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Molecular analysis of selective gas adsorption within composites of ionic polyimides and ionic liquids as gas separation membranes

Asghar Abedini, Ellis Crabtree, Jason E. Bara, C. Heath Turner*

Department of Chemical and Biological Engineering, The University of Alabama, Box 870203, Tuscaloosa, AL 35487, USA

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ABSTRACT

The CO_2 separation characteristics of ionic polyimides (i-PIs) are modeled using molecular dynamics simulations in combination with grand canonical Monte Carlo calculations. The performance of neat i-PI systems is evaluated, as well as composite structures containing both i-PIs and various ionic liquids (ILs). The i-PI + IL composites are based on combinations of 1-*n*-butyl-3-methylimidazolium ($[C_4mim^+]$) cations with three common molecular anions: (bis(trifluoromethylsulfonyl)imide ($[Tf_2N^-]$), tetrafluoroborate ($[BF_4^-]$), and hexafluorophosphate ($[PF_6^-]$). It is found that 50 mol% IL inclusion can increase CO_2/CH_4 selectivity by 16% in $[BF_4^-]$-based materials and by 36% in $[PF_6^-]$-based materials from mixtures of 5% CO_2/95% CH_4. While the $[BF_4^-]$-based system shows higher CO_2/CH_4 selectivity, the $[Tf_2N^-]$-based system shows higher CO_2/N_2 gas selectivity. A comprehensive structural analysis (fractional free volume (FFV), pore size distribution, surface area, etc.) is used to highlight the underlying differences among the different i-PI + IL systems that lead to the different adsorption properties.

1. Introduction

Carbon dioxide (CO_2) is the most well-known greenhouse gas (GHG) with many industrial emission sources contributing to the detriment of the atmosphere. CO_2 removal from natural gas has been successfully applied for over 80 years [1]. Although amine-based solvents, such as monoethanolamine (MEA) exhibit multiple disadvantages including corrosion, volatility, toxicity, and high-energy demand for recovery, carbon capture processes still heavily depend on typical MEA solvents during CO_2 absorption due to the high cost or low efficiency of other alternatives [2]. The design of alternative materials for CO_2 capture is of high importance due to a growing need for control of CO_2 emissions to the atmosphere and for increasing the efficiency of energy supply lines by reducing CO_2 in pre-combustion gases. Several different adsorbents such as activated carbons [3], zeolites [4], metal organic frameworks (MOFs) [5], and covalent organic frameworks (COFs) [6] have been widely studied for CO_2 adsorption. These materials provide a high capacity for gas adsorption, but they typically suffer from other limitations (selectivity, cost, or stability).

In addition to these porous materials, different types of ionic liquid (IL) solvents have also been studied and proposed as effective alternatives for CO_2 absorption [7]. These IL solvents have previously been shown to be effective at dissolving CO_2, and they tend to possess high thermal and physical stability and low vapor pressure. In particular, imidazolium-based ILs have received a great deal of attention, due to their high solubility and selectivity for CO_2 in post-combustion capture and natural gas sweetening [8–14]. However, their high cost and high viscosity as well as their limited adsorption capacity for CO_2 render them to be uncompetitive with traditional gas absorbents used in industrial-scale applications [8,9].

There have been some previous efforts to circumvent the inherent IL performance limitations. For instance, dissolving ILs in an amorphous structure of polymers and crystal structures consisting of MOFs [11] and COFs [15] can alleviate the low capacity of ILs by providing more void volume [14]. Recently, to explore the directed orientation of IL molecules and the resulting effect on gas separation, others have investigated the properties of ILs confined within solid pores [5,8,14,16–18]. In those works, a thick layer of IL solvent was confined between solid surfaces [19], and gas diffusion in that confined layer was studied, as well as the influence of confinement on CO_2 solubility [14,20,21]. Budhathoki et al. used molecular dynamics (MD) simulations to study CO_2 solubility selectivity, diffusion selectivity, and permselectivity from binary mixtures of CO_2/CH_4 and CO_2/H_2 within a $[C_4mim][Tf_2N]$ confined IL solvent [8]. The IL was confined within graphite nanopores of 2–5 nm in diameter. The ILs confined within the pores demonstrated enhanced permselectivity of CO_2 (compared to the

* Corresponding author.
E-mail address: hturner@eng.ua.edu (C.H. Turner).

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empty nanopores), but the diffusivity of all gas species decreased, relative to bulk ILs. Expelling captured CO_2 during adsorption and absorption and recycling the adsorbent and absorbent liquids is already a cost effective process in separation columns. However, membrane separation mitigates the need for frequent adsorbent replacement and absorbent recovery by providing continuous gas separation and purification [22–24].

Porous organic polymers [25–27] have been considered in gas separation studies due to their stability [28,29], large surface area [30,31], and fine-tuned microporosity resulting from the voids created in their rigid molecular structure (due to frustrated polymer chain packing) [32–35]. Supported ionic liquid membranes (SILMs) [36] and polymers of intrinsic microporosity (PIMs) [23,37] are now receiving much attention due to the combined advantages of both ILs and membranes in gas separation [24,38–41]. For instance, CO_2 mass transfer can be significantly enhanced when ILs are dissolved into polymers and porous solid structures [5,42]. Also, nitrogen-rich polymer building blocks can help promote CO_2 uptake within amorphous microporous polymers (AMPs) by increasing the heat of adsorption [33,43].

Ionic polyimides (i-PIs) are one of these promising polymers for membrane-based CO_2 separations (pre-combustion, gas sweetening, and CO_2 post-combustion capture) [42,44]. This novel class of materials, like poly(ionic liquids)s (PILs) [45,46], contain imidazolium cations within the polymer monomer unit. In the poly(ionic liquid) structure, IL molecules are bonded to the polymer backbone. However, the i-PI monomer structure is composed of an IL segment and an organic linker to provide an additional degree of structural and chemical design. In the i-PI structure, 1-(3-aminopropyl)imidazole is reacted with pyromellitic dianhydride (PMDA) to form a difunctional bis(imidazole) molecule which is then reacted with p-dichloroxylene to form the ionic polyimide. The chloride (Cl^-) anions resulting from the polymer synthesis (Menshutkin Reaction) are subsequently exchanged to bistriflimide (Tf_2N^-), hexafluorophosphate (PF_6^-) or tetrafluoroborate (BF_4^-) in the presence of aqueous solutions of the corresponding alkali metal salt in excess. PMDA was chosen as an organic ligand because of its low cost and reports that the PMDA-API molecule forms triply helical nanostructures in the presence of silver salts [47]. Each monomer contains two imidazolium cations in the backbone, along with two balancing anion molecules, as illustrated in Fig. 1. Composite structures were prepared by dispersing IL molecules inside the i-PI polymer in different concentrations.

Our previous experimental work [42] reports the significantly enhanced CO_2 permeability (up to 2200%) by adding [C_4mim][Tf_2N] to the neat i-PI system. The high permeability in the composite system (i-PI + IL) was directly correlated with diffusivity enhancement of CO_2 (up to 2300%), while solubility of CO_2 in the material was essentially identical in the presence/absence of IL. In order to characterize the molecular-level behavior of different gas adsorbents (CO_2, CH_4, N_2) in this system, our previous work [44] focused on pure gas solubility in [Tf_2N^-]-based structures. However, due to the intriguing potential for creating different composites by combining different ILs with the same i-PI backbone, the current work explores the selective adsorption behavior of binary gas mixtures with a range of different i-PI + IL composite materials. For instance, adding bulkier anions may increase the void volume of the composite and specific interactions with different anions may be used to tune the selectivity. In bulk ILs, it has been found that the anions can have a large influence on CO_2 solubility [9]. In the current study, the prepared composite structures contain i-PIs and different ILs with [C_4mim^+] as the cation in combination with one of three anions [Tf_2N^-], [BF_4^-], and [PF_6^-]. MD calculations and grand canonical Monte Carlo (GCMC) simulations are used to study structural changes of the i-PIs and their composites during binary mixtures of CO_2/CH_4 and CO_2/N_2 adsorption by analyzing the fractional free volume (FFV), pore size distribution (PSD), and the surface area.

In our current study, the neat i-PI with [BF_4^-] as the counter ion shows high CO_2/CH_4 selectivity at 1 bar and 294 K, and this is also observed when additional [C_4mim][BF_4] is added to generate the composite material. A high CO_2 solubility is found with the [PF_6^-]-based i-PI and i-PI + IL composites. The high solubility is accompanied by a large calculated surface area within the materials and a larger fraction of wider pores, while the FFV is not a very sensitive indicator of the solubility. Among the three different types of anions studied in this work, the [PF_6]-based structures showed the strongest interaction with gas molecules, regardless of gas type.

2. Simulation details

Our simulation procedure is comprised of several different steps in order to generate the initial configurations, relax the system, perform gas adsorption, and analyze the dominant molecular-level interactions. First, quantum mechanical calculations are used to assign partial charges on the atom sites of the i-PI monomer units (Fig. 1) using the B3LYP functional[48] and a 6-31G(d,p) basis set in Gaussian09 [49]. Then MD simulations are used to prepare the relaxed initial structure of the neat i-PI and i-PI + IL composite. This involves a polymerization scheme followed by several stages of structural relaxation. The initial system also contains an *N*-methyl-2-pyrrolidone (NMP) solvent, which is eventually removed and replaced with the IL species following polymerization. This is intended to qualitatively follow the experimental synthesis procedure during the polymerization and prepare enough vacant space for IL molecules by deleting NMP molecules [42]. Finally, using an iterative combination of molecular dynamics and GCMC simulations, the selectivity of CO_2/CH_4 and CO_2/N_2 is modeled over a wide range of concentrations within the neat i-PI and different combinations of i-PI + IL composite materials. The details of each stage are described below, which follows our previous approach [44].

The details of the electronic structure calculations and geometric optimization of the monomers, as well as the partial charge calculation and polymerization were provide in our previous work [44]. Force field parameters for [C_4mim^+], [Tf_2N^-], [BF_4^-], and [PF_6^-] were taken from Lopez et al. [50–52] while parameters for NMP molecules were extracted from Aparicio et al. [53] The TraPPE [54] force fields for CO_2, CH_4, and N_2 were used, based on the previous experience of others modeling gas adsorption in ILs. [54–57] The Lorentz-Berthelot mixing rules were used for cross-term interactions.

Following the assignment of the force fields, the i-PI and i-PI + IL systems were constructed and conditioned according to the following default procedure (with specific variations noted later in the text):

a) i-PI molecules (as single repeat units) were inserted into the simulation box using PACKMOL [58], followed by energy minimization using the steepest descent algorithm [59].
b) In addition to the monomers, NMP molecules were also inserted at three different ratios: 1:4, 1:6, and 1:8 (monomer:NMP) in order to produce additional replicas of the polymer structure. The experiments used a ratio of approximately 1:60 during polymerization [42]. The effect of different NMP solvent concentrations has been studied in our previous work [44], and it was found to be negligible. We have reached the same conclusion in this work (with different ILs).
c) The monomer + NMP molecules were relaxed with MD simulations using a cycle of canonical ensemble (NVT) simulations to increase temperature up to 2000 K, followed by isothermal-isobaric (NPT) ensemble simulations at high temperature and pressure. After, the systems were slowly quenched to 294 K.
d) The individual units were polymerized, using a nearest-neighbor algorithm (described in previous work) [44], followed by additional relaxation with MD.
e) The NMP was then removed from the system, and the i-PI + IL samples were generated by inserting the IL molecules (anion and cation) in the cavities left by the NMP molecules, again using

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