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Theoretical Studies on Interaction Between CO_2 Gas and Imidazolium-Type Organic Ionic Liquid Using DFT and Natural Bond Orbital Calculations

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The interaction between 4,5-dibromo-1-butyl-3-methylimidazolium trifluoromethanesulfonate; [DBBIM][TFMSO$_3$] ionic liquid and CO_2 gas has been studied using DFT calculations. With the help of natural bond orbital (NBO) analyses, the second order perturbation energies of the most interacting natural bond orbitals and natural atomic charges have been predicted by the density functional theory (DFT) computations at the X3LYP/6-31++G(d,p) level of theory. The natural charge calculations showed that in the ionic liquid-CO_2 system, the [DBBIM][TFMSO$_3$] ionic liquid is the electron donor while CO_2 gas is an electron acceptor. Further stabilization of the imidazolium ring π-system is produced due to the interaction of the CO_2 gas with the ionic liquid. The polarization of the C–O and S1–O3 bonds are affected significantly by such interactions. The charge decomposition (CDA) analysis revealed the strong interactions between the [DBBIM]$^+$ and [TFMSO$_3$]$^-$ ions of the ionic liquid and the weak interaction between the ionic liquid and the CO_2 gas. The mp2 interaction energy of ionic liquid-CO_2 system is only 3.6107 kcal/mol.

Keywords: Ionic liquid, Charge transfer, Natural bond orbital analysis, DFT/X3LYP, Charge.

INTRODUCTION

Several processes have been developed to remove CO_2 from the burning fossil fuels. Unfortunately, there are several obvious disadvantages in these processes [1]. The emissions of acid gas such as CO_2 in flue gases have drawn worldwide attention because it is a significant source of atmospheric pollution that threatens the environment. The increase of the atmospheric concentration of CO_2 gas has significant implications for the global climate. Reduction of the green house gas emissions has become one of the most impending global issues. Moreover, innovative technological development for removing acid gases such as CO_2 from natural gas (NG) and other sources is indispensable for clean energy production. The presence of this gas in natural gas deteriorates its quality (heating value) as well as liquefaction process performance. Thus, removal of such acid gases (CO_2) up to an acceptable specification is mandatory prior to its transportation for domestic and commercial use. As a result, it is important to develop new materials that can efficiently and economically capture this acid gas. Recently, a new class of material called ionic liquids (ILs) having a set of exceptional physicochemical properties have been proposed as selective absorbents for CO_2 capture [2], as they were found to show high CO_2 solubility and, therefore, a high loading capacity for acid gases [3].

The quantum chemical calculations are considered as effective tool to study the interaction between molecular systems and fragments. The calculations of net atomic charges and partial atomic charges have a significant importance to analyze the polarization effects of molecules and the electrostatic interactions processes as well as for molecular modeling [4]. The natural bond orbital (NBO) calculation is considered one of the best methods used to calculate the atomic charges using quantum chemical calculations [5-23]. It is considered as an effective tool for the elucidation of the charge transfer interactions of a molecule and describing its Lewis structure, charge, bond order, bond type, hybridization, resonance, donor-acceptor interactions among the natural bond orbitals. For that reason, this study aims to shed the light on the different molecular and electronic structure aspects of the 4,5-dibromo-1-butyl-3-methylimidazolium trifluoromethanesulfonate [DBBIM][TFMSO$_3$] ionic liquid and its complex with CO_2 gas in the framework of the DFT calculations.

COMPUTATIONAL METHODS

The electronic structures of the [DBBIM][TFMSO$_3$], CO_2 and [DBBIM][TFMSO$_3$]-CO_2 were optimized by solving the self-consistent field equation and the optimized structures corresponding to a single point minima were obtained by using the extended hybrid density functional X3LYP [24]. This method is widely used for ionic liquids [25,26] calculations. The 6-31++G(d,p) basis set has been employed in all the calculations since they can give a fine compromise between accuracy and computational cost. No symmetry constraint was imposed on the optimization of initial structures. To examine the nature of interactions, the electronic properties for stationary points were illustrated in terms of natural bond orbital (NBO) analysis [22] as employed in Gaussian 09W [27] software at the same level of theory.

RESULTS AND DISCUSSION

Molecular structure: The structures of $[DBBIM]^+$, $[TFMSO_3]^-$, $[DBBIM][TFMSO_3]$ (**1**) and the $[DBBIM][TFMSO_3]CO_2$ (**2**) were optimized with no symmetry constraint at the X3LYP/6-31++G(d,p) level of theory. The optimized structures were exhibited in Fig. 1. The length of C14-H16 and C24-H25 in $[DBBIM]^+$ cation are 1.094 and 1.095 Å respectively. The length of these bonds in $[DBBIM][TFMSO_3]$ ionic liquid are 1.092 and 1.091, respectively. These bonds are slightly shorter than that of corresponding C-H bonds in the isolated $[DBBIM]^+$ cation due to the C-H---O hydrogen bonding formation. Compared with the isolated $[TFMSO_3]^-$ anion, the lengths of S1-O3 and S1-O4 in $[DBBIM][TFMSO_3]$ (**1**) are increased by 0.011 and 0.006 Å, respectively, while the length of S1-O2 decreases (0.013 Å), in agreement with the principle of conservation of bond order. Therefore, hydrogen bonds are the main interactions between $[DBBIM]^+$ cation and $[TFMSO_3]^-$ anion.

The optimized structure of $[DBBIM][TFMSO_3]$ is shown in Fig. 1, with one stronger H---O interaction between O4 and H16 (2.344 Å) and one weaker H---O interaction between O3 and H25 (2.550 Å). These interacting distances are longer and hence weaker than those predicted for the 1-butyl-3-methylimidazolium methylsulfate [28] ionic liquid. The replacement of the methoxy group by the electron withdrawing CF_3-group tends to weaken these interactions. Anyway, these interacting distances are shorter than the sum of the Batsanov's van der Waals radii of both elements [29], hence these results indicate that the H---O interactions may occur. Moreover the C11---O3 distance is predicted to be 2.791 Å which is shorter than the sum of the Batsanov's van der Waals' radii of carbon (1.70 Å) and oxygen atoms (1.52 Å) [29] indicating the strong interaction between the O3 atom of the $[TFMSO_3]^-$ and the C11 of the $[DBBIM]^+$.

The optimized molecular structure of $[DBBIM][TFMSO_3]$ $-CO_2$ system is also shown in Fig. 1. There is one strong H---O interaction between the O3 and H12 with 2.436 Å and two strong C11---O3 and C11---O4 interactions having C---O distances of 2.823 and 2.949 Å, respectively. Moreover a weaker O4---C17 (3.064 Å) interaction is noted. The CO_2 gas significantly interact with the $[DBBIM]^+$ and $[TFMSO_3]^-$ *via* H16---O35 (2.433 Å) and O4---C34 (2.796 Å), respectively. It is evident that the ionic liquid-CO_2 gas increased the interactions between the $[DBBIM]^+$ and $[TFMSO_3]^-$ ions, hence stabilize the ionic liquid system and explain the high ability of ionic liquid towards absorption of CO_2 gas [3].

Natural population analysis: The calculated natural atomic charges for the optimized structures of $[DBBIM][TFMSO_3]$ and $[DBBIM][TFMSO_3]$-CO_2 are given in Table-1. In the case

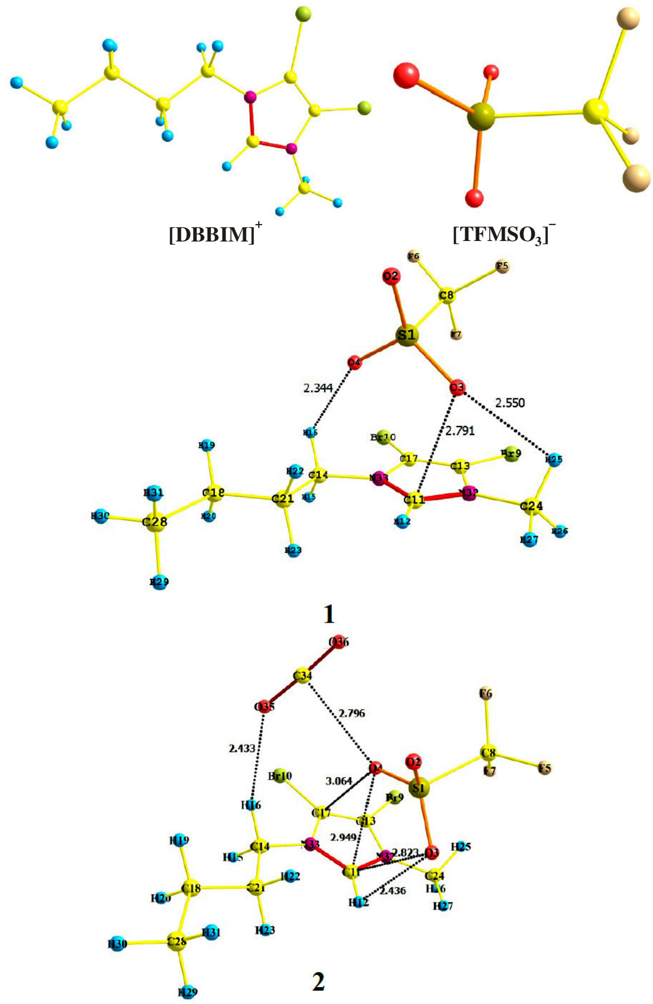

Fig. 1. Optimized molecular structures of $[DBBIM]^+$, $[TFMSO_3]^-$, **1** and **2**

of $[DBBIM][TFMSO_3]$, the most electropositive charge of 2.3558 e is accumulated at the S1 atom. From electrostatic point of view, the S-atom has the tendency to accept electrons. In contrast, the most electronegative charges -0.9586 e, -1.0501 e and -1.0366 e are accumulated at O2, O3 and O4 atoms, respectively. These atoms have the most tendencies to donate electrons. As a result, one could conclude strong electron polarization for the S-O bonds towards the O-atoms.

However, in case of $[DBBIM][TFMSO_3]$-CO_2, the most electropositive charge of 2.3500 e is also accumulated at the S1-atom. On other hand, the negative charges at the O2 and O4 atoms increased upto 0.002 e. In contrast, the negative charge at the O3 atom decreased by the same magnitude. These variations are mainly caused due to the interaction between the ionic liquid and CO_2 gas. Interestingly, the calculated natural charges at the C34, O35 and O36 are 1.0509, -0.5532, -0.4991 instead of 1.0229, -0.5114 and -0.5115 for the free CO_2, respectively. It could be seen that the C34 is shifted to higher positive charge while the O35 is shifted to more negative charge due to its interaction with H16-atom of the $[DBBIM][TFMSO_3]$ ionic liquid system. We noted that the net natural charge at the $[DBBIM][TFMSO_3]$ and CO_2 molecules in **2** are +0.0013 e and -0.0013e, respectively. As a result, we propose that CO_2 acts as an electron acceptor when it interacts with $[DBBIM][TFMSO_3]$ ionic liquid.

TABLE-1
CALCULATED NATURAL ATOMIC CHARGES OF THE STUDIED SYSTEMS

	Charge (e)				
Atom	**1**	**2**	Atom	**1**	**2**
S1	2.3558	2.3500	H19	0.2421	0.2395
O2	-0.9586	-0.9603	H20	0.2236	0.2243
O3	-1.0501	-1.0311	C21	-0.4799	-0.4806
O4	-1.0366	-1.0496	H22	0.2581	0.2558
F5	-0.3599	-0.3553	H 23	0.2218	0.2263
F6	-0.3564	-0.3519	C24	-0.4459	-0.4471
F7	-0.3811	-0.3832	H 25	0.2806	0.2712
C8	0.8162	0.8199	H26	0.2441	0.2404
Br9	0.1938	0.1928	H27	0.2479	0.2637
Br10	0.2012	0.1925	C28	-0.6599	-0.6607
C11	0.3144	0.3101	H29	0.2214	0.2227
H12	0.2740	0.2898	H30	0.2357	0.2353
C13	0.0072	0.0103	H31	0.2336	0.2358
C14	-0.2405	-0.2433	N32	-0.3518	-0.3554
H15	0.2441	0.2454	N33	-0.3430	-0.3483
H16	0.2916	0.2824	C34	1.0229	1.0509
C17	0.0096	0.0126	O35	-0.5114	-0.5532
C18	-0.4530	-0.4524	O36	-0.5115	-0.4991

Table-2 lists the most interacting natural bond orbital's along with their percentage of hybrid atomic orbital contribution. It is shown that all the atoms in imidazolium ring adopt sp^2 hybridization. These hybridized orbitals form the delocalized π-bonds of the imidazolium ring. On other hand, almost a 100 % *p*-character in both atoms forming the double bonds has been predicted. The natural bond orbital analyses showed that all the C–N, C-O and S–O bond orbitals are polarized towards the nitrogen and oxygen atoms. The polarization coefficients at the N and O atoms of the C–N, C–O and S–O bonds are in the range of 0.7918-0.8430, 0.8046-0.8753 and 0.8105-0.8157, respectively. Therefore, the maximum electron densities are mainly localized over the oxygen atoms of the $[TFMSO_3]^-$. The polarization coefficients at the σ(C-O) bonds are increased while that for the π(C-O) bonds are decreased due to the interactions between the CO_2 and the [DBBIM][$TFMSO_3$] ionic liquid.

The natural bond orbital analysis provides an efficient method for studying intra- and intermolecular bonding and also provides a convenient basis for investigating charge transfer or conjugative interactions in molecular systems. Intermolecular interactions are representative of donor–acceptor bonding, such as lone pair→anti-bonding orbital mixtures. In the natural bond orbital analysis, the second order perturbation stabilization energy E(2) associated with the delocalization indicate the strength of the electron delocalization. The most significant ICT interactions are given in Table-3. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors natural bond orbital.

In the [DBBIM][$TFMSO_3$], the π→π* and n→π* hyperconjugative interaction energies upto 17.56 and 76.11 kcal/mol, respectively, have been predicted. Interestingly, the energies of these π→π* and n→π* hyperconjugative interactions in the [DBBIM][$TFMSO_3$]-CO_2 are increased upto 18.17 and 84.05 kcal/mol, respectively and further stabilization of the imidazolium ring π-system is produced. The higher the E(2) value, the more electron transfer from donor orbitals to acceptor orbitals leading to more stable system [30,31].

In [DBBIM][$TFMSO_3$], the LP(1)O4→σ*C14-H16, LP(2)O4→σ*C14-H16, LP(1)O3→σ*C24-H25 and LP(3)O3 →σ*C24-H25 are 0.87, 0.11, 0.10 and 0.24 kcal/mol, respectively, indicating the presence of non covalent H---O interactions. The E(2) of LP(1)O3→π*C11-N33 has 0.48 kcal/mol indicates the presence of interaction between the O3-atom of the $[TFMSO_3]^-$ and the C11 of $[DBBIM]^+$. The calculated natural charges (Table-1) of the O3 (-1.0501), O4 (-1.0366), H16 (0.2916), H25 (0.2806) and C11 (0.3144) reveal that these interactions are mainly electrostatic.

The LP(1)O4→π*C34-O36, LP(2)O4→π*C34-O36, LP(1)O35→σ*C14-H16, LP(2)O35→σ*C14-H16 ICT interaction energies are calculated to be 0.47, 1.20, 1.13 and 0.89 kcal/mol, respectively. These results indicate the presence of electrostatic interactions between the delocalized LP(1)O4 of the $[TFMSO_3]^-$ and the antibonding π-bond of the C34-O36. These small E(2) values reveal that the interactions between

TABLE-2
LINEAR COMBINATION OF NATURAL ATOMIC ORBITALS (NAOs) OF SOME ATOMIC PAIRS IN [DBBIM][$TFMSO_3$] AND [DBBIM][$TFMSO_3$]-CO_2 SYSTEMS

Bonds	Population number		Linear combination of natural atomic orbitals	
	1, CO_2	**2**	**1**, CO_2	**2**
σC11-N32	1.9783	1.9785	$0.6048(sp^{2.27})_{C11}+0.7964(sp^{1.96})_{N32}$	$0.6038(sp^{2.30})_{C11}+0.7971(sp^{1.95})_{N32}$
πC11-N32	1.8947	1.8947	$0.5380(p)_{C11}+0.8430(p)_{N32}$	$0.5380(p)_{C11}+0.8430(p)_{N32}$
σC11-N33	1.9783	1.9778	$0.6052(sp^{2.28})_{C11}+0.7961(sp^{1.97})_{N33}$	$0.6043(sp^{2.31})_{C11}+0.7968(sp^{1.96})_{N33}$
σC13-C17	1.9820	1.9820	$0.7076(sp^{1.45})_{C13}+0.7066(sp^{1.47})_{C17}$	$0.7076(sp^{1.45})_{C13}+0.7066(sp^{1.47})_{C17}$
πC13-C17	1.8571	1.8587	$0.7076(p)_{C13}+0.7066(p)_{C17}$	$0.7065(p)_{C13}+0.7077(p)_{C17}$
σC13-N32	1.9781	1.9784	$0.6107(sp^{2.39})_{C13}+0.7918(sp^{2.11})_{N32}$	$0.6107(sp^{2.40})_{C13}+0.7918(sp^{2.10})_{N32}$
σC17-N33	1.9776	1.9778	$0.6108(sp^{2.39})_{C17}+0.7918(sp^{2.13})_{N33}$	$0.6108(sp^{2.38})_{C17}+0.7918(sp^{2.12})_{N33}$
σC34-O35	1.9988	1.9952	$0.5938(sp)_{C34}+0.8046(sp^{1.74})_{O35}$	$0.5867(sp^{1.01})_{C34}+0.8098(sp^{1.84})_{O35}$
σC34-O36	1.9988	1.9978	$0.5938(sp)_{C34}+0.8046(sp^{1.74})_{O36}$	$0.5902(sp^{1.07})_{C34}+0.8072(sp^{1.77})_{O36}$
πC34-O36	1.9986	1.9966	$0.4836(p)_{C34}+0.8753(p)_{O36}$	$0.4869(p)_{C34}+0.8735(p)_{O36}$
πC34-O36	1.9986	1.9966	$0.4836(p)_{C34}+0.8753(p)_{O36}$	$0.4869(p)_{C34}+0.8734(p)_{O36}$
σS1-O2	1.9822	1.9817	$0.5857(sp^{2.45})_{S1}+0.8105(sp^{3.16})_{O2}$	$0.5857(sp^{2.46})_{S1}+0.8105(sp^{3.16})_{O2}$
σS1-O3	1.9808	1.9806	$0.5785(sp^{2.65})_{S1}+0.8157(sp^{3.16})_{O3}$	$0.5804(sp^{2.63})_{S1}+0.8144(sp^{3.20})_{O3}$
σS1-O4	1.9806	1.9805	$0.5797(sp^{2.61})_{S1}+0.8148(sp^{3.16})_{O4}$	$0.5794(sp^{2.64})_{S1}+0.8150(sp^{3.18})_{O4}$

TABLE-3
SOME DONOR (Di)–ACCEPTOR (Aj) INTERACTIONS IN [DBBIM][TFMSO$_3$] AND [DBBIM][TFMSO$_3$]-CO_2
AND THEIR SECOND ORDER PERTURBATION STABILIZATION ENERGIES, E(2) (kcal/mol)

[DBBIM][TFMSO$_3$]			[DBBIM][TFMSO$_3$]-CO_2			[DBBIM][TFMSO$_3$]			[DBBIM][TFMSO$_3$]-CO_2		
Di	Aj	E(2)	Di	Aj	E(2)	Di	Aj	E(2)	Di	Aj	E(2)
		Within [TFMSO$_3$]$^-$						**Within [DBBIM]$^+$**			
LP(2)O2	σ*S1-O3	18.37	LP(2)O2	σ*S1-O3	18.13	πC11-N33	π*C13-C17	17.56	πC11-N32	π*C13-C17	18.17
LP(2)O2	σ*S1-O4	18.28	LP(2)O2	σ*S1-O4	18.57	πC13-C17	π*C11-N33	12.16	πC13-C17	π*C11-N32	11.77
LP(3)O2	σ*S1-C8	26.04	LP(3)O2	σ*S1-C8	26.03	LP(1)N32	π*C11-N33	76.11	LP(1)N33	π*C11-N32	84.05
LP(2)O3	σ*S1-O2	16.70	LP(2)O3	σ*S1-O2	17.04	LP(1)N32	π*C13-C17	36.92	LP(1)N33	π*C13-C17	37.67
LP(2)O3	σ*S1-O4	14.25	LP(2)O3	σ*S1-O4	14.33			**Within CO_2**			
LP(3)O3	σ*S1-C8	21.07	LP(3)O3	σ*S1-C8	21.85	LP(1)O35	σ*C34-O36	17.07	LP(1)O35	σ*C34-O36	16.63
LP(2)O4	σ*S1-O2	15.88	LP(2)O4	σ*S1-O2	15.41	LP(2)O35	π*C34-O36	139.60	LP(2)O35	π*C34-O36	110.44
LP(2)O4	σ*S1-O3	16.30	LP(2)O4	σ*S1-O3	15.97				LP(2)O35	π*C34-O36	9.75
LP(3)O4	σ*S1-C8	22.30	LP(3)O4	σ*S1-C8	21.77				LP(3)O35	σ*C34-O35	12.95
		[TFMSO$_3$]$^-$ → [DBBIM]$^+$				LP(3)O35	π*C34-O36	139.60	LP(3)O35	π*C34-O36	128.29
LP(1)O3	π*C11-N33	0.48	LP(2)O4	π*C11-N32	0.40	LP(1)O36	σ*C34-O35	17.06	LP(1)O36	σ*C34-O35	17.18
LP(1)O4	σ*C14-H16	0.87	LP(1)O3	σ*C11-H12	0.35			**[DBBIM]$^+$[TFMSO$_3$]$^-$ → CO_2**			
LP(2)O4	σ*C14-H16	0.11	LP(3)O3	σ*C11-H12	0.36				LP(1)O4	π*C34-O36	0.47
LP(1)O3	σ*C24-H25	0.10	LP(3)O3	π*C11-N32	0.86				LP(2)O4	π*C34-O36	1.20
LP(3)O3	σ*C24-H25	0.24	LP(1)O4	π*C11-N32	0.08				LP(1)O35	σ*C14-H16	1.13
			LP(2)O4	σ*C11-N33	0.07				LP(2)O35	σ*C14-H16	0.89
			LP(3)O4	π*C11-N32	0.25						
			LP(3)O4	π*C13-C17	0.06						

the CO_2 and the [DBBIM][TFMSO$_3$] are week. Also, another interaction occurs between the delocalized LPO35 of the CO_2 and the antibonding σ-bond of the C14-H16 bond. The electron delocalization within the CO_2 molecule affected strongly due to the interactions between it and the [DBBIM][TFMSO$_3$] where the number of ICT interactions are increased but most of these electron delocalization processes are destabilized. The net energy of these electron delocalization processes are decreased from 313.33 kcal/mol for the free CO_2 to 295.24 kcal/mol for the CO_2-ionic liquid systems respectively.

Charge decomposition analysis (CDA): The charge decomposition analysis [32] is used to provide deep insight on how charges are transferred between fragments in a complex to achieve charge equilibrium. This idea is fundamental on fragment orbital, which denotes the molecular orbital of fragment in its isolated state. In the original paper of the charge decomposition analysis, three important terms were presented d_i, b_i and r. The term d_i indicates the amount of electron donated from fragment A to B *via* molecular orbital i of complex; similarly, the term b_i indicates the electron back donation from B to A. Hence, the difference between d and b is that which fragment provides its electrons from its occupied fragment orbitals to virtual fragment orbitals of another fragment. The term r reveals close–shell interaction between two occupied fragment orbitals in different fragments; Positive value of r_i means that due to molecular orbital i, the electrons of the two fragments are accumulated in their overlap region and shows bonding character, while negative value indicates that the electrons are depleted from the overlap region and thus reflecting electron repulsive effect. The sum of all r_i terms is always negative, because overall interaction between filled orbitals are always repulsive. r is also known as ''repulsive polarization''.

The charge decomposition analysis of fragments [DBBIM]$^+$, [TFMSO$_3$]$^-$ and the [DBBIM][TFMSO$_3$] ionic liquid indicates that LUMO of the [DBBIM][TFMSO$_3$] is mainly contributed by 82.90 % of LUFO of [BMIM]$^+$ and the HOMO of the [DBBIM][TFMSO$_3$] ionic liquid is mainly contributed by the HOFO of [TFMSO$_3$]$^-$ by 96.52 %. These results suggest that the [DBBIM][TFMSO$_3$] ionic liquid is stable. The charge decomposition analysis of fragments [DBBIM][TFMSO$_3$], CO_2 and the complex [DBBIM][TFMSO$_3$]-CO_2 were analyzed. It is interesting that HOMO and LUMO of the complex are both mainly contributed by HOFO (99.51 %) and LUFO (100.00 %) of [DBBIM][TFMSO$_3$], respectively and the HOFO and LUFO of CO_2 contribute very little to the frontier molecule orbitals of the complex, hence the orbital interactions between [DBBIM][TFMSO$_3$] and CO_2 is considered to be weak.

The b, d and r values of charge decomposition analysis of [DBBIM][TFMSO$_3$] and [DBBIM][TFMSO$_3$]-CO_2 are given in Table-4. The charge decomposition analysis of [DBBIM][TFMSO$_3$] showed that HOMO, HOMO-1, HOMO-3 and HOMO-6 lead to electron donation from [TFMSO$_3$]$^-$ to [DBBIM]$^+$ upto 0.0397 electron, which is the primary source of the donor-acceptor bonding. The negative r values indicate the presence of electron accumulation upto 0.0371 electron between [DBBIM]$^+$ and [TFMSO$_3$]$^-$ from respective occupied fragment orbitals to the overlap region, which must be beneficial to the bonding between the two fragments while π-back donation has little significant. In case of the [DBBIM][TFMSO$_3$]-CO_2, electron donation upto 0.0066 electron from [DBBIM][TFMSO$_3$] to CO_2, which have also negative r values. These interactions between the [DBBIM][TFMSO$_3$] are CO_2 are week. The mp2 interaction energy including the BSSE correction using the same level of

TABLE-4
b, d AND r VALUES OF THE CHARGE DECOMPOSITION ANALYSIS OF [DBBIM][TFMSO$_3$] AND [DBBIM][TFMSO$_3$]-CO_2

	d	b	d-b	r
[DBBIM][TFMSO$_3$]				
HOMO	0.0081	0.0000	0.0081	-0.0253
HOMO-1	0.0124	0.0065	0.0059	-0.0645
HOMO-3	0.0113	0.0037	0.0150	-0.0072
HOMO-6	0.0397	0.0045	0.0352	-0.0371
[DBBIM][TFMSO$_3$]-CO_2				
HOMO	0.0020	0.0001	0.0021	-0.0058
HOMO-1	0.0011	0.0000	0.0011	-0.0019
HOMO-2	0.0066	0.0013	0.0053	-0.0051
HOMO-5	0.0043	0.0015	0.0028	-0.0177
HOMO-6	0.0020	0.0001	0.0021	-0.0058
HOMO-7	0.0011	0.0000	0.0011	-0.0019

theory at the optimized structure of **2** is calculated using the Counterpoise method. The interaction energy is predicted to be only 3.6107 kcal/mol. The small interaction energy indicates the weak interaction between ionic liquid and CO_2 gas.

Conclusion

The [DBBIM][TFMSO$_3$] ionic liquid and its complex with CO_2 have been calculated using the X3LYP/6-31++G(d,p) level of theory. The natural atomic charges of both systems have been predicted using the natural bond orbital (NBO) calculations. The most interacting natural bond orbitals and natural atomic charges have been predicted. The natural charges revealed that the CO_2 acts as an electron acceptor when it interacts with [DBBIM][TFMSO$_3$] ionic liquid. The different intra- and intermolecular charge transfer interactions have been calculated using the second order perturbation theory. The results gave insight on the presence of weak interactions between the [DBBIM][TFMSO$_3$] ionic liquid and the CO_2 gas. The performed charge decomposition (CDA) analysis indicated the strong interactions between [DBBIM]$^+$ and [TFMSO$_3$]$^-$ ions of the ionic liquid. In contrast, the interaction between [DBBIM][TFMSO$_3$] and CO_2 gas is weak.

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