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Gas Molecule Absorption in Ionic Liquids [EMIM][BF_4] and [EMIM][DCA]: a Molecular Dynamics Study

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Abstract. Addressing global environmental concerns necessitates effective strategies to restrain and reduce greenhouse gas emissions. Ionic liquids (IL) have emerged as promising candidates for capturing gases due to their unique properties. This study investigates the permeation mechanisms of CO_2, H_2S, and CH_4 molecules within: 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) 1-Ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) ILs using molecular dynamics (MD) simulations. The free energy profiles were computed at different temperatures to elucidate the temperature-dependent absorption behavior of these gases. Results reveal distinctive behaviors: CO_2 and H_2S exhibit spontaneous permeation into the IL bulk without energy barriers, whereas CH_4 indicates an adsorption preference solely at the vacuum-IL interface. Rising temperatures impede the viability of gas absorption, especially in higher temperature conditions. These insights offer crucial understanding for optimizing gas separation technologies employing ILs.

Keywords: Ionic Liquid, Gas Absorption, Carbon Capture, Gas Permeation, gas emission

I. INTRODUCTION

The unprecedented challenge of global climate change hinges largely on the relentless rise in greenhouse gas concentrations within the Earth's atmosphere [1, 2]. Notably, carbon dioxide (CO_2), originating predominantly from industrial activities, stands as the primary contributor to the intensifying greenhouse effect, amplifying environmental degradation [3, 4]. Reports by the Intergovernmental Panel on Climate Change (IPCC) underscore the pivotal role of emissions from fossil fuels, particularly CO_2, emanating from energy production, industrial sectors, and vehicular traffic, as the foremost driver of global warming [4, 5]. Based on IPCC statistics, a substantial 89 % of the total CO_2 emissions in 2018 originated from fossil fuels and industrial activities. This underscores the imperative to develop an effective gas-capturing technology to mitigate further ecological impacts [5, 6]. CCUS, standing for Carbon Capture, Utilization, and Storage, arises as a pivotal approach in reducing CO_2 emissions [7]. In the context of fossil fuel combustion, various techniques, such as precombustion capture, oxy-fuel combustion, and post-combustion capture, have surfaced as strategies to reduce the production of CO_2. Among these, post-combustion capture, employing mechanisms like physisorption chemisorption, membrane separation, and calcium looping, has gained traction as a widely implemented technology [8–12]. Chemical adsorption using aqueous amine solutions has been a reliable method in industrial settings, owing to its operational maturity, stability, reactivity, and high capacity for CO_2 absorption [13]. However, inherent drawbacks such as solvent volatility, corrosion concerns, and substantial energy requirements for regeneration highlight the pressing need for economically viable and sustainable alternative solvents to advance large-scale industrial deployment [14–16].

In the face of these obstacles, ILs have surfaced as a hopeful frontier within CO_2 capture and gas separation technologies. These liquids exhibit remarkable characteristics including negligible vapor pressure, high thermal stability, customizable molecular structures, and low flammability and toxicity, which position them as a strong candidate for mitigating emissions [17–21]. Their versatility, derived from diverse combinations of cations and anions, presents cost-effective pathways for isolating CO_2

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from industrial waste streams [22]. Notably, the choice of cation-anion combinations profoundly influences CO_2 solubility within ILs, prompting extensive investigations into specific anions like [Tf_2N], [BF_4], and [PF_6] revealing their direct impact on CO_2 solubility trends [23–25]. This atomic-scale understanding, facilitated by free energy calculations, offers a promising avenue to unravel the intricate molecular interactions underlying CO_2 capture within ILs.

However, the implementation of ILs in industrial settings is hindered by their high viscosity, impeding efficient gas diffusion. Even in light of this obstacle, specific ILs like[EMIM][BF_4]] and [EMIM][DCA] exhibit lower viscosity at room temperature, potentially offering solutions to this impediment [26, 27]. While conventional wisdom dictates that gas solubility decreases with rising temperatures, comprehensive insights into the permeation free energy barriers of gases into ILs remain limited [28–32]. Understanding these intricacies is pivotal for advancing the development of advanced gas capture technologies.
In this study, our primary emphasis is on exploring the complex dynamics of CO_2, H_2S, and CH_4 permeation from a vacuum into ILs ([EMIM][BF_4] and [EMIM][DCA]) bulk. By employing umbrella sampling MD simulations, our initiative aims to calculate free energy profiles. The objective is to offer a comprehensive understanding of the intricate molecular mechanisms that govern gas permeation into ILs across different temperatures. This thorough investigation has the capacity to reveal crucial understandings about how gases are absorbed in ILs, Establishing the fundamental framework to advance eco-conscious gas capture technologies on a global scale.

II. COMPUTATIONAL METHOD

The MD simulations utilized the GROMACS 5.1.4 package, employing GPU acceleration [33]. Employing [EMIM][BF_4] and [EMIM][DCA] ionic liquids along with CO_2, H_2S, and CH_4 gases, the study commenced with 200 anion-cation pairs arranged in a cubic box via Packmol software. Energy minimization and a 100 ps equilibration run using NVT and NPT ensembles were conducted. This preceded a 40 ns production run at two distinct temperatures, maintaining 1 atm pressure via the velocity rescaling thermostat [34] and Parrinello Rahman barostat [35]. Long-range electrostatic interactions were handled with the PME method, using a 1 nm cutoff radius [36]. Subsequently, densities of [EMIM][BF_4] and [EMIM][DCA] at varying temperatures were computed from trajectory data. The densities were cross-validated with experimental data, detailed in the figure 1.

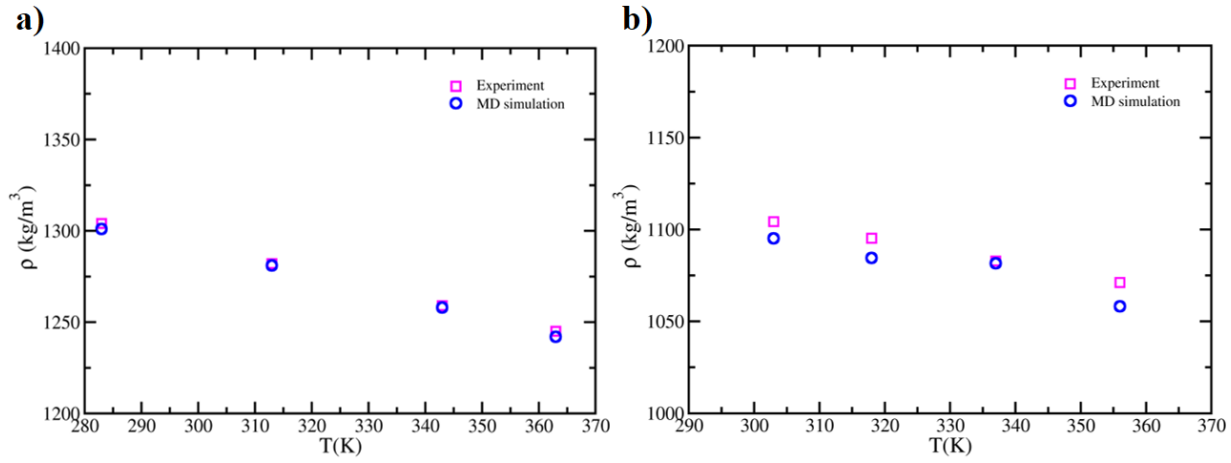


FIG. 1. a) The calculated density values of $EMIMBF_4$ at different temperatures: experimental vs model-ling results; b) The calculated density values of EMIMDCA at different temperatures: experi-mental vs modelling results.

The equilibrated model system was then relocated into a tetragonal box (dimensions: x = 3.7, y = 3.7, and z = 9.7 nm) to establish the vacuum and IL interface (see Figure 1d). Another 40 ns equilibration ensured a uniform distribution of IL molecules between the vacuum and IL bulk. Density distribution along the z-axis is documented in the figure 2.
Umbrella sampling (US) simulations within the tetragonal box [37] facilitated the computation of free energy profiles (FEP) along selected reaction coordinates. Gas molecules were positioned at 1 nm intervals along the z-axis in the model system (see Figure 3a) to optimize computational efficiency. Preceding the US simulations, energy minimization, short NVT simulations, and subsequent 6 ns runs with the last 4 ns trajectory were conducted. Multiple repetitions (4 to 15 times) of US simulations were carried out, randomizing gas molecule positions on the x-y plane (Figure 3a, b). The obtained individual FEPs (70 windows) were averaged using the weighted histogram analysis method (WHAM) [38], culminating in the final FEP. A total of 400 and 600 ns, incorporating 1050 US simulations, were conducted for the mentioned systems. Visual molecular dynamics tools were employed to visualize the model system [39].

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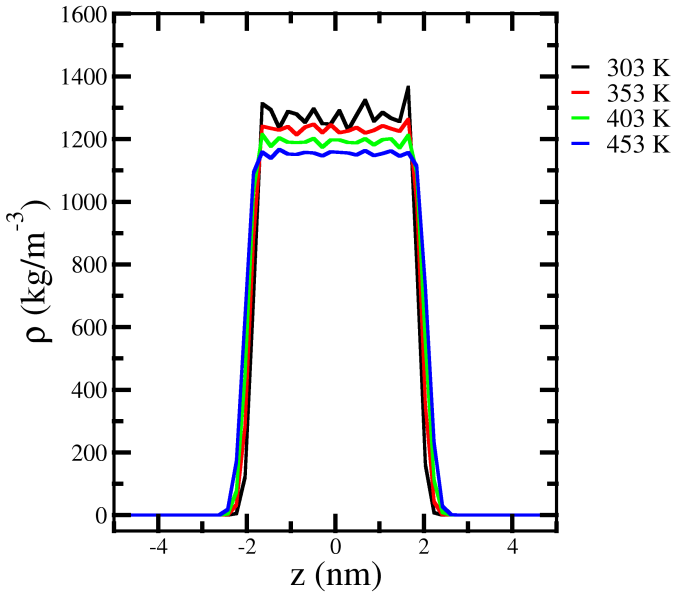


FIG. 2. *The density plot of EMIMBF$_4$ along z-axes;*

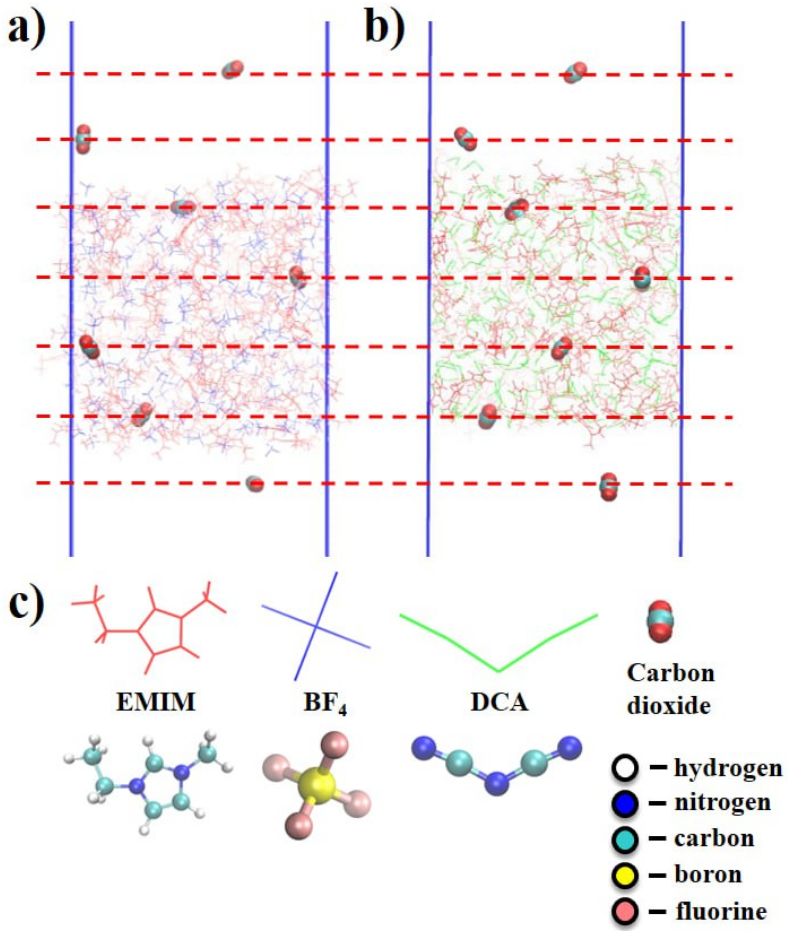


FIG. 3. (a,b) Slabs of [EMIM[[BF_4] (a) and [EMIM][DCA] (b) ionic liquids with embedded CO_2 molecules. (c) Optimized structures of EMIM, BF_4 and DCA molecules. These molecules are located at a 1 nm distance apart along the z-axis.

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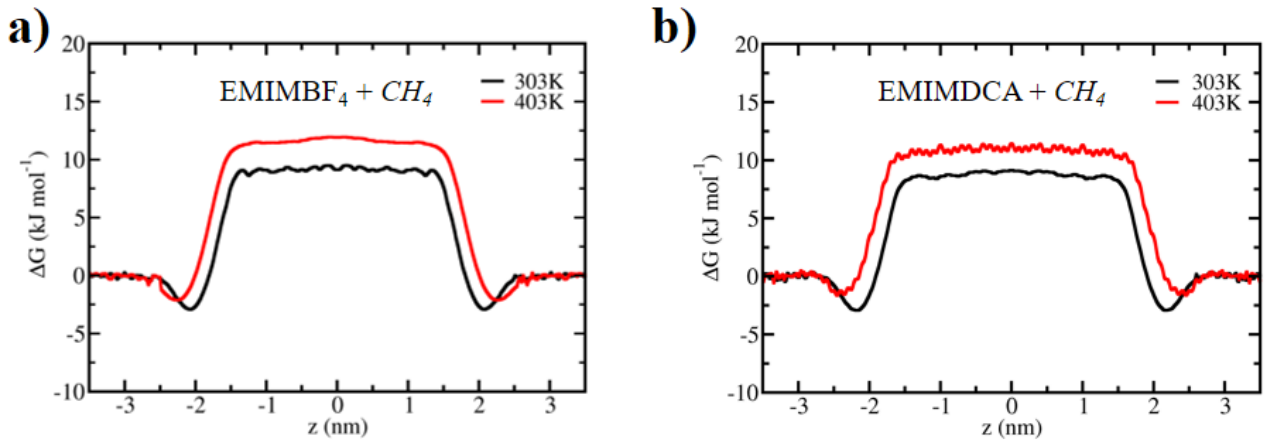


FIG. 4. *a) The FEPs of Methane (CH_4) in[EMIM] [BF_4]; b) The FEPs of Methane (CH_4) in [EMIM][DCA].*

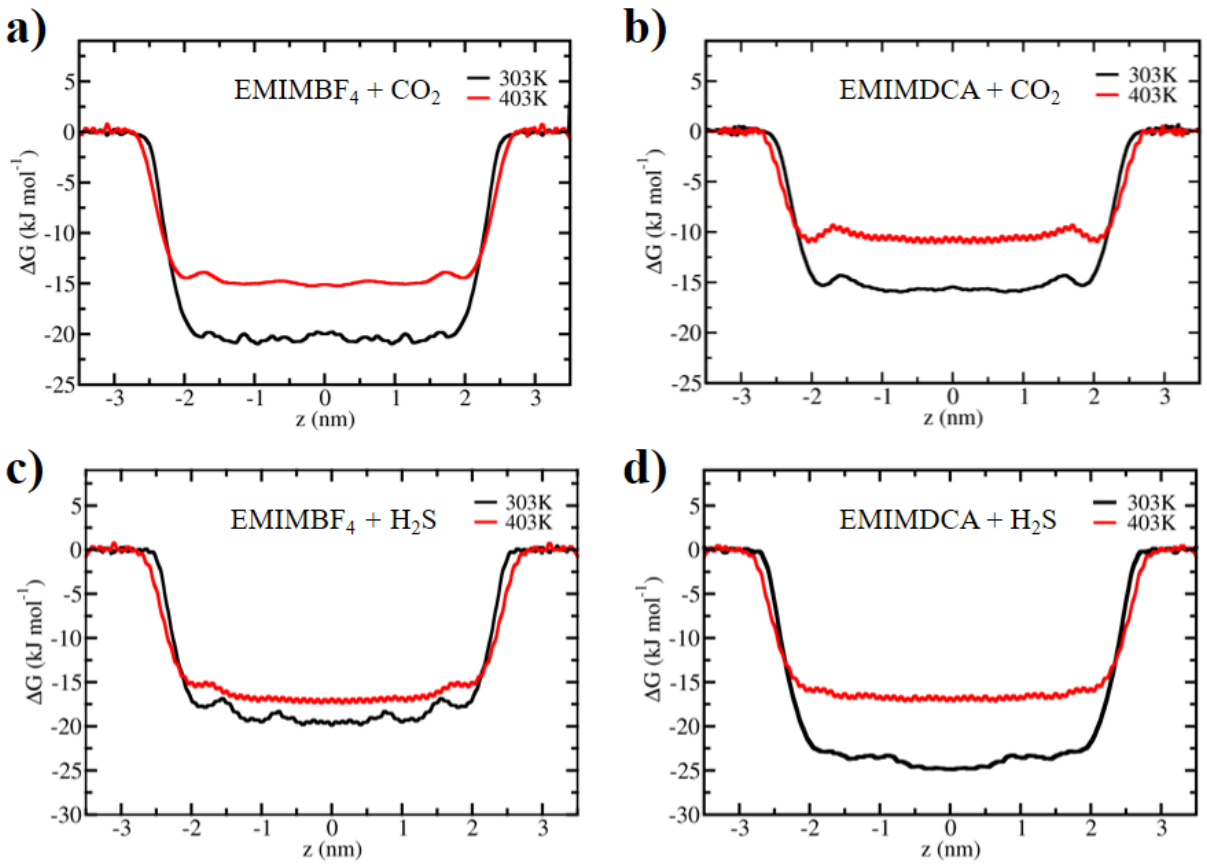


FIG. 5. a) The FEPs of Methane (CH_4) in[EMIM][BF_4]; b) The FEPs of Methane (CH_4) in [EMIM][DCA].

III. RESULTS AND DISCUSSION

To examine the solvation equilibrium behavior of gas molecules, we computed free energy profiles for CO_2, H_2S, and CH_4 within the vacuum-liquid interfaces of [EMIM][BF_4] and [EMIM][DCA]. Simulations were conducted at 303 K and 403 K to deeply probe the impact of temperature on the gas absorption process.

In the context of both ILs, we observed an abrupt change in free energy profile (FEP) for CO_2 and H_2S within the 0.5 nm range, while maintaining almost constant average values in the bulk (Figure 4 a-d). Specifically, the FEP values for CO_2 and H_2S in the

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bulk of[EMIM][BF_4] at 303 Remained close to approximately -20 kJ mol-1 and -18 kJ mol-1, correspondingly. Meanwhile, in [EMIM][DCA], these values were approximately -15 kJ mol-1 and -23 kJ mol-1. Crucially, the FEP curves illustrate an absence of energy barriers for these gases to permeate the IL interface. The notable decline in FEPs from the interface toward the bulk suggests the spontaneous movement of these gas molecules into the bulk upon nearing the IL interface. Increasing the temperature to 403 K intensified the FEP values for both CO_2 and H_2S in both ILs (see Figure 5), signifying a decreased favorability for gas permeation at higher temperatures.

However, the behavior of CH_4 presented a distinct scenario in both ILs (see Figure 4). While the FEP at the vacuum-IL interface remained around -3 kJ mol-1 at 303 K, there existed a considerable energy barrier of approximately 12 kJ mol-1 hindering its transfer into the bulk. Consequently, it appears that methane might solely be adsorbed at the interface in both ILs. Notably, akin to other gas molecules, the temperature dependency of CH_4 permeation revealed an analogous trend, with FEPs escalating as temperature increased, indicating the reduced feasibility of absorption at higher temperatures in both ILs.

This intricate analysis underscores the distinct behavior of CO_2, H_2S, and CH_4 within [EMIM][BF_4] and [EMIM][DCA], shedding light on the Complex dynamics governing gas absorption in these ionic liquids. Such findings hold immense promise in guiding the design of efficient gas separation and carbon capture technologies.

IV. SUMMARY AND CONCLUSION

The detailed examination performed on CO_2, H_2S, and CH_4 absorption within [EMIM][BF_4]and [EMIM][DCA] ILs underscores the nuanced nature of gas permeation mechanisms. The absence of energy barriers for CO_2 and H_2S suggests their easy movement into the IL bulk, contrasting sharply with CH_4, which exhibits an affinity for adsorption solely at the vacuum-IL interface. Furthermore, the temperature dependency of gas absorption indicates a reduced favorability for permeation at higher temperatures. Such intricate findings not only enrich our fundamental understanding of gas-IL interactions but also hold immense promise for guiding the development of efficient gas separation and carbon capture technologies, crucial for mitigating the impacts of greenhouse gas emissions on the environment.

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