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Evaluating the Interactions of Co_2-Ionic Liquid Systems through Molecular Modeling

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***Abstract*—**Owing to the stringent environmental legislations, CO_2 capture and sequestration is one of the viable solutions to reduce the CO_2 emissions from various sources. In this context, Ionic liquids (ILs) are being investigated as suitable absorption media for CO_2 capture. Due to their non-evaporative, non-toxic, and non-corrosive nature, these ILs have the potential to replace the existing solvents like aqueous amine solutions for CO_2 separation technologies. Thus, the present work aims at studying the important aspects such as the interactions of CO_2 molecule with different anions (F^-, Br^-, Cl^-, NO_3^-, BF_4^-, PF_6^-, Tf_2N^-, and $CF_3SO_3^-$) that are commonly used in ILs through molecular modeling. In this, the minimum energy structures have been obtained using Ab initio based calculations at MP2 (Moller-Plesset perturbation) level. Results revealed various degrees of distortion of CO_2 molecule (from its linearity) with the anions studied, most likely due to the Lewis acid-base interactions between CO_2 and anion. Furthermore, binding energies for the anion-CO_2 complexes were also calculated. The implication of anion-CO_2 interactions to the solubility of CO_2 in ionic liquids is also discussed.

***Keywords*—**CO_2, Ionic liquids, capture, molecular modeling, sequestration.

I. Introduction

ESCALATING concentrations of CO_2 and other greenhouse gases (GHG) in the Earth's atmosphere have the potential add to the natural greenhouse effect, which may result in climatic changes [1]. A major contributor to increased atmospheric CO_2 levels is fossil fuel combustion. Therefore, energy industry can be part of the solution to reduce greenhouse gas emissions by capturing and permanently sequestering CO_2 [2]. Carbon sequestration, which captures CO_2 from large point sources such as fossil fuel-fired electrical power-generation plants, and stores it in geological formations, has been proposed as a prominent solution to this problem. Efficient separation of CO_2 is a prominent solution to the economically viable sequestration efforts. The current methods of CO_2 capturing include, (a) absorbing into amine based solvents (b) carbonate based systems (c) ammonia based wet scrubbing (d) separation through polymeric membranes like Polyether-polyimide copolymer (e) adsorption on to carbonate based sorbents and amine based sorbents, and (f) metal organic frame works[3]. However, these methods have certain disadvantages like energy intensive, amine loss and degradation, release of volatile organic compounds, and equipment corrosion [4].

Ionic liquids are a new and exciting class of compounds that have the potential to overcome many of the problems associated with the current CO_2 capture techniques. Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions [5]. Typical ILs usually have either imidazolium, quaternary ammonium, pyrrolidinium, pyridinium, or tetra alkylphosphonium as the base for the cation. Possible anions include hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, bis(trifluoromethylsulfonyl) imide $[(CF_3SO_2)_2N]^-$, triflate $[CF_3SO_3]^-$, acetate $[CH_3CO_2]^-$, trifluoroacetate $[CF_3CO_2]^-$, nitrate $[NO_3]^-$, chloride $[Cl]^-$ bromide $[Br]^-$ or iodide $[I]^-$, among many others [6,7]. Adjusting the structure of either the anion or the cation can have huge effects on many properties including melting points, viscosities, densities, and gas and liquid solubilities [8]. ILs are regarded as potentially environmentally-benign solvents due to their immeasurably low vapor pressure, which essentially eliminates the opportunity for solvent release to the atmosphere [9]. ILs can dissolve CO_2 and are stable at temperatures up to several hundred degrees centigrade. Since ILs have excellent thermal stability, these can be used extensively for the recovery of CO_2 from flue gas. CO_2 interacts with the anion through a weak Lewis-acid-base interaction. Gases with large dipole moments (e.g. water) or quadrupole moments (e.g. CO_2 and N_2O), as well as the gases (eg: SO_2, NO_X) which have an opportunity for hydrogen bonding have the highest solubilities in the ILs [10]. Changing the cation from imidazolium to quaternary ammonium or pyrrolidinium, all with a similar anion, makes little difference in the CO_2 and O_2 solubilities. Anions containing fluorine such as bis[(trifluoromethyl) - sulfonyl] imide, Tf_2N- have great affinity toward CO_2. Thus, anion in ILs plays an important role in the CO_2 absorption. Previous studies showed that CO_2 solubility for 1-butyl- 3-methylimidazolium ($[bmim]^+$) based ILs at 60 °C increased in the order: nitrate ($[NO_3]^-$) < tetrafluoroborate ($[BF_4]^-$) < dicyanamide ($[DCA]^-$) ~ hexafluorophosphate ($[PF_6]$-) ~ trifluoro methanesulfonate ($[TfO]^-$) < bis[(trifluoro methyl)-sulfonyl] imide ($[Tf_2N]$-) < tris (trifluoro methylsulfonyl) methide ($[methide]^-$) [11]. For the cation, the CO_2 solubility increases with increasing chain length of alkyl substituents. Due to the variety of possible cations and anions, there are virtually an infinite number of possible combinations, which means there should be ample opportunities to tailor and optimize the properties of these

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solvents for CO_2 capture. For example, Bates et al[10]. developed a task-specific ionic liquid for CO_2 capture by introducing an amine ($-NH_2$) group to the ionic liquid These amine tethered ILs show substantial increase in CO_2 solubility than usual ionic liquids. Recently it was found that polymerization of Ionic Liquid monomers into Poly Ionic Liquids increases CO2 absorption capacity 6 to 8 times [12]. These Poly ILs are made by Free radical polymerization or atom transfer radical polymerization. Since these poly ILs are solids, they can be made into finer particles and can be used as promising solid sorbents and as membrane materials for CO2 capture and separation from flue gases[12].

II. Interaction of CO_2 with Ionic Liquid through Ab initio (MP2-Moller plesset perturbation level)

The solubility of CO_2 in ionic liquids has been the subject of experimental and theoretical investigations, but aspects concerning the molecular sites in the ionic liquids to which CO_2 associates more strongly can be studied through molecular simulations [13]. Ab initio calculations at the MP2 (Moller plesset) level of theory provide an insight into the nature of CO_2 interaction with ionic liquids 14]. Since the solubility of CO_2 in a particular IL mainly depends on the interaction of CO_2 with the type of anion of the IL, there is a need to study how CO_2 is interacting with different anions. In this paper we report Ab initio based zero Kelvin calculations that explore minimum energy structures of several anion-CO_2 pairs in gas phase helps in anticipating the interaction [15]. Anticipating the results, among all the anions studied, fluorine based anions show greater affinity towards CO_2. It was also observed that the solubility of CO_2 is inversely proportional to the anion-CO_2 binding energy. The distortion in the geometry of CO_2 is due to the interaction between the anion-CO_2.

Molecular Modeling Details

Geometry optimizations of different anions were carried out using ab-initio (MP2 (Moller-Plesset perturbation) level) calculations with 6-311+G* basis set using GAUSSIAN 03 software[17]. Anions like fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), tetrafluoroborate(BF_4^-), hexafluorophosphate (PF_6^-), trifluoromethylsulfonyl ($CF_3SO_3^-$), bis-(trifluoromethyl sulfonyl)imide ($N[CF_3SO_3^-]_2$) were studied in the present study. The input for the simulation was the Z-matrix of the molecule that was made in MOLDEN (software used to visualize the molecules) [16]. Initially each anion is geometry optimized. Thermo chemistry of each of the anion obtained through frequency optimization. For each of the anion, CO_2 molecule was placed at different positions around the anion to explore the potential energy surface better. The structures and binding energies reported here are those corresponding to the lowest energies. The binding energy of each pair was obtained by subtracting the total energy of the isolated anion and that of isolated CO_2 molecule from the total energy of the pair. The minimum distance of CO_2 from the anion, the distortion in the structure, and the binding energy between CO_2 and anion were obtained and are presented in the Table I. A comparison between the present data and the literature values (given in the brackets [15]) is also made in Table I.

The experimental solubility values of CO_2 in different [bmim] based ILs with various anions was used for establishing a relationship between binding energy and solubility [8].

III. Results and Discussion

Of all the anions studied, it is clear from Table I that the fluorine reacts spontaneously with CO_2 molecule to form FCO_2^-, with a distance of 1.51 Å. Though the distance is larger when compared to the F-C bond distance in carbon tetra fluoride (1.355 Å), the formation of the bond was clear. The CO_2 molecule in the complex was highly distorted from its original linear structure showing a O-C-O bond angle of 137.92°. The binding energy of the complex was found to be -105.1 kJ/mol. The complex appears to be a distorted planar trigonal structure. The CO_2 molecule was found to bend away from the F^- ion in order to minimize the interaction between the electronegative fluorine and the oxygen. Furthermore, comparison of the data for halide ions showed a systematic trend with increasing halogen size: the distance of the carbon atom from the halide ion increases; the OCO angle increases; and the binding energy of the CO_2-halide complex decreases. The optimized structural configuration for Bromide – CO_2 dimer is shown in the Fig. 1.

TABLE I
Comparisons for Nearest Distance of Anion in the Corresponding Complex, OCO Bond Angle and Binding Energy

Anion	Min Distance (Å)	OCO Angle (°)	Binding energy (kJ/mol)	Solubility in bmim IL
F^-	1.51 (1.59)	137.92 (139.4)	-105.1 , (-118.3)	-
Cl^-	2.89 (2.75)	171.59 (162.2)	-22.86 (-26.9)	0.26
Br^-	3.14 (3.09)	173.46 (167.6)	-19.38 (-20.7)	0.31
NO_3^-	2.74 (2.75)	172.47 (172.6)	-25.46 ((-24.8)	0.22
BF_4^-	2.76 (2.77)	175.1 (175.1)	-19.5 (-18.8)	0.30
PF_6^-	2.78 (2.80)	176.1 (176.1)	-14.0 (13.8)	0.31
Tf_2N^-	3.00 (2.84)	179.8 (176.9)	-7.8 (-9.9)	0.42
$CF_3SO_3^-$	3.39 (2.91)	173.4 (175.4)	-10.705 (-14.6)	0.34

The geometry of the dimer was similar for the other halogen anions except for the C-X distance and the OCO angle. All the mono atomic anions were observed to lie in the plane of the CO_2 molecule. Furthermore, CO_2 has bent away

from the anions so as to minimize the repulsive interaction of the oxygen atoms with the halide ions. Other anions that exhibited a greater affinity towards CO_2 molecules were NO_3^-, BF_4^-, PF_6^-, Tf_2N^-, and $CF_3SO_3^-$.

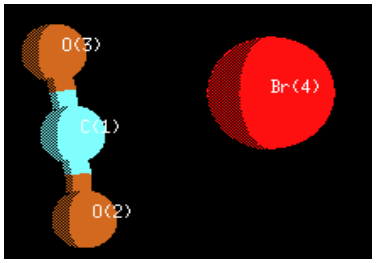

Fig. 1 Minimum energy structure of Bromide-CO_2 dimer

Fig. 2 shows the minimum energy geometries of some of the anions studied with CO_2. It was observed that in the complex with NO_3^- , CO_2 is located in such a way that it is equidistance from the two oxygens of nitrate ion with the carbon of CO_2 lying in the plane of the anion. Also the oxygens of the CO_2 bent outwards to reduce the repulsive interaction with the electronegative oxygens of the nitrate ion. In the tetrafluoroborate-CO_2 complex, the carbon of CO_2 lies in the plane formed by two BF bond vectors and the CO_2 molecule is perpendicular to this plane just as in the case of nitrate ion.

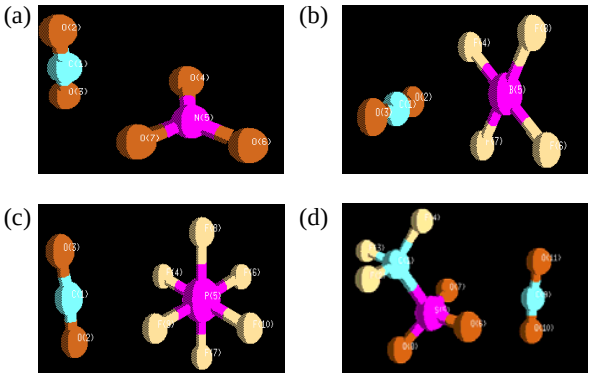

Fig. 2 Minimum energy structures of different anion-CO_2 complexes (a) NO_3^- (b) BF_4^- (c) PF_6^- (d) $CF_3SO_3^-$

It was reported that the optimized structures of anion-CO_2 complexes mainly dominated by Lewis acid-base interactions, with the carbon atom of CO_2 as the electron acceptor (acid) and the anion as the donor (base). This interaction leads to the varying degrees of distortion of the CO_2 molecule. The extent of bending of CO_2 is generally considered to be a measure of the basicity of the anion.

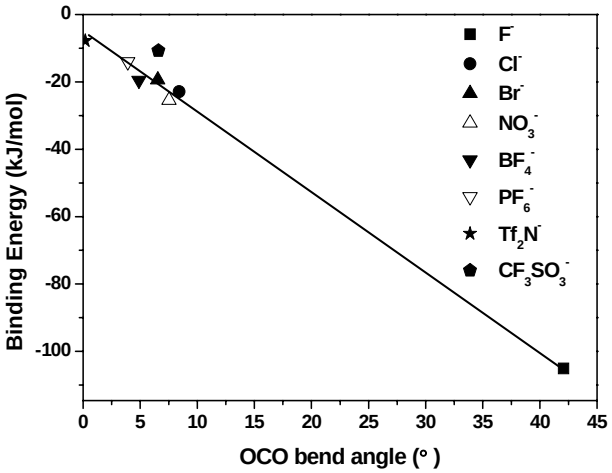

Fig. 3 Binding energy of anion-CO_2 dimer versus deviation of OCO angle of CO_2 molecule from 180° in various complexes. The dots represent various anions. The continuous line is the best fit to the data

Furthermore, the variation of binding energy with OCO angle deviation (from linearity) is illustrated in Fig. 3 for different anions studied. It appears that the extent of distortion from the linear geometry upon complexation appears to be proportional to the binding energy.

It is also clear from Table I that the anions containing fluoro-alkyl groups (Tf_2N^-, $CF_3SO_3^-$) possess lower binding energies of anion-CO_2 complex compared to that of inorganic fluorine-based anion (F^-, BF_4^-, PF_6^-) complexes. This in turn results in the higher CO_2 solubilities (see Fig. 4) for fluoro-alkyl groups.

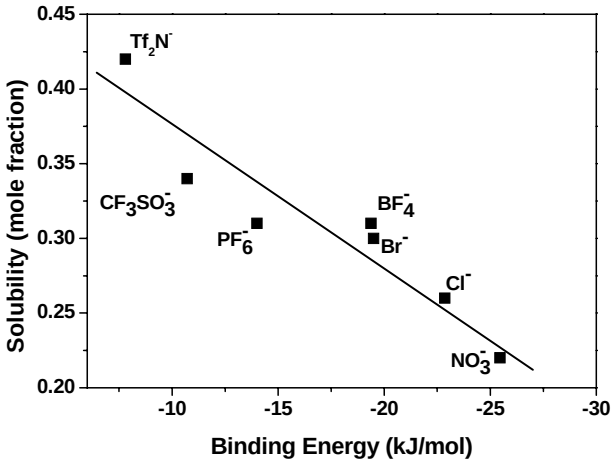

Fig. 4 Comparison of experimentally measured solubility of CO_2 in ionic liquids of different anions containing the same cation (bmim) with binding energy of corresponding complex

IV. Conclusion

The interactions of CO_2 molecule with various anions (F^-, Br^-, Cl^-, NO_3^-, BF_4^-, PF_6^-, Tf_2N^-, and $CF_3SO_3^-$) employed in

ionic liquids have been studied using Ab initio (MP2 level) calculations. The anion-CO_2 interactions revealed various degrees of distortions (OCO angle) of CO_2 molecule from its linearity, presumably due to the role of Lewis acid-base interaction between CO_2 and the anions. In case of halide ions, the interaction strength (binding energy) found to be decreased with increasing size of anion. Furthermore, the binding energy of CO_2-anion complexes was observed to be inversely proportional to the solubility of CO_2 in the respective ionic liquid.

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