



Investigations of CO₂ capture by 1-(3-aminopropyl)-3-ethylimidazolium tetrafluoroborate ionic liquid

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Abstract: CO₂ capture by 1-(3-aminopropyl)-3-ethylimidazolium ([Apeim]⁺) tetrafluoroborate ([BF₄]⁻) ionic liquid (IL) was systematically explored at the B3LYP/6-311++G** and mp2/6-311++G** levels. The stable geometries of the ILs and the capture products were optimized, the energies of these geometries were obtained and corrected by zero-point-vibration-energy and basis set superposition error correction. The results show that the interactions between [Apeim]⁺ and [BF₄]⁻ are mainly displayed as hydrogen bonds, but the interaction energies exceed –328 kJ mol⁻¹. Further analysis found that the interactions are reinforced by charge dispersion and charge redistribution of the ion-pair, and that electrostatic attraction contributes a great deal to the interaction energies. This IL system capturing CO₂ belongs to the class of physical absorption with a 1:1 molar absorption ratio; the absorption energy is nearly –18 kJ mol⁻¹ and thus, this IL may require low energy consumption when regenerated from IL–CO₂.

Keywords: ionic liquid; CO₂ capture; absorption; charge redistribution.

INTRODUCTION

Nowadays, CO₂ capture is an urgent issue in the academic circles. On the one hand, as one of the main greenhouse gases, the dramatic increase in the emission of CO₂ is becoming a potential hazard to the environment. On the other hand, CO₂ is also widely used in many fields as a raw material. Due to the unique properties (negligible vapor pressures, high thermal stabilities, excellent CO₂ solubility, and designability),^{1–11} ionic liquids (ILs) may offer a new opportunity for developing novel capture technologies that are capable of reversibly capturing CO₂ with high efficiency. However, many problems have not been solved for the limitations of the experimental technology, such as the structures, the interactions between cations and anions, the mechanisms for capturing CO₂,

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etc. These problems have become a bottleneck in the design of functional ILs for special purpose. Therefore, it is necessary and important to perform studies on series of ILs to solve the above-mentioned problems by using theoretical methods, which will reduce the experimental blindness and help in the design and synthesis of functional ILs with satisfactory properties.

The focus of the present work was 1-(3-aminopropyl)-3-ethylimidazolium ([Apeim]⁺) tetrafluoroborate ([BF₄]⁻) IL and its reactions with CO₂. Computational quantum chemistry methods were used for optimizing the possible stable geometries of the ILs and the capture products. By employing natural bond orbital (NBO) calculations, the influence of charge redistribution on interaction force between the ion-pair, as well as between the IL and CO₂. In addition, the interaction characteristics and the absorbing interaction mechanism were investigated using the atom in molecular theory (AIM) and the electron density topological theory.

THEORETICAL METHODS

Bearing in mind that the DFT method can yield reliable characteristics for geometries with low computational cost, all the geometry optimization works were performed to a minimum for all initial geometries with full freedoms and with no constraints for the symmetry of their initial structure, except for [BF₄]⁻ for T_d, and frequency analysis was employed to check the correctness of the minimum points at the B3LYP/6-311++G(d,p) level. However, B3LYP may not be able to offer sound and reliable energy results when describing systems with very weak interactions, such as ILs capturing CO₂, thus the single point energy of stable geometries were computed at the MP2/6-311++G** level. *ZPE* corrections for the total energy (*E_t*) and the relative energies (*E_r*) were obtained based on B3LYP/6-311++G(d,p) frequency results. The interaction characteristics and mechanisms were predicted by adopting NBO and AIM calculations and electron density topological analysis. All the computation works were completed by employing Gaussian 03¹² and AIM 2000¹³ programs.

RESULTS AND DISCUSSION

In order to find the stable geometries of the IL and the capture products resulting from the absorption of CO₂ by the IL, the possible geometries of the IL were guessed. First, the geometries of [BF₄]⁻ and [Apeim]⁺ were optimized, and the optimized [BF₄]⁻ were placed in the possible positions around the optimized geometry of [Apeim]⁺, and then, eight geometries of the IL were guessed totally. Subsequently, optimization calculations for these guessed geometries were performed and two stable conformers, named ^AIL and ^BIL are shown in Fig. 1. Finally, the geometries of the capture products were predicted when CO₂ was introduced into the possible positions around ^AIL and ^BIL, and the optimization calculations found two stable geometries, which are named ^AIL-CO₂ and ^BIL-CO₂ (shown in Fig. 2). All the geometry optimizations were performed with all the degrees of freedom relaxed and no symmetry constraints, except for the isolated [BF₄]⁻ for T_d.

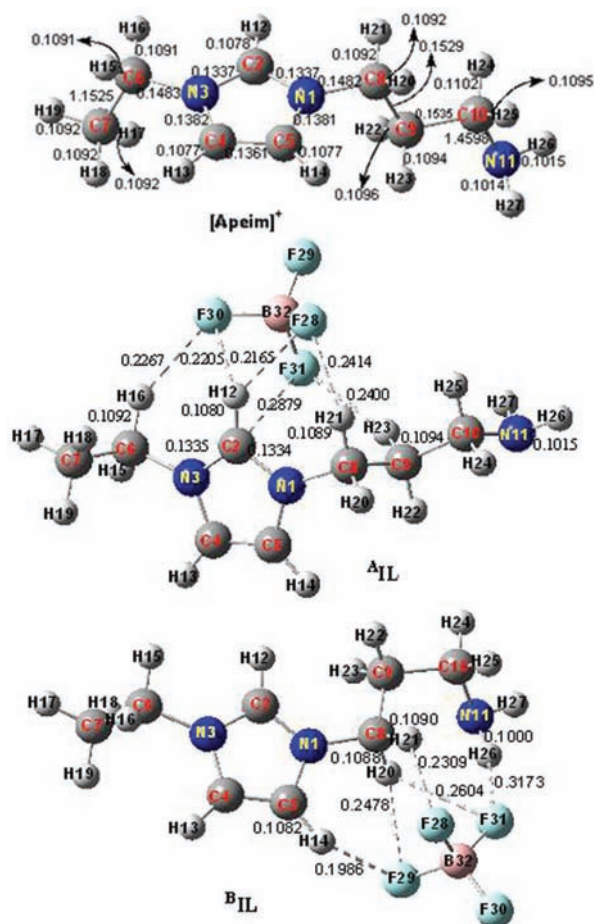


Fig. 1. Geometry of the isolated cation of the IL with atomic numbering and bond lengths in nm. A solid line denotes a normal chemical bond; a dot line denotes a hydrogen bond or a weak chemical bond.

Energies of the stable species

The total energies (E_T), relative energies (E_r), zero-point energy (ZPE) and basis set superposition error (BSSE) of all species are given in Table I. The total energy of isolated $[\text{Apeim}]^+$ and $[\text{BF}_4]^-$ and the total energy of isolated $^{\text{A}}\text{IL}$ and CO_2 were set as zero point datum marks of energy.

The energy change ($\Delta E(\text{IL})$) between an IL and the isolated ions is commonly used to estimate the interaction energy between the ion-pair of an IL, which, in the present case, can be calculated from $\Delta E(\text{IL}) = E([\text{BF}_4]^-) + E([\text{Apeim}]^+) - E(\text{IL})$. It could be observed that $\Delta E(^{\text{A}}\text{IL})$ is $359.69 \text{ kJ mol}^{-1}$ and $\Delta E(^{\text{B}}\text{IL})$ is $328.19 \text{ kJ mol}^{-1}$, which indicates that $\Delta E(^{\text{A}}\text{IL})$ is only 31.5 kJ mol^{-1} greater than that of $\Delta E(^{\text{B}}\text{IL})$. Hence, it could be predicted that both $^{\text{A}}\text{IL}$ and $^{\text{B}}\text{IL}$ are stable geometries and that $^{\text{A}}\text{IL}$ may be the main geometry of the $[\text{Apeim}][\text{BF}_4]$ IL. Whereas, it can be observed from Fig. 1 that the interactions

between $[[\text{Apeim}]^+]$ and $[\text{BF}_4]^-$ are mainly displayed as hydrogen bonds (HBs) and the energy of these HBs is far less than the value of $\Delta E(\text{IL})$, so there must be other stronger interaction forces between the ion-pair besides these HBs, and it is necessary to perform further NBO and AIM investigations.

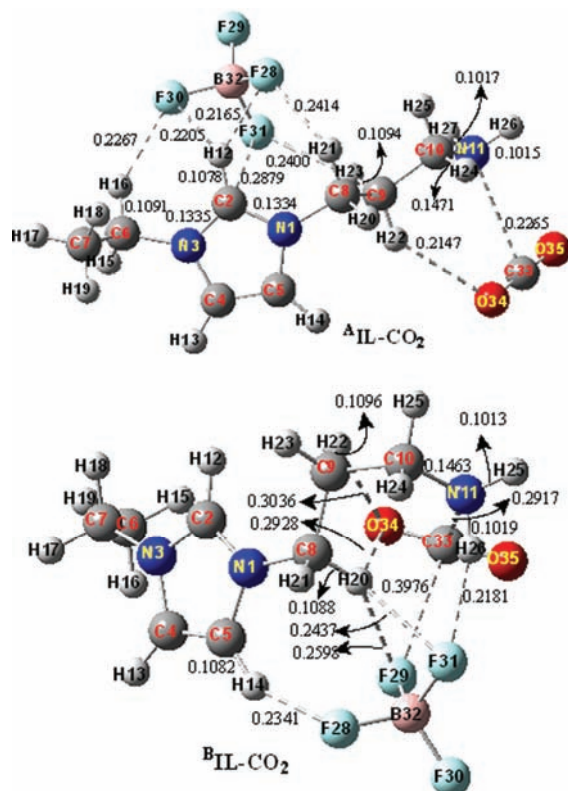


Fig. 2. Geometry of $^{\text{A}}\text{IL}-\text{CO}_2$ and $^{\text{B}}\text{IL}-\text{CO}_2$ with atomic numbering and bond lengths in nm. A solid line denotes a normal chemical bond; a dot line denotes a hydrogen bond or a weak chemical bonds.

TABLE I. The energies of all species corrected by *ZPE* and *BSSE*

Species	<i>ZPE</i> a.u.	<i>BSSE</i> a.u.	E_t a.u. mol ⁻¹	E_r kJ mol ⁻¹
$[[\text{Apeim}]^+ + [\text{BF}_4]^-]$	0.2564	0.0000	-900.7603	0.0000
$^{\text{A}}\text{IL}$	0.2583	0.0024	-900.8973	-359.69
$^{\text{B}}\text{IL}$	0.2585	0.0023	-900.8853	-328.19
$^{\text{A}}\text{IL} + \text{CO}_2$	0.2700	0.0024	-1089.0918	0.0000
$^{\text{A}}\text{IL}-\text{CO}_2$	0.2706	0.0026	-1089.0999	-21.01
$^{\text{B}}\text{IL} + \text{CO}_2$	0.2702	0.0023	-1089.0797	31.76
$^{\text{B}}\text{IL}-\text{CO}_2$	0.2709	0.0034	-1089.0923	-1.26

Table I also shows that the relative energies of $^{\text{A}}\text{IL}-\text{CO}_2$ and $^{\text{B}}\text{IL}-\text{CO}_2$ are -21.01 and 31.76 kJ mol⁻¹, respectively, *i.e.*, $^{\text{A}}\text{IL}$ capturing CO_2 is an exothermic reaction while $^{\text{B}}\text{IL}$ capturing CO_2 is an endothermic reaction. Thus, the relative

energy of ${}^A\text{IL}-\text{CO}_2$ is $52.77 \text{ kJ mol}^{-1}$ lower than that of ${}^B\text{IL}-\text{CO}_2$ and furthermore, ${}^A\text{IL}$ is the most likely geometry; hence, ${}^A\text{IL}-\text{CO}_2$ is the most likely stable product of this IL capturing CO_2 . $\Delta E(\text{IL}-\text{CO}_2)$ was also used to estimate the interaction energy between IL and CO_2 , calculated according to $\Delta E(\text{IL}-\text{CO}_2) = E(\text{IL}) + E(\text{CO}_2) - E(\text{IL}-\text{CO}_2)$. $\Delta E({}^A\text{IL}-\text{CO}_2)$ is $20.01 \text{ kJ mol}^{-1}$, which means that the interaction between ${}^A\text{IL}$ and CO_2 is a strong intermolecular interaction force, the reaction of ${}^A\text{IL}$ capturing CO_2 is physical absorption and $\text{IL}-\text{CO}_2$ is a molecular complex. It could be further speculated that the desorption of CO_2 from ${}^A\text{IL}-\text{CO}_2$ might be a low energy consumption process. For the sake of simplification, ${}^A\text{IL}$ together with ${}^A\text{IL}-\text{CO}_2$ are used as examples to illustrate the research details throughout this paper.

Geometry structures of the ionic liquid

The geometries given in Fig. 1 show that there are five hydrogen bonds (HBs) and a weak bond of $\text{F31}\cdots\text{C2}$ between the ion-pair in ${}^A\text{IL}$. The five HBs are $\text{F28}\cdots\text{H12}-\text{C2}$ (0.2165 nm), $\text{F28}\cdots\text{H21}-\text{C8}$ (0.2414 nm), $\text{F30}\cdots\text{H16}-\text{C6}$ (0.2267 nm), $\text{F30}\cdots\text{H12}-\text{C2}$ (0.2205 nm) and $\text{F31}\cdots\text{H23}-\text{C9}$ (0.2400 nm). The HB strength order is $\text{F28}\cdots\text{H12}-\text{C2} > \text{F30}\cdots\text{H12}-\text{C2} > \text{F30}\cdots\text{H16}-\text{C6} > \text{F28}\cdots\text{H21}-\text{C8} > \text{F31}\cdots\text{H23}-\text{C9}$. Obviously, the bond length could be a simple criterion for the formation of HBs or weak chemical bonds when classic HBs or weak chemical bonds are investigated, and the shorter the bond length, the stronger is the bond. The bond lengths of the five HBs are slightly shorter than the van der Waals radii (Pauling) of F and H (0.245 nm)¹⁴, that is to say, they pertain to normal HBs. The bond length of $\text{F31}\cdots\text{C2}$ (0.2879 nm) is much longer than a normal F–C chemical bond, which means that it is a very weak. However, the interaction energy between the ion-pair in ${}^A\text{IL}$ is far beyond the bond energy of the five HBs and $\text{F31}\cdots\text{C2}$. It could be observed from Fig. 1 that the $\text{C2}-\text{H12}$ bond length is lengthened resulting from the electrons on the H atom transferring to form the HB or another weak chemical bond, this phenomenon being called an “electron transfer effect”. Moreover, the $\text{C2}-\text{N1}$ and $\text{C2}-\text{N3}$ bond lengths are shortened by 0.0003 and 0.0002 nm, respectively, in spite of C2 involvement in $\text{F31}\cdots\text{C2}$ formation. These abnormal bond length changes depart from the “electron transfer effect”. In addition, another particular phenomenon is that H12 participates in the formation of two HBs, *i.e.*, $\text{F30}\cdots\text{H12}-\text{C2}$ and $\text{F28}\cdots\text{H12}-\text{C2}$, simultaneously despite the saturation characteristic of a HB.

Geometries of the molecular complexes

It can be seen from Fig. 2 that ${}^A\text{IL}-\text{CO}_2$ is produced when CO_2 is absorbed by ${}^A\text{IL}$ and the molar absorption ratio is 1:1. The main interactions between ${}^A\text{IL}$ and CO_2 are through the $\text{C33}\cdots\text{N11}$ (0.2265 nm) and $\text{O34}\cdots\text{H22}-\text{C9}$ (0.2147 nm) bonds. The bond lengths of these two chemical bonds are shorter than the

van der Waals radii of the corresponding two atoms. Additionally, C10–N11, N11–H26 and N11–H27 participate in the formation of C33···N11 and they are elongated by the “electron transfer effect”. The C9–H22 bond is abnormally shortened, although it is involved in the formation of the C10–H26···O38 HB. This particular phenomenon possibly influences the absorption of CO₂ by ^AIL. Therefore, it was essential to determine the reasons for these abnormal phenomena by using NBO and AIM research.

Frequency analysis

The frequency calculations suggest that the two optimized geometries of the IL and the two capture products have no imaginary vibration frequency, which confirmed their stability. The interactions between cation and anion resulted in the breakage of T_d symmetry in [BF₄][−] and a shift of the vibration frequencies, which are consistent with the bond strength changes.

The NBO analysis

In order to reveal how the charge population affects the interaction forces between the ion-pair, as well as between the IL and CO₂, NBO atomic charges were calculated and analyzed. The NBO net charges of atoms and group fragments are given in Tables II and III, respectively. Here, ^AIL and ^AIL–CO₂ are considered.

TABLE II. The net integral atomic charges in all stable species

Atom	Cation	^A IL	^A IL–CO ₂	^B IL	^B IL–CO ₂	[BF ₄] [−]
N1	−0.34404	−0.35775	−0.35546	−0.33081	−0.32983	B 1.33356
C2	0.29607	0.32491	0.32493	0.27236	0.28145	F −0.58339
N3	−0.35099	−0.36037	−0.36168	−0.36669	−0.36724	F −0.58339
C4	−0.00877	−0.01895	−0.02289	−0.03748	−0.03488	F −0.58339
C5	−0.00410	−0.02061	−0.02134	0.01462	0.01487	F −0.58339
C6	−0.16613	−0.17909	−0.17901	−0.16426	−0.16321	CO ₂
C7	−0.58896	−0.58095	−0.58031	−0.58466	−0.58438	C 0.99076
C8	−0.16354	−0.16242	−0.16145	−0.19660	−0.18859	O −0.49538
C9	−0.40064	−0.41316	−0.42047	−0.40706	−0.41165	O −0.49538
C10	−0.17975	−0.17647	−0.17471	−0.17147	−0.17216	−
N11	−0.84167	−0.84403	−0.85638	−0.87076	−0.88013	−
H12	0.23630	0.27921	0.28054	0.22692	0.22765	−
H13	0.24574	0.22713	0.22774	0.23053	0.22943	−
H14	0.24523	0.22997	0.23247	0.29558	0.29032	−
H15	0.22086	0.20377	0.20338	0.21133	0.20896	−
H16	0.21553	0.25894	0.25852	0.20730	0.20628	−
H17	0.21250	0.21861	0.21855	0.21063	0.21067	−
H18	0.21443	0.20878	0.20912	0.20998	0.21471	−
H19	0.23457	0.19838	0.19838	0.21871	0.21653	−
H20	0.22006	0.19693	0.19742	0.25522	0.26627	−

TABLE II. Continued

Atom	Cation	^A IL	^A IL-CO ₂	^B IL	^B IL-CO ₂	[BF ₄] ⁻
H21	0.21526	0.24130	0.24235	0.25503	0.22318	-
H22	0.20094	0.19589	0.20497	0.20054	0.20738	-
H23	0.21524	0.24133	0.24157	0.18781	0.19170	-
H24	0.16436	0.17229	0.17368	0.16834	0.16705	-
H25	0.18832	0.17168	0.17477	0.18433	0.18599	-
H26	0.3550	0.35272	0.35744	0.39004	0.39408	-
H27	0.36816	0.35385	0.35852	0.35529	0.35817	-
F28	-	-0.58795	-0.58899	-0.58497	-0.58436	-
F29	-	-0.53967	-0.53958	-0.58687	-0.58917	-
F30	-	-0.58580	-0.58571	-0.54363	-0.54143	-
F31	-	-0.57938	-0.57888	-0.58416	-0.58078	-
B32	-	1.33093	1.33156	1.33484	1.33664	-
C33	-	-	1.00935	-	1.02160	-
O34	-	-	-0.52348	-	-0.54636	-
O35	-	-	-0.49491	-	-0.47876	-

TABLE III. The net integral charges of the main groups

Species	[Apeim] ⁺	^A IL	^A IL-CO ₂	^B IL	^B IL-CO ₂
Ethyl	0.34280	0.32844	0.32863	0.30903	0.30956
Imidazole	0.31544	0.30354	0.30431	0.30503	0.31177
Aminopropyl	0.34174	0.32991	0.33771	0.35071	0.34129
[BF ₄] ⁻	-	-0.96187	-0.96160	-0.96479	-0.95910
CO ₂	-	-	-0.00904	-	-0.00352

Theoretically, the unit charge of isolated [Apeim]⁺ should belong to the N3 atom, but from Table III it can be seen that some of the unit positive charge disperses over the whole cation, with +0.34280 charge transferring to the ethyl, +0.34174 charge transferring to the aminopropyl group, and the remaining +0.31544 charge disperses over the imidazole ring. The unit negative charge disperses over the whole [BF₄]⁻, which leads to an increase in the net negative charges of the F atoms (see Table II), which is beneficial for the HBs.

It could be observed from the charge data of the isolated ions and ^AIL in Table III that the negative charge of [BF₄]⁻ becomes -0.96205 when ^AIL is formed; in other words, the unit negative charge of [BF₄]⁻ disperses over the whole ^AIL, with -0.03813 electrons transferring from [BF₄]⁻ to [Apeim]⁺, which results in the positive charges of imidazole, ethyl and aminopropyl decreasing by 0.01190, 0.01436 and 0.01183, respectively. Additionally, the atomic positive charges in ^AIL must decrease and the atomic negative charges must increase after receiving the electrons coming from [BF₄]⁻. The atomic charges given in Table II suggest that most of the atomic charges changes accord with the above theoretical deduction, yet some deviate. For example, the atomic positive charge of C2, H12, H16, H17, H21, H23 and H24 are increased by 0.02884, 0.04291,

0.04341, 0.00611, 0.02604, 0.02609 and 0.00793, respectively, the atomic negative charge of C7, C8 and C10 are decreased abnormally by 0.0080, 0.0011 and 0.0033, respectively. These abnormal atomic charge changes imply that the unit positive charge of $[Apeim]^+$ must redistribute together with the dispersing of the unit negative charge of $[BF_4]^-$. Furthermore, the charge dispersion and distribution may have some influence on the interactions between the ion-pair, as well as between IL and CO_2 , which will be discussed in the next paragraph.

It is obvious that $F31 \cdots C2$ is a very weak chemical bond and the bond length of the five $C-H \cdots F$ HBs in ${}^A\text{IL}$ are much longer than that of a normal $C-H \cdots F$ HB (about 0.163 nm), which means that each of the hydrogen-bonding energy in ${}^A\text{IL}$ should be smaller than that of a normal $C-H \cdots F$ HB (about 28 kJ mol^{-1}), whereas it is directly opposite. All these extraordinary phenomena may be due to the electrostatic attraction force between the ion-pair. The atomic charge of F in isolated $[BF_4]^-$ is -0.58339 (Table II), which is so large that it can easily form a strong HB. Moreover, the charges of F28 and F30 in ${}^A\text{IL}$ become -0.58795 and -0.58580 ; the atomic positive charges of H12, H16 and H21 change from 0.23630 to 0.27921, from 0.21553 to 0.25894 and from 0.21526 to 0.24130, respectively. Both the increasing of negative charge of the F atom and the positive charges of the H atoms are propitious to strengthening the electrostatic attraction between F and H, so the hydrogen-bonding energies of the five HBs are far beyond those of normal HBs. The strengthened electrostatic attraction force is displayed as HBs and it is the reason of the involvement of F28 and F30 in two HBs simultaneously. Additionally the atomic negative charge of F31 (-0.57938) in ${}^A\text{IL}$ is slightly smaller than in a single $[BF_4]^-$, but it is enough to form an HB, and the positive charge of H23 becomes larger (from 0.21524 to 0.24133), therefore, $F31 \cdots H23-C9$ can be formed. Overall, all the atomic positive charges of H involved in HB formation are increased, which is beneficial to reinforce the interaction forces between the ion-pair and stabilize the IL system.

The atomic charge changes caused by charge dispersion and redistribution can also explain the abnormal shortening of the $C2-N1$ and $C2-N3$ bonds. Both the atomic positive charge of C2 (changes from 0.29607 to 0.32491) and the atomic negative charges of N1 (changes from -0.34404 to -0.35775) and N3 (changes from -0.35099 to -0.36037) contribute to the strengthening of the $C2-N1$ and $C2-N3$ bonds, and the strengthening effect exceeds the weakening effect caused by the "electron transfer effect". Thus, the comprehensive result is that $C2-N1$ and $C2-N3$ bonds are strengthened. In addition, some of the other normal chemical bonds are either strengthened or weakened because of the atomic charge changes, but these changes are not remarkable.

${}^A\text{IL}$ is the main geometry and ${}^A\text{IL}-CO_2$ is the main product of CO_2 capture by IL. Thus in this part, ${}^A\text{IL}-CO_2$ is taken as an example to discuss the charge distributions and their consequences for CO_2 capture by ${}^A\text{IL}$.

Table III shows that -0.00904 electrons transfer from ${}^{\text{A}}\text{IL}$ to CO_2 when ${}^{\text{A}}\text{IL}$ combines with CO_2 . The charge change of $[\text{BF}_4]^-$ is only -0.00027 . In other words, the -0.00904 electron mostly comes from $[\text{Apeim}]^+$, which should theoretically result in increasing atomic positive charges or decreasing atomic negative charges in $[\text{Apeim}]^+$. However, the atomic negative charges of N3, C4, C5, C9 and N11 are somewhat increased and the atomic positive charge of H15, H16, H17 and F28 are somewhat decreased (Table II). Hence, the charge must redistribute over the whole ${}^{\text{A}}\text{IL}-\text{CO}_2$ system for a secondary time during the process of ${}^{\text{A}}\text{IL}$ combination with CO_2 , which results in some changes in the atomic charges in $[\text{Apeim}]^+$ and the second charge redistribution contributes further to reinforcement of the absorptive interaction force. For instance, the atomic negative charge of N11 is increased by -0.00124 , the positive charge of C33 (1.00935) is greater than that of the C atom (0.99076) in an isolated CO_2 molecule. Both these atomic charge changes on N11 and C33 are beneficial to the electrostatic attraction force between the two atoms. The atomic charge of H22 changes from 0.19589 to 0.20497, and the atomic charge of O34 (-0.52348) is greater than that of an isolated CO_2 molecule; thus the reinforced electrostatic attraction between O34 and H22 reinforce the combination interactions between ${}^{\text{A}}\text{IL}$ and CO_2 .

The above analysis suggests that the charge dispersion and redistribution are beneficial by reinforcing both the interactions between the ion-pair and the combination interaction force between ${}^{\text{A}}\text{IL}$ and CO_2 . In order to research the energy contribution of electrostatic attraction force, the orbital interaction energy of these weak chemical bonds in ${}^{\text{A}}\text{IL}$ and ${}^{\text{A}}\text{IL}-\text{CO}_2$ were calculated. The results show that the total orbital interaction energy of the six weak chemical bonds in ${}^{\text{A}}\text{IL}$ are less than 10 kJ mol^{-1} ; hence, most of the interaction energy comes from a non-orbital interaction force, which proves the prediction that electrostatic interaction force plays a dominant role in this IL system. In a word, when attempts are made to change the physical or chemical properties of an ionic liquid, the electrostatic attraction force has to be considered. The total orbital interaction energy of the two weak chemical bonds between ${}^{\text{A}}\text{IL}$ and CO_2 are 1.65 kJ mol^{-1} , *i.e.*, most of the interaction energy between ${}^{\text{A}}\text{IL}$ and CO_2 is non-orbital interaction energy and electrostatic attraction may play a dominant role in CO_2 capture by ${}^{\text{A}}\text{IL}$. Thus, this is a further evidence that CO_2 capture by ${}^{\text{A}}\text{IL}$ is a physical absorption process and the interactions between ${}^{\text{A}}\text{IL}$ and CO_2 are strong intermolecular interactions. Therefore, in future studies, it is vital that a series of research on how to influence the charge distribution be realized, which could aid in the design of functionalized ILs to satisfy the set requirements.

Electronic density topological analyses

Based on the Bader¹³ theory of Atoms in Molecules (AIM), if there is a bond critical point (BCP) between two atoms in a molecule, they must form a chemi-

cal bond. The values $\rho(r_c)$ (the electron density at the BCP), $\nabla^2\rho(r_c)$ (Laplacian value of the electron density) and ε (the ellipticity value of a bond) are used to characterize the properties of a bond. The larger the $\rho(r_c)$ value, the stronger is the bond. A $\nabla^2\rho(r_c)$ value close to zero means a weak bond; a $\nabla^2\rho(r_c)$ value less than zero means a covalent bond, and the smaller the $\nabla^2\rho(r_c)$ value, the stronger is the covalence of the bond; a $\nabla^2\rho(r_c)$ value larger than zero suggests an ionic bond, and the larger the $\nabla^2\rho(r_c)$ value, the stronger is the ionic nature of the bond. The ε value is used to characterize the σ or π nature of a bond, the greater the ε value, the more obvious is the π character of the bond; conversely, the σ character of the bond is stronger. In this section, the AIM theory was employed to analyze further the characteristics of the interaction between the ion-pair and between the IL and CO₂.

The AIM molecular graphs of ILs and ILs-CO₂ are drawn by AIM200 program package (Fig. 3), the little red dots between two atoms represent the BCPs, the bond parameters at the BCPs were calculated and are listed in parentheses beside the little red dots, and they are ρ values, $\nabla^2\rho(r_c)$ values and ε values from the top down. In this section, the electron density topological theory was applied in discussing and predicting the interaction characteristics in the IL, as well as the absorption characteristics between the IL and CO₂.

As shown in the AIM structure of ^AIL, the BCPs of the five HBs prove their formation. According to their $\rho(r_c)$ values, the bond strength order is F28...H12-C2 > F30...H12-C2 > F30...H16-C6 > F28...H21-C8 > F31...H23-C9, which agrees with the conclusion drawn from the bond lengths. The $\rho(r_c)$ values of F28...H12-C2 and F30...H12-C2 are greater than 0.015, indicating two strong H-bonds; the $\rho(r_c)$ values of the other three HBs are about 0.01, which indicates they are normal HBs. All the $\nabla^2\rho(r_c)$ values of these five HBs are close to zero and their ε values at the BCPs are very small; thus, the five HBs are weak chemical bonds of typical σ bond characteristics. The $\rho(r_c)$ and $\nabla^2\rho(r_c)$ values of F31...C2 are 0.0100 and 0.0400, respectively, hence F31...C2 is a weak chemical bond. However F31...C2 has some π characteristics as indicated by its larger ε value (0.9127). It could be predicted that the π electrons on C2 and F31 contribute a great deal to the F31...C2 bond. The AIM analysis proved that the interaction forces between the ion-pair are weak chemical bonds, with electrostatic attraction playing dominant role in reinforcing the interaction forces.

Two new BCPs between O34 and H22, as well as between C33 and N11 in the AIM geometry of ^AIL-CO₂ confirmed the formation of O34...H22-C9 and C33...N11 bonds. The $\rho(r_c)$ value of the C33...N11 bond is 0.0105 and that of O34...H22-C9 bond is 0.0059, and the $\nabla^2\rho(r_c)$ values of for these bonds are close to zero. Thus, both the $\rho(r_c)$ and $\nabla^2\rho(r_c)$ values indicate that the two bonds belong to molecular interactions and that ^AIL-CO₂ may be a bimolecular complex; therefore, the reaction of ^AIL and CO₂ is physical absorption. The

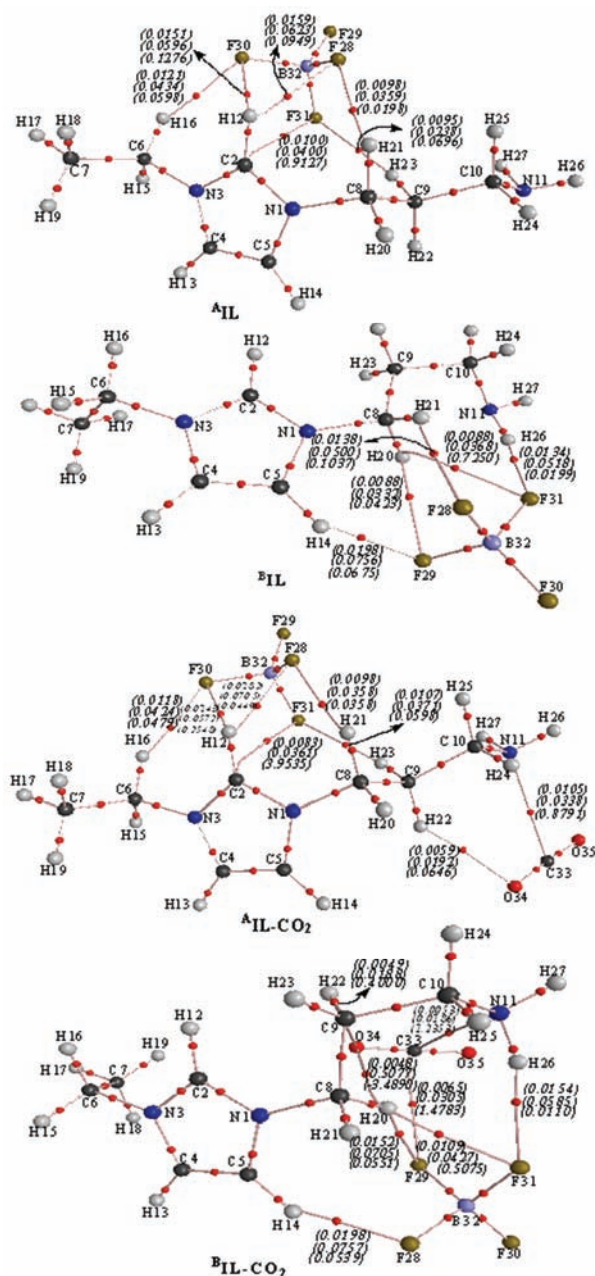


Fig. 3. AIM structures of A_{IL} , B_{IL} , A_{IL-CO_2} and B_{IL-CO_2} . The little red balls denote the BCP. Some bond parameters at the BCPs, *i.e.*, the ρ values, $\nabla^2\rho(r_c)$ values and ε values from the top down, are listed in parentheses beside the little red dots.

$O34 \cdots H22-C9$ bond has typical σ characteristics according to its ε value. The ε value of the $C33 \cdots N11$ bond (0.8791) implies greater π characteristics and it

could be inferred that π electron interactions contribute a great deal to the C33...N11 bond. In addition, the weak chemical bonds between the ion-pair in ${}^A\text{IL}-\text{CO}_2$ changed somewhat owing to geometry changes and the secondary charge redistribution effect, but the changes are negligible and have little effect on the absorbing interaction.

CONCLUSIONS

The CO_2 capture by the $[\text{Apeim}][\text{BF}_4]$ ionic liquid has been systematically discussed at the electron level and the conclusions could be summarized as follows:

1. Two stable geometries, named ${}^A\text{IL}$ and ${}^B\text{IL}$, were optimized, ${}^A\text{IL}$ is the main geometry and the interaction energy between ion-pair is nearly 360 kJ mol^{-1} . CO_2 capture by ${}^A\text{IL}$ is physical absorption and the molar absorbing ratio is 1:1, the absorbing energy is about 20 kJ mol^{-1} . Thus ${}^A\text{IL}$ may absorb CO_2 effectively and the energy consumption for its regeneration is low.

2. Electrostatic attractive forces resulting from charge dispersion and redistribution of $[\text{Apeim}]^+$ and $[\text{BF}_4]^-$ help in the stabilization of this IL system and reinforce the absorbing interaction forces between IL and CO_2 .

3. Electrostatic attractive forces play a dominant role in the interactions between the ion-pair. The main absorption mechanism is the π electron interaction between C33 and N11, and a weak hydrogen bond between CO_2 and $[\text{Apeim}]^+$.

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ИЗВОД

ИСПИТИВАЊЕ ЈОНСКЕ ТЕЧНОСТИ 1-(3-АМИНОПРОПИЛ)-3-ЕТИЛ-ИМИДАЗОЛИЈУМ-ТЕТРАФЛУОРОБОРАТА КОЈА ВЕЗУЈЕ CO_2

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1-(3-Аминопропил)-3-етил-имидазолијум ($[\text{Apeim}]^+$) тетрафлуороборат ($[\text{BF}_4]^-$) је јонска течност (IL) која везује CO_2 . Ово једињење је систематски проучавано на нивоу ВЗЛУР/6-311++G** и mp2/6-311++G**. Геометрије за IL и продукте везивања CO_2 су оптимизоване и њихове енергије одређене. Резултати показују да се интеракција између $[\text{Apeim}]^+$ и $[\text{BF}_4]^-$ углавном оставарује преко водоничних веза, али да енергија интеракције превазилази -328 kJ mol^{-1} . Даљом анализом смо нашли да је интеракција појачана дисперзијом наелектрисања и њеном редистрибуцијом, као и да електростатичко привлачење знатно доприноси енергији интеракције. Овај IL систем за везивање CO_2 спада у класу физичке сорпције са молским односом 1:1 и апсорпционом енергијом око -18 kJ mol^{-1} . Због тога би регенерација ове IL из $\text{IL}-\text{CO}_2$ захтевала малу потрошњу енергије.

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