Multiscale Modeling and Experimental Study of CO₂ Absorption into Ionic Liquid Reverse Micelle

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ABSTRACT

In this work, we have used both atomistic simulations and device-scale modeling of our experimental data to investigate CO₂ absorption in ionic liquid reverse micelle (ILRM). The ILRM consisted of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) ionic liquid (IL) as the micelle core, the benzylhexadecylmethylammonium ([BHDC]+) cation ([Cl⁻]⁻), and benzene was used as the continuous solvent phase in this study. The atomistic simulations show that CO₂ molecules are absorbed in four different regions of the ILRM system, that is, (I) in the IL inner core, (II) in the [BHDC]+ surfactant cation layer, (III) at the interface between the [BHDC]⁺ surfactant cation layer and benzene solvent, and (IV) in the benzene solvent. The CO₂ solubility was found to decrease in the order II > III > IV > I, while the CO₂ diffusivity and permeability decrease in the following order: IV > III > II > I. Finally, by using a device-scale modeling of our experimental CO₂ absorption solubility data, it was found that apparent CO₂ mass transport in the ILRM could be one magnitude faster compared with CO₂ mass transport in the corresponding neat IL and surfactant.

Keywords: Atomistic simulation, device-scale modeling, CO₂ absorption, ionic liquid, reverse micelle

1 INTRODUCTION

Highly viscous solvents for gas absorption will lead to large pumping power requirement and large absorption/desorption tower, resulting in high capital cost. Ionic liquids (ILs) represent such examples even though ILs have been extensively studied for gas separation due to their favorable properties, such as negligible volatility and large CO₂ solubility. In addition to the high viscosity, ILs are typically hygroscopic due to strong anion-water interactions. This IL hygroscopicity implies that water must be removed before CO₂ is captured. Both the high viscosity and hygroscopicity degrade the efficiency and economics of carbon capture by using ILs. In order to overcome the above two drawbacks, we have recently investigated IL reverse micelle (RM) for CO₂ capture [1]. The nano size and consequently the large specific surface area for the ILRM nanodroplet (IL core and surfactant) will significantly help gas mass transport. Additionally, a hydrophobic oil is used as the solvent phase to minimize water permeation through the ILRM system, which may alleviate problems related to water absorption in ILs.

In this talk, we present both atomistic and device scale modeling to investigate CO₂ absorption in ILRM. The ILRM consisted of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) IL as the micelle core, the benzylhexadecylmethylammonium ([BHDC]+) cation ([Cl⁻]⁻) was the cationic surfactant, and benzene as the continuous solvent phase. Both our atomistic simulations and experiments show that the IL inside the RM diffuses 5-26 times faster than the neat IL, which is partly due to the fast particle diffusion for the ILRM nanodroplet (IL and surfactant) as a whole in benzene solvent compared with neat [bmim][BF₄] diffusion. Furthermore, atomistic simulations show that CO₂ molecules are absorbed in four different regions of the ILRM system, that is, (I) in the IL inner core, (II) in the [BHDC]+ surfactant cation layer, (III) at the interface between the [BHDC]⁺ surfactant cation layer and benzene solvent, and (IV) in the benzene solvent. The CO₂ solubility was found to decrease in the order II > III > IV > I, while the CO₂ diffusivity and permeability decrease in the following order: IV > III > II > I. By combing the device-scale modeling with the unsteady-state CO₂ absorption data obtained from our experimental Sievert’s apparatus, it was found that the apparent CO₂ mass transport in the ILRM could be one magnitude faster compared with CO₂ mass transport in the corresponding neat IL and surfactant. This is partly due to the large specific area for the ILRM nanoparticle. Both our simulations and experiments show that the ILRM is a promising material for CO₂ capture applications.

2 SIMULATION DETAILS

2.1 Atomistic Simulations

The molecular structures for the [bmim]+ cation, [BF₄]⁻ anion, [BHDC]⁺ surfactant cation, [Cl⁻]⁻ surfactant anion, and benzene solvent are shown in Figure 1. The classical force field (FF) potential used to simulate the [bmim][BF₄] IL, [BHDC]⁺ surfactant, benzene solvent, CO₂, and the interactions between these molecules is given by
the gas phase [1].

Figure 1. Molecular structures for 1-butyl-3-methylimidazolium cation ([bmmim]+), tetrafluoroborate anion ([BF4]-), benzylhexadecyldimethylammonium surfactant cation ([BHD]+), chloride surfactant anion ([Cl]-), and benzene (C6H6). A vertical dashed line was used to divide [BHD]+ into two groups, that is, the head group with a charge of +0.767 e and the alkyl chain tail group with a charge of +0.233 e. Note that the charges were obtained from quantum ab initio calculations of [BHD]+ in the gas phase [1].

\[
\mathcal{V}(r) = \sum_{\text{bonds}} k_b (r - \tau_b)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_b)^2 + \sum_{\text{dihedrals}} k_\gamma [1 + \cos(n_\gamma \chi - \delta_\gamma)] + \sum_{\text{impropers}} k_\text{improp} (\psi - \psi_0)^2 + \frac{\beta}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ 4e^{\left(\frac{r_{ij}^2}{\tau_g}\right)} - \left(\frac{r_{ij}}{\tau_g}\right)^6 + \frac{q_i q_j}{r_{ij}} \right\}
\]

(1)

Standard Lorentz–Berthelot combining rules were used to calculate the mixed Lennard-Jones (LJ) interaction parameters. The LJ potential was switched from 10.5 to 12.0 Å. A Verlet neighbor list with a 13.5 Å radius was used. The intra molecular electrostatic and LJ interactions for atoms separated by exactly three consecutive bonds were scaled by 0.5 and were neglected for atoms separated by less than three consecutive bonds. The classical FF parameters for [bmmim]+, [BF4]-, and CO2 were obtained from previous work [1].

2.2 Device Scale Modeling

CO2 concentration in the liquid sample changes with time during the experimental CO2 solubility measurement until an equilibrium is obtained. It is very important to note that stirring was not used in the experiment. The CO2 mass transport in the liquid sample is completely due to CO2 Fickian diffusion mechanism. By assuming 1-dimensional CO2 Fickian diffusion along the Z-direction of the cylindrical tube containing the liquid sample, CO2 concentration in the liquid sample was obtained as below

\[
C(z,t) = C_s \left[1 - \text{erf}\left(\frac{z}{2\sqrt{D}t}\right)\right] \quad (2),
\]

where \(C(z,t)\) is the CO2 concentration in a unit of mol/liter at time \(t\) and position \(z\), \(C_s\) is the CO2 concentration at the top of the liquid surface (\(z=0\)). The \(\text{erf}\) is the mathematical error function, \(D\) is the CO2 diffusivity in the liquid. Note that when deriving the equation (2), the following initial and boundary conditions were used: \(C(z,0)=0\); and \(C(0,t)=C_s\), \(C(L,t)=0\), where \(L\) indicates the liquid thickness in the tube in \(Z\) direction; this boundary condition implies that \(C_s\) is a constant and there is no CO2 absorbed at the bottom of the liquid sample in the tube. During CO2 absorption experiment, after some time \(t_0\), CO2 will be diffused to the bottom of the tube and the above equation (2) will not be appropriate. But at \(t < t_0\), \(C(L,t)=0\) would hold. Consequently, only the experimental data at the initial time stage were used to fit equation (2). Additionally, at \(t < t_0\), CO2 pressure in the gas phase only slightly changes and \(C_s\) could be reasonably assumed to be a constant. For example, for CO2 absorption in neat [bmmim][BF4] IL, only the CO2 absorption experimental data at \(t < 36\) minutes were used. During this time, CO2 pressure in the gas phase only slightly decrease from 13.84 bar to 13.65 bar; the CO2 pressure in the gas phase and \(C_s\) for CO2 could be reasonably assumed a constant. Additionally, at \(t < 36\) minutes, CO2 concentration at the bottom of the tube \((C(L,t))\) was calculated from equation (2) and was found to be negligibly small, very close to 0. Consequently, at \(t < 36\) minutes, equation (2) would be appropriate to describe CO2 concentrations in the IL sample. Note that in experiment the total number of CO2 absorbed in the whole IL solvent sample, \(N_{CO2}(t)\), instead of CO2 concentrations at different IL position \(C(z,t)\), was measured. In the modeling calculation, the \(N_{CO2}(t)\) can be calculated from \(C(z,t)\) by using the following integration equation,

\[
N_{CO2}(t) = \int_0^t A \times C(z,t) dz = C_s \times A \int_0^t \left[1 - \text{erf}\left(\frac{z}{2\sqrt{D}t}\right)\right] dz \quad (3),
\]

where \(A\) is the cross-section area for the tube \((\pi/4 \times (18.98\text{mm})^2)\). By tuning \(D\) and \(C_s\), the \(N_{CO2}(t)\) could be calculated from (2) and compared with the experimental data. For CO2 absorption in [bmmim][BF4], for the time period 2.95 min. \(\leq t \leq 35.95\) min., there are totally 34 sets of experimental \(N_{CO2}(t)\) data for comparison with the modeling. The following minimization function was
Consequently, constructed, 
\[
\text{obj} = \sum_{i=1}^{N_{\text{CO}_2}} N_{\text{CO}_2}(\exp) - N_{\text{CO}_2}(\text{cal}) = \int_0^L A \times C(z,t)dz
\]
\[= Cs \times A \int_0^L 1 - \text{erf} \left( \frac{z}{2\sqrt{Dt}} \right) dz \]  
(4)

The \(Cs\) and \(D\) values were obtained by minimizing the above \(\text{obj}\) function.

3 RESULTS AND DISCUSSIONS

3.1 Diffusion of IL Enclosed in the ILRM

A snapshot from molecular dynamics simulation for the ILRM was shown in Figure 2. The [bmim][BF4] IL diffusion enclosed in the ILRM (Figure 2) was calculated.

![Figure 2](image)

Figure 2. Representative snapshots obtained from NPT molecular dynamics simulations at 298 K and 1 bar. The ionic liquid reverse micelle (ILRM) system has 55798 atoms and contains 50 [bmim][BF4] IL, 100 [BHDC] surfactant, and 7833 benzene molecules. The simulation was started (corresponding to time \(t = 0\) ns) from a predefined ILRM nanodroplet (IL and surfactant) structure. Benzene molecules are indicated by gray sticks. [1]

The mean square displacement (MSD) (Figure 3) show that the [bmim]+ cation and [BF4]- anion enclosed in the ILRM diffuse much faster than the neat [bmim][BF4] IL. Obtained from the MSD values, it was found that the self-diffusion coefficients for the [bmim][BF4] IL enclosed in the ILRM diffuses about 16-35 times larger compared with the neat [bmim][BF4] IL. The significantly enhanced IL self-diffusion in RM is partly due to the ILRM nanodroplet particle diffusion in less viscous benzene.

![Figure 3](image)

Figure 3. Mean squared displacement (MSD) for the [bmim]+ cation (black line) and [BF4]- anion (red line) at 298 K and 1 bar in the ionic liquid reverse micelle (ILRM) (solid line) and neat ionic liquid (IL) (dashed line) systems. The ILRM system consists of 50 [bmim][BF4] IL, 100 [BHDC], and 7833 benzene molecules [1].

3.2 CO2 Absorption in ILRM

As shown in Figure 4, in the ILRM CO2 could be absorbed in the benzene solvent phase (IV), the interace between benzene and the [BHDC] surfactant tail (III), [BHDC] surfactant tail (II), and inside the ILRM nanodroplet (I).

![Figure 4](image)

Figure 4. Representative snapshot for CO2 absorption in an ionic liquid reverse micelle (ILRM) system at 298 K and 1 bar. The ILRM system contains 50 [bmim][BF4] IL, 100 [BHDC] surfactant, and 7833 benzene molecules, in which 500 CO2 molecules are absorbed. The CO2 molecules are indicated as purple VDW. The IL and surfactant molecules
are represented in the same way as in Figure 2. Benzene solvent molecules are not shown for clarity [1].

CO₂ Henry’s law constant, self-diffusivity and permeability were calculated (Table 1). The β values are close to 1, which suggest that the simulations are long enough to obtain reliable CO₂ self-diffusivity data. Note that the larger the Henry’s law constant, the smaller gas solubility. The CO₂ solubility was found to decrease in the order II > III ~ IV > I, while the CO₂ diffusivity and permeability decrease in the following order: IV > III > II > I.

Table 1. Simulated CO₂ Henry’s Law Constant (H), CO₂ Self-Diffusivity (D), and CO₂ Permeability (perm.) in Four Different Regions (Figure 4) of the Ionic Liquid Reverse Micelle (ILRM) System at 298 K [1]

<table>
<thead>
<tr>
<th>Region</th>
<th>H (bar)</th>
<th>D (m²/s)</th>
<th>β</th>
<th>perm. (barrier)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>333.33</td>
<td>9.1(5) × 10⁻¹¹</td>
<td>1.05(6)</td>
<td>76 ± 4</td>
</tr>
<tr>
<td>II</td>
<td>55.31</td>
<td>3.4(1) × 10⁻¹⁰</td>
<td>0.92(3)</td>
<td>143 ± 42</td>
</tr>
<tr>
<td>III</td>
<td>89.29</td>
<td>4.3(6) × 10⁻⁹</td>
<td>0.91(2)</td>
<td>14300 ± 200</td>
</tr>
<tr>
<td>IV</td>
<td>88.90</td>
<td>5.9(4) × 10⁻⁹</td>
<td>0.97(1)</td>
<td>22270 ± 150</td>
</tr>
</tbody>
</table>

aThe ILRM system contains 50 [bmim][BF₄]/100 [BHDC]/7833 C₆H₆. A total number of 500 CO₂ molecules are absorbed in the ILRM system. Note that the summation of cation and anion numbers rather than the number of IL pairs was used to compute the CO₂ molar fraction and Henry’s law constant. The β = d(log Δr²)/d(log t) values obtained from simulations are also shown. The uncertainty in the last digit is given in parentheses.

3.3 CO₂ Diffusivity in Benzene, [bmim][BF₄] IL, and ILRM

The experimental CO₂ amounts of absorption in neat [bmim][BF₄] IL versus time are shown in Figure 5. The CO₂ Fickian diffusivity in [bmim][BF₄] at 298 K was calculated to be 1.146 × 10⁻¹⁰ m²/s by fitting to the experimental data (Figure 5); which is comparable to the simulated CO₂ self-diffusivity of 9.9 ± 0.1 × 10⁻¹¹ m²/s [1] and the experimental data of 7.3 × 10⁻¹¹ m²/s obtained by Shiflett et al. The CO₂ Cs value was calculated to be 2.2393 mol/L by fitting to the experimental data. The fitted NCO₂(t) values (Figure 5) are close to the experimental value, with an absolute average difference of 5.5%. The equilibrium amount of absorbed CO₂ was estimated to be 1.027 ± 0.001 mmol based on the experimental data at t > 26 hr (inset Figure 5), which corresponds to a CO₂ mole fraction of 0.188 at 13.059 ± 0.001 bar; this CO₂ equilibrium solubility data is comparable to the experimental data obtained by Shiflett et al. with a difference of about 10%.

Similarly, CO₂ diffusivity in benzene at 298 K was calculated to be 0.5-2 × 10⁻⁸ m²/s, which is reasonably close to the simulation value of 0.6 × 10⁻⁸ m²/s obtained from molecular dynamics simulations [1].

For CO₂ absorption in the ILRM, the above fitting procedure by using equations (3-4) to obtain D and Cs does not work. There are large difference between the fitting and the experimental data; this is because the above equations (3-4) work only for a homogeneous solvent system and the diffusivity D is assumed to be a constant. However, in the ILRM CO₂ diffusivity values are very different from each other in different regions of the ILRM system (Table 1). In the ILRM system, if we assume that CO₂ diffuses three layers of benzene, the IL, and the surfactant in series, it takes about 10 times longer time than the experimental data. This is due to the large specific area of the ILRM nanoparticle, in which CO₂ diffuses into many ILRM nanoparticles parallel instead of serially.

**REFERENCES**