Effect of [emim][BF₄] ionic liquid concentration on ionic liquid-polymeric membrane (ILPM) for CO₂/CH₄ separation

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Abstract. In the current study, polyethersulfone based (emim)[bf₄] ionic liquid polymeric membranes (ILPMs) were synthesised for CO₂ separation from CH₄. Two weight percentages (10% and 20%) of (emim)[bf₄] ionic liquid was added in the prepared doped solution; flat sheet dense membranes were synthesised by the dry phase inversion method. Field Emission Scanning Electron Microscope (FESEM) was used to analyse membranes morphology. Elemental composition of the membranes was examined using Energy Dispersive X-ray (EDX). Distribution of IL in the polymer matrix was observed with the help of mapping. The gas permeation experiments were performed at ambient room temperature and 4 bar pressure. All membranes showed dense and non-porous structure which depicted the good compatibility of polymer and ionic liquid. Presence of additional elements such as nitrogen and fluorine in PES/[emim][bf₄] membranes confirmed the presence of ionic liquid in the polymer. Mapping of fluorine element shown the uniform distribution of ionic liquid in the synthesised ILPMs. Membrane having ionic liquid 20 weight % showed a nearly 39-fold increase in CO₂ gas permeability compared to pure polyethersulfone membrane and 2.31-fold increase in ideal selectivity of CO₂/CH₄. The synthesised ILPMs have immense potential for CO₂ separation from natural gas.

1. Introduction
Natural gas (NG) composition changes one region to another, and it comprises mainly of methane and a different amount of CO₂, many gaseous hydrocarbons, water vapors and other gases such as nitrogen [1]. Removal of CO₂ is the focus due to its higher concentration in raw natural gas. Separation of CO₂ from natural gas increases its calorific value and avoids corrosion in pipes. So, CO₂ removal benefits, directly and indirectly, to make NG fuel cheap, efficient and environmentally green. Membrane in gas separation is attaining significance because of its benefits over remaining separation processes, because membrane technology consists of lower energy demand, compact size, lower operational cost. Polymers are getting importance because of its good mechanical stability and lower cost. Such as polysulfone, polyethersulfone, and polyamides are famously used in the gas separation membranes. Still, performance of these polymers is facing limitation by tradeoff between permeability and selectivity. To improve CO₂/CH₄ Separation performance, there is a need to explore new additives that can be helpful in the enhancement of CO₂/CH₄ Separation performance. Different ionic liquids as additives are under study in membrane synthesis, and the incorporation of ionic liquids in polymeric materials improves the gas separation performance [2] The ILs present in the polymer aids to absorb CO₂ in the polymer matrix, as a result rise in CO₂ permeance and CO₂/CH₄ selectivity [3].
In this study, a novel PES/[emim][bf_4] ionic liquid polymeric membrane has been synthesised with different weight % of the ionic liquid. The synthesized membranes were characterized using FESEM to examine the morphology of the synthesized membranes and EDX elemental analysis was used to determine the presence of ionic liquid in the polymer matrix and the distribution of IL was observed with the help of mapping and synthesized membranes were tested for CO_2 and CH_4 gas separation performance.

2. Materials and method

2.1. Materials
PES was obtained from BASF Germany having MW of 50,000 g/mol. NMP with reported purity of 99.99 % is chosen as solvent because of good miscibility of PES in NMP solvent. [emim][bf_4] was purchased from Sigma-Aldrich.

2.2. Membrane synthesis
IPLMs were synthesized by mixing PES/(emim)[bf_4] with weight % ratio of 10:1 and 5:1 as provided in table 1. PES/IL blend along with NMP solvent was mixed for 24 h. to attain a clear solution. Trapped bubbles from dope solution were removed by placing dope solution for 30 min on table. After that, the casting-solution was spread on the plate, and the casting knife was moved over it to make dense membranes. The synthesized dense films allowed to grow the membrane skin. After that, for drying and evaporating the solvent, the membranes were kept in an oven at 130˚C for 24 h. FESEM analysis was performed for surface and cross-section morphology observation, and the presence of elements and the distribution of (emim)[bf_4] in the synthesized ILPMs was investigated using EDX.

| Polymer | IL         | Membrane            |
|---------|------------|---------------------|
|         | 0          | PES                 |
| PES     | (EMIM)[BF_4] | PES/IL(10%)       |
|         | (EMIM)[BF_4] | PES/IL(20%)       |

2.3. Membrane characterization

2.3.1. Membrane morphology. With help of FESEM the morphology of the membranes was evaluated. Samples were inserted for a minimum of 30 s before fracture, into liquid nitrogen to get good cross-section surface. Cross-section and surface view were observed using FESEM.

2.3.2. Energy dispersive X-ray (EDX) analysis and mapping. EDX was used to determine the existence and distribution of [emim][bf_4] in the synthesized ILPMs. Samples cross-section was chosen to perform EDX analysis.

2.4. Gas permeation studies
Synthesised membranes performance was analyzed at 4 bar pressure. Full details of the gas separation equipment used details given in the article [4]. The permeability of membranes in barrer was calculated as:
where $N$ is the flux of CO$_2$ gas, $l$ is the thickness of the membrane and $\Delta P$ is the pressure difference at inlet and outlet of the testing module. Correspondingly, the CH$_4$ permeability was determined from the equation (1). The ideal selectivity ($\alpha$) was measured by the following equation (2):

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}}$$

3. Results and discussion

3.1. Membrane morphology

Figure 1 shows cross section view of PES and PES/[emim][bf$_4$] membranes at 1KX magnification. Cross sectional image showed that the developed PES and PES/[emim][bf$_4$] membranes are symmetric, dense and homogenous. Morphology of the membranes depends on the polymer-solvent interactions. It is noticeable that the membrane cross-sectional view did not show any phase separation, no pores, voids or defects in the membrane structure which demonstrates good compatibility between PES polymer, NMP solvent and [emim][bf$_4$] ionic liquid. Dense, pore free ionic liquid polymeric membrane showed the compatibility of ionic liquid and PES [5]. Pure PES membrane showed regular structure, additionally mixing of ILs in PES exhibited the more smooth structure of the membranes [6].

3.2. Energy dispersive X-ray (EDX) analysis:

Presence of ionic liquid in the polymer matrix was confirmed by EDX elemental analysis and distribution of IL was observed with the help of mapping. Figure 2 (a) shows the elemental spectra of the PES membrane and figure 2 (b) is presenting elemental spectra of the PES/[emim][bf$_4$] (20 weight %) membrane. In PES membrane, C, O$_2$, and S are the main essential constituent of the polyethersulfone membranes due to PES polymer chains. In PES/[emim][bf$_4$] (20 weight %) additional elements such as nitrogen and fluorine are present because of [emim][bf$_4$] ionic liquid. The distribution of the fluorine element is also reflected in the mapping in figure 3 (a) and (b). The indigo dots represent the fluorine element in the synthesized ILPMs. It can be observed that the ionic liquid is well distributed in the membranes.
Figure 2. EDX elemental spectrum of (a) Pure polymeric membrane, and (b) PES/IL (20 wt. %) membrane.

Figure 3. Fluorine element in ILPMs (a) PES/(emim)[bf$_4$] (10 wt. %), and (b) PES/(emim)[bf$_4$] (20 wt. %) membrane.

3.3. Gas permeability studies

The influence of ionic liquid concentration on CO$_2$, CH$_4$ is shown in figure 4. Both gases exhibited an increase in permeability values; however, CO$_2$ showed more permeability enhancement compared to CH$_4$. CO$_2$ permeability for PES membrane is 2.9 barrer, while, for PES/(emim)[bf$_4$](10wt. %) and PES/IL(20wt. %) is 51.12 and 115 barrer correspondingly. This improvement in permeability exhibited that the ILs have a significant impact on CO$_2$ [7]. Addition of ILs aided the absorption of CO$_2$ in the polymer matrix, increasing CO$_2$/CH$_4$ gas separation [3]. CO$_2$ diffuses more conveniently in ionic liquid than in polymer [8].

Moreover, ILs decreases the stiffness of polymer matrix [9] this allows easy diffusion of CO$_2$ in the polymer matrix. Other factors are, ILs having with lower viscosity possesses more CO$_2$ solubility [10], and shorter alkyl chain also decreases the viscosity of the ILs, resulting in permeation increase of CO$_2$ gas [11]. Consequently, the blending of PES and with [emim][bf$_4$] IL that has lower viscosity and shorter alkyl chain length has enhanced the CO$_2$ permeability gas separation performance of the membrane in this study.
(a) CO₂ Permeability

(b) CH₄ Permeability
4. Conclusion

In the present work, synthesis, characterization and gas separation testing of ionic liquid polymeric membranes (ILPMs) was studied. Miscibility of IL in the polymer was evaluated by FESEM, EDX and mapping analysis. The gas separation results of membranes exhibited that the addition of ionic liquid in PES enhanced the performance of the synthesized membranes. The enhancement from 2.9 to 115 barrer CO$_2$ permeability for pure PES and PES/[emim][bf$_4$](20wt. %) respectively, with 2.31-fold increase in ideal selectivity of CO$_2$/CH$_4$. PES/[emim][bf$_4$] (20 weight %) contributed improved gas separation performance than polyethersulfone membrane and PES/(emim)[bf$_4$] (10 weight %) membranes.

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