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Molecular simulation of [P8883][Tf₂N] ionic liquid decorated silica in 6FDA-ODA based mixed matrix membrane for enhanced CO₂/CH₄ separation

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Mixed-matrix membranes (MMMs) have been reported to have considerable scope in gas separation applications because of their merged inherent strength of a durable polymer matrix and the exceptional performance capabilities of inorganic fillers. The selection of comparatively suitable polymers with fillers that can match each other and boost interfacial compatibility while ensuring uniform dispersion of filler within the polymer is still intensively demanding and is challenging at the experimental scale. Ionic liquids (ILs) are effective in promoting better dispersion and compatibility, leading to improved separation performance. A computational molecular simulation approach is employed in current work to design a hybrid membrane having Trioctapropyl phosphonium bis(trifluoromethylsulfonyl)imide [P8883][Tf₂N] IL decorated silica as a filler and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride-4,4'-oxydianiline (6FDA-ODA) polymer for carbon dioxide (CO₂) separation from methane (CH₄). Thermophysical and gas transport properties under pure and mixed gas condition (30, 50, and 70% CO₂/CH₄) within the MMMs with varying filler loadings (5, 10, and 15 wt% IL-silica) are examined *via* Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) simulations. Membrane characteristics like glass transition temperature (*T*_g), Fractional Free Volume (*v*_f), X-Ray Diffraction (XRD), solubility, diffusivity, permeability, and selectivity for neat and IL-silica filled 6FDA-ODA are computed. The results show that the *T*_g of the composite membrane with 5 wt% IL-silica is found to be considerably higher (with 305 °C) than that of the pure 6FDA-ODA polymer having 298 °C. A higher *T*_g value highlights the effective dispersion and higher adhesion between the filler and polymer membrane. Additionally, CO₂ permeability for 5 wt% IL-silica/6FDA-ODA MMM is significantly improved, measuring 319.0 barrer while maintaining a CO₂/CH₄ selectivity of 16.2. These values are 89% and 56% respectively, greater than the corresponding values of neat 6FDA-ODA membrane. Published data from the literature review is used to validate the findings and guarantee their reliability. The obtained results exhibited an error in the range of 0.7–9%. Hence, it is concluded from the study that molecular simulation can be used to design IL decorated silica incorporated within 6FDA-ODA matrix, which is able to boost the interfacial compatibility, with elevated CO₂/CH₄ selectivity and CO₂ permeability.

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1 Introduction

Raw natural gas, a fuel source of considerable global importance, contains a high level of CO₂, requires its purification to prevent issues such as pipeline degradation, increased

compression costs, reduced heating efficiency, and increased greenhouse gas emissions.^{1,2} Among the various separation technologies, membrane separation offers several advantages, including environmental friendliness, simple fabrication, trouble-free application, low capital cost, low energy

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consumption, well-space utility, and excellent thermal suitability.³ However, polymeric membranes have some shortcomings to meet industrialization standards due to the well-known “trade-off” between permeability and selectivity.⁴

Mixed matrix membranes (MMMs) are designed to exceed Robeson's upper bounds to get around the tradeoff between permeability and selectivity. MMMs consist of a polymer matrix with distributed inorganic components, allowing them to possess the advantageous characteristics of both inorganic and polymer membranes.⁵ In the MMM, the dispersed inorganic filler disrupts the effective packing of polymer for the creation of void channels to facilitate gas transport while also enhancing affinity for a specific molecule to improve separation performance.⁶ This gives MMMs a significant performance boost over a basic polymeric membrane.⁷ However, improper filler dispersion and low interfacial compatibility between the filler and polymer led to a tradeoff between permeability and selectivity, common issues faced by MMM, causing a bottleneck in its further enhancement. To tackle this concern and improve CO₂/CH₄ separation, supporting ionic liquids onto the surface of fillers or polymers has been proposed.^{8,9}

To date, several studies have been conducted to support ionic liquids (ILs) on polymers and fillers to improve their CO₂ separation performance. There are various methods to support ILs on the surface of polymer and filler,¹⁰ which encompass impregnation,¹¹ physical stirring,¹² supercritical fluid deposition (SCFD),¹³ blending,¹⁴ and grafting.¹⁵ A study was conducted on the synthesis of Ethyl Cellulose (EC) supported with 1-carboxymethyl-3-methylimidazolium tetrafluoroborate [HOOC-MIM][BF₄]. The resulting EC exhibited a permeability of 199 barrer, which was significantly higher than that of the pure EC (46.8 barrer). Furthermore, the selectivity for CO₂/CH₄ increased from 9.0 to 19.¹⁶ A. S. Aquino *et al.*¹⁷ studied methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride [MTMSP-Im][Cl] supported on mesoporous material (MCM-41) and found that at 25 °C and 1 bar, the CO₂ adsorption capacity of IL supported on MCM-41 was 57% higher than that of the bare MCM-41 with merely 0.62 mmol CO₂ per g sorbent. Wang *et al.*¹⁸ synthesized 1-*n*-butyl-3-methylimidazolium chloride [BMIM][Cl] decorated Santa Barbara Amorphous-15 (SBA-15) and observed that under similar conditions, the CO₂ adsorption of SBA-15-IL was 63% higher than that of the neat SBA-15. Using the same method, Vishwanath Hiremath *et al.*¹⁹ studied four amino acid (AA) functionalized 1-methyl-3-ethyl-imidazolium [EMIM] based IL supported on ordered mesoporous silica (OMS-IL (AA)) and compared its CO₂ sorption capacity with bare silica (0.11 mmol g⁻¹). They observed that the CO₂ sorption capacity of OMS-IL (AA) was 63% higher than that of the neat silica. Bahadori *et al.*²⁰ prepared 1-(2-aminoethyl)-3-methyl imidazolium bromide [NH₂-EMIM][Br] grafted on MIL-101(Cr) and found that the CO₂ sorption capacity of the grafted sample was 7.84 times higher than the MOFs present at that time. Zhu *et al.*¹⁵ synthesized triocetapropyl phosphonium bis(triflimide) [P8883][Tf₂N] grafted silica and obtained the CO₂ capture performance increased from 0.07 mmol g⁻¹ to 0.99 mmol g⁻¹.

Preparing MMMs using the incorporation of IL modified filler in the polymeric matrix is another widely used method.

Ilyas *et al.*²¹ conducted a study where they developed a mixed matrix membrane consisting of zeolite 4A filler supported by an IL called 3-(trimethoxysilyl)propan-1-aminium acetate [APTMS][AC] and polysulfone (PSF) polymer. Their research revealed that incorporating a filler content of 34 wt% in the membrane led to an enhanced separation performance. Specifically, the modified filler demonstrated an increase in the selectivity of CO₂/CH₄ by 37% and CO₂/N₂ by 43% as compared to the original unmodified filler in the MMMs. Li *et al.*²² synthesized 1-butyl-3-methylimidazolium bis(triflimide) [Bmim][Tf₂N] embedded in ZIF-8/Pebax-1657 based MMM and observed membrane performance at various loadings of [Bmim][Nf₂T]@ZIF-8. They reported the highest CO₂ permeability of 104.9 barrer at 15 wt% loading, which was 28% greater than that of the pure Pebax-1657 (72 barrer) and the selectivity was also increased from 18 to 34.5. To separate CO₂ from CH₄ and N₂, Ahmad *et al.*²³ employed 1-ethyl-3-methylimidazolium bis(triflimide) [EMIM][Tf₂N] supported on zeolite SAPO-34, which was subsequently integrated into PSF. Compared to the unmodified MMM, they observed a substantial improvement in the CO₂ separation ability of a composite containing SAPO-34 modified with the IL, with an approximately 486% rise in CO₂/CH₄ and a 232% increase in CO₂/N₂ selectivity. Nevertheless, the process of identifying an appropriate filler and polymer that complement one another, as well as an ionic liquid that can enhance the surface-to-surface compatibility and propagation of the filler within the polymer, will inevitably involve numerous attempts and mistakes. Additionally, membrane morphology and performance of the new generation hybrid materials are difficult to measure *in situ*, causing testing of membranes on an experimental scale to be potentially costly, labor-intensive, and time-consuming. For instance, Liu *et al.*²⁴ synthesized a MMM consisting of a fluorinated metal organic framework (NbOFFIVE-1-Ni) filler and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride-2,4,6-trimethyl-1,3-diaminobenzene (6FDA-DAM) polymer. The composite membrane (NbOFFIVE-1-Ni/6FDA-DAM) exhibited diminished CO₂/CH₄ selectivity compared to the base 6FDA-DAM membrane, likely due to incompatibility between the polymer and filler materials.

Computational chemistry has grown as an effective tool that provides fast, atomistic-level elucidation of material properties in the creation and analysis of different materials. It offers modeling and simulation environment that can be used to anticipate and understand the connections between molecular structure of a material and its properties while circumventing the difficulty, cost, or time associated with lab-scale manufacturing.^{25,26} Several computational studies have been conducted on polymers and MMMs. Velioğlu *et al.*²⁷ conducted a comprehensive investigation on the molecular simulation of gas transport on three distinct polyimides, namely 4,4-hexafluoroisopropylidene-diphthalic anhydride-2,4,6-trimethyl-*m*-phenylene diamine (6FDA-DAM), 4,4-hexafluoroisopropylidene-diphthalic anhydride-4,4-oxydianiline (6FDA-ODA), and 4,4-hexafluoroisopropylidene-diphthalic anhydride-2,5-dimethyl-*p*-phenylenediamine (6FDA-DPX). Their investigation involved the computation of diffusion and sorption coefficients of CO₂, CH₄, N₂, and O₂ gases

