



Insights into IL-modified silica/6FDA-DAM ionic liquid mixed matrix membranes for CO₂/CH₄ separation: Integrated computational approach

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ABSTRACT

Mixed Matrix Membranes (MMMs) are considered a promising alternative to conventional natural gas sweetening processes. However, their performance is often hindered by poor filler dispersion and weak polymer-filler compatibility, which result in non-selective gas transport. Ionic liquids (ILs) can improve dispersion and enhance interfacial interactions, thereby improving separation performance, but identifying an appropriate polymer-filler-IL combination at the experimental scale is challenging due to the vast structural variations of ILs. This study introduces a novel integrated computational approach that combines quantum mechanics with atomistic computations to investigate IL-supported silica (IL-Si)/6FDA-DAM ILMMMs, aiming to establish a predictive mechanistic framework for the material formulation in CO₂/CH₄ separation. COSMO-RS was employed to screen 150 ILs using activity coefficient (γ) predictions, from which [P8888][Tf₂N] was identified as the most CO₂-philic candidate. This IL was then supported on silica and incorporated into a 6FDA-DAM matrix. The influence of IL-Si loading (0, 8, and 16 wt%) on thermophysical and transport properties was systematically examined under pure and mixed-gas environments (30, 50, and 70% CO₂/CH₄) at 35 °C and 1 atm, enabling molecular-level insight into the effect of gas composition on separation performance. Results showed that the glass transition temperature (T_g) of the hybrid membrane increased from 409 °C (neat 6FDA-DAM) to 421 °C at 8 wt% IL-Si, indicating strong filler dispersion and interfacial adhesion. For separation performance, the optimized membrane at 16 wt% IL-Si achieved a CO₂ permeability of 1413.9 Barrer and a CO₂/CH₄ selectivity of 62.1 under 50 vol% CO₂/CH₄ conditions, corresponding to improvements of 114% in permeability and 193% in selectivity compared to neat 6FDA-DAM. The obtained results exhibited an error in the 0.7–9% range, confirming the reliability of the simulation framework. Overall, this study demonstrates the potential of simulation-driven design for tailoring IL-functionalized MMMs with enhanced stability, permeability, and selectivity for natural gas upgrading, while pointing toward future integration of molecular simulations with AI-based tools for accelerated discovery and optimization of next-generation membranes.

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1. Introduction

Membrane gas separation has been a widely used technique for purifying and refining natural gas. In recent decades, this industrial application has gained more recognition for its inherent advantages, including reduced environmental impact, enhanced energy efficiency, cost-effectiveness, and user-friendly operation in comparison to conventional separation methodologies [1]. The utilisation of membranes for the extraction of impurities from natural gas, specifically in the separation of carbon dioxide (CO₂) from methane (CH₄), is expected to undergo more rapid expansion in comparison to other process technologies for gas separation [2]. The proposed application commonly utilises membranes made from various polymers, such as polyethersulfone (PES) [3], cellulose acetate (CA) [4,5], polypropylene (PP) [6], polyvinyl alcohol (PVA) [7], polyethylene (PE) [8], and polyimides (PIs) [9]. Among them, PIs captured the attention of the researchers due to their high mechanical strength, high temperature operation capability, chemical resistance, and remarkable gas permeability and selectivity coefficients [10]. Nevertheless, polymeric membranes fail to satisfy the requirements of industrialisation due to the infamous “trade-off” between selectivity and permeability.

Mixed matrix membranes (MMMs) have been developed to overcome this limitation and exceed the upper limit set by Robeson [11]. MMM has attracted significant recognition over the past decade due to its ability to combine the benefits of polymeric and inorganic membranes [12]. Among the various reported MMM fillers, silica stands out due to its high surface area and porosity, as well as its customisable pore structure and low density. These characteristics make silica highly promising for the development of excellent-performance MMMs [13]. Wang et al. [14] studied polyimide/silica MMMs and found that adding 10 wt% silica nanoparticles improved CO₂ permeability by 394%. Ghadimi et al. [15] found that adding 25 wt% silica to PEBA/silica MMMs boosted their CO₂/CH₄ selectivity by 150%. Despite their numerous benefits, the lack of compatibility between the polymer and filler at the interface is a major challenge in the development of efficient MMMs. This incompatibility can lead to the creation of non-selective gaps, which decrease gas selectivity, or the consolidation of the interface, which reduces gas permeability. Furthermore, attaining optimal dispersion of the filler inside the polymer matrix is a significant obstacle in the development of MMMs. ILs are highly effective in enhancing dispersion and improving compatibility, resulting in enhanced separation performance. Incorporating IL-supported filler into the polymeric matrix to produce ILMMMs is a common, widespread technique [16]. Ilyas et al. [17] constructed a ILMMM using polysulfone (PSF) polymer and zeolite 4A infill supported by an IL 3-(trimethoxysilyl) propane-1-aminium acetate [APTMS][AC]. The outcomes of their investigation demonstrated that adding a filler content of 34 wt% to the membrane improved its separation performance. In comparison to the initial unmodified filler in the MMMs, the modified filler exhibited a notable enhancement in the selectivity for CO₂/CH₄ by 37% and CO₂/N₂ by 43%. Li et al. [18] synthesised 1-butyl-3-methylimidazolium bis(triflimide) [Bmim][Tf₂N] supported on ZIF-8/Pebax-1657-based ILMMM. They subsequently assessed the efficiency of the membrane at different loadings of [Bmim][NTf₂]@ZIF-8. At a concentration of 15 wt%, they achieved the highest CO₂ permeability of 104.9 barrer, which was 28% greater than that of pure Pebax-1657 (72 barrer). Additionally, CO₂/CH₄ selectivity increased from 18 to 34.5. Ahmad et al. [19] utilised 1-Ethyl-3-methylimidazolium bis(triflimide) [EMIM][Tf₂N] supported on zeolite SAPO-34, which was subsequently incorporated into PSF, to extract CO₂ from a gas mixture composed of CO₂, (CH₄), and (N₂). A membrane incorporating SAPO-34 modified with the IL exhibited a significant enhancement in its ability to separate gases. Specifically, the CO₂/CH₄ selectivity increased by around 486%, and the CO₂/N₂ selectivity rose by 232%, in comparison to the unmodified MMM. Despite the rise of IL-based MMMs (ILMMMs) as next-generation membrane materials, selecting a suitable combination of polymer, filler,

and IL remains challenging, which may require labour-intensive trial-and-error and lengthy experiments.

Computational chemistry has emerged as a powerful tool for rapidly and precisely understanding the properties of materials, particularly in the field of membrane synthesis and analysis, at the atomic level [20]. This provides a modeling and simulation platform that enables the prediction and understanding of the relationship between a substance's molecular structure and its characteristics without the typical challenges, costs, or time constraints of laboratory-scale production [21,22]. For example, Velioglu et al. [23] employed molecular simulations to investigate the movement of gases through three different polyimides. These were 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-phenylenediamine (6FDA-DPX). They successfully replicated the experimental findings with great accuracy. Golzar et al. [24] conducted a simulation study on a mixed matrix membrane composed of silica and PSF under pure gas conditions, including O₂, N₂, CO₂, and CH₄. They found that for 20 wt% silica, the CO₂ permeability was 22.5 barrer, which was 470% higher than neat PSF (3.95 barrer). Asif et al. [25] extended Golzar's research by modifying silica with amine, resulting in an optimal CO₂ permeability of 60 barrer and selectivity of 10.9 at a loading of 20%. These values were greater than those observed in the unmodified silica/PSF MMM, and the simulation results were comparable to the experimental values. Despite the promising potential of MMMs incorporating IL-functionalized filler for CO₂/CH₄ separation, identifying a compatible combination of IL, polymer and filler remains challenging. For example, Loh et al. [26] developed a computational framework to study ILMMMs and showed that binding-energy analysis confirmed a two-to-three-fold stronger integration of silica and [EMIM][Tf₂N] with 6FDA-durene membranes. Silica incorporation increased CO₂ and CH₄ diffusivity by 40.7% and 13.9%, respectively, whereas the ionic liquid generally reduced gas diffusivity by approximately 20%. This challenge is compounded by the vast structural diversity of ionic liquids, the limited use of predictive computational tools to guide membrane design and the variety of IL-incorporation strategies employed in the literature.

COSMO-RS, a computational tool, provides a robust framework for thermodynamic screening of ILs based on CO₂ affinity [27]. For example, Ramdin et al. [28] utilised Monte Carlo simulations to perform a molecular simulation study aimed at forecasting the solubility of the gases CO₂, CH₄, N₂, H₂, H₂S, and CO in the [Bmim][Tf₂N] IL. Islam et al. [29] utilised the Conductor-like Screening Model for Real Solvents (COSMO-RS) to identify ILs that would be effective in removing greenhouse gases (GHGs). To predict the solubility of gases, they looked at 240 different ILs combos, with 30 anions and 8 cations for each GHG. Zhang et al. [30] screened suitable ILs to capture CO₂ using COSMO-RS. In their investigation, they examined 408 combinations of ILs, comprising 17 anions and 24 cations per GHG. They selected the top three ILs for solubility measurements based on predicted results, and the results they obtained were in good agreement with the screening results. Although both COSMO-RS and molecular dynamics (MD) simulations have independently proven to be powerful tools in predicting gas solubility, filler-polymer compatibility, and transport properties, their isolated use provides only a fragmented understanding of complex mixed matrix membrane systems. COSMO-RS offers rapid screening of ILs based on thermodynamic affinity, yet it lacks the structural and dynamic insights necessary to capture transport behaviour within polymeric networks. Conversely, MD simulations can unravel atomistic interactions and diffusion pathways but rely heavily on prior knowledge of suitable filler and IL candidates, making the process computationally demanding without effective pre-screening. To the best of our knowledge, no previous study has systematically screened a large library of ionic liquids (150 candidates) using COSMO-RS and subsequently immobilized the selected IL on a solid support for integration into a