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Removal of Carbon Dioxide by Phosphonium-Based Amino Acid Ionic Liquids: Molecular Dynamics Simulation

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Abstract

Molecular dynamics simulation was performed to capture CO_2 by using non-toxic solvents. Tetrabutylphosphonium cation coupled with glycinate amino acid anion was simulated in order to compare the functionalization effect on gas capturing. The results demonstrated that functionalized ionic liquid with carboxylic group is the most favoured ionic liquid and its interaction with CO_2 is due to the anion.

Keywords: Molecular Dynamics Simulation; Carbon Dioxide Capture; Phosphonium-based Ionic Liquids; Radial Distribution Function.

I. I. Introduction

The main reason for global warming is greenhouse gases; these gases include water vapor, carbon dioxide, methane, and nitrous oxide. Excessive emission of carbon dioxide has adverse effects on the global climate, leading to social and economic consequences. For this reason, the removal of carbon dioxide gas has been considered [1]. Phosphonium-based ionic liquids are of interest due to the chains around the phosphonium cation and the large space volume. They have a higher solubility compared to imidazolium ionic liquids [2]. In the present study, the removal of carbon dioxide gas with ionic liquids that have unique properties such as low vapor pressure, high thermal stability and physical and chemical adjustment has been done through proper coupling of cation and anion. These solvents are used as harmless environmental solvents and green ones [3].

II. Methods

Molecular dynamics simulation was performed with Materials Studio software [4] for 3 ns to investigate the removal of carbon dioxide. Here, glycinate amino acid anion coupled with tetrabutylphosphonium cation, $[P_{4444}][GLY]$, was simulated at ambient temperature and pressure. In addition, the studied ionic liquid cation was functionalized using different functional groups including –OH, –COOH, $–NH_2$, and $–OCH_3$. The geometry optimization in the gas phase for CO_2 and all target ionic liquids was carried out using DFT at B3LYP/6-311++G(d,p) level of theory. The wave number calculation was also performed at the same level of theory. The absence of negative values of Hessian matrix confirmed that the stationary point corresponds to a real minimum. In addition, the electrostatic surface potential (ESP) at the same level of theory was conducted to access more

accurate atomic charges. The temperature and pressure of NPT ensemble simulation box were controlled by with Andersen thermostat and Berendsen barostat.

III. Results and discussion

Ion pair binding energy is the highest in [P_{4444}][Gly] and is the lowest in [P_{4444}COOH][Gly]. According to the cation…anion pair correlation function, Figure 1, it can be understood that cation functionalization does not change the compactness of the system and the average distance between cation and anion is 4.80 Å. However, the intensity of the interaction shows reduction due to the functionalization. It can also shed light on the more space available for the gas to be absorbed in the [P_{4444}COOH][Gly]. Noticeably, comparing the radial distribution function, RDF, between the ionic liquid and the gas demonstrates that anion has the major role in gas solubility. The average distance between the glycinate anion and absorbed CO_2 gas is 3.40 Å and the [P_{4444}COOH][Gly] shows the most favorable interaction between the liquid and the CO_2 gas. Figure 2 illustrates that the target ionic liquids are able to absorb the CO_2 uniformly and make it dissolved.

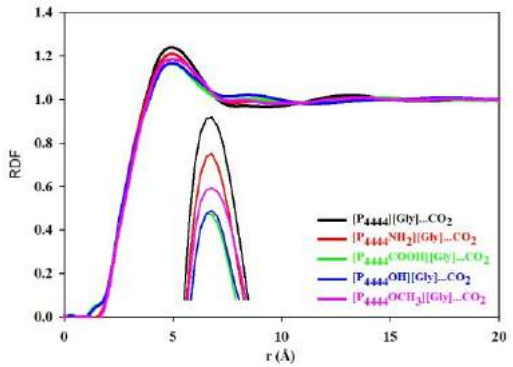

Fig. 1. Anion… cation RDF at the presence of CO_2. Magnification of the first peak is shown as a legend from COMPASS (version 2.8) force field.

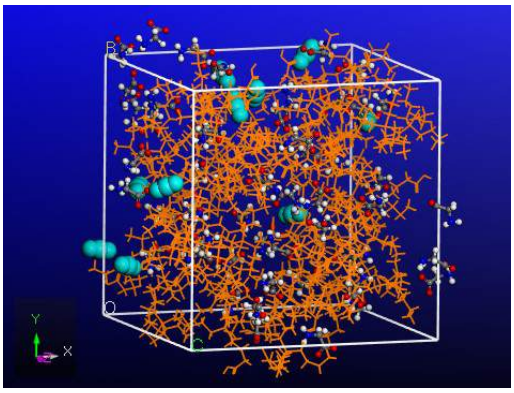

Fig. 2. Final snapshot of the simulation box; the orange is cation, the cyan is CO_2, and anion is shown in stick and ball model with O in red, C in dark gray, N in blue, and H atoms in white.

IV. Conclusions

It was observed that the functional group addition to the cation not only decreases the cation and anion interaction but also density of the liquid. As a result, the ionic liquid anion does tend to interact with the carbon dioxide. In general, the anion plays a critical role in the interaction because its radial distribution function occurred at a shorter distance. The compactness of ion pairs as well as the least mobility of captured gas demonstrated that functionalization with carboxylic acid is more favored for this purpose.

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