Bangladesh J. Sci. Res. **29**(1): 41-46, 2016 (June)

INVESTIGATION OF THE ABSORPTION OF CO_2 IN IONIC LIQUID

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Abstract

Due to environmental concerns, current interest is the development of technologies that may be able to remove CO_2 efficiently from exhaust gases and thus avoid its dispersion in the atmosphere. The density functional theory (DFT) calculations with the modern continuum solvation model (IEFPCM-SMD) was used to study the mechanism of CO_2 absorption in room temperature ionic liquid such as, [EMIM][BF_4] (1-ethyl-3-methylimidazolium tetrafluoroborate). We determine the minimum energy structures and to determine the possible binding sites for CO_2 absorption process in [EMIM][BF_4]; by comparing the relative minimum energy of [EMIM][BF_4] in the presence and absence of CO_2.

Key words: Density functional calculations, absorption of $CO_{2,}$ ionic liquids, anionic effect, ionic liquid

Introduction

Ionic liquids (ILs) are generally liquid salts with a very low melting point, often lower than room temperature (Dhar and Cavalloti 2014). There are a lot of properties that make ILs interesting as process electrolytes. For instance, they reveal very small vapor pressure, are good solvents for many substances, are not flammable or nontoxic and 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 (Ludwig *et al*. 2012). The use of ILs for the absorption of CO_2 is a broad field of research both from experimental as well as theoretical standpoint that has emerged recently. CO_2 absorption in room temperature ionic liquid solvents is at present among the most promising technologies for the capture of CO_2. Efforts are on going to improve and make it more attractive technology for large scale applications, to use in carbon capture and storage and to reduce CO_2 emissions from the atmosphere.

However, the most important technologies to absorb CO_2 can be divided into two classes; the first one based on the sequestration and storage of CO_2 and the second on its reactive conversion to chemicals. In this framework, a technology that has been recently attracted much attention is the absorption of CO_2 in room temperature ionic liquids (RTILs). This is the principle of possible application of IL for absorption of CO_2 (Karadas and Aparacio 2010). Since so many parameters affect the properties of the ILs, it became attractive to calculate CO_2 absorption in ILs with a

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rigorous method, so that we may have a rational guide to select the best IL to use as a function of the composition of the CO_2 feed to process. The counter anions BF_4 containing ILs are often soluble in water and in the CO_2 atmosphere.

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 are the ensemble of minimum energy structures accessible to CO_2 when absorbed in the [EMIM][BF_4] and the analysis of the main reaction channels possible for CO_2 binding site when absorb on a RTIL both in water and in presence of a [EMIM][BF_4]. The choice of the [EMIM][BF_4] IL for the simulations was determined by the fact that this is the system for which it was shown that CO_2 absorption is possible. Noteworthy [EMIM][BF_4] ionic liquid can be obtained with low cost compared to other ionic liquids. The solubility and diffusion ability of CO_2 in IL were described elsewhere in this paper (Cadena *et al*. 2004). The purpose of the present paper is therefore to increase the knowledge of this process from a theoretical standpoint.

Experimental Methods

To determine the absorption of CO_2 in [EMIM][BF_4] ionic liquid, simulations were performed by studying the ionic pair in presence and absence of CO_2. 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 of complexes, reactants, products were determined using density functional calculations (DFT) (Pople *et al*. 1992).

Quantum mechanical calculations were performed using the B3LYP hybrid functional (Raghavachari 2000) 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 (Schaftenaar and Noordik 2000).

Results and Discussion

The results of the calculations are presented below on the basis of computed minimum-energy structures of [EMIM][BF_4] and their corresponding interaction energies in CO_2 .

Absorption of CO_2: The subject of this section is the investigation of the structures and energies of interaction of CO_2 with [EMIM][BF_4]. BF_4^- is probably the most common anion used in RTIL research. Moreover, [EMIM][BF_4] is water-soluble and can be obtained easily with low price from the chemical market (Lei *et al*. 2010). The first part of this study was thus devoted to determine the minimum energy structures assumed by the [EMIM][BF_4]. Simulations were performed both in vacuum and using an implicit water model, as described in the method section. Though it is known that implicit models are unsuitable to study ionic liquid structures, in this particular case they are reasonably appropriate since the electrochemical CO_2 reduction is performed using a 1 : 5 IL-water ratio, thus indicating that each ion pair will be surrounded by a significant number of water molecules, probably more than sufficient to complete the first solvation shell. Five minimum energy structures located for [EMIM][BF_4] are reported in Fig. 1. Structures 1 and 2 are similar to those determined by (Katsyuba *et al*. 2009) when studying the same ionic liquid in a dichlomethane (DCM) continuum.

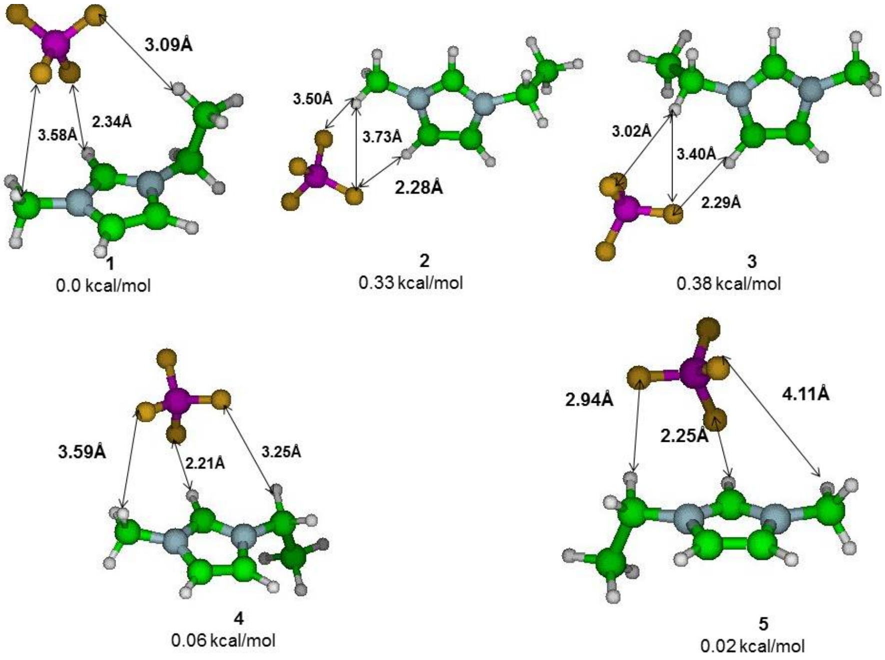
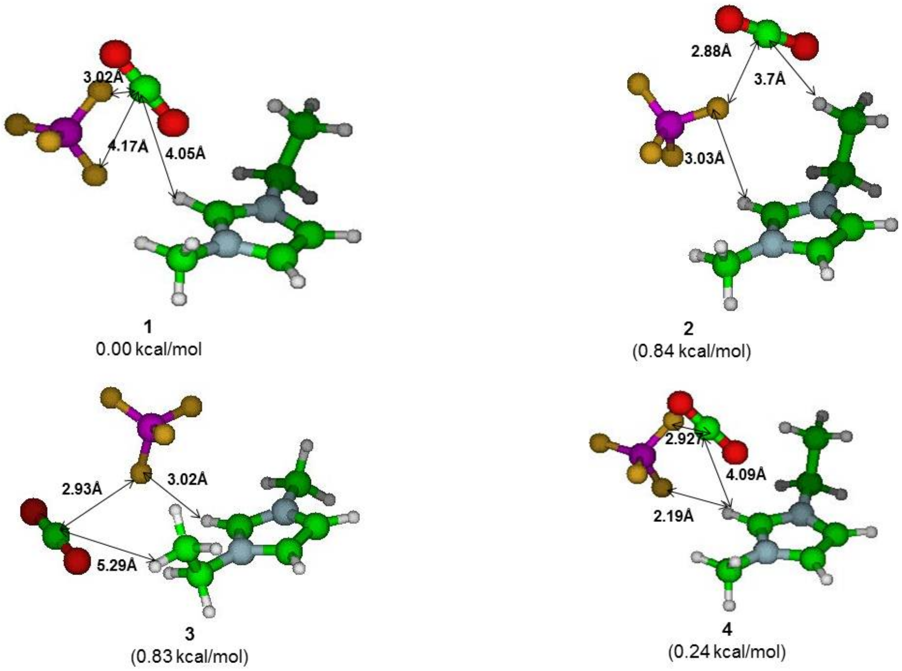


Fig. 1. Minimum energy structure of the [EMIM][BF_4] ion pair calculated in water using the PCM implicit model performing the calculation at the B3LYP/6-31 + g(d, p) level. Relevant distances between F and H atoms are reported in angstrom (indicated with arrows). Relative energies are reported in kcal/mol. Energies not corrected for ZPE.

It is, however, interesting to observe that the structures in which BF_4 is located in proximity of the –CHCH- groups of the imidazole ring have energies that do not differ substantially from that of the minimum energy structure, while in the calculation reported by (Katsyuba *et al*. 2009), the same structures had energy differing by about 2 kcal/mol. This is probably determined by screening effect of the water dielectric, which decreases the interaction energy between the ion pair more than the DCM continuum. This same effect can be observed comparing the decrease of the relative energies reported in Table 1 computed for the gas phase and for the liquid.

Table 1. 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.

IL $[EMIM]^+[BF_4]^-$ ion pair	Gas phase relative energies (kcal/mol)	Liquid relative energies (kcal/mol)
Ion pair **1**	0.00	0.00
Ion pair **2**	8.02	0.33
Ion pair **3**	8.10	0.38
Ion pair **4**	0.41	0.06
Ion pair **5**	0.56	0.02



1
0.00 kcal/mol

2
(0.84 kcal/mol)

3
(0.83 kcal/mol)

4
(0.24 kcal/mol)

Fig. 2. Minimum energy structure of the $[EMIM][BF_4]$ CO_2 ion pair calculated in water using the PCM implicit model performing the calculation at the B3LYP/6-31+g(d, p) level. Relevant distances (Å) between F and H, C and H atoms also indicated.

$[EMIM][BF_4]$ and CO_2 in $[EMIM][BF_4]$, it is possible to study on binding site of anion as well as possible position of CO_2 in $[EMIM][BF_4]$ and finally minimum-energy structures of complexes. Important minimum energy structures and the preferred interaction site, possible binding sites of CO_2 in our reference IL were also investigated. Anion and their interaction with CO_2 are supposed to be the most important part for absorption of CO_2 by ionic liquids.

Table 2. Ionic liquid, CO_2 in ionic liquid and their corresponding interaction energies were calculated at the B3LYP level in gas and liquid phase at 6-31+G(d, p) basis set.[a]

CO_2 in IL $[EMIM]^+[BF_4]^-$	Gas phase relative energies (kcal/mol)	Liquid relative energies (kcal/mol)
Conformer **1**	0.07	0.00
Conformer **2**	1.18	0.84
Conformer **3**	0.56	0.83
Conformer **4**	0.42	0.20

[a]Energies 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).

Interaction between CO_2 and BF_4^- are therefore fundamental. From this framework CO_2-BF_4 and their corresponding binding energy, optimized z-matrix orientation and frequency are calculated by DFT. CO_2 interacts primarily with BF_4 (acid behavior). Present experiment and also different reports indicated that the anion is playing the major role in RTIL and CO_2 absorption process. Additionally from our experimental DFT simulations show that CO_2 has a common tendency to stay close with our selected anion BF_4^-. The geometric parameters of anion and CO_2 are reported. Absorption or CO_2 reduction IL anion always gives us vision that they have much more capability to bind CO_2 in IL compared to IL cation. From this background our experiment suggested that CO_2 absorption in RTIL, anion was highly favorable to bind CO_2 compared to RTIL cation.

Conclusions

The present investigation shows that RTIL provides an ideal candidate for absorption of CO_2. We performed theoretical calculation of the $[EMIM][BF_4]$ ionic liquid structure and of the CO_2 absorption process. Minimum energy structures and interactions energy of the IL are calculated. CO_2 minimum energy structure in $[EMIM][BF_4]$ systems is estimated. Simulations of CO_2 absorption in the $[EMIM][BF_4]$ ionic liquid showed that the absorption process is slightly exothermic. Multiple minimum energy structures were found for the absorbed CO_2 molecules, which differ slightly for the calculated interaction energies. This means that the mobility of CO_2 in the ionic liquid is probably high. Also the simulations showed that significant interactions are formed between CO_2 and the BF_4^- anion, which can be described to the acid properties of CO_2.

Acknowledgements

This work was supported by Technical University of Milan Research Grant in 2012. The authors would like to thank the CFA laboratory of the Politecnico di Milano, Milan, Italy.

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(Manuscript received on 25 November, 2015; revised on 9 August, 2016)