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MECHANISM OF THE ABSORPTION OF CO_2 IN IONIC LIQUID DIMER

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Abstract

The density functional theory (DFT) calculations with the modern continuum solvation model (IEFPCM-SMD) was used to study the mechanism of CO_2 absorption at room temperature using ionic liquid such as, [EMIM][BF_4] (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 determined the minimum energy structures and to determine the possible binding sites for CO_2 absorption in [EMIM][BF_4] monmer and dimer; by comparing the relative minimum energy of [EMIM][BF_4] in the presence and in absence of CO_2. It was found that CO_2 is stabilized by the multiple interactions with several anions. When CO_2 penetrates the IL monomer or dimer, through gas-to-liquid diffusion, the O-C-O (CO_2)-BF_4 intermolecular bond is likely to be formed immediately and bind the CO_2 molecule. This result suggests that ionic liquid dimer is suitable for the absorption of CO_2.

Key words: Density functional calculations, Absorption of CO_2, Anionic effect, [EMIM][BF_4], CO_2.

Introduction

Currently, because of environmental concerns, there is much interest in the development of technologies that may be able to efficiently remove CO_2 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 lower than room temperature. There are many properties that make IL interesting as process electrolytes. For instance they have very small vapor pressure, good solvents for many substances, 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 (Dhar and Fahim 2016). Ionic liquids are strongly characterized by ionic pairs. The properties can be modified by changing cations and anions. Moreover, modulation of physico-chemical properties (e.g. hydrophobicity) can be obtained by suitable combination of anions and cations. The systems investigated

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described in the results and discussion sections, is the ensemble of minimum energy structures accessible to CO_2 when absorbed in the [EMIM][BF_4] ionic liquid monomer, dimer, and the analysis of the main reaction channels possible for CO_2 absorption (Dhar and Cavallotti 2014).

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 (Dhar 2014). This approach was followed in this work. The adopted computational approach consisted of DFT simulations performed using an implicit solvation model. The two systems investigated described in the results and discussion sections, are the ensemble of minimum energy structures accessible to CO_2 when absorbed in the [EMIM][BF_4] monomer and dimer and the analysis of the main reaction channels possible for CO_2 binding site when absorbed 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 CO_2 absorption is possible. Noteworthy [EMIM][BF_4] ionic liquid can be obtained at a low cost compared to other ionic liquids. The solubility and diffusibility of CO_2 in IL were investigated in this work.

Materials and Methods

To study the adsorption of CO_2 in ionic liquid, simulations were performed by studying the [EMIM][BF_4] monomer and dimer in presence and in 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 and clustering 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). 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 were 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

Absorption of CO_2 in dimer: Firstly the computed energy structures of dimers [EMIM][BF_4] IL and secondly the absorption of CO_2 in dimer [EMIM][BF_4]$_2$ have been described. By dimer, we refer to system including two ionic pairs.

Absorption of CO_2 in 2[EMIM]$^+$2[BF_4^-]$^-$dimer: An analysis of the structures of [EMIM][BF_4] IL dimer is reported and the relationship of such structures with CO_2-[EMIM][BF_4] 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. (Figs 1 to 3). The same level of theory is then used to study the absorption of CO_2. 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][BF_4] and [EMIM][BF_4]-CO_2 system have been collected in Tables 1 to 3. IL dimer comprise two couples of anions and cations, so that more intermolecular interactions are established than in the single IL pair. It was observed that the formation of H bonds between oxygen and hydrogen atoms could stabilize the structure of the complex. Similarly it was also found that CO_2 is stabilized by the formation of multiple interactions with several anions. When CO_2 penetrates the IL monomer or dimer, through gas-to liquid diffusion, the O-C-O (CO_2)-BF_4 intermolecular bond will be formed immediately and bind the CO_2 molecule. The energy of interaction between two ion pairs in solution was established for the gas phase and in solution and is presented in Table 1. It can be observed the clustering energies are small, thus indicating that the mutual interaction between dimer and the interaction with water are comparable.

Table 1. Ionic liquid monomer, dimers and their corresponding clustering energies calculated at the B3LYP level in gas and liquid phase at 6-31+g(d,p) basis set.[a]

IL([EMIM]+[BF4]$^-$	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

[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).

However, for the sake of simplicity, the liquid phase computed minimum energy structure of the monomer with CO_2 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 CO_2 are shown in Figs 1-3. Their corresponding x, y, z coordinates are reported. It is worth to point out that the ion pair dimer is a better model to study CO_2 absorption than the single ion pair. It is also affordable in terms of computational cost. The absorption energy of CO_2 calculated using the IL monomer and pair model is reported in Table 3. It can be observed that the bonding energy of CO_2 in [EMIM][BF_4] monomer is –2.05 kcal/mol, whereas the ion pair dimers bonding energy is –2.80 kcal/mol. In Fig.1 (ion pair monomer) and Fig. 2 (the ion pair dimer) are reported. The structures monomer -CO_2 and Dimers -CO_2 (Complex 2), are reported in Figs 3-4 respectively. It can be seen that the two imidazolium rings have parallel positions in the case of the dimer CO_2-[EMIM][BF_4] 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 two ion pair is thus a good model to absorb CO_2 in this system. The alkyl group of the ionic liquid is sufficient to obtain larger surface area and bigger specific molar volume (V_M). Generally free volume (V_f) of a molecule has a linear correlation with V_M. The larger volume of this IL complex results higher solubility of CO_2 than smaller ones**.** This is another critical pathway to increase the solubility of CO_2 in [EMIM][BF_4] ionic liquid. Minimum energy structures of monomer ion pair and dimer ion pair are reported in Figs 1 and 2, respectively.

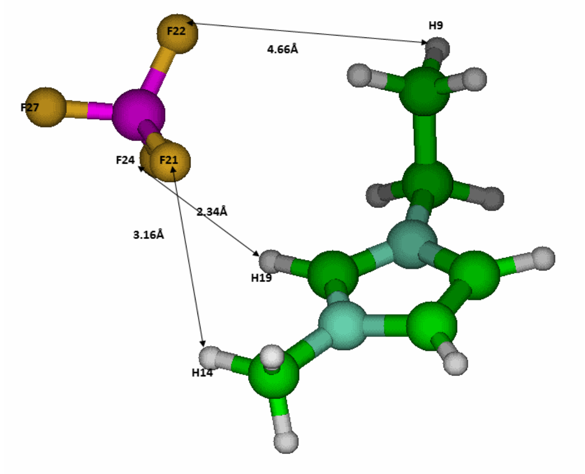

Fig. 1. Optimized ion pair monomer minimum energy structure in liquid phase.

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

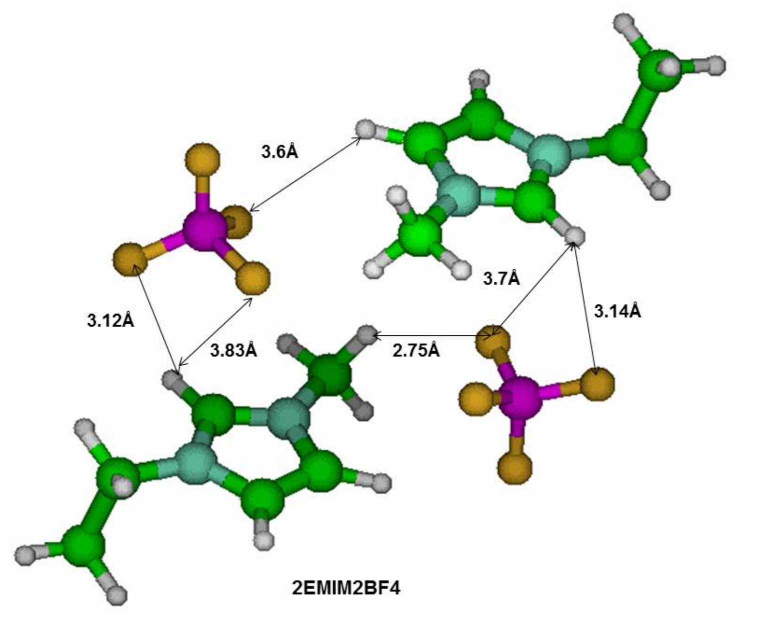

Fig. 2. Optimized ion pair dimers in liquid phase.

The structure of [EMIM][BF_4]-CO_2 dimer in liquid phase is reported in Fig. 4. Structures are stable and fully optimized. Monomer CO_2 system are less stable in comparison to the liquid phase energy than dimer by 2.05 and 2.81 kcal mol^{-1}. In the system of CO_2-monomer, the BF_4 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 CO_2 is almost coplanar with the imidazolium ring. C-F distances between the C atom of CO_2 and the nearest F atom. The corresponding C-H distances between the C atom of CO_2 and the nearest H is shown in Fig. 3 i.e. atom (C (25) –H (24)) distance is 4.05Å.

Complex 2 (Fig. 4) indicates the possible binding site of the CO_2 molecule. It is also reported that the EMIM ring is parallel and the anionic interaction between CO_2 molecules is always higher than the cation. Dimer-CO_2 and the optimized distances between F (14) - C (CO_2) at 3.05 Å and the F (11) - C (CO_2) at 2.95 Å are reported in the figure. Minimum energy structure is the most stable, where CO_2 is located near the methyl group in [EMIM][BF_4] IL.

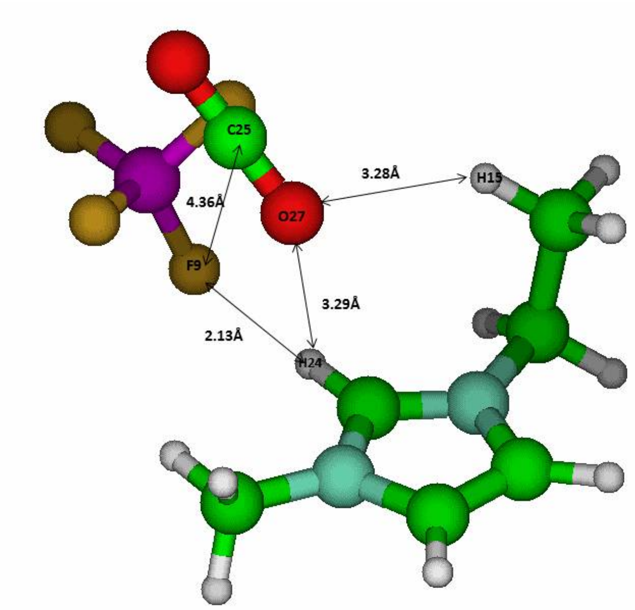

Fig. 3. Complex-1 (monomer) and the possible binding site of the CO_2 molecules. Optimized ion pair monomer with CO_2 in liquid phase.

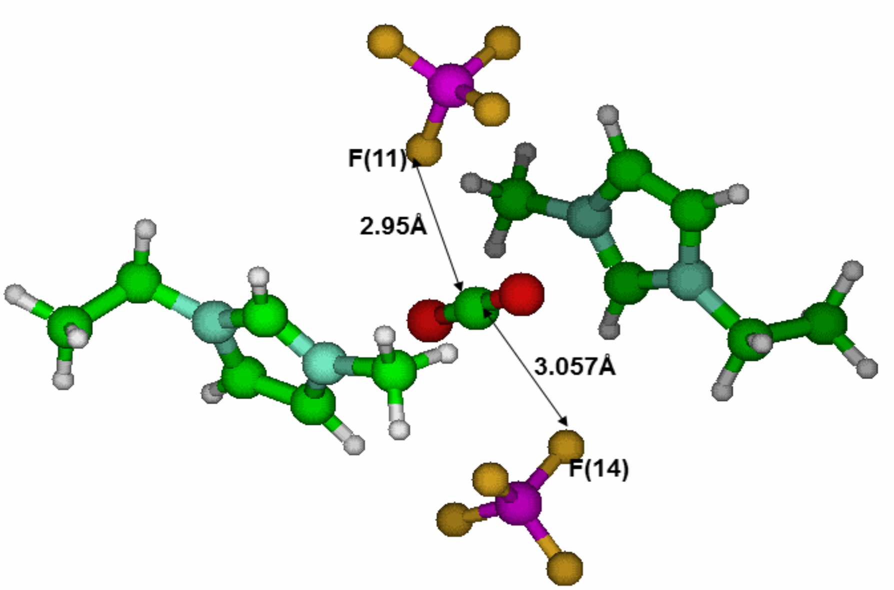

Fig. 4. Complex-2 optimized ion pair dimers with CO_2 in liquid phase.

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 EMIMBF4		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 CO_2 absorption process in [EMIM][BF_4].

Table 3. CO_2 in Ionic liquid and their corresponding interaction energies calculated at the B3LYP/6-31+G(d,P) level using the IEF-PCM model for implicit solvent simulations.

CO_2 in IL([EMIM] + $[BF4]^-$	Gas phase	Liquid phase
	Binding energies (kcal/mol)	Binding energies (kcal/mol)
Monomer	–3.45	–2.05
Dimer	–1.81	–2.80

The CO_2 absorption process is better to carry out in liquid phase with di-electric constant 12. Simulations are used to analyze the structural behavior of CO_2+ ionic liquids systems as a function of composition. The results show the different structuring of CO_2 around cation and anion, the anionic effect is explained considering the larger expansion upon CO_2 absorption for $[BF_4]^-$ containing systems.

The author performed theoretical calculation of the [EMIM][BF_4] ionic liquid structure and of the CO_2 absorption process. Minimum energy structures, interactions energy, clustering energies and binding energy of the IL were calculated. CO_2 minimum energy structure in [EMIM][BF_4] IL and $[EMIM][BF_4]_2$ IL systems is estimated. As it can be observed that the clustering energies are small, thus indicating the mutual interaction between dimer and the interaction with water are comparable. It is found that monomer CO_2 system are less stable in comparison with the ionic liquid phase energy than dimer. Moreover the bigger volume of this IL complex dimer result higher solubility of CO_2 than smaller ones. The result shows that the structure of ionic liquid monomer and ion pair dimer are absorbing CO_2 due to structure sensitivity of anion.

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