

The Absorption Mode of CO₂ in Ionic Liquids: DFT Study

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Abstract

Economic and environmental factors drive research into energy efficient processes and CO₂ capture materials. Currently, amine-based (e.g., monoethanolamine) technologies dominate CO₂ capture, but they are energy intensive and environmentally unfriendly due to volatile solvent emissions. Ionic liquids have been proposed as a viable alternative to conventional volatile solvents. This remarkable interest has resulted in a rapid growth of literature. The goal of this paper is to provide a general idea of the successes and challenges in finding an ionic liquid for CO₂ capture from flue gas streams. This article covers the computational data of CO₂ solubility in various ionic liquids. There is a focus on anions, cations and functional groups in ionic liquid CO₂ solubility. Solvent designers can use these trends to sort through the vast number of theoretically possible ILs and their CO₂ absorption capacity by using suitable ionic liquids.

Keywords— Density functional calculations, absorption of CO₂, room temperature ionic liquids, anionic effect, ionic liquid.

1. Introduction

Currently, because of environmental concerns, there is much interest in the development of technologies that may be able to efficiently remove CO₂ from exhaust gases and thus avoid its dispersion in the atmosphere. Ionic liquids (IL) are generally liquid salts with a very low melting point, often smaller than room temperature. There are a lot of properties that make IL interesting as process electrolytes. For instance, they reveal very small vapor pressure, are good solvents for many substances, are not flammable or toxic, have high thermal stability. Efficient CO₂ removal from flue gas is difficult economically and technically. For large-scale CO₂ removal from flue gas/ natural gas, the energy penalty is too high, making it unattractive [1].

Many new processes/ materials, particularly ionic liquids (ILs), have been proposed to solve this issue [2]. We aimed to present trends in CO₂ solubilities and selectivity in IL, effect of anions, cations and functional groups on physical properties, volatility, biodegradability and toxicity of ionic liquids [3]. The main finding is that post-combustion CO₂ solubility in conventional ILs is still dominating by anion-CO₂ interaction. As IL molecular weight, molar volume and free volume increase, so does the Henry's constant (CO₂ solubility). Solubility of CO₂ in ILs should be compared in molality (mol/kg) or molarity (mol/m³) rather than mole fraction. In industrial separation processes, selectivity is as important as solubility. [4]. CO₂ is much more soluble than other simple gases (e.g., H₂, N₂, O₂), but SO₂ and H₂S are the most soluble in ILs. That is, selectivity will be high for CO₂-simple-gas systems and low for CO₂-sour-gas systems. Using ILs with a low molar volume should improve CO₂/N₂ and CO₂/CH₄ selectivity [5]. The high viscosity of all functionalized or non-functionalized ILs prevents industrial

application. The paper shows trends that can be used to design ILs for CO₂ absorption process. DFT simulations with an implicit solvation model were used to compute the results. On an RTIL, in both water and ionic liquid, the ensemble of minimum energy structures accessible to CO₂ when absorbed is investigated in the results and discussion sections. Solubility and diffusibility of CO₂ in ILs also investigated.

2. Computational Methods

To study CO₂ absorption in ionic liquids, simulations was run on a variety of ionic liquids with CO₂. The Polarized Continuum Model also used to model the latter (ICF-PCM). The minimum energy structures, interaction energies, binding energies and preferred interaction sites of complexes, reactants and products were determined using DFT [6]. It was also used to perform quantum mechanical calculations [7]. All simulations was carried out the Gaussian 09 quantum chemistry software suite packakge to calculate the minimum energy structures. The implicit PCM model was used to model the solvent in the simulations. In the SMD model, a solute molecule's charge density interacts with a continuum description of the solvent. Solute electron density is used instead of partial atomic charges to define the model, which is known as SMD. Solute-solvent boundary surface tension refers to a dielectric medium rather than an explicit representation of the solvent. The SMD model calculated the cavitation and non-polar contributions to energy. All minimum energy structures will be frequency checked for stability. All graphics in this paper were created using the Molden 4.4 visualization program [8].

3. Results and Discussions

3.1. Absorption of CO₂ in IL:

1-Ethyl-3-methylimidazoliumhexafluorophosphate (EMIM-PF₆), Tetramethyl ammonium

tetra-fluoro-borate (TMA-BF₄) and chlorotetramethyl-phosphate (TMP-Cl) 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), 1-methyl-3-methylimidazolium tetrafluoroborate (MMIMBF₄), ionic liquids are investigated in the presence of CO₂. Simulations were done in vacuum and with the implicit polarized solvation model. Ionic liquids structures are optimized using B3LYP/6-31+G(d,p) ab initio calculations. (Fig. 1).

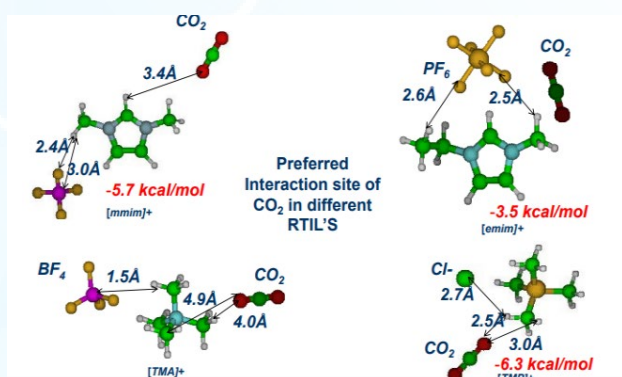


Figure 1: CO₂ preferred interaction sites on various ionic liquids (Optimized ion pair monomer minimum energy structure in liquid phase).

The formation of H bonds between oxygen and hydrogen atoms can stabilize the complex structure. CO₂ is also stabilized by multiple interactions with anions.

When CO₂ diffuses into an IL via gas-to-liquid diffusion, CO₂-BF₄ anion, CO₂-PF₆, CO₂-Cl anionic interaction and intermolecular bond are formed instantly. Since ionic liquids and water have similar interactions and the interaction energies are low.

As stated, before that the calculations were done in water using the PCM implicit model at the B3LYP/6-31 level of theory and basis set respectively. Relevant distances between the C-F and O-H atoms (indicated with arrows) are reported. The binding and interaction energies are calculated and reported as kcal/mol. Distances are shown in figure 1. Both values are probably close to the experimental values of

chemisorption states. EMIMBF₄ and MMIMBF₄ show almost the same C-F and O-H distance (Å) but differences in their binding energies, the bond distance is not enough to distinguish between the absorbate species. A vibrational analysis checks for negative frequencies and a true minimum was also performed to understand the true minimum structures. Notably, the ion pair and CO₂ absorption process differs slightly from our experimental data.

One feature of these conformers is that each anion shares the H5 side of one cation and the H4 side of the other. The larger the IL complexes, the more CO₂ are soluble. We found that ionic liquids with low molecular weights and compact structures have better selectivity. Low temperature and pressure improve separation performance in CO₂ absorption. Lan-yun Wang 2018 et al. stated that ionic liquids with small molecular weights and compact structures usually have better selectivity; low temperature and pressure are favorable for increasing separation performance in physically selective absorption [9-12]. On the other hand Daniel W. Armstrong et al. (2002) also described that the selectivity which is involving chemisorption, increasing temperature possibly enhances CO₂ selectivity, which is caused by the reduction of CO₂ capacity, dominated by physisorption, rather than an increase of CO₂ capacity. From this benchmark, it is concluded that feeding gas ratio, ionic liquid dosage, temperature and pressure are significant factors required to be adjusted to approach great real gas selectivity. It is worth to point out here our results also suggest the same. The energy of interaction between IL in solution was established for the gas phase and in solution and is sketched in Table 1.

As it can be observed the binding energies are small, thus indicating that the mutual interaction between monomer and the interaction with

water are comparable. The table below also shows the different sets of ionic liquids including EMIMBF₄-CO₂, MMIMBF₄-CO₂, EMIMPF₆-CO₂, TMABF₄-CO₂ and TMPCL-CO₂ and their key distances and interaction energies are reported.

TABLE 1: Optimized structures and some key distances of different ionic liquids

CO ₂ in ionic liquids	C-F distance(Å)	O-H distance(Å)	Binding energies (kcal/mol)
EMIMBF ₄	2.13	3.29	-2.05
MMIMBF ₄	2.4	3.4	-5.7
EMIMPF ₆	2.5	--	-3.5
TMABF ₄	2.7	4.0	--
TMPCL	--	3.0	-6.3

^AEnergies not corrected for BSSE and ZPE and reported in kcal/mol. Geometry and energy optimized at the same level of theory. Relative energies are reported in kcal/mol (1 Hartree/particle = 627.5 kcal/mol).

The common characteristic feature of this conformer is that each anion shares the H5 side of one cation and the H4 side of the other cation. The two-ion pair is thus a good model to absorb CO₂ in this system. Generally free volume (V_f) of a molecule has a linear correlation with Molar Volume (V_M). The bigger volume of this IL complex results higher solubility of CO₂ than smaller ones. This is another critical pathway to increase the solubility of CO₂ in [EMIM][BF₄] ionic liquid.

4. Conclusion

Ionic liquids have been around since the early 1980s, but are still poorly understood. These processes include electrochemical CO₂ reductions and other atomic processes. Our work begins with atomic steps. Determining the macroscopic process requires basic knowledge of chemical phenomena in the gas or liquid phase and on surfaces. Quantum chemistry was used to investigate CO₂ absorption in ionic liquids. The research shows RTIL can absorb CO₂. The four ionic liquid structures are discussed theoretically. Their preferred interaction sites also calculated. The CO₂ minimum energy structures were designed. CO₂ absorption in [EMIM][BF₄] ionic liquid is

slightly exothermic. Multiple minimum energy structures for absorbed CO₂ molecules were discovered. The IL anion binds CO₂ better than the IL cation. We discovered that RTIL anion binds CO₂ better than RTIL cation. Because of their long-term stability, ILs are being studied to increase CO₂ absorption capacity. But many hurdles must be overcome before ILs can be widely used commercially.

5. Acknowledgments

This work was supported by Technical University of Milan Research Grant for Research fellowship in 2020-2021. The author would like to thank the CFA laboratory of the Politecnico di Milano, Italy, University of Dhaka, University of Liberal Arts and Shyamoli Textile Engineering College. The author is also grateful to Prof. Carlo Cavallotti for his constant support and encouragement.

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