distillation cannot be applied to this separation. For the first time, this work has taken advantage of the combination of ionic liquids and polymeric membranes for the separation of the constituents of the R410A mixture. Results show a remarkable improvement in terms of R32 permeability and R32/R125 selectivity in the composite membranes containing 40 wt % [C<sub>2</sub>mim][SCN] ( $\alpha_{R32/R125}$  up to 14.5) and [C<sub>2</sub>mim][BF<sub>4</sub>] ( $\alpha_{R32/R125}$  up to 11.0) with respect to the neat polymer membranes ( $\alpha_{R32/R125}$  up to 6.9). Besides, the long-term stability was successfully tested for 25 days under high pressure conditions (7 and 12 bar), which makes these composite membranes excellent candidates for the development of membrane-based R32 separation and recovery processes.

## 1. Introduction

The refrigeration and air conditioning sector (RAC) is facing drastic changes worldwide to reduce the emissions of fluorinated greenhouse gases (GHG), which account for 2–3% of the global GHG emissions [1–3]. In Europe, the amount of hydrofluorocarbons (HFCs) placed on the market must be reduced by 21% with respect to the annual average reported during the period 2009–2012 by 2030 [4]. Moreover, the Kigali Amendment to the Montreal Protocol established further restrictions among the signatory parties to cut HFC emissions worldwide by 80–85% by 2047. Consequently, the HFCs must be replaced in the short-term by environmentally friendly alternatives. In particular, the widely used refrigerants R134a, R404A and R410A are the most affected because of their high global warming potential (GWP). In this sense, several low GWP replacement refrigerants involving mixtures of HFCs, hydrofluoroolefins (HFOs), hydrocarbons and CO<sub>2</sub> (R744) are being developed and commercialized [5].

In the present work, we focus our attention on the refrigerant R410A (GWP = 2088), which is an equimass mixture of difluoromethane (R32, GWP = 675) and pentafluoroethane (R125, GWP = 3500). Among the

alternative refrigerants to R410A, the use of pure R32 is proposed because of its good thermophysical properties, higher coefficient of performance (COP) and lower GWP, which is below the European threshold for air conditioning applications. In addition, several mixtures have been postulated as alternative refrigerants to R410A in order to increase the overall energy performance of RAC equipment, and overcome the main technical drawbacks presented by R32, namely, its flammability (ASHRAE category A2L) and higher discharge temperature than R410A [5]. Very interestingly, these alternative mixtures also contain R32, typically ranging between 29 and 68 wt %, which is balanced primarily with very low-GWP HFOs such as 1,3,3,3- and 2,3,3,3-tetrafluoropropene (R1234ze(E) and R1234yf, respectively), and with other HFCs to a lesser extent. Within this framework, the selective separation of the value-added R32 from the refrigerant blend R410A could be sought as a good operating practice to reclaim waste HFCs contained in end-of-life RAC equipment, with the final goal of using the recovered R32 for the formulation of new HFC/HFO refrigerant mixtures. This approach would minimize the amount of new HFCs placed on the market as well as the release to the environment or incineration of waste HFCs.

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The separation of R410A into its individual constituents poses a great challenge because R410A is a near-azeotropic mixture with very low temperature glide ( $\sim 0.1$  K) in the whole composition range. Moreover, the R32 + R125 binary system exhibits a positive azeotrope at the composition near 90 mol % R32 that is almost independent of temperature [6], and thus, conventional distillation cannot be applied to the separation of the components that constitute the R410A blend. Nevertheless, several strategies have been described to overcome this issue. Shiflet and Yokozeki [7,8] proposed the use of ionic liquids (ILs) as entrainers to perform the separation of R32 and R125 from R410A by extractive distillation. Since then, the phase behaviour of these and other HFCs have been widely studied in ILs [9–11], providing very relevant information that can serve as the basis for engineering novel processes for separating HFC mixtures [12–14]. In addition, the adsorption separation of R410A have been successfully addressed by means of the preferential uptake of one of the components of the mixture in zeolites and activated carbons [15,16].

Yet, to the best of our knowledge, the separation of R32 apart from the mixture R410A using membrane technology has never been reported. In fact, the study of the gas permeation properties of refrigerant gases through polymer membranes remains a quite unexplored field of research. To date, only a few works provide data on the membrane permeation properties of fluorinated hydrocarbons. In particular, high permeability values of several chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and perfluorocarbon gases (PFCs) were found in high-free volume glassy PTMSP [17,18]. In addition, Hirayama et al. [19] reported the permeability of PFCs and CFCs in several poly(ethylene oxide)-containing membranes. Regarding the most common refrigerants used nowadays, Stern et al. [20] assessed the influence of pressure and temperature on the gas permeability of trifluoromethane (R23) in rubbery polyethylene, and recently, we reported for the first time on the permeation properties of the widely used HFCs 1,1,1,2-tetrafluoroethane (R134a, GWP = 1430) and R32, and the HFO 2,3,3,3-tetrafluoropropene (R1234yf, GWP = 4) in several poly(ether-block-amide) (under the trade name Pebax®) membranes [21]. Findings from that work showed that R32 exhibits the highest permeability of them because of its small size and high solubility in Pebax® copolymers. This fact, coupled with the exceptional properties of Pebax® films in terms of ease of casting and good mechanical resistance, makes Pebax® an excellent candidate to explore the recovery of R32 from the R410A mixture. In addition, this thermoplastic copolymer has already been employed to synthesize high IL content polymer gels as a promising strategy to further enhance the separation performance towards target compounds [22–28], yet these composite ionic liquid polymer membranes (CILPMs) have never been applied to the separation of HFCs gases. Moreover, critical information for process design regarding the influence of pressure on gas permeability and membrane stability, the permeability under mixed-gas conditions, and the long-term performance of this type of membranes is seldom reported.

Therefore, we herein report for the first time on the performance of dense polymer membranes based on Pebax® copolymer and its blends with ILs to separate the refrigerant gas R32 from the near-azeotropic mixture R410A formed by R32 and R125. Polymer-IL blends were prepared with four low-viscosity ILs exhibiting different degrees of anion fluorination and a wide range of molar volumes in order to assess the influence of these variables, as well as the IL content within the CILPMs, on the mixed-gas permeability of R32 and R125 at pressures up to 12 bar. Eventually, a long-term stability assay was addressed with the CILPM that provided the best separation performance.

## 2. Experimental

### 2.1. Materials

Butan-1-ol (99.9%) purchased from VWR, was used as solvent for membrane preparation by the solvent casting method. The polymer used

**Table 1**

Properties of the ILs used at 30 °C and 1 bar.

Ionic Liquid	CAS No.	$\eta$ (mPa·s)	$\rho$ (g·cm <sup>-3</sup> )	$M$ (g·mol <sup>-1</sup> )	$V_m$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
[C <sub>2</sub> mim]	331717-	20.8	1.114	169.3	151.9 [29]
[SCN]	63-6	[29]	[29]		
[C <sub>2</sub> mim]	143314-	32.3	1.279	198.0	154.8 [30]
[BF <sub>4</sub> ]	16-3	[30]	[30]		
[C <sub>2</sub> mim]	145022-	36.3	1.382	260.2	188.3 [29]
[OTf]	44-2	[29]	[29]		
[C <sub>2</sub> mim]	174899-	27.2	1.514	391.3	258.5 [31]
[Tf <sub>2</sub> N]	82-2	[31]	[31]		

**Table 2**

Physical properties of refrigerants R32 and R125 and their equimass mixture (R410A).

Property	R32	R125	R410A blend
CAS No.	75-10-5	354-33-6	–
$M$ (g·mol <sup>-1</sup> )	52.02	120.02	–
$V_c$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	122.4	211.9	–
Normal boiling point (K)	221.5	225.1	–
$T_c$ (K)	351.3	339.2	–
$P_c$ (bar)	57.8	36.2	–
Acentric factor	0.277	0.306	–
Dipole moment (D) [32,33]	1.978	1.563	–
Chung diameter (Å) [34]	4.02	4.82	–
GWP (100 years, CO <sub>2</sub> -eq)	675	3500	2088
Vapor pressure at 30 °C (bar)	19.27	15.68	18.89

was poly(ether-block-amide) (Pebax 1657®MH grade), which was kindly provided as pellets by Arkema (Spain). The IL 1-ethyl-3-methylimidazolium thiocyanate [C<sub>2</sub>mim][SCN] (>98%) was purchased from IoLiTec, whereas 1-ethyl-3-methylimidazolium tetrafluoroborate [C<sub>2</sub>mim][BF<sub>4</sub>] (>98%), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [C<sub>2</sub>mim][OTf] (>98%) and 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [C<sub>2</sub>mim][Tf<sub>2</sub>N] (>98%) were purchased from Sigma-Aldrich.

All reagents employed in the preparation of membranes (polymer, solvent and ILs) were used as received. Properties of each IL, viscosity ( $\eta$ ), density ( $\rho$ ) and molar volume ( $V_m$ ) are summarized in Table 1. The R410A mixture (50 wt % R32 and 50 wt % R125) was purchased from Coproven Climatización (Gas Servei licensed supplier, Spain). Table 2 shows the properties of the R410A blend and its constituents (R32 and R125). Chemical formulas and 3D structures of the constituents of the R410A mixture, the ILs used and the chemical formula of the repeated unit of the Pebax®1657 copolymer are shown in Tables S1–S2 and Fig. S1 of the Supplementary Information.

### 2.2. Membrane preparation

Dense polymer films were prepared by solving Pebax®1657 pellets in butan-1-ol, 3 wt % solution, under magnetic stirring at 100 °C for 24 h. The polymer solution was poured in a glass Petri dish and solvent evaporation was conducted in a vacuum oven at 300 mbar and 40 °C for 24 h. The Pebax®1657 polymer is a thermoplastic elastomer made of rigid polyamide (40 wt %) and flexible polyether (60 wt %) units. The polyamide segments (PA, melting point at 215 °C) confer stability and mechanical resistance to the polymer, whereas the polyether blocks (PEO, melting point at 67 °C) give flexibility and higher chain mobility.

The CILPMs were prepared by adding the desired amount of IL to the polymer solution once the Pebax®1657 pellets were completely dissolved. To avoid gelation, the mixture IL + solvent + polymer was stirred for 1 h at 100 °C. Next, the solution was casted under the same vacuum and temperature conditions used for casting the neat polymer membranes. Note that butan-1-ol was used as solvent instead of water-based mixtures in order to avoid the formation of undesired by-

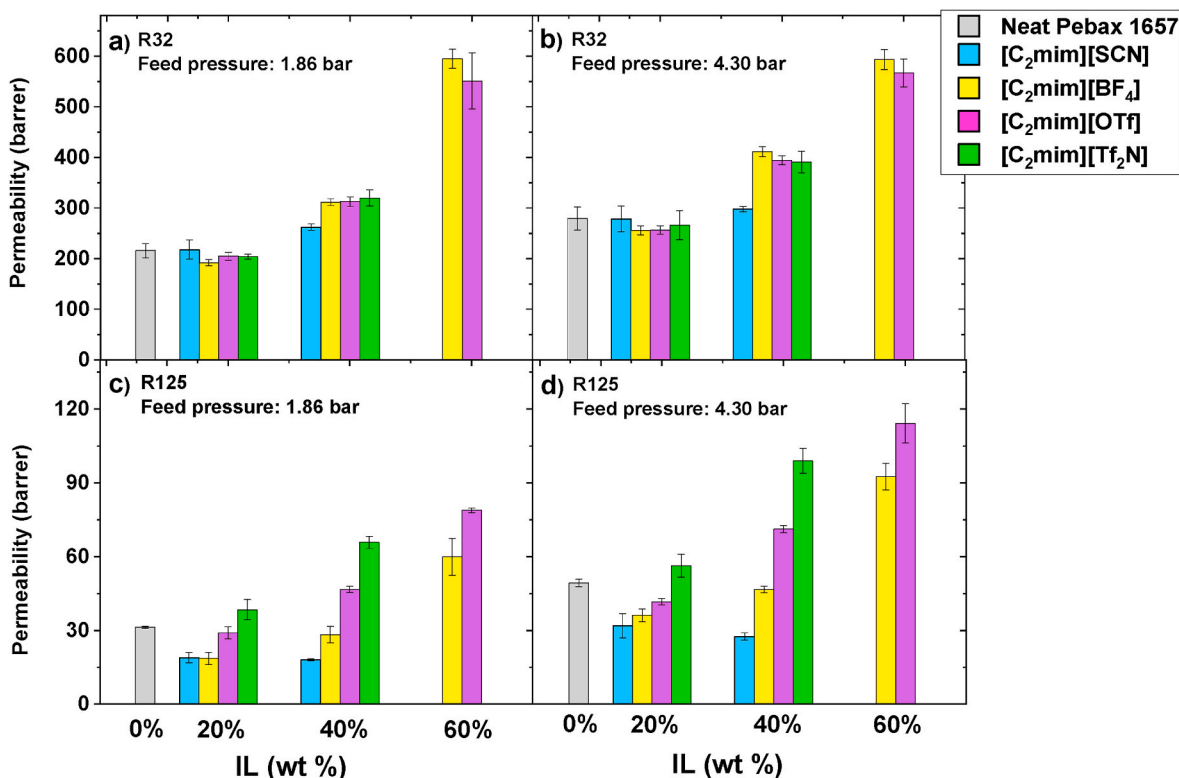


Fig. 1. R32 (1a, 1b) and R125 (1c, 1d) mixed-gas permeability through neat Pebax®1657 and several CILPMS at 30 °C as a function of IL content and R410A feed pressures of 1.86 bar (1a, 1c) and 4.3 bar (1b, 1d).

products, like HF, which may result from hydrolysis of the fluorinated ILs used in this work [35,36]. Membrane thickness was measured at 9 different positions with a digital micrometer (Mitutoyo MDC-25PX, accuracy  $\pm 1 \mu\text{m}$ ), being the average value of all prepared membranes  $100 \pm 10 \mu\text{m}$ .

Apart from the neat Pebax®1657 membrane, 12 different CILPMS were fabricated varying the IL anion (SCN<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, OTf<sup>-</sup> and Tf<sub>2</sub>N<sup>-</sup>) and the IL content between 20 and 60 wt %. However, free standing membranes could not be fabricated with 60 wt % IL content of [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][Tf<sub>2</sub>N] as they exhibited fragile behaviour, a fact that can be ascribed to the use of butan-1-ol as solvent instead of alcohol/water mixtures [23]. Notably, all CILPM membranes prepared with up to 40 wt % IL were able to withstand a feed pressure of 12 bar without damage. However, the CILPMS with 60 wt % IL content did not exhibit enough mechanical stability to be tested at feed pressures higher than 4.3 bar.

The thermal properties of the films were determined by differential scanning calorimetry (DSC Q100, TA Instruments). Samples of 10–15 mg were encapsulated in hermetic aluminum pans and subjected to a heating/cooling/heating cycle in the range from  $-80$  to  $220 \text{ }^\circ\text{C}$  at a rate of  $15 \text{ }^\circ\text{C min}^{-1}$ . The thermograms corresponding to the second heating run, shown in Fig. S2 of the Supplementary Information, reveal that the melting temperature of the rigid PA block, observed at  $200 \text{ }^\circ\text{C}$  for the neat Pebax®1657 sample, is shifted to lower temperatures as the IL content increases in the CILPMS. Besides, the area of that melting peak also decreases with increasing IL content, which may be attributed to a decreased polymer crystallinity. On the other hand, the peak associated to the melting temperature of PEO segments, observed at  $11 \text{ }^\circ\text{C}$  in the neat polymer, becomes almost imperceptible in the CILPMS. In conclusion, the DSC results suggest that the ILs studied in this work have preferential interactions with the PEO blocks of the Pebax®1657 copolymer. This behavior is consistent with the DSCs observed for other Pebax®1657-based CILPMS prepared using ILs that share the anion with those used in this work, e.g., [C<sub>4</sub>mim][OTf] and [C<sub>4</sub>mim][Tf<sub>2</sub>N], among others [22,23,26,28].

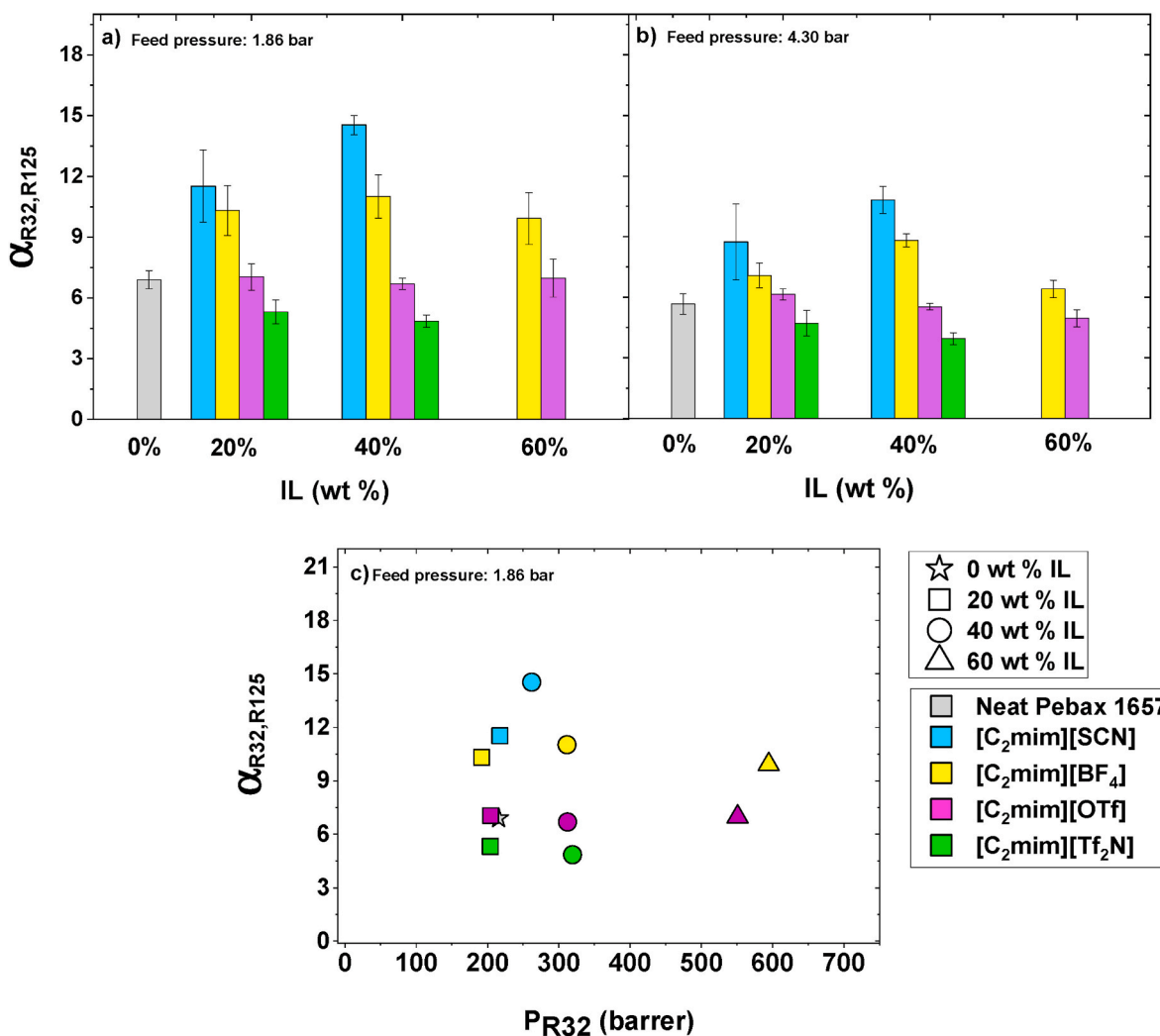
In addition, SEM images of the surface morphology and cross-section of CILPMS with Pebax®1657 and 40 wt % of [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>] were taken by scanning electron microscopy (SEM, Carl Zeiss EVO MA 15). Samples were prepared by freeze-fracturing after immersion in liquid nitrogen, followed by gold thin film deposition using a sputter coater (Balzers Union SCD040). Photographs and SEM images, provided as Supporting Information in Figs. S3 and S4, respectively reveal that the composite membranes consisted of dense homogeneous structures with no porosity.

### 2.3. Gas permeability measurements

In this work, the membrane permeability of each gas was determined using an experimental setup designed for continuous operation in which the flat membrane was placed inside a custom-made stainless-steel permeation cell. In all experiments, the feed gas was the refrigerant R410A, an equimass mixture of R32 and R125. During the permeation experiment, an argon stream ( $4 \text{ cm}_{\text{STP}}^3 \text{ min}^{-1}$  and 1 bar) swept the permeate side of the membrane and the steady state concentration of R32 and R125 in the permeate was quantified by gas chromatography (Agilent 490 micro GC, equipped with a Pora Plot U column and a thermal conductivity detector). Further details regarding the experimental setup and measuring procedure can be found in Ref. [37,38]. Permeation experiments were performed at  $30 \text{ }^\circ\text{C}$  varying the R410A feed pressure in the range 1.3–12 bar. In addition, the long-term stability of the composite membrane formed by Pebax®1657 and 40 wt % [C<sub>2</sub>mim][SCN] was tested at 7 bar feed pressure for 18 days, followed by testing at 12 bar during 7 additional days.

Gas permeability through the membrane was calculated according to Eq. (1)

$$P_i = \frac{Q_i \cdot \delta}{A \cdot (\hat{f}_{R,i} - \hat{f}_{P,i})} \quad (1)$$



**Fig. 2.** R32/R125 selectivity as a function of IL content and anion type in CILPMs at 30 °C and R410A feed pressures of 1.86 bar (2a) and 4.3 bar (2b). Summary of R32/R125 selectivity vs. R32 permeability (30 °C and 1.86 bar R410A feed pressure) as a function of IL content in the CILPMs (2c): 0 (star), 20 (squares), 40 (circles) and 60 wt % IL (triangles).

where  $P_i$  is the permeability of gas  $i$  through the membrane,  $Q_i$  is the transmembrane flux of component  $i$ , calculated as the experimental concentration of the gas in the permeate stream multiplied by the permeate flowrate,  $\delta$  is the membrane thickness,  $A$  is the membrane area and  $\hat{f}_{R,i}$  and  $\hat{f}_{P,i}$  are the fugacity of component  $i$  in the gas mixtures of the retentate and permeate streams, respectively. The component fugacity in the mixture was calculated with Eq. (2),

$$\hat{f}_i = \hat{\phi}_i p_i \quad (2)$$

where  $\hat{\phi}_i$  and  $p_i$  represent the fugacity coefficient of component  $i$  in the R410A binary mixture calculated by the Peng-Robinson equation of state, and the partial pressure of  $i$ , respectively [39]. Eventually, the competitive permselectivity ( $\alpha_{ij}$ ) was calculated according to Eq. (3),

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (3)$$

where  $i$  and  $j$  are the most and least permeable gases, respectively.

### 3. Results and discussion

#### 3.1. Influence of IL content and anion moiety on R410A separation

Fig. 1 shows the mixed-gas permeability of the constituents of R410A mixture (R32 and R125) in the neat Pebax®1657 membrane (0 wt % IL) and through CILPMs as a function of the IL content (20–60 wt % IL) and anion moiety at two different pressures (1.86 and 4.3 bar). The results show that R32 permeates faster than R125 in all membranes tested, thus proving our initial hypothesis that the separation of the components of the near-azeotropic mixture R410A can be efficiently performed with membrane technology, thus enabling the recovery of the value-added R32 in the permeate stream.

The transport of fluorinated hydrocarbons through polymeric membranes can be described according to the solution-diffusion model [21]. In this sense, R32 diffusivity is expected to be higher than that of R125 because of its smaller molecular size (see Table 2). On the other hand, gas solubility may depend on several intrinsic properties of the gases, such as condensability, molecular size and polarity [17]. Therefore, despite having similar condensability ( $T_B^{R32} = 221.5$  K;  $T_B^{R125} = 225.1$  K), R32 would also be more soluble in the polymer matrix than R125 because of its smaller molecular size and higher polarity ( $\mu^{R32} = 1.978$  D,  $\mu^{R125} = 1.563$  D). It is important to note that more polar gases

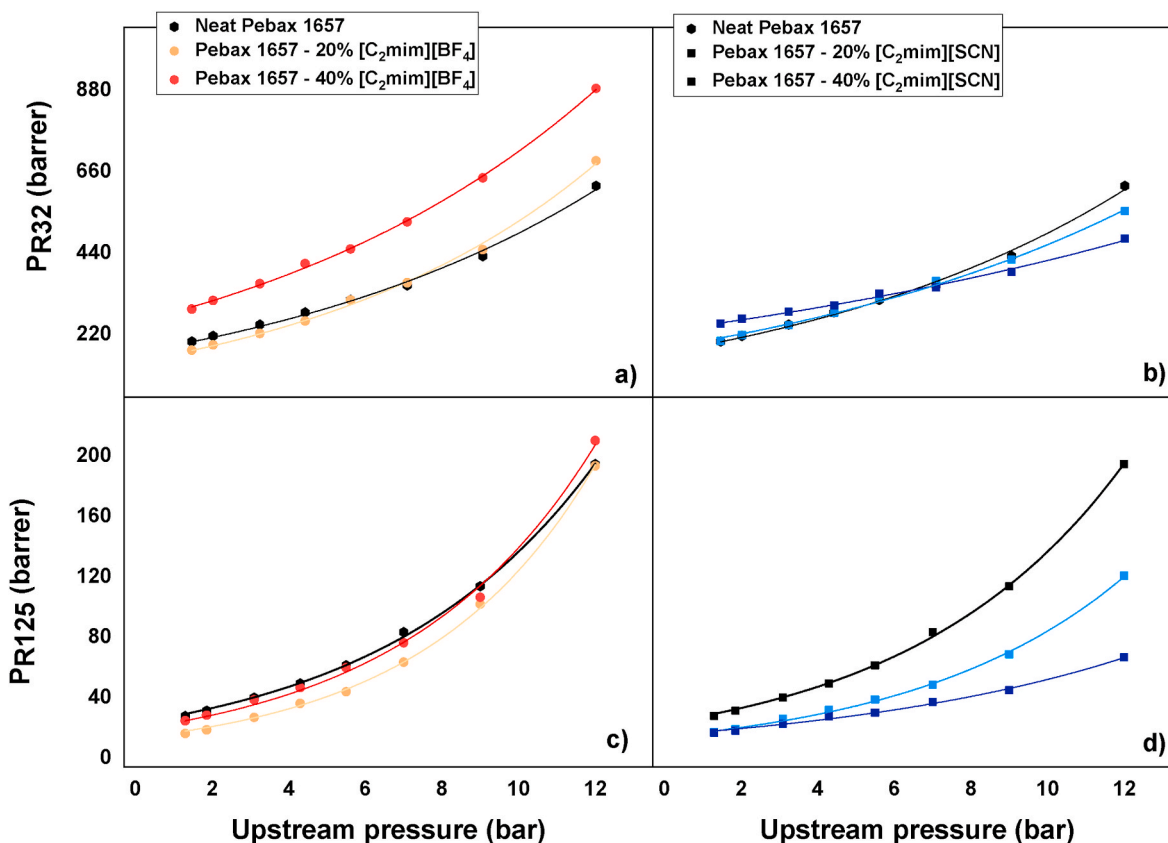


Fig. 3. R32 (3a, 3b) and R125 (3c, 3d) mixed-gas permeability at 30 °C through several CILPMs as a function of R410A feed pressure and IL content and anion type.

may have preferential interactions both with the polar ether linkages of the PEO groups in the Pebax® membrane [40] and with the ILs contained in the structure of CILPM [41]. Therefore, the differences observed between R32 and R125 permeability through the CILPMs can also be ascribed to the higher solubility of R32 over that of R125 in ILs [41–43]. Furthermore, these results are in good agreement with our previous work [21], in which the exceptional ability of R32 to permeate through neat Pebax® membranes was attributed to its high solubility and diffusivity in the polymeric matrix compared to that of other fluorinated hydrocarbons.

Although permeation of HFCs gases in CILPM is a topic still unexplored, the influence of IL concentration in CILPMs has been reported in studies focused on the separation of CO<sub>2</sub> from N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> [44–47]. For Pebax®-based CILPMs, several authors [22,26,28] reported an enhancement of gas solubility and diffusivity with increasing IL content that in turn resulted in improved gas permeability, which was particularly significant, as observed in this work, for IL loadings above 20–30 wt %. In this work, a noticeable increment is observed in R32 permeability as the IL content increases, from 204.3 barrer in the neat polymer to ~600 barrer in the CILPMs containing 60 wt % [C<sub>2</sub>mim][BF<sub>4</sub>] and [C<sub>2</sub>mim][OTf]. However, no significant R32 permeability differences are noticed among the fluorinated ILs tested. In the case of the non-fluorinated IL [C<sub>2</sub>mim][SCN], R32 permeability is also enhanced with increasing IL content, yet this increment is less marked than for the fluorinated ILs, a fact that can be ascribed to the much higher solubility of R32 in fluorinated ILs [9,10,43]. In contrast, there is a clear influence of IL anion on the permeability of R125 through CILPMs, which increases in the order: [C<sub>2</sub>mim][SCN] < [C<sub>2</sub>mim][BF<sub>4</sub>] < [C<sub>2</sub>mim][OTf] < [C<sub>2</sub>mim][Tf<sub>2</sub>N]. Interestingly, this trend is consistent with the order of increasing IL molar volume (see Table 1), which is known to play a crucial role in determining gas solubility in both ILs and CILPMs. In fact, similar trends have been observed for the absorption of CO<sub>2</sub> [48–50] and fluorinated gases [10,43,51,52] in ILs, as well as for CO<sub>2</sub> permeability

and solubility through CILPM membranes [26]. Moreover, it is interesting to note that the addition of [C<sub>2</sub>mim][BF<sub>4</sub>] and [C<sub>2</sub>mim][SCN] leads to a decrease of R125 permeability with respect to the neat Pebax®1657 membrane, except for CILPMs prepared with 60 wt % [C<sub>2</sub>mim][BF<sub>4</sub>], a fact that can be exploited to enhance R32/R125 selectivity. This permeability decrease might be attributed to the expected lower solubility of R125 in small molar volume ILs with low degree of anion fluorination, such as [C<sub>2</sub>mim][BF<sub>4</sub>] and [C<sub>2</sub>mim][SCN], compared to its solubility in the neat Pebax®1657 copolymer.

The resulting R32/R125 competitive selectivity ( $\alpha_{R32/R125}$ ), shown in Fig. 2a and 2b, exhibits values between 4 and 15 depending on the IL content and anion moiety. Selectivity follows an opposite trend to that of gas permeability, i.e., [C<sub>2</sub>mim][SCN] > [C<sub>2</sub>mim][BF<sub>4</sub>] > [C<sub>2</sub>mim][OTf] > [C<sub>2</sub>mim][Tf<sub>2</sub>N]. To elucidate the separation efficiency of the CILPMs tested, Fig. 2c shows a Robeson type diagram where  $\alpha_{R32/R125}$  is plotted against the permeability of the most permeable gas at 1.86 bar. It can be observed that the CILPMs with [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>] significantly improve the performance of neat Pebax®1657 in terms of both permeability and selectivity. On the other hand, CILPMs based on [C<sub>2</sub>mim][OTf] and [C<sub>2</sub>mim][Tf<sub>2</sub>N] only improve the R32 permeation rates without enhancing the separation selectivity. This fact suggests that the separation performance of CILPMs containing more than 60 wt % [C<sub>2</sub>mim][OTf] would not be attractive in terms of R32/R125 selectivity. Overall, the highest permeability improvement is observed for the CILPMs functionalized with [C<sub>2</sub>mim][BF<sub>4</sub>], which triplicate the permeability of R32 in neat Pebax®1657. Conversely, the functionalization of the Pebax® polymer with [C<sub>2</sub>mim][SCN] provides the highest selectivity for the R32/R125 separation, which is up to two-fold higher than in the neat Pebax®1657 membrane.

### 3.2. Effect of feed pressure on R410A separation

According to the previous results, the CILPMs prepared with

Table 3

Parameters of the exponential fitting of R32 and R125 permeability as a function of transmembrane partial pressure (Eq. (4)). Pressure range: 1.3–12 bar. Temperature: 30 °C.

Gas	Parameter	Neat polymer	CILPM-[C <sub>2</sub> mim][SCN]		CILPM-[C <sub>2</sub> mim][BF <sub>4</sub> ]	
			20 wt %	40 wt %	20 wt %	40 wt %
R32	$P_0$ (barrer)	174.5	186.5	232.1	148.4	256.1
	$m$ (bar <sup>-1</sup> )	0.161	0.139	0.090	0.194	0.156
	$r^2$	0.995	0.997	0.994	0.997	0.999
R125	$P_0$ (barrer)	22.9	14.1	15.2	13.0	18.8
	$m$ (bar <sup>-1</sup> )	0.602	0.598	0.408	0.757	0.670
	$r^2$	0.999	0.998	0.995	0.995	0.996

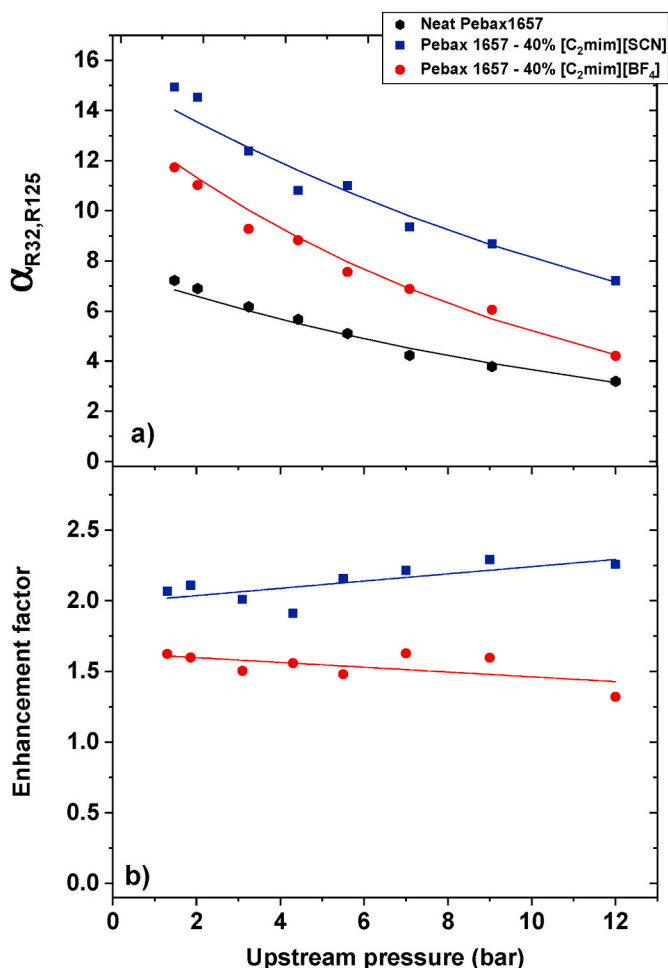


Fig. 4. (a) R32/R125 selectivity and (b) R32/R125 selectivity enhancement of CILPMs containing 40 wt % [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>] as a function of R410A feed pressure at 30 °C. Solid lines are a guide to the eye.

[C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>] were selected to further characterize their performance to separate the components of the R410A refrigerant mixture. Fig. 3 shows the permeability of R32 and R125 as a function of the upstream pressure, which was varied between 1.3 and 12 bar. As can be seen, the permeability of each gas exponentially increases with pressure, which is the expected behavior of highly condensable gases permeating through rubbery polymers [53–56]. Therefore, the experimental data were accurately fitted ( $r^2 > 0.99$ ) to an exponential function (Eq. (4)) [56].

$$P_i = P_{0,i} \cdot e^{m \cdot \Delta P_i} \quad (4)$$

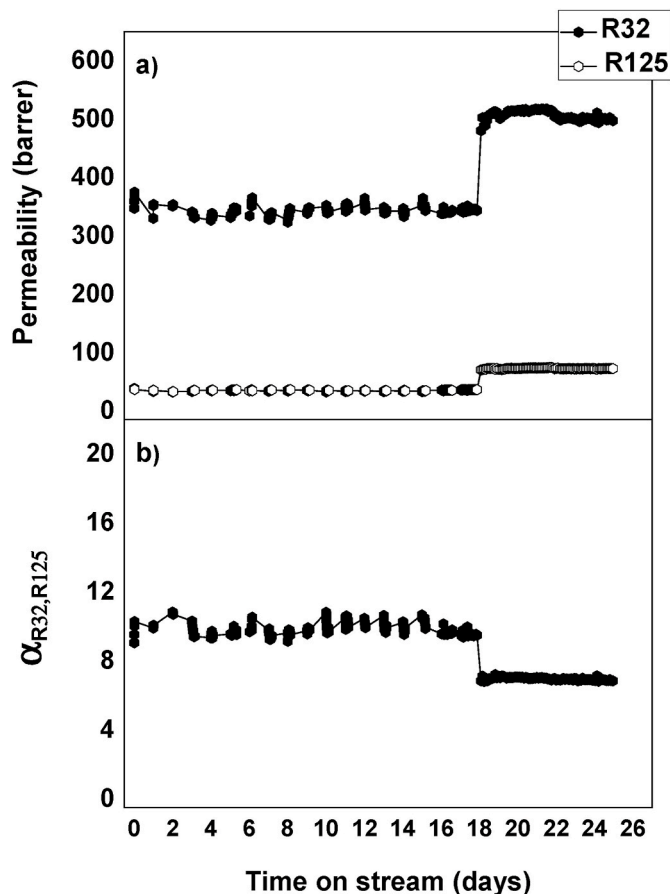


Fig. 5. R32 and R125 permeability (5a) and R32/R125 selectivity (5b) vs. time on stream at 30 °C through the 40 wt % [C<sub>2</sub>mim][SCN] CILPM. The feed gas is R410A mixture at 7 bar (until day 18) and 12 bar (from day 18).

where  $P_{0,i}$  is a preexponential factor and  $m$  is a constant that provides information of the pressure influence on gas permeability. Table 3 presents the fitting of experimental data to Eq. (4), showing that the feed pressure has a stronger effect on R125 permeability than on R32 permeation rate (i.e.,  $m_{R125} > m_{R32}$ ). In addition, increasing the IL content from 20 to 40 wt % slightly decreases the pressure influence on gas permeability. This effect is particularly significant for R125 permeability through the CILPM containing 40 wt % [C<sub>2</sub>mim][SCN], a fact that will improve R32/R125 separation performance. With respect to the anion type, the pressure effect on gas permeability is stronger in CILPMs prepared with [C<sub>2</sub>mim][BF<sub>4</sub>] than with [C<sub>2</sub>mim][SCN].

As a result of the pressure influence on gas permeability, the R32/R125 separation selectivity decreases with increasing feed gas pressure as observed in Fig. 4a for the CILPMs containing 40 wt % [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>]. This effect can be ascribed to the strong plasticizing ability of the gas penetrants, which typically increases polymer chain mobility and decreases its size-sieving ability and the resulting separation selectivity [54,57,58]. Indeed, this effect is more pronounced as feed pressure increases because of the higher penetrant concentration within the polymer [59]. Finally, the R32/R125 selectivity enhancement ( $E_{R32/R125}$ ) achieved with these CILPMs with respect to the neat polymer was calculated with Eq. (5) and plotted in Fig. 4b as a function of pressure.

$$E_{R32/R125} = \frac{\alpha_{R32/R125}^{CILPM}}{\alpha_{R32/R125}^{Neat\ Pebax\ 1657}} \quad (5)$$

Fig. 4b reveals that the selectivity of the R32/R125 separation with 40 wt % [C<sub>2</sub>mim][SCN] CILPM is two times higher than the selectivity of

the neat polymer, and that this factor is slightly benefitted by operating the membrane process at increasing feed pressures. With respect to the 40 wt % [C<sub>2</sub>mim][BF<sub>4</sub>] CILPM, the selectivity enhancement achieved is lower than with [C<sub>2</sub>mim][SCN] CILPMs and slightly decreases with pressure.

According to these results, the 40 wt % [C<sub>2</sub>mim][SCN] CILPM not only exhibits a significant improvement in the separation of the components of the R410A refrigerant blend compared to the neat polymer, but also achieves a reasonably high R32 permeability, which is close to 480 barrer at 12 bar. Therefore, the novel membrane materials prepared in the present study could meet the separation needs for the recovery of the still valuable R32 refrigerant from the R410A commercial mixture, which is on the verge of being phased out. The recovery of R32 would boost its reuse for the reformulation of more environmentally friendly HFC/HFO refrigerant mixtures that meet the needs of reduced global warming potential index.

### 3.3. Long-term separation performance of R410A with CILPMs

The long-term stability and separation performance of the 40 wt % [C<sub>2</sub>mim][SCN] CILPM was tested for 25 days. Fig. 5 presents the permeability and selectivity data obtained in continuous mode of operation feeding the refrigerant mixture R410A (50 wt % R32 and 50 wt % R125). Focusing on the permeability (Fig. 5a), both R32 and R125 maintained stable permeation rates working at 7 bar for 18 days. As shown in Fig. 5b, R32 permeability (~350 barrer) was 9.5 times higher than R125 permeability. In the next period of 7 days, the feed pressure was increased to 12 bar. As expected, the permeability of both R32 and R125 were enhanced, although at the expense of a moderate reduction in the separation selectivity. Overall, the CILPM prepared with 40 wt % [C<sub>2</sub>mim][SCN] and Pebax®1657 polymer exhibited a stable behaviour during the 25 days of testing. In this sense, these results demonstrate that this type of composite membranes can be operated to yield very good permeability and selectivity values for a reasonably long period of operation.

## 4. Conclusions

This work addresses for the first time the separation of the constituents of the refrigerant mixture R410A, formed by 50 wt % difluoromethane (R32) and 50 wt % pentafluoroethane (R125), using functionalized CILPMs based on Pebax® copolymer. Several CILPMs were prepared by tuning the IL type and content within the polymer matrix. The recovery of value-added R32 is sought because this compound still has potential to be used in the formulation of future refrigerant blends due to its relatively low GWP compared to that of other HFCs. The results revealed that all CILPMs outperformed the performance of the neat polymer membrane in terms of permeability; however, only the CILPMs based on [C<sub>2</sub>mim][SCN] and [C<sub>2</sub>mim][BF<sub>4</sub>] were able to improve the separation selectivity of the neat Pebax®1657 films. Furthermore, these membranes also exhibited good mechanical performance, being able to withstand feed pressures up to 12 bar with IL contents up to 40 wt %. Finally, the CILPM containing 40 wt % [C<sub>2</sub>mim][SCN] also showed an outstanding stability for 25 days of continuous operation under 7 and 12 bar of feed pressure. Thus, this type of hybrid material can be considered as a good candidate towards the practical application of membrane technology for the recovery of value-added compounds from azeotropic or close boiling point refrigerant mixtures.

### Authors' statement

**Fernando Pardo:** Methodology; Formal analysis; Investigation; Resources; Writing- Original draft

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### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.memsci.2020.118744>.

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