

On the Mechanism of the Absorption of CO₂ in Ionic Liquid Dimer

Kalyan Dhar

Dept. di Chimica Materiali e Ingegneria chimica G. Natta
Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy
and

Department of EEE
University of Liberal Arts, Dhaka, Bangladesh
Email: kalyankumar.dhar@polimi.it

Abstract

The density functional theory (DFT) calculations with the modern continuum solvation model (IEFPCM-SMD) was used to study the mechanism of CO₂ absorption in room temperature ionic liquid such as, [EMIM][BF₄] (1-Ethyl-3-Methylimidazolium Tetrafluoroborate) monomer and dimer. Ionic liquid [IL] dimer comprises two couple of anions and cations, so that more intermolecular interactions are established than in the single IL pair. In this paper, we determine the minimum energy structures and to determine the possible binding sites for CO₂ absorption process in [EMIM][BF₄] monomer and dimer; by comparing the relative minimum energy of [EMIM][BF₄] in the presence and absence of CO₂. It was found that CO₂ is stabilized by the formation of multiple interactions with several anions. When CO₂ penetrates the IL monomer or dimer, through gas-to liquid diffusion, the O-C-O (CO₂)-BF₄ intermolecular bond is formed immediately and bind the CO₂ molecule. This result suggests that ionic liquid dimer is more suitable for the absorption of CO₂.

Keywords— Absorption of CO₂, Anionic effect, [EMIM][BF₄] ionic liquid, Density Functional theory

© University of Liberal Arts Bangladesh
All rights reserved.

Manuscript received on 29 November 2018 and accepted for publication on 2 December 2018.

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. The low melting point is favored by the use of bulky, barely symmetric and (often) charge delocalized cations or polarizable and charge delocalized anions, which determine what is known as packing frustration [1]. Ionic liquids are strongly characterized by ionic pairs. Changing cations and anions the properties can be modified. Moreover modulation of physico-chemical properties (e.g. hydrophobicity) can be obtained by suitable combination of anions and cations. The systems investigated described in the results and discussion sections, is the ensemble of minimum energy structures accessible to CO₂ when absorbed in the [EMIM][BF₄] ionic liquid monomer, dimer, and the analysis of the main reaction channels possible for CO₂ absorption [2]. The density functional study (DFT) of the IL structure and the understanding of the reaction mechanism of the absorption process is one of the possible approaches that can be used to improve this technology. This is the approach that was followed in this work. The adopted computational approach consisted of DFT simulations performed using an implicit solvation model, as described in detail in the method section.

The two systems investigated described in the results and discussion sections, are the ensemble of minimum energy structures accessible to CO₂ when absorbed in the [EMIM][BF₄] monomer and dimer and the analysis of the main reaction channels possible for CO₂ binding site when absorb on a RTIL both in water and in presence of a [EMIM][BF₄].

The choice of the [EMIM][BF₄] IL for the simulations was determined by the fact that this is the system for which it was shown that CO₂ absorption is possible. Noteworthy [EMIM][BF₄] ionic liquid can be obtained with low cost compared to other ionic liquids. The solubility and diffusion ability of CO₂ in IL were described in [3] and [8-15]. The purpose of the present paper is therefore to increase our knowledge of this process from a theoretical stand-point.

2 EXPERIMENTAL METHODS

To study the adsorption of CO₂ in ionic liquid, simulations were performed by studying the [EMIM][BF₄] monomer and dimer in presence and absence of CO₂. Simulations were performed both in vacuum and in solution, which was modeled using the Polarized Continuum Model (PCM) Minimum energy structures, interaction energies, binding energies and clustering energies of complexes, reactants, products were determined using density functional calculations (DFT) [4]. Quantum mechanical calculations were performed using the B3LYP hybrid functional [5] is a three-parameter functional developed by Becke, which combines the Becke gradient-corrected exchange functional and the Lee-Yang-Parr functional for exchange and correlation. All simulations were performed with the Gaussian 09 quantum chemistry software suite program using the minimum energy cluster structures. Simulations were performed in water, modeling the solvent with the implicit PCM model. SMD model is based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent. The model is called SMD, where the "D" stands for "density" to denote that the full solute electron density is used without defining partial atomic charges. "Continuum" denotes that the solvent is not represented explicitly but rather as a dielectric medium with surface tension at the solute-solvent boundary. The SMD model was used to calculate the cavitation and non-polar contributions to the energy. The stability of all minimum energy structures was checked through frequency calculations. All the graphical sketches inserted in this paper were produced using the Molden 4.4 visualization program [7].

3 RESULTS AND DISCUSSIONS

In this section first we describe the computed energy structures of dimers [EMIM][BF₄] IL and secondly we describe absorption of CO₂ in dimer [EMIM][BF₄]. By dimer, we refer to system including two ionic pairs. An analysis of the structures of [EMIM][BF₄] IL dimer is reported and the relationship of such structures with CO₂-[EMIM][BF₄] monomer is discussed. Simulations were performed both in vacuum and using the implicit polarized solvation model. Ionic liquids Structures are optimized by ab initio calculations at B3LYP/6-31+G(d,p) level. (Figure 1 to 3). The same level of theory is then used to study the absorption of CO₂. Their x,y,z coordinates are given in the supporting information. Energies not corrected for BSSE and ZPE. The SCF energies, vibrational frequency, and lastly interaction energies of the [EMIM][BF₄] and [EMIM][BF₄]-CO₂ system have been collected in Table 1 to 3. IL dimer comprises two couples of anions and cations, so that more intermolecular interactions are established than in the single IL pair. It was in fact observed that the formation of H bonds between oxygen and hydrogen atoms could stabilize the structure of the complex. Similarly, it was found that also CO₂ is stabilized by the formation of multiple interactions with several anions. When CO₂ penetrates the IL monomer or dimer, through gas-to-liquid diffusion, the O-C-O (CO₂)-BF₄ intermolecular bond is formed immediately and binds the CO₂ molecule. The energy of interaction between two ion pairs in solution was established for the gas phase and in solution and is sketched in Table 1. As it can be observed the clustering energies are small, thus indicating that the mutual interaction between dimer and the interaction with water are comparable.

However, for the sake of simplicity, the liquid phase computed minimum energy structure of the monomer with CO₂ is introduced in order to facilitate the interpretation of the peculiarities of the dimer structure. For this purpose the structures of the ionic pair and monomer with and without CO₂ are shown in Figures 1, 2, and 3. Their corresponding x, y, z coordinates is reported.

TABLE 1

IONIC LIQUID, MONOMER AND DIMERS AND THEIR CORRESPONDING CLUSTERING ENERGIES WERE CALCULATED AT THE B3LYP LEVEL IN GAS AND LIQUID PHASE AT 6-31+G(D,P) BASIS SET.^A

IL([EMIM]+[BF ₄]-	Gas phase energies	Liquid Phase energies
1EMIM1BF ₄ (monomer)	-769.27	-769.31
2EMIM2BF ₄ (Dimer)	-1538.57	-1538.62
Clustering Energies	-1.08 kcal/mol	0 kcal/mol

^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).

It is worth to point out that the ion pair dimer is much better model to study CO₂ absorption than the single ion pair. It is also affordable in terms of computational cost. The absorption energy of CO₂ calculated using the IL monomer and pair model is reported in Table 3. It can be observed that the bonding energy of CO₂ in [EMIM][BF₄] monomer is -2.05,

whereas the ion pair dimers bonding energy is -2.80 kcal/mol. In Figure 1 (ion pair monomer) and Figure 2 (the ion pair dimer) is reported. While structures Monomer -CO₂ (complex 1) and Dimer -CO₂ (Complex 2), are reported in Figure 3 and 4 respectively. It can be seen that the two imidazolium rings have parallel positions in the case of the dimer CO₂[EMIM][BF₄] system. 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 ion pair is thus a good model to absorb CO₂ in this system. The alkyl group of this ionic liquid structure is sufficient to obtain larger surface area and bigger specific molar volume (VM). Generally free volume (V_f) of a molecule has a linear correlation with VM. 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. Minimum energy structures of monomer ion pair and dimer ion pair are reported in Figure 1 and Figure 2 respectively.

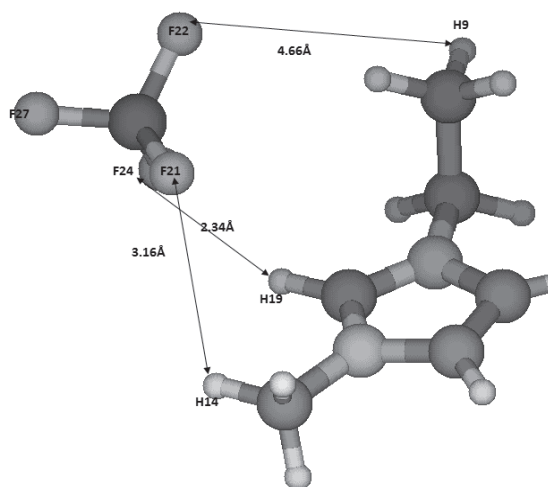


Figure 1: Optimized ion pair monomer minimum energy structure in liquid phase.

Some key distances are reported in Figure 1. H(19)-F(24) distance 2.34 Å. All distances are reported in Angstrom. Corresponding vibrational analysis is carried out to ensure the absence of negative frequencies and verify the existence of a true minimum.

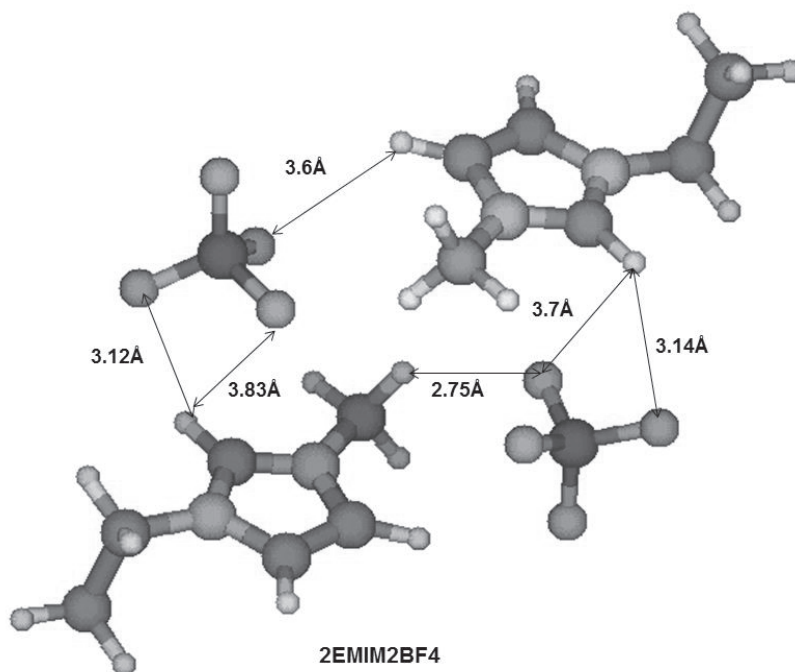


Figure 2: Optimized ion pair dimers in liquid phase.

Figure 2: Optimized ion pair dimers in liquid phase.

The complex-2 structure of [EMIM][BF₄]-CO₂ dimer in liquid phase is reported in Figure (4). Structures are stable and fully optimized. Monomer CO₂ system are less stable in comparison of the liquid phase energy than dimer by 2.05 and 2.81 kcal mol⁻¹. In the system of CO₂-monomer, the BF₄ anion is located on the methyl side and the ethyl side at the back of the imidazolium ring, respectively.

However, It is interesting to mention that oxygen atom of CO₂ is almost coplanar with the imidazolium ring. C-F distances between the C atom of CO₂ and the nearest F atom i.e. C(25)-F(9) distance is 4.36Å, H(24)-O(27) distance 3.29Å is reported. The corresponding C-H distances between the C atom of CO₂ and the nearest H is reported in Figures 3 i.e. atom (C (25) –H (24)) distance is 4.05Å.

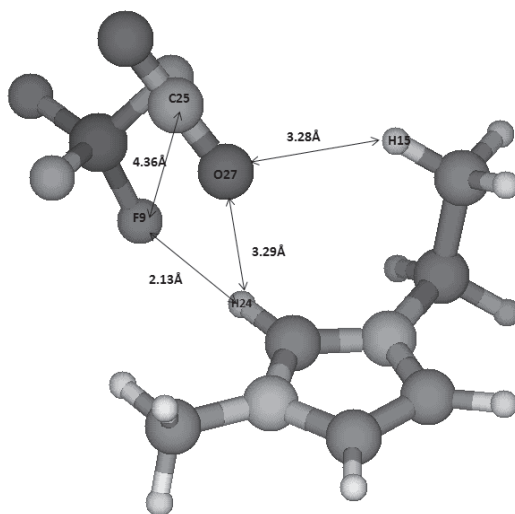


Figure 3: Complex 1 (Monomer) and the possible binding site of the CO₂ molecules. Optimized ion pair monomer with CO₂ in liquid phase.

Complex 2 (Figure 4) indicates the possible binding site of the CO₂ molecule. It is also nice to report that the EMIM ring is parallel and the anionic interaction between CO₂ molecules is always higher than the cation.

Dimer-CO₂ and the optimized distances between F (14) – C (CO₂) at 3.05 Å and the F (11)-C (CO₂) at 2.95 Å are reported in figure. Minimum energy structure is the most stable, where CO₂ is located near the methyl group in [EMIM][BF₄] IL.

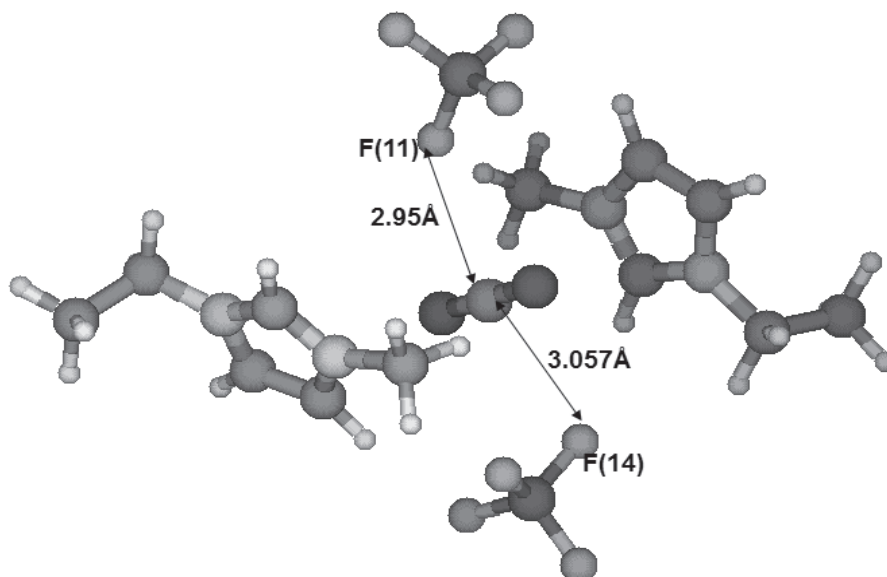


Figure 4: Optimized ion pair dimer with CO₂ in liquid phase.

TABLE 2

OPTIMIZED STRUCTURES AND SOME KEY DISTANCES

CO ₂ IN EMIM BF ₄	C-H distance (Å)	C-F distance(Å)	O-H distance(Å)
Ion pair EMIMBF ₄		2.34	
Conformer1 (Monomer)	4.05	3.02	3.18
Ion pair dimer	--	2.75	--
Conformer (Dimer)	4.09	2.95	3.29

It is worth to point out that (Table 3) the binding energy in gas phase vary from -3.45 kcal/mol (monomer) to -1.81 kcal/mol (dimer). This is also a new insight for the CO₂ absorption process in [EMIM][BF₄]. The CO₂ absorption process is better to carry out in liquid phase with dielectric constant 12. Simulations are used to analyze the structural behavior of CO₂ + ionic liquids systems as a function of mixture composition.

TABLE 3

CO₂ IN IONIC LIQUID AND THEIR CORRESPONDING INTERACTION ENERGIES WERE CALCULATED AT THE B3LYP/6-31+G(D,P) LEVEL USING THE IEF-PCM MODEL FOR IMPLICIT SOLVENT SIMULATIONS.

CO ₂ in IL([EMIM] ⁺ [BF ₄] ⁻	Gas phase Binding energies(kcal/mol)	Liquid Phase Binding energies(kcal/mol)
Monomer	-3.45	-2.05
Dimer	-1.81	-2.80

The results show the different structuring of CO₂ around cation and anion, the anionic effect is explained considering the larger expansion upon CO₂ absorption for [BF₄] anion containing systems.

4 CONCLUSION

We performed theoretical calculation of the [EMIM][BF₄] ionic liquid structure and of the CO₂ absorption process. Minimum energy structures, interactions energy, clustering energies and binding energy of the IL are calculated. CO₂ minimum energy structure in [EMIM][BF₄] IL & 2[EMIM]2[BF₄] IL systems is estimated. As it can be observed the clustering energies are small, thus indicating that the mutual interaction between dimer and the interaction with water are comparable. It is found that monomer CO₂ system are less stable in comparison of the ionic liquid phase energy than dimer. Moreover, the bigger volume of this IL complex dimer result higher solubility of CO₂ than smaller ones. The result shows that the structure of ionic liquid monomer and ion pair dimer are absorbing CO₂ due to structure sensitivity of anion.

ACKNOWLEDGMENT

This work was supported by Technical University of Milan Research Grant for Postdoc Research fellow in 2014-2015. The author would like to thank to the CFA laboratory of the Politecnico di Milano, Italy and University of Liberal Arts Bangladesh. The author is also grateful to Prof. Carlo Cavallotti for his constant support and encouragement.

REFERENCES

- [1] Kalyan Dhar and Carlo Cavallotti, "Investigation of the initial steps of the electrochemical reduction of CO₂ on Pt electrodes," *Journal of Physical Chemistry, ACS*, vol. 118(38), pp: 8676-8688, 2014.
- [2] Kalyan Dhar and Syed Fahim, "Investigation of the Absorption of CO₂ in Ionic Liquid," *Bangladesh Journal of Scientific Research*, vol. 29(1), pp: 41-46, 2016.
- [3] Karadas Ferdi, M. A. Santiago Aparicio, "Review on the use of Ionic Liquids (ILs) as alternative fluids for CO₂ capture and natural gas sweetening," *Energy Fuels*, vol. 24 (11), pp: 5817–5828, 2010.
- [4] Pople J. A., P. M. W. Gill and B. G. Johnson. "Kohn-Sham Density-functional theory within a finite basis set," *Chemical Physics Letters*, vol. 199 (6) pp: 557-560, 1992.
- [5] Raghavachari K., Perspective on "Density functional thermochemistry. III. The role of exact exchange- Becke AD" (1993) *J Chem Phys* vol. 98 pp: 5648-52, 2000.
- [6] Cadena. C, Jennifer L. Anthony and Jindal K. Shah. "Why is CO₂ so soluble in Imidazolium-based ionic liquids?," *J. Am. Chem. Soc.*, vol. 126 (16) pp: 5300–5308. 2004.
- [7] Schaftenaar G. and J. H. Noordik. "Molden: a pre- and post-processing program for molecular and electronic structures," *Journal of Computer-Aided Molecular Design*, vol. 14 (2) pp: 123-134, 2000.
- [8] Mahinder Ramdin, Theo W. de Loos, and Thijs J.H. Vlugt W.-K. Chen, "State-of-the-Art of CO₂ Capture with Ionic Liquids," *Ind. Eng. Chem. Res.* Vol.51, pp:8149–8177, 2012,
- [9] Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. "Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3- methylimidazolium hexafluorophosphate," *Journal of physical chemistry* ,ACS,06, 7315–7320. 2002.
- [10] Freemantle, M. *An Introduction to Ionic Liquids*; RSC Publishing, London, 2010.
- [11] *Carbon Dioxide Capture from Existing Coal-Fired Power Plants*; DOE-NETL: Pittsburgh, PA, 2007
- [12] *Research and Development Goals for CO₂ Capture Technology*; DOE-NETL: Pittsburgh, PA, 2011
- [13] Kilaru, P. K.; Condemarin, R. A.; Scovazzo, P. "Correlations of low-pressure carbon dioxide and hydrocarbon solubilities in imidazolium-, phosphonium-, and ammonium-based room-temperature ionic liquids," Part 1. using surface tension. *Ind. Eng. Chem. Res.* Vol.47, pp:900–909, 2008.
- [14] Shannon, M. S.; Tedstone, J. M.; Danielsen, S. P. O.; Hindman, M. S.; Irvin, A. C.; Bara, J. E. "Free volume as the basis of gas solubility and selectivity in imidazolium-based ionic liquids," *Ind. Eng. Chem. Res.* Vol.51, pp: 5565–5576. 2012.
- [15] Kalyan dhar, DFT study on the absorption and adsorption of CO₂ in Ionic liquid unpublished (Unpublished manuscript).

Kalyan Kumar Dhar was born on 15 October 1980 in Narail, Bangladesh. He received his PhD in 2014 on Industrial Chemistry and Chemical Engineering from Politecnico di Milano Italy and MS in 2010 on Materials Engineering jointly from Politecnico di Milano, Italy and Technical University of Berlin, Germany and BSc in 2005 on Applied Chemistry and Chemical Engineering from the University of Dhaka. He worked as a Research Fellow at CFA Lab Politecnico di Milano, Italy in 2014 to 2015. In 2015 to 2017 he also worked as an Assistant Professor in the Department of Chemical Engineering at Z.H. Sikder University of Science and Technology, Bangladesh. Currently, he works as an Adjunct Faculty in the Department of EEE, University of Liberal Arts Bangladesh. He received various scholarships, research and travel grants as recognition of his research works. He is a member of American Chemical Society. His current research is focused on ionic liquids and computational chemistry, nanomaterials and CO₂ adsorption.