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Transport and Energetics of Carbon Dioxide in Ionic Liquids at **Aqueous Interfaces**

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the viscosity of the liquids using the standard Einstein-Stokes relation. Moreover, we calculated the free energy of translocation for various species across the aqueous-IL interface, including CO₂ and HCO₃⁻. Free energy profiles demonstrate that CO₂ exhibits a more favorable partitioning behavior in the RTILs compared to that in pure water, while a significant barrier hinders the movement of HCO_3^- from the aqueous layer. Experimental measurement of the CO_2 transport in the RTILs corroborates the model. These findings strongly suggest that hydrophobic RTILs could serve as a promising option for selectively transporting CO_2 from aqueous media and concentrating it as a preliminary step toward storage.

INTRODUCTION

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The escalating growth of anthropogenic carbon dioxide (CO_2) emissions has led to a wide range of detrimental environmental impacts, including global warming, rising sea levels, and ocean acidification.¹⁻³ Consequently, the development of efficient CO₂ separation, capture, and storage technologies has become imperative. The use of traditional organic solvents like aqueous amines for postcombustion capture (PCC) of CO_2^4 has several notable drawbacks, including high energy consumption, volatile solvents, and exorbitant costs.^{5,6} In contrast, ionic liquids (ILs) have emerged as a promising alternative PCC technology, exhibiting notable CO₂ solubility and possessing advantageous properties like nonvolatility and low operating temperatures.⁷⁻⁹ ILs are more expensive than traditional solvents, and some techno-economic analyses have suggested that using large quantities of physically absorbing ILs may not be viable.^{10,11} Nevertheless, the development of novel IL systems, such as thin film and membrane systems, would dramatically reduce the quantity, and thus the cost, of the IL systems.^{12,13}

selected ILs compared to what would be predicted solely based on

Extensive research has been dedicated to enhancing the CO₂ solubility and transport in ILs since the initial discovery of CO₂ solubility in 1-butyl-3-methylimidazolium hexafluorophosphate $([BMIM][PF_6])$. Those studies have explored the effects of temperature, pressure, and the vast array of possible IL molecular structures on CO₂ solubility and transport.^{14–19} Brennecke and co-workers have reported that increasing the quantity of fluoroalkyl groups in anions and increasing alkyl chain length in cations enhance CO₂ solubility.^{20–22} However, the effect of cation alkyl chain length is relatively small and occasionally exhibits a reversed trend.²³ Shiflett and Yokozeki developed a gravimetric method to measure CO2 diffusion within ILs experimentally and observed diffusion coefficients ranging from 10^{-6} to 10^{-7} cm² s⁻¹ for CO₂ in [BMIM][PF₆] and [BMIM][BF₄].²⁴ Gonzalez-Miquel et al. utilized gravimetric analysis to elucidate the effect of specific anions on CO₂ thermodynamics and kinetics, revealing different orders for

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(c) [TFSI]⁻

Figure 1. Molecular structural representation of imidazolium-based ionic liquids: (a) 1-ethyl-3-methylimidazolium $[EMIM]^+$, (b) 1-octyl-3-methylimidazolium $[OMIM]^+$, and (c) bis(trifluoromethanesulfonyl)imide $[TFSI]^-$. This study used the atoms highlighted with red circles for quantitative analyses.

solubility ([FAP]⁻ > [TFSI]⁻ > [PF₆]⁻) and diffusion coefficients ($[TFSI]^- > [FAP]^- > [PF_6]^-$), where $[FAP]^- =$ tris(perfluoroalkyl)trifluorophosphate and [TFSI]⁻ = bis-(trifluoromethanesulfonyl)imide.²⁵ Moya et al. later showed that a minimum mass of IL is required to obtain accurate gravimetric diffusion coefficients and determined that the diffusion coefficient of CO_2 in [BMIM] [PF₆] is almost 1 order of magnitude larger than previously reported.²⁶ They also fitted the diffusion coefficients to empirical and theoretical models, yielding mean absolute percentage errors ranging from 25% to 82%.²⁶ Furthermore, Zhang and Maginn employed molecular dynamics (MD) simulations to investigate IL dynamics and found that the general rules governing liquid properties do not necessarily apply to ILs.²⁷ For instance, smaller ILs do not always exhibit faster dynamics than larger ILs.²⁷ Consequently, selecting the ideal IL for CO₂ separation and capture remains challenging.

Despite being investigated primarily in pure phases, ILs have also been integrated into gas-selective membranes.^{28–34} Pioneering work by Richard Noble's group demonstrated the potential of supported IL membranes, achieving CO_2/N_2 selectivity as high as 61 and permeability/selectivity exceeding that of existing polymer membranes.^{35,36} The exceptional performance of supported IL membranes can be attributed to the enhanced solubility and transport of CO_2 when confined within a membrane structure.^{37,38} However, optimizing selectivity and permeability simultaneously remains challenging due to the inherent trade-off between the two parameters.²⁸ Nonetheless, Fu et al. successfully mitigated this trade-off by incorporating several innovative strategies, resulting in a $\rm CO_2$ separation membrane with an unprecedentedly high $\rm CO_2$ flux (2600 GPU) and a $\rm CO_2/N_2$ selectivity of 788.¹² Their approach involved using an ultrathin liquid membrane to stabilize the carbonic anhydrase (CA) enzyme at concentrations higher than those achievable in bulk water.¹²

It is conceivable that the innovative techniques reported by Fu et al. could be applied to supported IL membranes to achieve high-performance CO_2 separation and capture and, ultimately, storage. This endeavor would involve developing a dual-layer membrane consisting of a thin CA-stabilized aqueous layer^{39,40} followed by an IL layer. Such a configuration would combine the superior separation efficiency of the previously reported enzymatic membrane with the ability to dissolve and concentrate CO_2 in a condensed phase, allowing further processing into value-added products, such as by electrochemical conversion.⁴¹⁻⁴³ As existing research predominantly focuses on pure IL phases, a deeper understanding of the dynamics of CO_2 at the aqueous–IL interface is crucial.

In this study, we investigate the potential of roomtemperature ionic liquids (RTILs) as materials for the transport and concentration of CO_2 . Our investigation centers on characterizing the behavior of CO_2 at the interfaces of aqueous-[EMIM][TFSI] and aqueous-[OMIM][TFSI] phases, where [EMIM]⁺ =1-ethyl-3-methylimidazolium and [OMIM]⁺ = 1-ethyl-3-methylimidazolium. We present the findings of our comprehensive study that combines molecular dynamics simulations spanning microseconds with experimental data quantifying the CO_2 absorption rates and transport through the aqueous-RTIL phases.

MATERIALS AND METHODS

Molecular Dynamics Simulations. Atomistic simulations were performed using the GROMACS package version 2021.^{44,45} The force field parameters for anion bis-(triuoromethanesulfonyl)imide [TFSI]⁻ and cations 1-ethyl-3-methylimidazolium [CMIM]⁺ and 1-octyl-3-methylimidazolium [OMIM]⁺ were obtained from Doherty et al.^{46,47} (Figure 1). The SPC/E force field parameters were applied to model water, whereas the force field parameters proposed by Cygan et al.⁴⁸ were utilized to represent CO₂. Parameters for the HCO₃⁻ ion were obtained from the LigParGen webserver⁴⁹ using the OPLS-AA/1.14*CM1A parameters. The integration of Newton's equations of motion was performed using the leapfrog algorithm with a time step of 2 fs. The initial structures of the ILs were obtained from PubChem.⁵⁰

For IL systems with CO₂ dissolved, we created a simulation box with 512 IL pairs, either [EMIM][TFSI] or [OMIM]-[TFSI], and included 100 CO₂ molecules. For IL-aqueous systems, we simulated a rectangular box with 392 IL pairs and ~4000 water molecules to produce a system with roughly equal volumes of each phase. The IL layer also contained 100 CO₂ molecules, while the water layer contained 100 HCO₃⁻ ions with 100 neutralizing sodium ions.

The system temperature was maintained using a velocityrescaling thermostat⁵¹ with a coupling constant of 1 ps. The pressure was controlled using a stochastic cell-rescaling barostat⁵² with a coupling constant of 1 ps. Periodic boundary conditions were applied in all three dimensions. The LINCS algorithm was used to constrain the bond lengths.⁵³ A cutoff of 13 Å was set for the short-range electrostatic and Lennard-Jones interactions. The particle mesh Ewald (PME) method was used to treat long-range electrostatic and Lennard-Jones interactions.⁵⁴ Trajectory position coordinates and velocities were recorded every 5 ps.

For each system, energy minimization was performed by using the steepest descent algorithm for 500 steps. This was followed by thermal stabilization and production simulations, carried out at three different temperatures (25, 70, and 120 °C) under the isothermal and fixed pressure (NPT) ensemble with a reference pressure of 1 atm. 2 μ s trajectories were generated, and the first 500 ns of the trajectories were excluded from the data analysis to allow proper equilibration of the system.

For IL–aqueous interfacial systems, free energy profiles were generated using the histogram reweighting method, which involves sampling from a multinomial distribution based on likelihood maximization estimation of a collective variable or reaction coordinate. Here, we use the center-of-mass position of the atoms along the *z*-axis as the collective variable for constructing the histogram. To calculate the free energy, G(s), as a function of the collective variable s(z) related to the marginal distribution P(s), we used the PLUMED plugin^{55,56} command line tool in conjunction with the GROMACS MD code. The free energy profiles were calculated using the following equation:

$$G(s) = -k_{\rm B}T \ln P(s) \tag{1}$$

where $k_{\rm B}$ is the Boltzmann constant and T is the temperature.

We examined the diffusion of the cations (D_+) , the anions (D_-) , and CO_2 within the RTILs solutions by using the Einstein relation. This relation allowed us to capture the essence of the linear regime and analyze the intricate dynamics over a significant time scale of approximately 2 μ s while considering the temperature-dependent variations. Equation 2 describes how to calculate the mean-squared displacement (MSD) of the ion center of mass by summing the squared differences between the center of mass positions at different times for all of the ions in the system.

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$$MSD = \frac{1}{N_i} \langle \sum_{n=1}^{N_i} |r_i^c(t) - r_i^c(0)|^2 \rangle = \Delta |r(t)|^2$$
(2)

Here, N_i represents the total number of ions considered in the system, the angled brackets denote the ensemble average, $r_i^c(t)$ is the position vector of the center of mass of ion i at time t, and $r_i^c(0)$ is the initial position vector of the center of mass of ion i at the starting time, t = 0.

Spontaneous CO₂ Transport through RTIL/Water Interface. Under a 75 sccm N₂ blanket (Matheson, ultrahigh purity, 99.999%), ultrapure water (Millipore, 18.2 M·cm) was brought to boiling and then cooled to room temperature to remove dissolved atmospheric CO₂. About 1.5 mL of roomtemperature water was collected in a syringe. Under an N₂ blanket, the ionic liquid was brought to 100 °C for 30 min and then to room temperature. 5 mL of the ionic liquid was collected in a syringe. The RTILs [EMIM][TFSI] (io-li-tec, 99%) and [OMIM][TFSI] (Solvonic, 99.5%) were used.

The addition funnel was purged with N₂ for at least 30 min before use. The RTILs were added to the main chamber, followed by the water layer. 1.5 mL of water was required to cover the ionic liquid completely, resulting in a 0.36 cm thick water layer. The two components are immiscible, making the interface between RTIL/water distinct (Figure 2). CO2 (Matheson, >99%) was fed through the addition funnel from the bottom through the neck up to the main chamber. The top of the addition funnel was capped with a septum stopper and syringe needle to allow for outlet flow and to prevent pressurizing of the main compartment. CO₂ flow was continued for 4 h. The sample of RTIL was collected through the bottom of the funnel into a preweighed scintillation vial, which was N₂ purged, and the vial was capped and reweighed. The scintillation vial was connected to a gas chromatograph (3000A Micro GC, Agilent) using a custom-made cap. The vial with ionic liquid was brought to 50 °C and heated for 30 min. A single gas chromatograph measurement was taken after 30 min of heating. A previously established CO₂ calibration curve was used as a reference for the analysis.

CO₂ Transport through RTIL Supported on an Alumina Membrane. As shown in Figure 3, a Whatman Anodisc 100 nm alumina membrane was encased in polyimide donut tape, with a 0.97 cm² membrane exposed on each side. 5 μ L of RTIL ([EMIM][TFSI] or [OMIM][TFSI]) was deposited on one side of the membrane and spread evenly over the surface. The membrane was placed under -9.5 psi vacuum (relative to atmospheric pressure) for 30 min to remove remaining air from the nanopores. The membrane with ionic liquid was braced in the center of a two-chamber cell with one side connected to a gas chromatograph (3000A Micro GC, Agilent). The maximum CO₂ percentage the gas chromatograph was capable of measuring was 25% in a given gas mixture. Both chambers were purged with N₂. Simultaneously,



Figure 2. Schematic of the experimental setup of an addition funnel for measuring the spontaneous CO_2 absorption into an RTIL through a thin layer of water. The CO_2 flow path through the funnel is represented by solid black arrows.



Figure 3. Schematic of the experimental setup with RTILs ([EMIM][TFSI] or [OMIM][TFSI]) loaded on a membrane and held between the CO_2 flow (25% $CO_2/75\%$ N_2) and sealed chamber (100% N_2). The CO_2 that entered the sealed chamber was measured using gas chromatography.

one chamber (feeding to the gas chromatograph) was sealed, and through the other chamber, a mix of 24.8% $CO_2/75.2\% N_2$ (Matheson) was flowed at 100 sccm, venting to outside the cell. The chromatograph was sampled hourly from the sealed chamber to quantify the CO_2 that had crossed the membrane. A previously established CO_2 calibration curve for the gas chromatograph was used as a reference for the analysis.

RESULTS

CO₂ Transport in RTILs. We used atomistic molecular dynamics simulations to explore the fundamental properties of the two RTILs ([EMIM][TFSI] and [OMIM][TFSI]) and to understand the differences in CO₂ transport and energetics of CO₂ within the RTIL systems at various temperatures. The allatom force field parametrization used here has been characterized extensively and is known to reproduce physical

quantities such as the mass density of a broad range of RTILs.^{46,47}

 $\rm CO_2$ diffusion is expected to be slower within RTILs as compared to that in water and other traditional hydrocarbon solvents. The diffusion coefficient of a dissolved gas depends on various factors, including the temperature, the molecular size of the gas, and the viscosity of the liquid; however, it has been observed that the correlation between viscosity and diffusion coefficient varies for gases dissolved in RTILs. Previous investigations have demonstrated that, in the case of imidazolium ILs such as the ones studied here, the diffusion coefficient of $\rm CO_2$ ($D_{\rm CO_2}$) correlates with ionic liquid viscosity (η), with $D_{\rm CO_2}$ being proportional to η raised to the power of -0.6.^{57,58}

Table 1 provides a summary of the MD computed diffusion coefficients of the ions and CO_2 at various temperatures. In the

Table 1. Diffusion Coefficients of Individual Ions and CO₂ Obtained from MD Simulations of RTILs

system	T (°C)	$\binom{D_+}{(10^{-6} \text{ cm}^2/\text{s})}$	D_{-} (10 ⁻⁶ cm ² /s)	$D_{\rm CO_2}$ (10 ⁻⁶ cm ² /s)
[EMIM] [TFSI]/CO ₂	25	0.114 ± 0.008	0.088 ± 0.004	1.62 ± 0.06
	70	0.679 ± 0.014	0.520 ± 0.023	7.08 ± 0.26
	120	2.311 ± 0.11	1.759 ± 0.166	17.4 ± 1.1
[OMIM] [TFSI]/CO ₂	25	0.035 ± 0.001	0.037 ± 0.002	1.36 ± 0.14
	70	0.279 ± 0.009	0.312 ± 0.003	5.63 ± 0.05
	120	1.15 ± 0.06	1.30 ± 0.04	16.5 ± 0.7

[EMIM][TFSI]/CO₂ systems, we observe faster diffusion coefficients for [EMIM]⁺ compared to the [TFSI]⁻ anion across all temperatures tested. In contrast, the diffusion coefficients observed for the ions in the [OMIM][TFSI]/CO₂ system at room temperature were similar in value, and at higher temperatures, the [OMIM]⁺ cation showed slower diffusion compared to [TFSI]⁻. Assuming that diffusion follows the known Einstein–Stokes relation, slower diffusion coefficients in the [OMIM][TFSI]/CO₂ systems are to be expected as the longer alkyl chain in [OMIM]⁺ increases the viscosity of the IL.⁵⁹

At 25 °C, the diffusion coefficients of the ions in [EMIM][TFSI] are 2.4–3.3 times faster than those observed in [OMIM][TFSI], which is in agreement with the experimentally measured viscosities of these two ILs, where the [EMIM][TFSI] viscosity (33.0 cP) is ~2.8 times lower than that of [OMIM][TFSI] (93.1 cP).⁵⁹ Similarly, at 70 °C, the diffusion coefficients of the ions in [EMIM][TFSI] are 1.7–2.4 times faster than those observed in [OMIM][TFSI], where the ratio of the [EMIM][TFSI] experimental viscosity (9.8 cP) is ~1.9 times lower than that of [OMIM][TFSI] (17.4 cP) at that temperature.⁵⁹

Diffusion of the CO₂ molecules in the ILs tested is significantly faster compared to that of the individual ions, as shown in Table 1. The values of D_{CO_2} are ca. 14–18 times larger in the [EMIM][TFSI]/CO₂ system at 25 °C, while for the [OMIM][TFSI]/CO₂ system, they are ca. 36–88 times larger. Diffusion of CO₂ in the ILs is still an order of magnitude slower compared to that measured in pure water ($D_{CO_2}^{water} = 22.7 \pm 0.4 \times 10^{-6} \text{ cm}^2/\text{s}$). Moreover, the values of D_{CO_2} are much closer in magnitude when comparing the [EMIM][TFSI]/CO₂

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Figure 4. Mean-squared displacement as a function of simulation time for (a) CO_2 , [EMIM]⁺, and [TFSI]⁻ in the [EMIM][TFSI]/ CO_2 system, and (b) CO_2 , OMIM⁺, and TFSI⁻ in the [OMIM][TFSI]/ CO_2 system at 25 °C.

 $(D_{\rm CO_2} = 1.62 \pm 0.06)$ and [OMIM][TFSI]/CO₂ $(D_{\rm CO_2} = 1.36 \pm 0.14)$ systems at 25 °C. Although CO₂ has faster diffusion in the lower viscosity [EMIM][TFSI], the moderate differences (~ 6–26%) in the calculated $D_{\rm CO_2}$ values between the two ILs at all temperatures tested indicate that CO₂ diffusion does not follow the simple Einstein–Stokes relation. The mean-squared displacement (MSD) data clearly show a linear dependence as a function of time, and, therefore, it does not appear that the diffusion is anomalous (Figure 4).

Validation of our D_{CO_2} results with experimental data from the literature is challenging as most studies focus on pure RTILs. Diffusion coefficients for CO₂ in RTILs with different cation sizes, including [OMIM][TFSI], have been reported from gravimetric analysis.⁶⁰ However, the mass diffusion analysis used to extract the coefficients in those experiments directly imposes the inverse proportional dependence on the viscosity of the fluid. To address this issue, we conducted experiments that directly characterize the transport of CO₂ through the RTILs.

In our experimental setup, filled with the respective IL being tested, we placed a nanoporous alumina membrane between the two compartments. One compartment had a constant flow of CO2, while the other was filled with N2 and sealed off (Figure 3). The CO_2 would then have to transport through the IL to reach the sealed compartment. By measuring the amount of CO2 that diffused through the ionic liquid and into the sealed compartment, we compared the CO₂ transport capabilities of [EMIM][TFSI] and [OMIM][TFSI] (Figure 5). The volume of CO_2 collected over time shows a linear transport dependence in both RTILs. While the CO₂ transport rate is faster for [EMIM] [TFSI] (0.745 \pm 0.008 vol %/h) compared to [OMIM][TFSI] (0.514 \pm 0.002 vol %/h), the ratio of these two rates, 1.45, is much smaller than the ratio of the viscosities for the two RTILs, 2.8, and closer to the ratio of the CO₂ diffusion coefficients, 1.2, obtained from our MD simulations. Together, our simulation and experimental results indicate that the diffusion of CO₂ does not depend solely on the viscosity of the RTILs, but there may be other molecular interactions that modulate its transport. We make use of radial distribution functions (RDFs) in the next section to further characterize these interactions.

RTIL Structure around CO₂. To gain a deeper understanding of the interactions between CO_2 and RTILs that may be important for their transport properties, we characterize solute-solvent radial distribution functions (RDFs) based on



Figure 5. Experimentally measured volume percent (vol %) of CO_2 present in a sealed chamber separated from a 25% CO_2 gas environment by a nanoporous membrane loaded with [EMIM]-[TFSI] or [OMIM][TFSI]. The sealed chamber initially contained only N_2 (0 vol % CO_2 .).

site-specific pairs. The RDF is defined by the following expression:

$$g_{AB}(r) = \frac{\langle \rho_{B}(r) \rangle}{\langle \rho_{B} \rangle_{\text{local}}} = \frac{1}{\langle \rho_{B} \rangle_{\text{local}}} \frac{1}{N_{A}} \sum_{i \in A}^{N_{A}} \sum_{i \in B}^{N_{B}} \frac{\delta(r_{ij} - r)}{4\pi r^{2}}$$
(3)

where $\langle \rho_{\rm B}(r) \rangle$ is the average density of particles B at distance r from a particle of type A, $\langle \rho_{\rm B} \rangle_{\rm local}$ is the local average density of particles B, and $\delta(r_{ij} - r)$ is a Dirac delta function.

Focusing first on the interactions with the [EMIM]⁺ and [OMIM]⁺ cations, we computed the RDFs between the carbon atom of $CO_2(C_1)$ and a few key atoms near the imidazolium ring, as shown in Figure 6. The highest g(r) peak observed, indicating the most favorable solute-solvent interaction, corresponds to the pair with the C₈ atom (Figure 6a, orange curve), which is the methyl carbon bonded to one of the two nitrogen atoms (N₄). The g(r) curve for the N₄ atom (Figure 6a, blue curve) has a lower first neighbor peak that is also broader and shifted to larger distances, which indicates a weaker interaction with CO2. On the other side of the imidazolium ring, the methylene carbon (C_6) from the ethyl group that is bonded to the second nitrogen atom also shows a broader and less structured first neighbor interaction. For comparison, the g(r) for the interaction between water and CO₂ in a simple aqueous solution (dashed black line in Figure 6) shows a much smaller first neighbor peak, indicating that CO₂ interacts more favorably with the imidazolium cation compared to water.



Figure 6. Radial distribution functions, g(r), for the carbon atom of CO₂ and the carbon and nitrogen atoms of (a) [EMIM]⁺ and (b) [OMIM]⁺. The g(r) between the water oxygen atom (OW) and the carbon atom of CO₂ for carbon dioxide in a simple aqueous solution is included for reference. The mean error for all RDFs computed using block averaging is 0.02.



Figure 7. Radial distribution functions, g(r), for (a) C₇, a terminal carbon in [EMIM]⁺ and nonterminal (C₉) in [OMIM]⁺, with the carbon atom of CO₂. (b) Carbon and nitrogen atoms of [TFSI]⁻ with the carbon atom of CO₂. The g(r) between the water oxygen atom (OW) and the carbon atom of CO₂ for carbon dioxide in a simple aqueous solution is included for reference. The mean error for all RDFs computed by using block averaging is 0.02.



Figure 8. Snapshot of an MD simulation with CO_2 in a mixture of [EMIM][TFSI] and water. Atoms are represented as spheres to highlight the interface between the ionic liquid (IL) and water phases, as well as the distribution of CO_2 . The CO_2 molecules are predominantly observed in the IL phase.

The RDFs for the interactions between CO_2 and $[OMIM]^+$ (Figure 6b) show a pattern similar to that observed with $[EMIM]^+$. The linear geometry of the neutral CO_2 molecule prevents it from having a net polarity, as the dipoles formed by the carbon and its two electronegative oxygens cancel each other out. The balance between the moderate electrostatic interactions and van der Waals forces results in the CO_2 molecules preferring an optimal location in contact with mildly hydrophobic carbons and yet near the charged nitrogens of the imidazolium ring. The g(r) between CO₂ and the terminal methyl (C₇) in [EMIM]⁺ shows a slightly lower peak compared to the methylene carbon adjacent to it (Figure 7a). A similar trend is observed for carbon atoms positioned further away from the imidazolium ring in [OMIM]⁺ (Figure 7a). Our RDF calculations are in agreement with previous observations that peak intensity diminishes and width expands with increasing alkyl chain length on the imidazolium ring.^{61,62}

The RDF plot for the CO_2 carbon atom interacting with the central nitrogen atom (N) and the terminal carbon atoms (C)



Figure 9. Free energy (FES) profiles for CO_2 , HCO_3^- , and H_2O in the (a) [EMIM][TFSI]/ CO_2/HCO_3^- , and (b) [OMIM][TFSI]/ CO_2/HCO_3^- systems at 25 °C. The mean error for all free energy profiles computed using block averaging is 0.03 kJ/mol.

of $[TFSI]^-$ is depicted in Figure 7b. A distinct, well-defined peak is observed in the RDF plot corresponding to the C–N interaction, whereas a broad peak with a shoulder is observed for the C–C interaction. More notably, both peaks have lower values, indicating a less favorable interaction compared to the cation. While Figure 7b shows data only for $[TFSI]^-$ in the $[EMIM]^+$ system, the RDFs for $[TFSI]^-$ in the $[OMIM]^+$ system display nearly identical results (data not shown).

Energetics of CO₂ Transport across IL-Aqueous Interfaces. Beyond the simple IL systems with dissolved CO_{2} , we also simulated interfacial systems with IL-aqueous boundaries. For these systems, we modeled a roughly equal volume of IL and water with CO₂ in the IL region and HCO_3^{-} (bicarbonate anions) in the water phase, as illustrated in Figure 8 (see the Materials and Methods section). Neutralizing Na⁺ ions were added in the aqueous phase to balance the charges of the bicarbonate anions. The presence of bicarbonate in the aqueous phase is expected from the spontaneous conversion of CO₂ in solution and also from enzyme-catalyzed conversion, as in the case of carbonic anhydrase-containing membranes.¹² Based on the long microsecond trajectories, we used the spontaneous transition of the various species between phases to estimate the free energy as a function of the position normal to the interphase (the zcoordinate) through histogram reweighting (see the Materials and Methods section).

Free energy profiles for CO₂, HCO₃⁻, and H₂O in [EMIM][TFSI] and [OMIM][TFSI] aqueous interfaces are shown in Figure 9. Free energy differences on both systems show similar patterns, with CO₂ having a negative value in the RTILs relative to the aqueous solution in contrast to both HCO₃⁻ and H₂O, which have positive values. The negative solvation free energies (ΔG) for CO₂ in both RTILs relative to H₂O (Table 2) indicate favorable dissolution in that phase. For comparison, the solvation free energy of CO₂ in pure water has been estimated to be ~-1 kJ/mol.^{15,63} While CO₂ appears to partition more favorably into [EMIM][TFSI] ($\Delta G \sim -5.9$ kJ/

Table 2. Solvation Free Energies (ΔG) for CO₂ in RTILs Relative to H₂O

system	T (°C)	ΔG (kJ/mol)
[EMIM][TFSI]/CO ₂	25	-5.86 ± 0.02
	70	-5.40 ± 0.01
[OMIM][TFSI]/CO ₂	25	-5.66 ± 0.02
	70	-5.32 ± 0.01

mol) compared to [OMIM][TFSI] ($\Delta G \sim -5.7 \text{ kJ/mol}$), the small difference in energies is consistent with previous simulations studies,⁶⁴ where no significant influence of alkyl chain length on computed solvation free energies was observed in 1-*n*-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([C_n MIM][TFSI]) with varying chain lengths (n = 2, 4, 6, 8). Elevating the temperature to 70 °C results in a less negative free energy for CO₂, suggesting a less favorable interaction. This behavior is consistent with other findings in the literature.⁶⁵

Conversely, the solvation free energies for H_2O in the RTILs are positive and significantly larger in magnitude, indicating that the partitioning of water in the RTILs is much less favorable. The slightly larger value observed in [OMIM]-[TFSI] is due to the more hydrophobic nature of the [OMIM]⁺ cation, which has a longer alkyl chain. HCO_3^- ions were never observed to partition into the bulk RTIL regions. As a consequence, we were unable to estimate the free energy values for HCO_3^- in that phase accurately.

Spontaneous Absorption of CO₂ into ILs through a Thin Water Layer. To support our findings from MD simulations, we conducted experimental measurements of the spontaneous absorption of CO₂ into [EMIM][TFSI] and [OMIM] [TFSI] through a thin water layer. The absorption was performed using a continuous flow setup in an addition funnel (Figure 2). N_2 was first used to flush out the chamber before the addition of the N2-gas-purged IL and water, after which CO₂ was introduced to the chamber under a constant flow. The CO_2 first would absorb into the thin water layer and then into the IL below the water, confirming the spontaneous IL/H₂O transport from the model. After a 4 h period, we observed a slightly higher amount of absorbed CO₂ in [EMIM] [TFSI] compared to [OMIM] [TFSI] when normalized to the mass of each respective RTIL (Figure 10a). These experimental findings support our predicted FES calculations, which indicate favorable and similar CO2 solvation in the [EMIM][TFSI]/CO₂/H₂O/HCO₃⁻ and [OMIM][TFSI]/ $CO_2/H_2O/HCO_3^-$ systems, as illustrated in Figure 9. The increased affinity for CO₂ in the [EMIM][TFSI] RTILs in addition to its lower viscosity, compared to [OMIM][TFSI], result in faster overall absorption (Figure 10b).

CONCLUSIONS

We used MD simulations and experiments to characterize the transport and energetics of CO₂ in two RTILs, namely, [EMIM][TFSI] and [OMIM][TFSI], for capture applications in enzyme-based liquid membrane technology. While diffusion



Figure 10. Experimentally measured (a) amount of CO_2 per gram RTIL, and (b) rate of CO_2 absorbed into RTIL through the water layer when exposed to a constant stream of CO_2 for 4 h.

of CO₂ in [EMIM][TFSI] is faster compared to that in [OMIM][TFSI], the similar diffusion coefficients do not follow the significant difference in the viscosity of the two ionic liquids. This result suggests that diffusion of the smaller CO₂ molecule does not follow the conventional Stokes–Einstein relation. Experimentally measured CO₂ transport through the RTILs shows faster transport of CO₂ across [EMIM][TFSI] than [OMIM][TFSI] and supports our diffusion calculations. Analysis of the radial distribution functions indicates that the CO₂ molecules prefer to interact with the carbon atoms closest to the imidazole ring in both the [EMIM]⁺ and [OMIM]⁺ cations.

Furthermore, we modeled the transport of CO_2 across an RTIL–aqueous interface and characterized the free energy differences between the two phases. As expected, we found that the free energy of CO_2 in the RTILs is more negative compared to water and the free energy of both H_2O and HCO_3^- is largely positive as these two highly polar molecules prefer the aqueous environment. Similarly to our diffusion results, our calculations show that the solvation free energy for CO_2 in [EMIM][TFSI] is slightly more favorable compared to [OMIM][TFSI]. Experimental measurement of the CO_2 absorption shows that CO_2 will absorb spontaneously through a thin water layer into [EMIM][TFSI] and [OMIM][TFSI], with slightly more CO_2 absorbing into [EMIM][TFSI], which agrees with our computational findings.

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Notes

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