



Research Paper

An Investigation on Gas Transport Properties of Elvaloy4170/[Emim][Tf₂N] Hybrid Membranes for Efficient CO₂/CH₄ SeparationMahvash Gharedaghi ¹, Mohammadreza Omidkhah ^{1,*}, Sasan Abdollahi ², Ali Ghadimi ^{3,*}¹ Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran² Petroleum Engineering Department, Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran³ Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

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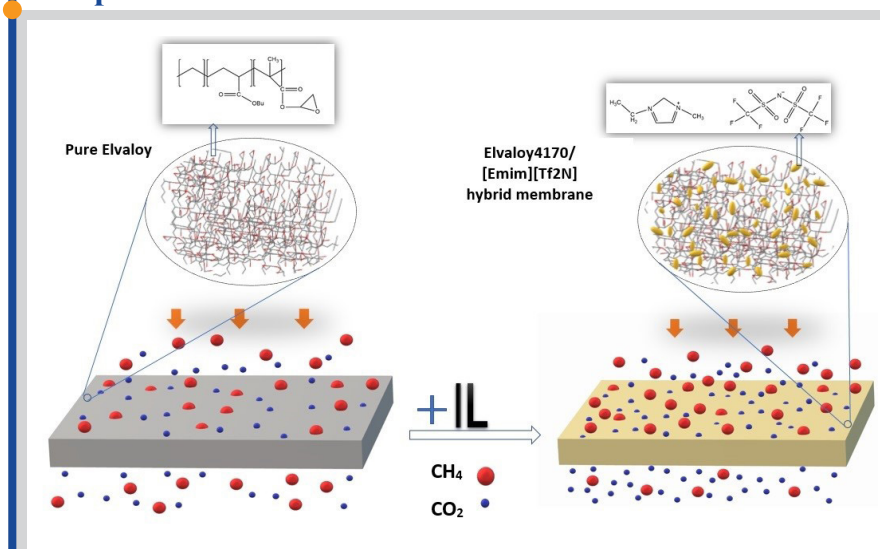
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Highlights

- Elvaloy4170/IL hybrid membranes were fabricated for efficient CO₂/CH₄ separation.
- All hybrid membranes showed greater CO₂ separation performance.
- Significant increase in selectivity (2.5 fold) was achieved in 40 wt. % IL hybrid membrane.
- All prepared membranes displayed great stability at pressure up to 16 bar.

Graphical abstract



Abstract

This study investigates the separation performance of a polymer-IL hybrid membrane comprised of Elvaloy4170 and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf₂N]) ionic liquid. The goal is to incorporate superior features of Elvaloy4170 as a cost-effective commercial polymer with desirable CO₂ permeability and mechanical strength, with those of [Emim][Tf₂N] such as high affinity to CO₂ molecules for fabricating high performance hybrid membranes. Results revealed that the presence of IL within the polymeric matrix leads to simultaneous enhancement of permeability and selectivity values. This is confirmed by the increase in CO₂ permeability from 88 to 141 Barrer accompanied with 2.5 fold increase in CO₂/CH₄ ideal selectivity in hybrid membrane containing 40 wt. % IL. Both SEM-EDX analysis and Maxwell predictions confirmed the heterogeneous structure of polymer/IL hybrid membranes with no specific chemical interactions confirmed by FTIR-ATR spectra. The hybrid membranes prepared in this study showed promising separation performance at low temperature levels, e.g. CO₂/CH₄ ideal selectivity reached to 24.3 at 15°C. Moreover, separation performance of the hybrid membranes displayed minute variation facing higher pressures of up to 16 bar.

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1. Introduction

Natural gas (NG) as one of the cleanest fuel resources supplies a significant proportion of the energy used worldwide. Presence of CO₂ in these resources results in considerable problems in gas compression and transportation sectors [1]. Hence, employment of an appropriate CO₂ removal process with minimal energy penalty to meet the pipeline specifications has become a concerning key issue. Natural gas processing using membrane technology enjoys several advantages over energy-intensive amine-based processes like simplicity, small footprint, low energy consumption, and being more

environmentally friendly [2-10].

Material selection is the cornerstone of membrane fabrication. In recent years, polymeric membranes have been proved to be reliable solution for several gas separation applications due to their excellent film forming property, mechanical stability, and low cost [11-13]. Despite the rapid growth in development of new polymers, certain tradeoffs between permeability and selectivity restricts separation performance of polymeric membranes. In addition, tendency of polymeric membrane to plasticization and consequently

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reduction in their separation performance when facing high partial pressures of condensable gases like CO₂ or vapor organic compounds (VOCs) is another challenging issue [14,15]. Therefore, evaluation of new polymers or hybrid polymeric composites is needed to fulfill the all requirements such as permeability and selectivity as well as thermal, mechanical, and chemical stability for developing reliable membrane-based separation systems [16-18].

One of the effective methods to obtain composite materials with enhanced gas transport properties is incorporating solid or liquid fillers with synergetic and unique properties into host polymeric matrices. In this regard, embedding of ionic liquids (ILs) into polymeric membranes for enhancing the separation properties is an interesting research scope which has attracted attention of researchers dealing with this topic [19]. ILs possess unique physico-chemical properties such as negligible vapor pressure and high CO₂ solubility; they also have adjustable structures providing opportunities for design of different polymer-IL hybrid membranes with promising properties compared to conventional polymeric membranes especially for CO₂ separation purposes [20-22]. For instance, mass transfer rate in ILs is much faster than polymeric membranes resulting in higher fluxes through the hybrid membranes and more beneficial separation [9,23,24].

ILs are salts with asymmetrical combination of the cation and anion with weak linkages which are in general in liquid state below 100 °C [25]. The good solubility of CO₂ in ILs is the result of the asymmetrical structure of the ionic segments [23]. Investigations have also manifested that presence of CO₂-philic groups such as fluorine, carbonyl and S=O groups in the anion segments could enhance CO₂ absorption [26,27]. In addition, the fluorinated anions like: [PF₆], [BF₄], and [Tf₂N] strongly associate with CO₂, and it is expected that this type of the anions provide higher CO₂ capture ability [27, 28]. Pringle et al. compared the CO₂ capture ability of a fluorinated IL like [Emim][Tf₂N] with a nonfluorinated form [Emim][NMe₂] and the results confirmed that [Emim][Tf₂N] with Henry's law constant of 47±6 atm has higher CO₂ absorption compared to [Emim][NMe₂] with Henry's law constant of 76±8 atm [29]. The appropriate CO₂ absorption of [Emim][Tf₂N] is most probably due to the combination of S=O and fluorine groups. Moreover, regarding ab initio calculations S=O group can augment the CO₂ philicity due to establishment of Lewis base-Lewis acid interactions with carbon atom of CO₂ [30]. Furthermore, among different cation groups, imidazolium-alkyl based ILs, with higher CO₂ solubility proportional to the others, have attracted more attention for CO₂ capture applications.

Up till now, various types of polymers such as poly(vinylidene fluoride) hexafluoropropylene P(VDF-HFP) [31-33], poly(vinylidene difluoride) (PVDF) [34], polyether-polyamide block-copolymer (Pebax) [23], Polyimide (PI) [35], poly(styrene-*b*-ethylene oxide-*b*-styrene) (SOS) and poly(styrene-*b*-methylmethacrylate-*b*-styrene) (SMS) triblock copolymers [36] have been employed to prepare polymer-IL hybrid membranes. In these hybrid membranes, interactions between polymer and IL could be either physical or chemical [37]. Among rubbery polymers with relative high permeability, Pebax is one of the mostly studied polymers in combination with different ILs for fabrication of hybrid polymer-IL membranes. Rabiee et al. fabricated reverse selective gel membranes for CO₂ separation by blending [C₂mim][BF₄] and Pebax®1657. They observed an increasing trend of CO₂ permeability against the IL loading contents [38]. Qiu et al. prepared Pebax®1657/[Emim][PF₆] hybrid membranes, they observed that incorporation of [Emim][PF₆] increases the gas solubility coefficients of CO₂, N₂, CH₄ and H₂, while permeability values of CO₂, N₂, CH₄ and H₂ decrease due to reduction of gas diffusion coefficients. Meanwhile, they reported a slight enhancement in the selectivity of CO₂/CH₄. Interestingly, Bernardo et al. reported a significant increment in gas transport properties of Pebax®1657 by incorporating [Bmim][CF₃SO₃], while no remarkable change was observed in separation performance of Pebax®2533 in presence of that IL [20]. Therefore, because of the presence of many complexities and contradictories, appropriate selection of polymer/IL pair is an essential factor to be considered. This work systematically investigate separation performance of Elvaloy4170 as a commercially available polymer in presence of [Emim][Tf₂N] as an IL enhancer.

The principal purpose of this study is the development and characterization of polymer-IL hybrid membranes composed of [Emim][Tf₂N] and low price commercial Elvaloy4170 polymer matrix. This rubbery polymer has been designed by Dupont to rectify the properties of asphalt binder used in paving. To the best of our knowledge, there is just one scientific report investigating gas transport properties of Elvaloy4170 as membrane, up to date. In 2015, Ranjbaran et al. used Elvaloy4170 for fabrication of mixed matrix membranes filled by functionalized multi-walled carbon nanotubes. Based on the results obtained in that study, this inexpensive polymer (almost one-fourth price of PEBA) with promising separation performance can be considered as a proper candidate for different membrane gas separation applications [39]. Elvaloy4170 is a commercially available polymer with multiple positive features including low price (Much

less expensive than laboratory synthesized polymers), great mechanical stability, excellent film formation, and promising separation performance. Separation performance of this polymer has not been well studied in the literature. It is worth noting that almost all the commercial membranes in gas separation fields are fabricated based on few commercial polymers; therefore, it is needed that the separation properties of available polymers be available in the literature. This study specifically tries to provide transport properties of Elvaloy4170 for two common penetrants including CO₂ and CH₄.

In the current study, various Elvaloy-[Emim][Tf₂N] hybrid membranes were fabricated via solution-casting method. Separation performance and structural properties of the hybrid membrane were investigated. Desirable solubility properties of [Emim][Tf₂N], led to enhancement of separation performance of Elvaloy4170 membranes. The hybrid membranes prepared in this study showed an increase in CO₂ permeability and also CO₂/CH₄ ideal selectivity compared to the neat membranes.

2. Experimental

2.1. Material

Elvaloy4170 or Reactive Ethylene Terpolymer (RET) was provided by Dupont, USA in the form of white pellets with density of 0.94 g/cm³. Elvaloy4170 is comprised of polyethylene, polar methyl methacrylate and epoxide functional groups. The polyethylene backbone and polar methyl methacrylate functional groups are responsible for the mechanical strength and corrosion resistance properties of this polymer, while the epoxide groups provide the reactivity property. Tetrahydrofuran (CAS number: 109-99-9) and dichloromethane (CAS number: 75-09-2) were used as solvent and purchased from Merck (Germany). 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf₂N]) ionic liquid (CAS number: 174899-82-2) with a purity of more than 97.0%, was acquired from Merck (Germany). N₂, CH₄ and CO₂ with the purity of 99.99% were provided by Farafan Gas Inc. (Iran). All the materials and the gases were used as received. In addition, some of physical properties of the materials are summarized in Table 1.

Table 1
Physical properties of the materials.

| Material | Melting point (°C) | Boiling point (°C) | Density (g/cm ³) |
|--|--------------------|--------------------|------------------------------|
| Elvaloy4170 properties (Dupont) | 72 | - | 0.94 |
| [Emim][Tf ₂ N] properties (Merck) | -15 | - | 1.52 |
| Dichloromethane (DCM) (Merck) | -95 | 40 | 1.33 |
| Tetrahydrofuran (THF) (Merck) | -108.5 | 65-66 | 0.89 |

2.2. Membrane preparation

Primarily, the polymer pellets were kept in a vacuum oven at 60 °C overnight to remove the possible absorbed moisture. Then, a 6 wt.% polymeric solution was prepared by dissolving Elvaloy4170 in THF, heating at 70 °C and magnetically stirring for 4 h to obtain a homogeneous polymer solution. Likewise, a 3 wt. % polymer solution was prepared in DCM at 50 °C to compare the morphology of the membranes prepared in DCM and THF. Investigations showed that concentration of the polymer solution has a great importance, due to two major reasons: firstly, proper dispersion of IL with no sedimentation depends on the solution concentration, and secondly, higher concentrations could make fabrication of defect free membranes challenging. Afterwards, different IL amounts were added to the polymer solution to prepare the polymer-IL solution containing 10 to 40 wt. % of the IL based on the polymer weight. The polymer-IL solutions were again stirred for 2 h under the same heating conditions, to ensure obtaining a completely homogeneous solution. After degassing, the polymer-IL solutions were cast on glassy petri dishes for preparing the free-standing dense membranes by solvent evaporation method. In the first drying step, the membranes prepared in THF and DCM were respectively kept in an oven at 50 °C and 37 °C for 30 min, and then, in the second drying step all the membranes were placed in vacuum oven at 50 °C for 2 h.

2.3. Membrane characterization

The structural properties of the membranes were characterized by different analysis including scanning electron microscopy (SEM, TESCAN VEGA II), Fourier transform infrared (FT-IR, BRUKER (VERTEX 80)) with attenuated total reflectance accessory (ATR) and differential scanning calorimetry (DSC, METTLER TOLEDO DSC 822). Further information for the instruments are available elsewhere [40].

2.4. Permeability and solubility measurements

Gas permeation properties of the membranes were measured by the constant volume method [41]. To control the temperature of the experiments, all equipment were immersed in a water bath equipped with a circulator set. Pressure regulators (PRs) were used to adjust the pressure. The experiments were continued until the steady state was attained. Permeability coefficients of the gases are calculated using Eq. (1):

$$\text{Permeability (Barrer)} = \frac{273.15 L \times V}{76 A \times T \times P} \times 10^{10} \times \left(\frac{dP}{dt}\right) \quad (1)$$

where L , V , P , T and A are membrane thickness (cm), permeate volume (cm^3), feed pressure (cmHg), operating temperature (K), and membrane effective surface area (cm^2), respectively. dp/dt is pressure increment in the permeate vessel versus time (cmHg/s), and Eq. (1) gives permeability in Barrer ($1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cmHg}$).

The ideal selectivity of the membranes is obtained using Eq. (2):

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (2)$$

Gas solubility experiments were conducted according to the dual-volumes/dual-sensors method [42]. Concentration of the dissolved gas into the membrane matrices is calculated by the following Eq. (3) [38]:

$$C = \frac{22414}{RT} (P_1 - P_2) \frac{V_m}{V_p} \quad (3)$$

where C is the concentration of dissolved gas ($\text{cm}^3(\text{STP})/\text{cm}^3$ membrane), P_1 and P_2 are initial and final pressure in the sample vessel, and V_m and V_p are volumes of the sample vessel and the membrane sample (cm^3), respectively. R is the universal gas constant, T defines absolute temperature and 22.414 is the Avogadro's number. The gas solubility coefficients (S) are calculated using Eq. (4):

$$S = \frac{C}{P} \quad (4)$$

All the experimental permeation and sorption data reported in this study are averaged values obtained from three different samples. The maximum relative errors for permeation and sorption measurements were almost equal to 7 and 5 %, respectively. The diffusion coefficients can be calculated using the solution-diffusion theory.

3. Results and discussion

3.1. Characterization

3.1.1. SEM results

SEM and SEM-EDX analyses were performed to investigate distribution of the IL through the host Elvaloy4170 matrix. Figure 1a, shows the cross-sectional morphology of the neat Elvaloy4170 membrane which is completely uniform and regular. Figures 1b and c depict cross-sectional morphology of Elvaloy4170/IL 20 and 40 wt. % hybrid membranes prepared in THF, respectively. Regarding these cross-sectional images, and also the surface morphology shown in Figure 1i it was concluded that this group of hybrid membranes could not provide a proper IL distribution in their structure. This improper distribution is more obvious at higher IL contents confirmed by the corresponding X-ray maps of fluorine in Elvaloy4170/40 wt. % IL (Figure 1d). This observation is explained according to the lower density of THF ($\rho = 0.89 \text{ g/cm}^3$) and Elvaloy ($\rho = 0.94 \text{ g/cm}^3$) compared to that of the IL ($\rho = 1.52 \text{ g/cm}^3$). Indeed, a solvent with closer density to

[Emim][Tf₂N] is needed for preparation of the hybrid membranes with a proper IL distribution. Therefore, DCM with a higher density value ($\rho = 1.33 \text{ g/cm}^3$), high solubility for Elvaloy4170 and also desirable

polarity was selected as solvent. Figures 1e-g show hybrid membranes synthesized in DCM, with the IL contents of 10, 20, and 40 wt. %, respectively. As can be seen in Figure 1e, Elvaloy4170/IL 10 wt. % hybrid membrane has a uniform structure, while significant structural changes are observed at the higher IL contents, (Figures 1f and g). With increasing the IL content to 20 and 40 wt. %, partial phase separation occurred between the polymer and the IL. However, SEM-EDX analyses confirmed the continuous and uniform distribution of the IL in body (Figure 1h) and at the surface (Figure 1j) of the hybrid membranes prepared by DCM. Similar observations have been reported by other researchers such as Chung et al. [34], Abdollahi et al. [43] and Filiz et al. [44]. Regarding the results obtained in this section, DCM was determined as a proper solvent.

3.1.2. DSC results

Thermal properties of the pure and the hybrid membranes were investigated by DSC analysis. Figure 2 presents DSC thermograms and Table 2 presents T_g values of those membranes prepared in this study. T_g of pure Elvaloy4170 membrane was obtained about -47°C . Considering Figure 2 and Table 2, presence of the IL into the polymeric matrix gradually decreases T_g values of the hybrid membranes compared to the pure membrane. For instance, for Elvaloy/IL 40 wt. % T_g value is 6.3°C lower than the corresponding value for the pure polymer. Indeed, presence of a low molecular weight additive enhances polymer chain mobility and results in lowering of the T_g values [33,34,43,45-47].

3.1.3. FTIR results

Figure 3 illustrates the FTIR-ATR spectra of Elvaloy4170, [Emim][Tf₂N], and Elvaloy4170/IL hybrid membranes. The characteristic peak in spectrum of [Emim][Tf₂N] at 2992cm^{-1} represents the stretching vibrations of aliphatic C-H groups and the peaks at 3124 and 3160cm^{-1} are related to the stretching vibrations of aromatic C-H group in the cation segment of the IL. In addition, the peaks located at 1574 , 1457 and 1351cm^{-1} are attributed to stretching vibrations of C=N, C=C, and C-N groups, respectively. The stretching vibrations of C-F and S=O in the anionic segment of IL are observed at 1190 and 1057cm^{-1} [48]. Considering the spectrum of Elvaloy4170, the observed peak at 721cm^{-1} is attributed to polyethylene chains and the peaks at 844 and 1065cm^{-1} are representative for epoxy and methyl methacrylate groups, respectively. The peaks depicted at 1464 and 1733cm^{-1} are attributed to the ester and the carbonyl groups, and derivatives of C-H are located around 2851 and 2914cm^{-1} . In the spectrum of Elvaloy/IL hybrid membranes, no significant change is observed toward pure IL and/or Elvaloy4170. Therefore, it is concluded that presence of [Emim][Tf₂N] into the matrix of Elvaloy4170 does not cause any chemical interactions and the two components are totally physically blended.

Table 2

T_g values for the pure and the hybrid membranes.

| Membrane | T_g ($^\circ\text{C}$) |
|---------------------------|----------------------------|
| Elvaloy4170 | -47.1 |
| EL/10 wt. % IL | -48.9 |
| EL/20 wt. % IL | -49.5 |
| EL/30 wt. % IL | -51.3 |
| EL/40 wt. % IL | -53.4 |
| [EMIM][Tf ₂ N] | -58.6 |

3.2. Transport properties of the membranes

3.2.1. Effect of IL loading

To investigate effect of IL loading contents on the separation performance of the membranes prepared in this study, gas permeability and ideal selectivity values were evaluated at 4 bar and 35°C . Figure 4 represents the permeability of pure CO_2 and CH_4 and also the CO_2/CH_4 ideal selectivity values of the membranes. As can be seen, presence of the IL leads to

significant increase of CO₂ permeability. Indeed, as the IL content increases up to 40 wt. % CO₂ permeability dramatically increases to 141 Barrer (about 64%). However, CH₄ permeability shows an opposite trend so that CH₄

permeability in Elvaloy4170/ 40 wt. % [Emim][Tf₂N] membrane is 55% lower than that of the pure polymer.

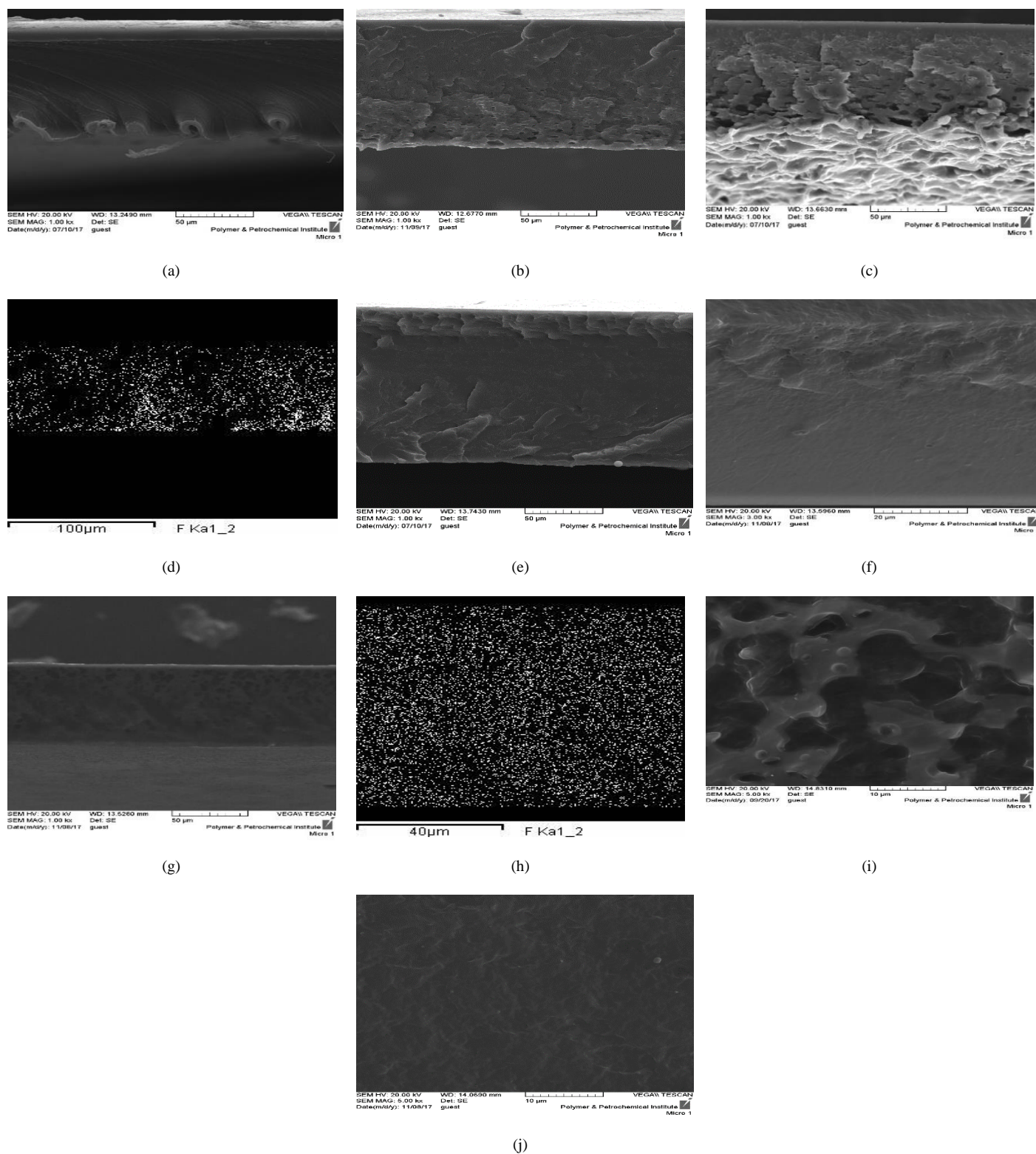


Fig. 1. SEM cross sectional images: (a) neat Elvaloy in THF, (b) Elvaloy4170/IL 20 wt. % in THF, (c) Elvaloy4170/IL 40 wt. % in THF, (d) SEM-EDX mapping of fluorine element of Elvaloy/IL 40 wt. % in THF, (e) Elvaloy4170/IL 10 wt. % in DCM, (f) Elvaloy4170/IL 20 wt. % in DCM, (g) Elvaloy4170/IL 40 wt. % in DCM, (h) SEM-EDX mapping of fluorine element of Elvaloy/IL 40 wt. % in DCM, (i) Surface SEM images of Elvaloy/IL 40 wt. % in THF, and (j) Surface SEM images of Elvaloy/IL 40 wt. % in DCM.

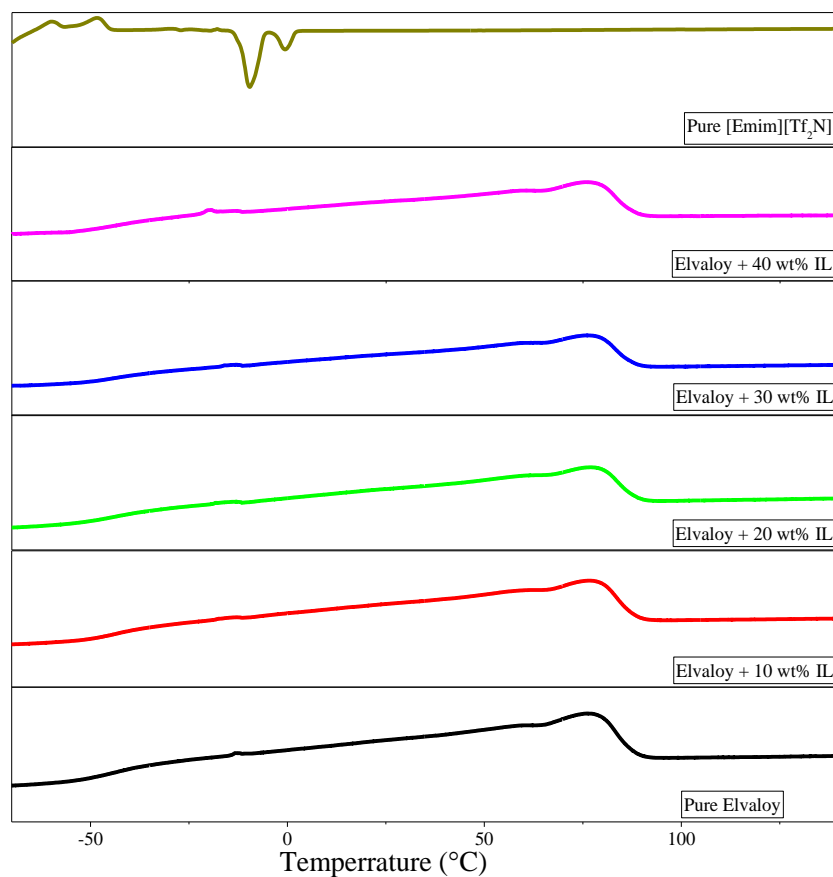


Fig. 2. DSC thermograms of Elvaloy4170, [Emim][Tf₂N], and Elvaloy4170/IL hybrid membranes.

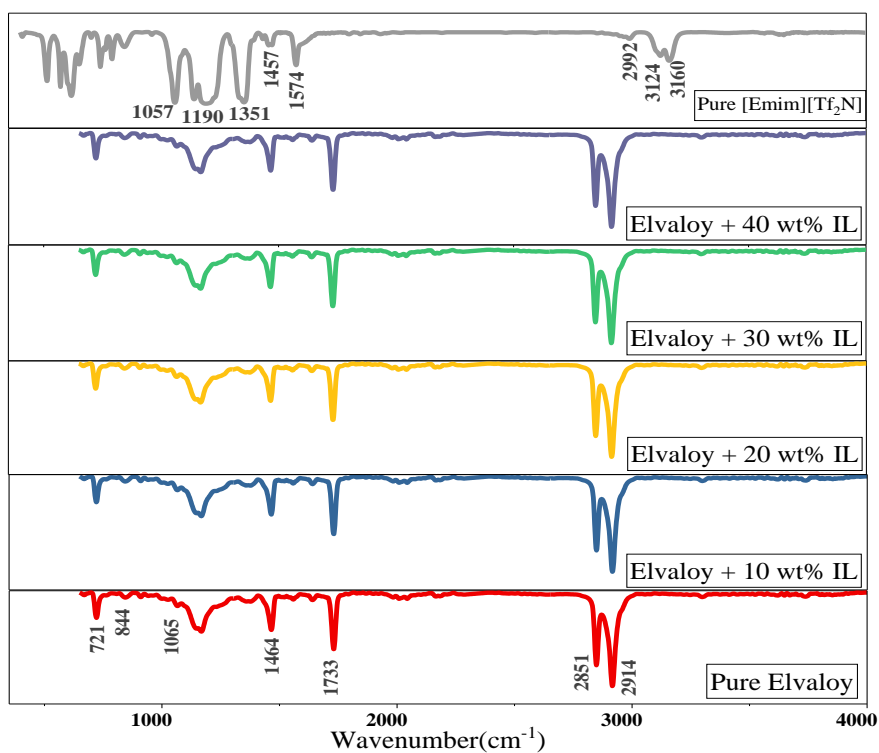


Fig. 3. FTIR-ATR spectra of Elvaloy4170, [Emim][Tf₂N], and Elvaloy4170/IL hybrid membranes.

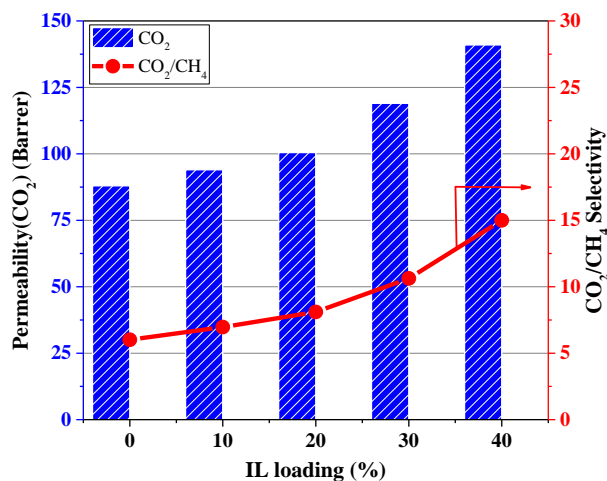


Fig. 4. Effect of IL loading contents on CO₂ permeability and ideal selectivity of CO₂/CH₄.

Since ILs possess higher fractional free volume (FFV) compared to polymers, presence of ILs facilitates diffusion of the CO₂ molecules through the hybrid membranes [34]. In general, in rubbery polymeric membranes solubility coefficients of penetrants governs permeability coefficients. Solubility coefficient of CO₂ in [Emim][Tf₂N] is equal to 2.55×10^{-2} (cm³(STP)/cm³.cmHg) at 4 bar and 35 °C, about 1.7 times more than the corresponding value in Elvaloy4170 [49]. This considerable solubility capacity for CO₂ molecules is justified by presence of the fluorinated and S=O groups in [Tf₂N] increasing the CO₂ philicity of the IL due to the Lewis base-Lewis acid interactions [30]. Therefore, positive interaction of [Emim][Tf₂N] incorporated in hybrid membranes could enhance the permeability coefficient of CO₂ molecules by enhancing their solubility coefficients [50]. In contrary, for CH₄ molecules there is no specific interaction with the IL and it has a solubility coefficient equal to one-tenth of that of CO₂, i.e. 0.206×10^{-2} (cm³(STP)/cm³.cmHg) [49]. Thus, it is expected that presence of IL into the matrix of Elvaloy4170 increases the CO₂/CH₄ solubility selectivity. For instance, a 2.5-fold growth in the CO₂/CH₄ solubility selectivity was observed for Elvaloy/IL 40 wt. %.

Due to the plasticization effect of ILs in hybrid membranes, reduction in the diffusivity selectivity is not an unexpected behavior. Nevertheless, predominant increase in the solubility selectivity compensates the diffusion effect and overall increases the ideal permeation selectivity. Rabiee et al. investigated transport properties of different penetrants through Pebax/[Emim][BF₄] hybrid membranes. They observed that enhancement of the solubility selectivity compensates the negative effect of the loss of molecular sieving ability and survives the ideal selectivity values [38]. Also, Ghasemi et al. reported increment of the ideal selectivity of Pebax/[Bmim][BF₄] hybrid membranes [23]. According to the results reported by other researchers and obtained in this study, it is concluded that presence of IL in hybrid membranes can improve the ideal selectivity by increasing the solubility selectivity.

The greater solubility selectivity of [Emim][Tf₂N] for CO₂/CH₄ compared to Elvaloy4170 along with its proper compatibility with the polymeric matrix caused a significant improvement in separation performance of the hybrid membranes prepared in this study. Elvaloy4170 is a commercially available and mechanically stable polymer which has high permeability for CO₂ gas molecules, despite its rather low CO₂/CH₄ selectivity. In the first study on Elvaloy4170 as membrane, Ranjbaran et al. tried to improve its separation performance by embedding multi walled carbon nanotubes (MWNTs) into the host matrix. The highest achieved ideal selectivity for CO₂/CH₄ pair was 7.38 for the MMMs with 4 wt % MWNTs, while in presence of the inorganic phase the CO₂ permeability decreased from 88 to 64.31 Barrer. However, results obtained in this study showed that incorporation of [Emim][Tf₂N] into Elvaloy4170 matrix simultaneously improves CO₂ permeability and CO₂/CH₄ selectivity to 141 Barrer and 15, respectively. However, addition of ILs into host polymeric matrices does not guarantee separation performance enhancement in all cases. For instance, Kanehashi et al. observed that presence of [Bmim][Tf₂N] in 6FDA glassy polyimide causes reduction of the CO₂ permeability from 1156 to 501 Barrer and also reduces the CO₂/CH₄ selectivity [48].

3.2.2. Maxwell model

The cross-sectional SEM images (section 3.1.1.) showed that the hybrid membranes prepared in this study have heterogeneous structures, especially at the high loading contents of the IL. To examine the possibility of contribution of these heterogeneous structures to the permeability of the membranes, the experimental permeability values were compared with the predicted permeability values using the Maxwell model. Eq. 5 presents the Maxwell model [51,52]:

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \right] \quad (5)$$

where P_{eff} is the effective permeability, P_d and P_c are permeability of the dispersed and the continuous phases, respectively. ϕ_d is the volume fraction of the dispersed phase into the host matrix. CO₂ permeability of the dispersed IL phase was considered equal to 1702 Barrer based on the solubility and diffusivity coefficients of CO₂ in [Emim][Tf₂N] reported by Scovazzo et al. [53]. As depicted in Figure 5 experimental results are in good agreement with the predictions of the Maxwell equation, especially at the higher IL loading contents. At the lower IL loading contents, the structure is more homogeneous, which causes negative deviation from the Maxwell equation. By increasing the IL contents and formation of the heterogeneous structures, lower mass transfer resistance and higher CO₂ permeability of the IL leads to higher permeability of the hybrid membranes. Therefore, it can be concluded that the isotropic heterogeneous structures of the hybrid membranes contribute to the permeation process [34].

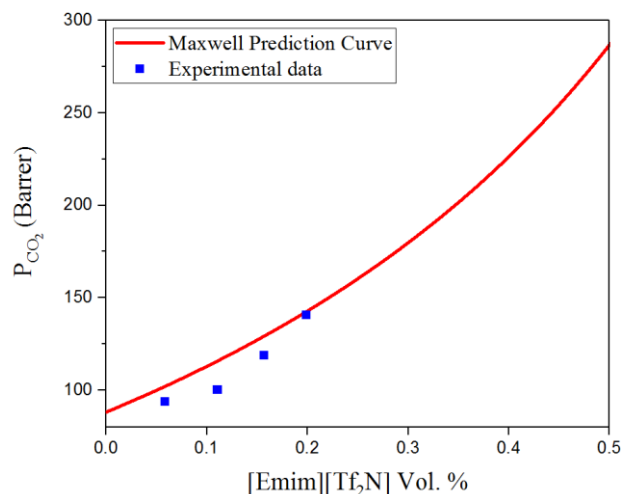


Fig. 5. Comparison between the Maxwell predicted values and experimental data.

It should be noted that the heterogeneous structures as observed in this study have a significant stability even at high loading contents of ILs. Different investigators have confirmed the possibility of incorporation of large amounts of ILs within different polymer matrix. There are various reports in the literature on Polymer/IL hybrid membranes containing 5-100 wt. % IL in their structure. For instance, Rabiee et al. reported incorporation of 100 wt. % [Emim][BF₄] in a polymer matrix [38]. In another study, Chen et al. demonstrated superior separation performance of a hybrid PVDF/RTIL membrane while the ratio of polymer/RTIL was increased up to 1/2 [34].

Considering the heterogeneous structure of the membranes prepared in this study, [Emim][Tf₂N] as the dispersed phase is encapsulated into the host polymeric matrix. Therefore, an excellent time durability is expected for these hybrid membranes.

3.2.3. Effect of temperature

Effect of operating temperature on gas transport properties of the neat and the polymer/IL hybrid membranes was investigated from 15 to 45 °C. Figure 6 shows that permeability of the gases through the membranes prepared in this study increases with increasing temperature. In the case of neat Elvaloy4170, the maximum permeability values obtained for CO₂ and

CH₄ at 45 °C are equal to 115 and 25 Barrer, respectively. For Elvaloy4170/40 wt. % [Emim][Tf₂N] hybrid membrane, the highest permeability values for CO₂ and CH₄ at 45 °C are 190 and 16 Barrer, respectively. At 45 °C, the ideal CO₂/CH₄ selectivity of Elvaloy4170/40 wt. % [Emim][Tf₂N] is 11.9 which is considerably higher than the corresponding value for the neat Elvaloy4170, i.e. 4.6, confirming better separation performance of the hybrid membranes. Investigations also reveal that the hybrid membranes have more promising performance at lower temperatures. As can be seen in Figure 6, at 15 °C the permeability values of CO₂ and CH₄ through Elvaloy4170/ 40 wt. % [Emim][Tf₂N] are respectively 85 and 3.5. Consequently, the CO₂/CH₄ ideal selectivity increases to 24.3.

In general, permeation temperature dependence through polymeric membranes is described by Arrhenius equation as follows:

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \quad (6)$$

where P , P_0 , E_p , T and R are permeability coefficient, pre-exponential coefficient, permeation activation energy, the absolute temperature, and the universal gas constant, respectively. E_p values calculated for the neat and the hybrid membranes are presented in Table 3. Higher permeation activation energy of CH₄ compared to CO₂ results in higher relative permeation increment of CH₄ and consequently lower CO₂/CH₄ ideal selectivity at higher temperatures. With increasing the IL loading contents in the hybrid membranes, E_p of CO₂ increases, while E_p of CH₄ remains almost constant. This phenomenon causes less reduction of CO₂/CH₄ ideal selectivity in the hybrid membranes at higher temperatures, see Figure 6.

In general, E_p is the sum of activation energy of diffusion (E_d) and molar enthalpy of sorption (ΔH_s) stated as follows:

$$E_p = E_d + \Delta H_s \quad (7)$$

$$S = S_0 \exp\left(-\frac{\Delta H_s}{RT}\right) \quad (8)$$

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \quad (9)$$

E_d is usually a positive value, therefore diffusivity coefficients of penetrants increases at higher temperatures. Moreover, larger molecules like CH₄ (3.8 Å) compared to CO₂ (3.3 Å), with greater E_d value, are rather more dependent to the temperature according to Eq. 9 that results in decrement of diffusivity selectivity at higher temperatures [38]. In addition, higher temperatures facilitate the diffusion of gas molecules through ILs. Considering Eq. 10 proposed by Scovazzo, there is a reverse relationship between diffusion coefficients of penetrants through ILs and their viscosity [54,55].

Table 3

Permeation activation energy of CO₂ and CH₄ through the neat and the hybrid membranes.

| Membrane | E_p (kJ/mol) | |
|----------------|-----------------|-----------------|
| | CO ₂ | CH ₄ |
| Elvaloy4170 | 15.52 | 38.55 |
| EL/10 wt. % IL | 15.89 | 38.31 |
| EL/20 wt. % IL | 16.28 | 38.74 |
| EL/30 wt. % IL | 18.38 | 38.62 |
| EL/40 wt. % IL | 20.25 | 38.15 |

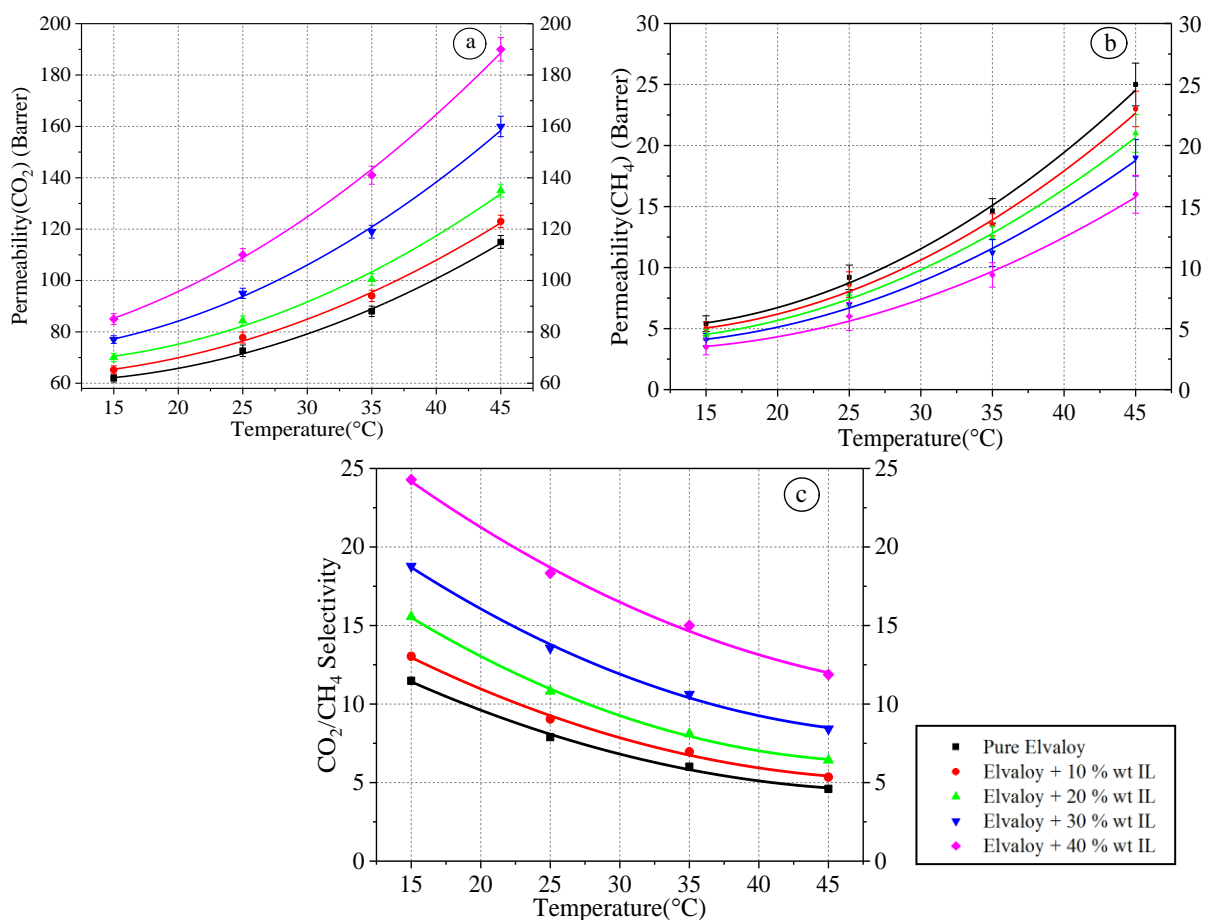


Fig. 6. Effect of temperature on permeability and ideal selectivity of CO₂/CH₄.

$$D_{IL} = A \frac{V_{IL}^a}{\mu_{IL}^b V_1^c} \quad (10)$$

where D_{IL} is the diffusivity coefficient of solutes in the ILs, V_{IL} is the IL molar volume, μ_{IL} is the IL viscosity, V_1 is the solute molar volume, and A , a , b , and c are IL-class specific parameters. Hence, higher diffusivity coefficients are expected at higher temperatures as observed in this study.

Furthermore, on the subject of enthalpy of sorption, ΔH_s can be negative or positive regarding to Eq. 11:

$$\Delta H_s = \Delta H_{cond} + \Delta H_{mix} \quad (11)$$

where ΔH_{cond} (J/mol) is the molar heat of condensation of penetrants and ΔH_{mix} is the molar heat of mixing of penetrants with polymer matrix.

According to the literature, solubility coefficients of CO_2 and CH_4 in polymer matrices have a descending trend by increasing temperature due to their dominant negative heat of condensation.

Table 4 presents the solubility coefficients of CO_2 in neat Elvaloy4170 and also the solubility coefficients of CO_2 and CH_4 in [Emim][Tf₂N] obtained from the literature [49]. The solubility coefficients of CH_4 in neat Elvaloy4170 was below the measuring limit of our device. While the solubility coefficient of CH_4 in [Emim][Tf₂N] is almost constant, the solubility coefficient of CO_2 decreases at higher temperatures and decreases the solubility selectivity of polymer/IL hybrid membranes against temperature. As a consequence, higher temperatures lead to higher diffusivity and consequently higher permeability for CO_2 and CH_4 through the Elvaloy4170/[Emim][Tf₂N] hybrid membranes. Although the solubility coefficients decrease with increasing the temperature, significant improvements observed in the permeation coefficients at higher temperatures are justified with dominant effect of diffusivity coefficients. Additionally, lower ideal permeability selectivity at higher temperatures is a direct result of reduced solubility selectivity as well as reduced diffusivity selectivity.

3.2.4. Effect of pressure

Effect of trans-membrane pressure (TMP), from 4 to 16 bar, on permeability coefficients of the penetrants were examined. In general, increasing the pressure has different effects on the permeability coefficient of condensable (like CO_2) and non-condensable (like CH_4) penetrants through dense polymeric membranes. On one hand, increasing the pressure leads to compactness of polymer and reduces its FFV, which causes reduction in gas diffusion rate; and the other, increasing the pressure motivates gas diffusion through the polymer matrix as a driving force. Besides, higher pressure causes higher concentration of penetrants into the membrane matrix and for more condensable gases like CO_2 , leads to CO_2 -induced plasticization effect. Plasticization is a pressure-dependent phenomena that is followed by a sudden rise in permeability and a drop in selectivity after a threshold pressure limit called plasticization pressure. Despite most of rubbery polymeric membranes where CO_2 permeability begin to increase at very low partial pressures followed by a lost in separation factor, Elvaloy4170 membrane represents more stable separation performance. For example, the CO_2 permeability through the neat Elvaloy4170 membrane is 88 Barrer at 4 bar and is 88.2 Barrer at 16 bar.

For all Elvaloy/IL hybrid membranes, such a stable trend is also observed within the pressure range studied in this study even at the higher IL loading contents. As it is observed in Figure 7a, For Elvaloy4170/40 wt. % [Emim][Tf₂N], the CO_2 permeability is 141 barrer at 4 bar and 140.3 barrer at 16 bar. A similar trend was observed for CH_4 gas that is shown in Figure 7b. Actually, there was no sign of penetrant-induced plasticization effect in all prepared membranes in the operating pressure ranges of CO_2 and CH_4 ,

although DSC results demonstrated more flexible structure of the hybrid membranes due to the plasticization effect of the IL. Mannan et al. also reported similar behavior for the CO_2 permeability through PES/[Emim][Tf₂N] hybrid membranes in a pressure range of 5 to 25 bar [56]. For example, for pure PES membrane, CO_2 permeability was reported 2.86 Barrer at 5 bar and 2.42 Barrer at 25 bar, while for PES-IL-50 the CO_2 permeability was increased from 298.84 up to 355.76 Barrer by increasing pressure from 5 to 25 bar. This behavior can be justified by this fact that most of CO_2 molecules diffuse through the IL matrix without interference in the polymer matrix. In another study Chen et al. also observed stable performance of PVDF/[Emim][B(CN)₄] hybrid membranes [34]. According to their observation, the CO_2 permeability remained almost constant in the range of testing pressures and CO_2/H_2 and CO_2/N_2 ideal selectivity values were also constant. The constant transport properties confirmed no plasticization effect in PVDF/[Emim][B(CN)₄] hybrid membranes. This result is also consistence with the study by Li et al. [57] for poly(RTILs)-RTIL membrane, where no remarkable chain swelling was noticed at pressures below 10 atm.

Consequently, incorporating [Emim][Tf₂N] with Elvaloy4170 is introduced as an efficient method to efficiently enhance the separation performance with insignificant variation under pressure as most transport is going through the ionic liquid which is an incompressible liquid.

3.2.5. Comparison with the Robeson's upper bound

Figure 8 depicts the separation performance of hybrid membranes prepared in this study, in comparison with some of PEG-based PU membranes and Elvaloy/MWNTs MMMs reported by other researchers. Moreover, this figure shows separation performance of Elvaloy4170/[Emim][Tf₂N] hybrid membranes with reference to the Robeson's (1991) upper bonds line for CO_2/CH_4 . Interestingly, it was observed that CO_2 permeability in Elvaloy/40 wt. % IL hybrid membrane is higher than cross-linked poly(ethylene glycol diacrylate) (XLPEGDA) reported by Lin and Freeman and also hybrid organic-inorganic poly(urethanesiloxane) (XSi-PPU2) membranes synthesized in our previous work [58,59]. Additionally, CO_2/CH_4 ideal selectivity of Elvaloy/40 wt. % IL hybrid membrane is almost comparable with the aforementioned PEG based membranes. It should be mentioned that PEG based membranes have high interaction with CO_2 molecules due to the presence of electronegative ether oxygen groups in their structure, and this feature makes them especially attractive candidates for separation of CO_2 from light gas streams like CH_4 . Additionally, investigations showed that the CO_2 permeability of Elvaloy/IL hybrids membranes prepared in this study is much higher than that of PEG containing thiol-ene network membranes, while they provide similar CO_2/CH_4 selectivity values [60].

4. Conclusions

Hybrid membranes using Elvaloy4170 and [Emim][Tf₂N] ionic liquid were prepared and used for CO_2/CH_4 separation. Presence of [Emim][Tf₂N] into the matrix of Elvaloy4170 led to formation of heterogeneous structures. Comparison of the experimental permeation results with the Maxwell equation confirmed contribution of these heterogeneous structures in separation process. [Emim][Tf₂N] with a considerable interaction with CO_2 molecules improved CO_2 solubility and also CO_2/CH_4 solubility selectivity of the hybrid membranes in comparison to the pure Elvaloy4170 membrane. The hybrid membranes prepared in this study also showed an increase in CO_2 permeability and also CO_2/CH_4 ideal selectivity compared to the neat membranes. Interestingly, it was observed that the pure and the hybrid membranes prepared in this study are pressure independent and their separation performance are more promising at lower temperatures.

Table 4
Solubility coefficients of CO_2 and CH_4 in different operating temperatures.

| Temperature | S_{CO_2} in Elvaloy4170 $10^2[\text{cm}^3(\text{STP})/\text{cm}^3.\text{cmHg}]$ | S_{CH_4} in Elvaloy4170 $10^2[\text{cm}^3(\text{STP})/\text{cm}^3.\text{cmHg}]$ | S_{CO_2} in [Emim][Tf ₂ N] $10^2[\text{cm}^3(\text{STP})/\text{cm}^3.\text{cmHg}]$ | S_{CH_4} in [Emim][Tf ₂ N] $10^2[\text{cm}^3(\text{STP})/\text{cm}^3.\text{cmHg}]$ |
|-------------|--|--|--|--|
| 15 | 2.1 | ND | 3.53** | 0.1960** |
| 25 | 1.8 | ND | 2.99* | 0.2011* |
| 35 | 1.5 | ND | 2.55** | 0.2060** |
| 45 | 1.3 | ND | 2.15** | 0.2120** |

ND Not determined

* Obtained from [49]

** Estimated by interpolation [49]

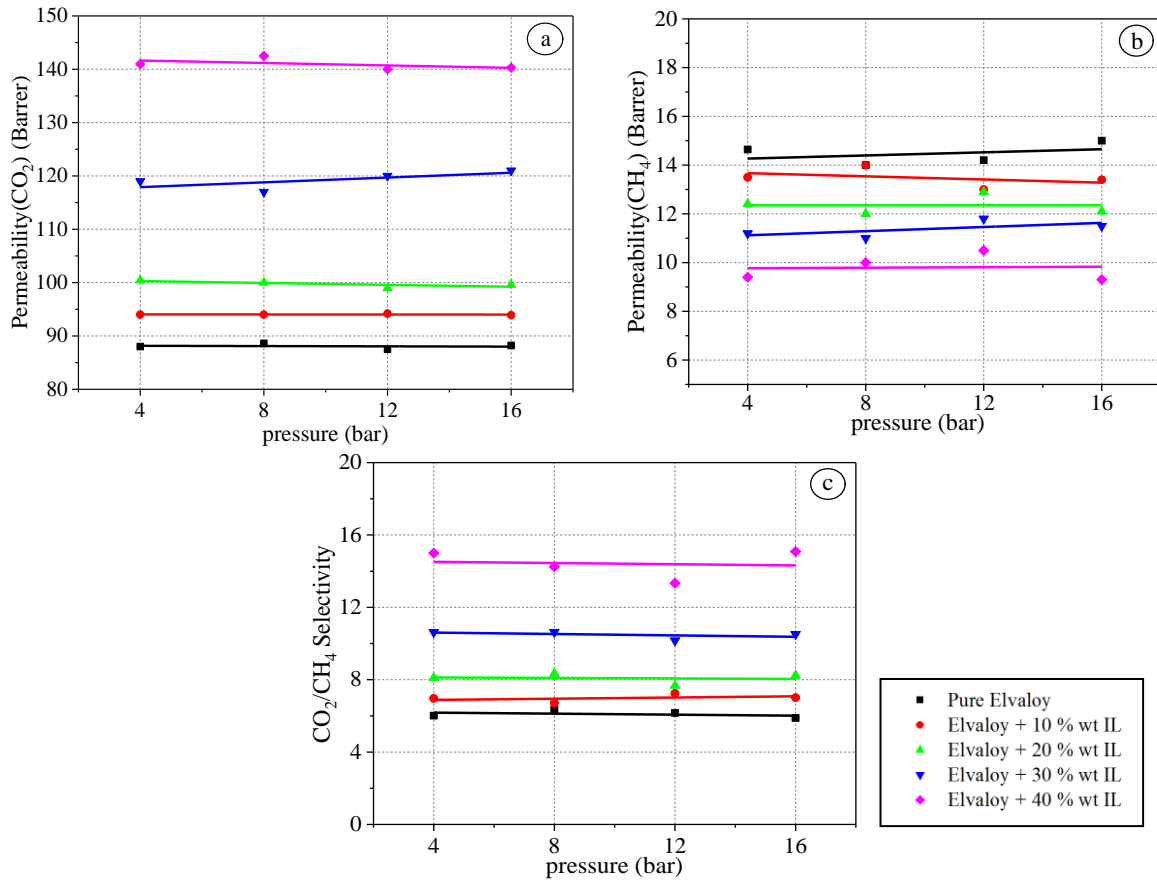


Fig. 7. Effect of trans-membrane pressure on permeability and ideal selectivity, at 35°C.

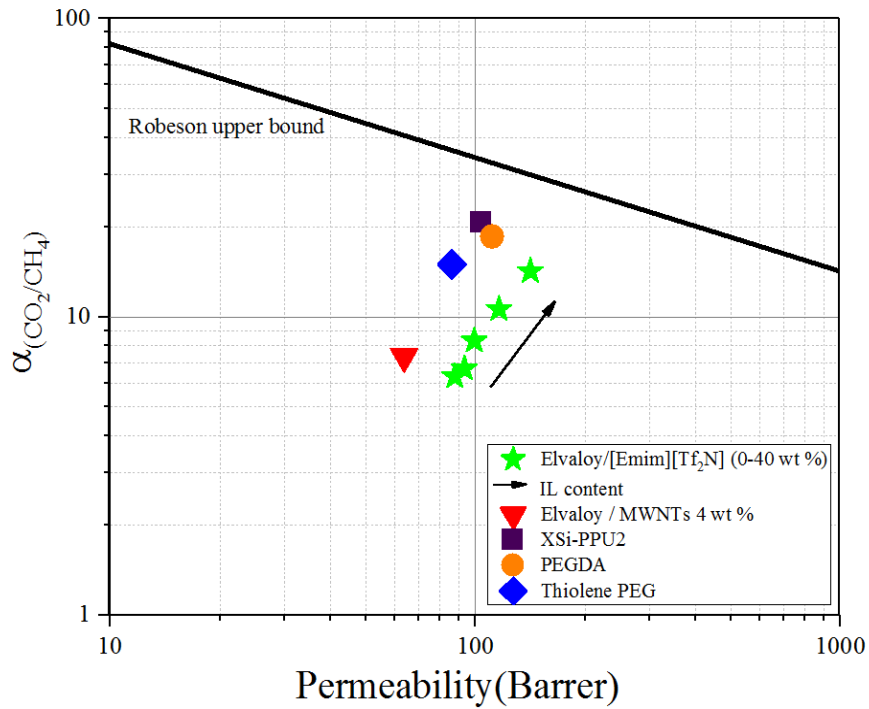


Fig. 8. Robeson's upper bounds for CO₂/CH₄ [61], the depicted data for the membranes prepared in this study have been obtained at 35 °C and 4 bar

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