



The electronic and topological properties of interactions between 1-butyl-3-methylimidazolium hexafluorophosphate/tetrafluoroborate and thiophene

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ARTICLE INFO

Article history:

Received 10 January 2012

Received in revised form 28 February 2012

Accepted 17 March 2012

Available online 28 March 2012

Keywords:

Ionic liquids

Thiophene

Electronic properties

Topological properties

Density functional theory

Desulfurization

ABSTRACT

Density functional calculations have been performed to explore the interactions of thiophene and two ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]⁺[PF₆][−]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]⁺[BF₄][−]). The electronic properties and topological properties of [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene were analyzed. The calculated results reveal that the dominant interactions of C2–H2...F hydrogen bonds in [BMIM]⁺[PF₆][−] or [BMIM]⁺[BF₄][−] were not destroyed by the thiophene interactions with [BMIM]⁺[PF₆][−] and [BMIM]⁺[BF₄][−]. The C–H ([BMIM]⁺)... π (thiophene) hydrogen bonds and H(thiophene)...F([PF₆][−] or [BF₄][−]) hydrogen bonds play crucial roles in the adsorption of thiophene on [BMIM]⁺[PF₆][−] and [BMIM]⁺[BF₄][−].

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1. Introduction

A modern refinery is a highly integrated industrial plant, the main task of which is to efficiently produce high yields of valuable products from the feed of crude oil with variable compositions. The crude oil is converted to products with higher values via different physical and chemical processes, such as distillation, extraction, reforming, hydrogenation, cracking, and blending. Currently, environmental restrictions regarding the quality of transportation fuels and the emissions from the refinery itself have become the most important issues. The primary goal of the recently proposed regulations is to reduce the sulfur content of transportation fuels [1]. Catalytic hydrodesulfurization (HDS) is the conventional method to remove sulfur from compounds, which requires both high temperature and high pressure of the hydrogen gas. Unfortunately, this method is not very effective for the removing of thiophene compounds and its alkylated derivatives [2]. So extraction of sulfur-containing compounds from the fuels under mild conditions with ionic liquids is proposed.

It has been found that ionic liquids can effectively remove a large amount of S-containing compounds from fuels, such as thiophene and methylthiophene [3–18]. Among the many types

of ionic liquids studied, those based on imidazolium cations and BF₄[−] or PF₆[−] anions showed high efficiency for the extraction of compounds containing organic sulfur as well as organic nitrogen. Recent efforts have been made using theoretical methods to model ionic liquids. The quantum chemical based COSMO-RS was used to predict the non-ideal liquid phase activity coefficient for mixtures containing 1-ethyl-3-methyl imidazolium thiocyanate [EMIM][SCN], thiophene, quinoline, pyridine, indoline, pyrrole, and water [19]. Kumar and Banerjee used the COSMO-RS predictions to evaluate the performance of 264 possible cation–anion pairs in the removal of thiophene from diesel oil [20]. The simultaneous separation of thiophene and pyridine from isooctane were investigated by the non-random two liquid (NRTL) and Universal QUASi-Chemical (UNIQUAC) models with 1-ethyl-3-methylimidazolium acetate [EMIM][OAc], 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][EtSO₄], and 1-ethyl-3-methylimidazolium methylsulfonate [EMIM][MeSO₃] as green solvents [21]. Aznar et al. used the UNIQUAC model to correlate the liquid–liquid equilibrium (LLE) of fifty ternary systems involving twelve different ionic liquids with the activity coefficient [22]. Molecular dynamics simulations of solutions of benzene in dimethylimidazolium chloride and dimethylimidazolium hexafluorophosphate have been performed to explain the better solubility of aromatic compounds compared to aliphatic compounds in the ionic liquids of dimethylimidazolium [23]. Extraction of thiophene or pyridine from *n*-heptane using ionic liquids was modeled

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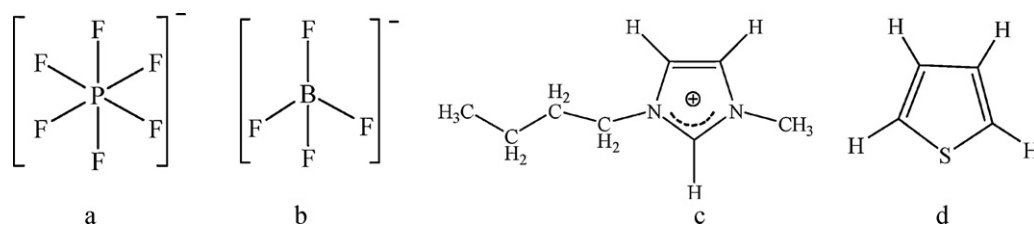


Fig. 1. The initial structures of (a) PF_6^- , (b) BF_4^- , (c) $[\text{BMIM}]^+$ and (d) thiophene.

by both NRTL and UNIQUAC approaches to correlate with the experimental results [24]. Quantum chemical calculations including natural bond orbital (NBO) analyses have also been carried out to investigate the simultaneous interactions of thiophene and pyridine with different ionic liquids, including 1-butyl-1-methyl pyrrolidinium tetrafluoroborate ($[\text{Pyr14}][\text{BF}_4]$), 1-butyl-1-methyl pyrrolidinium hexafluoro-phosphate ($[\text{Pyr14}][\text{PF}_6]$), 1-butyl-4-methyl pyridinium tetrafluoroborate ($[\text{BPY}][\text{BF}_4]$), 1-butyl-4-methylpyridinium hexafluorophosphate ($[\text{BPY}][\text{PF}_6]$) and 1-benzyl-3-methylimidazolium tetrafluoroborate ($[\text{BeMIM}][\text{BF}_4]$) [25]. Zhang et al. employed multinuclear NMR spectroscopy and ab initio calculations to study the interactions between thiophene and the ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}]^+[\text{PF}_6]^-$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}]^+[\text{BF}_4]^-$) [5,26]. In their studies, five clusters have been optimized, including thiophene interacting with anion (thiophene- PF_6^- , thiophene- BF_4^-), thiophene interacting with cation (thiophene- BMIM^+) and the neat ionic liquid ($[\text{BMIM}]^+[\text{PF}_6]^-$, $[\text{BMIM}]^+[\text{BF}_4]^-$). The optimized structures show that the anions of the ionic liquids are situated outside the ring plane of the thiophene, with the fluorine atoms interacting with the hydrogen atoms of the thiophene. On the other hand, the cations of the ionic liquids approach the thiophene with their positively charged atoms approaching the negatively charged atoms of thiophene. But the interactions of thiophene with cation–anion pairs of ionic liquids were neglected. Therefore, it is significant to investigate the simultaneous interactions between thiophene and the cation of 1-butyl-3-methylimidazolium ($[\text{BMIM}]^+$) and the anions of $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$.

The aim of the present work is to study the interactions of thiophene with the cation–anion pair of $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$ by means of density functional approach. The electronic and topological properties of $[\text{BMIM}]^+[\text{PF}_6]^-$ –thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ –thiophene were highlighted.

2. Specification of initial geometries

The structures of PF_6^- and BF_4^- anions, $[\text{BMIM}]^+$ cation, and thiophene molecule are shown in Fig. 1. Different initial structures of $[\text{BMIM}]^+[\text{PF}_6]^-$ –thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ –thiophene have been designed for optimization. Firstly, the possible π (imidazolium)– π (thiophene) interaction was considered with the anions of $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ arranged in different positions. Secondly, the optimized structures of thiophene– $[\text{PF}_6]^-$ and thiophene– $[\text{BF}_4]^-$ were used and the $[\text{BMIM}]^+$ cation was arranged around them at different positions [26]. Thirdly, $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ was placed around the optimized structure of thiophene– $[\text{BMIM}]^+$ [26]. Lastly, thiophene interactions with optimized $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$ were designed [26–31].

3. Computational details

All the density functional theory (DFT) calculations were performed with the package DMol³ [32,33]. This method uses fast convergent three-dimensional numerical integrations to calculate

the matrix elements occurring in the Ritz variation method. The double numerical basis sets plus polarization functional (DNP) was adopted. For the exchange correlation term of the energy functional, the generalized gradient corrected functional GGA and PW91 functional [34] were used for all the geometry optimizations, which are proved quite accurate in different situations, including the hydrogen-bonded systems. Although PW91 functional is unable to provide a good description of dispersion interactions, GGA/PW91/DNP can give good results of interactions between conjugated systems [35]. All the stationary structures in the gas phase have been fully optimized without geometrical constraints. Each stationary point was checked by computing the vibrational frequencies to make sure that the optimal geometries were minima without imaginary frequency. All the calculations employed a method based on Pulay's direct inversion of iterative subspace (DIIS) technique to accelerate the SCF convergence. The NBO analysis was obtained with 6-31++G** basis set to provide information of hydrogen bonding and halogen bonding [36]. In the NBO analysis, the second order perturbation stabilization energy $E(2)$ associated with the delocalization of $i \rightarrow j$ is estimated as

$$E(2) = \Delta E_{ij} = n_i \frac{(F_{ij})^2}{\varepsilon_j - \varepsilon_i}$$

where n_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements, and F_{ij} is the off-diagonal NBO Fock matrix element. Atoms in molecules (AIM) analyses were computed by AIM2000 to provide topological properties [37,38].

DMol³ uses numerical functions that are far more complete than traditional Gaussian functions, and therefore we expect BSSE contribution to be small [39]. The interaction energies between $[\text{BMIM}]^+[\text{PF}_6]^-$ / $[\text{BMIM}]^+[\text{BF}_4]^-$ and thiophene were defined as the following expression:

$$\Delta E = E([\text{BMIM}]^+[\text{PF}_6]^- / [\text{BMIM}]^+[\text{BF}_4]^- - \text{thiophene}) - [E([\text{BMIM}]^+[\text{PF}_6]^- / [\text{BMIM}]^+[\text{BF}_4]^-) + E(\text{thiophene})]$$

where $E([\text{BMIM}]^+[\text{PF}_6]^- / [\text{BMIM}]^+[\text{BF}_4]^- - \text{thiophene})$ represents the energies of $[\text{BMIM}]^+[\text{PF}_6]^-$ –thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ –thiophene, $E([\text{BMIM}]^+[\text{PF}_6]^- / [\text{BMIM}]^+[\text{BF}_4]^-)$ and $E(\text{thiophene})$ the individual energies of $[\text{BMIM}]^+[\text{PF}_6]^-$ or $[\text{BMIM}]^+[\text{BF}_4]^-$ and thiophene, and ΔE is the interaction energies between $[\text{BMIM}]^+[\text{PF}_6]^- / [\text{BMIM}]^+[\text{BF}_4]^-$ and thiophene.

4. Results and discussion

4.1. Geometric and electronic properties

The geometries of $[\text{BMIM}]^+[\text{PF}_6]^-$ –thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ –thiophene with the minimum energy were determined by performing density functional geometry optimizations and the results are displayed in Fig. 2. In the configurations of $[\text{BMIM}]^+[\text{PF}_6]^-$ –thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ –thiophene, the structural parameters of the $[\text{BMIM}]^+$ cations and thiophene rings did not change pronouncedly compared to those of isolated $[\text{BMIM}]^+$ and isolated thiophene rings, implying that the coplanar

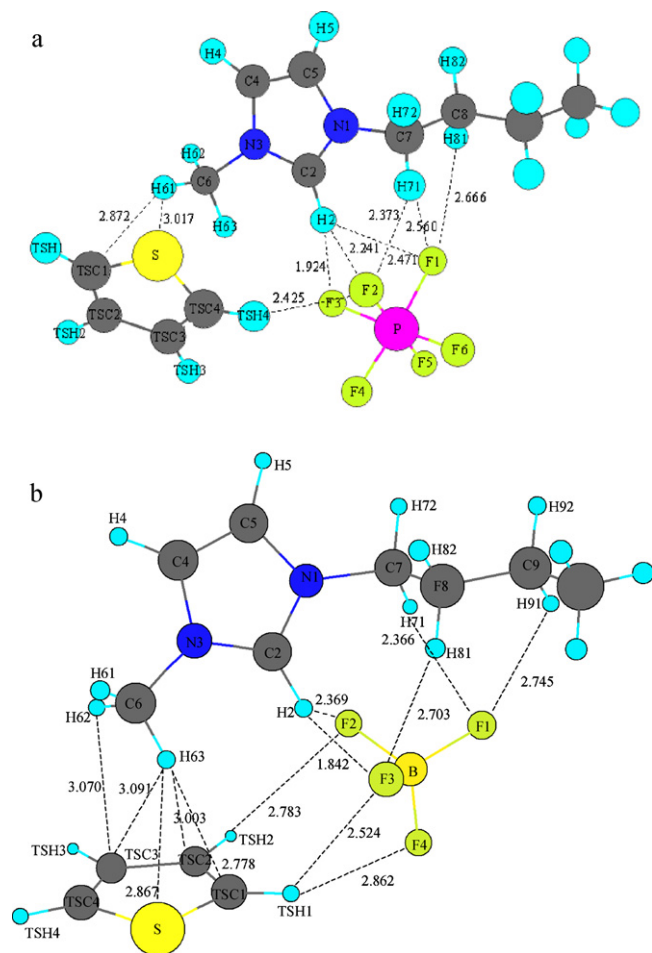


Fig. 2. The partial distances of (a) [BMIM]⁺[PF₆][−]-thiophene and (b) [BMIM]⁺[BF₄][−]-thiophene.

characteristics of the ion pairs maintain in the cation rings and thiophene rings. In [BMIM]⁺[PF₆][−]-thiophene, C6–H61 is situated above the thiophene ring with the distances of H61...S (3.017 Å) and H61...TSC1 (2.872 Å) equal to the sum of the Bondi's van der Waals radii (3.55 Å) of carbon (1.70 Å), hydrogen (1.20 Å), and sulfur (1.80 Å) approximately [40]. The F2...TSH4 distance is 2.425 Å, shorter than the sum of the Bondi's van der Waals radii of hydrogen (1.20 Å) and fluorine (1.47 Å) [35]. The bond length of C2–H2 is lengthened from 1.081 Å in isolated [BMIM]⁺ to 1.089 Å in [BMIM]⁺[PF₆][−]-thiophene due to the interactions of H2...F1 (2.471 Å), H2...F2 (2.241 Å), and H2...F3 (1.924 Å), in agreement with the principle of bond order conservation [41]. The other H...F distances below the sum of the Bondi's van der Waals radii of hydrogen and fluorine are 2.373 Å (H71...F2), 2.560 Å (H71...F1), and 2.666 Å (H81...F1). It can be that a single hydrogen atom may participate in two or three hydrogen bonds instead of one. This type of bonding is called "bifurcated hydrogen bonding (three

centered hydrogen bonding, $\text{X}-\text{H} \cdots \text{A}$ or "trifurcated hydrogen

bonding (four centered hydrogen bonding, $\text{X}-\text{H} \cdots \text{A}$) [42–44]. The results show that H71 and H2 in [BMIM]⁺[PF₆][−]-thiophene are involved in the formation of bifurcated hydrogen bonding, suggesting that C2-proton plays a crucial role in the interactions between [BMIM]⁺ and [PF₆][−]. The F...H contacts within the bifurcated hydrogen bonds are found to be unequivalent in terms

of the different F...H distances. These deviations from linearity of the C–H...F angles are common for bifurcated hydrogen bonds. In [BMIM]⁺[BF₄][−]-thiophene, the F1...H91, F1...H71, F2...H2, F2...TSH2, F3...H81, F3...H2, F3...TSH1, and F4...TSH1 distances are 2.745 Å, 2.366 Å, 2.369 Å, 2.783 Å, 2.703 Å, 1.842 Å, 2.524 Å, and 2.862 Å, respectively. The H...F contacts are near the higher end of the range of 1.84–2.87 Å, showing that C–H...F hydrogen bonds are medium or weak. Of all the H...F interactions, the H2 involved interactions are strong, in consonance with their short H...F distances and the reported dominating role of C2-proton hydrogen bonds in the interactions between cation and anion pairs [27–31,45]. Surprisingly, the H63...S, H63...TSC1, H63...TSC2, H63...TSC3, and H62...TSC3 distances are 2.862 Å, 2.778 Å, 3.003 Å, 3.091 Å, and 3.070 Å, respectively, indicating the existence of C6–H63...π interactions. Dupont et al. found that the CH=π bond is strongly responsible for the interactions of alkylbenzenes and sulfur heterocycles with the ionic liquids [46].

The NBO analysis can be employed as a useful tool for the investigation of partial charge transfer interaction within the parent compounds [25]. Based on the NBO charges, differences in the hydrogen-bonding and CH=π bonding interaction can be compared. The NBO analyses of isolated [BMIM]⁺, [PF₆][−], [BF₄][−], thiophene, [BMIM]⁺[PF₆][−]-thiophene, and [BMIM]⁺[BF₄][−]-thiophene were performed. According to the NBO analysis, the net NBO charges of [PF₆][−] (−0.95361) and thiophene (−0.00715) in [BMIM]⁺[PF₆][−]-thiophene suggest electron transfer from the [PF₆][−] anion to the [BMIM]⁺ cation and thiophene, while the net NBO charges of [BF₄][−] (−0.9448) and thiophene (+0.01104) in [BMIM]⁺[BF₄][−]-thiophene demonstrate that both [BF₄][−] and thiophene give electron charges to the [BMIM]⁺ cation.

The interaction energies between [BMIM]⁺[PF₆][−]/[BMIM]⁺[BF₄][−] and thiophene are 32.22 kcal/mol and 25.82 kcal/mol, respectively, implying that the interaction between [BMIM]⁺[PF₆][−] and thiophene is stronger than that between [BMIM]⁺[BF₄][−] and thiophene, in agreement with the experimental results that the absorption capacity of [BMIM]⁺[PF₆][−] for thiophene is larger than that of [BMIM]⁺[BF₄][−] for thiophene [47].

The σ, π occupancy and linear combination of NAOs of isolated [BMIM]⁺, isolated thiophene, [BMIM]⁺[PF₆][−]-thiophene, and [BMIM]⁺[BF₄][−]-thiophene give the orbital information of the rings of [BMIM]⁺ and thiophene. The nitrogen atoms in the imidazolium ring are close to the sp² hybridization, while the C4 and C5 atoms are sp^{2.7–2.8} hybridization in both isolated [BMIM]⁺, [BMIM]⁺[PF₆][−]-thiophene, and [BMIM]⁺[BF₄][−]-thiophene. The sulfur atoms in the thiophene ring are sp^{4.33–4.43} hybridization, while the two carbon atoms linking to the sulfur atoms are sp^{2.87–2.98}. The sulfur hybridization of sp^{4.35} in isolated [BMIM]⁺ is different from the sulfur hybridization in [BMIM]⁺[PF₆][−]-thiophene (sp^{4.33} and sp^{4.42}) and [BMIM]⁺[BF₄][−]-thiophene (sp^{4.43} and sp^{4.33}). For both of the rings of [BMIM]⁺ and thiophene, five hybridization orbitals form σ bonds, and the remaining five p orbitals perpendicular to the ring plane overlap to form the delocalized bond. The occupation of the five σ bonds and two π bonds of each [BMIM]⁺ and thiophene ring is 1.97–1.99 e and 1.82–1.91 e, respectively. Significant changes have happened for the π-system occupation of thiophene in [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene, which may be ascribed to the strong interactions between thiophene and the cation–anion pair.

The extent of electron delocalization from donors to acceptors can be evaluated by analyzing the second-order perturbation stabilization energy *E*(2). The value of *E*(2) indicates the intensity of the interactions between the orbitals of electron donors and acceptors. The higher the value of *E*(2), the more electrons tend to transfer from the donor orbitals to the acceptor

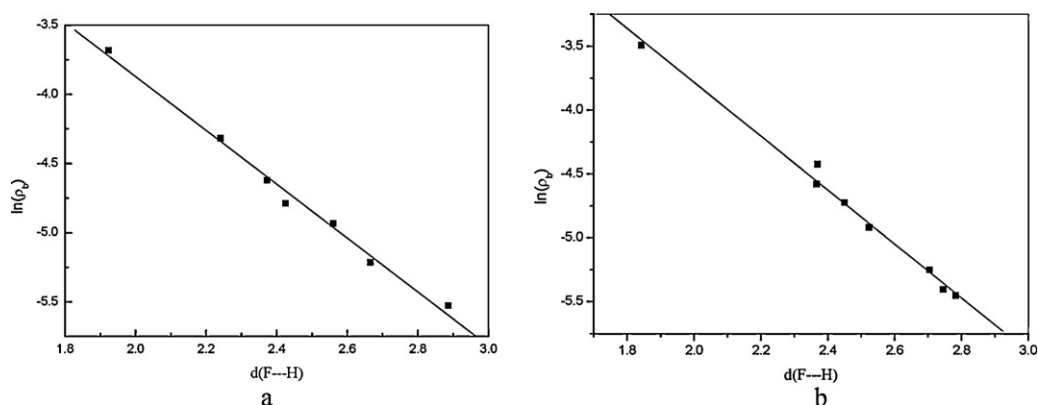


Fig. 3. Relationship between the F...H distances and their corresponding $\ln(\rho_b)$ of (a) [BMIM]⁺[PF₆][−]-thiophene and (b) [BMIM]⁺[BF₄][−]-thiophene.

orbitals. The interactions between the lone pairs of S and the orbitals of $\pi^*(\text{TSC4-TSC3})$ and $\pi^*(\text{TSC2-TSC1})$ are denoted as $\text{LP}(\text{S}) \rightarrow \pi^*(\text{TSC4-TSC3})$ and $\text{LP}(\text{S}) \rightarrow \pi^*(\text{TSC2-TSC1})$. The $E(2)$ value manifests a large extent of electron delocalization from LP(S) to the antibonds of $\pi^*(\text{TSC4-TSC3})$ and $\pi^*(\text{TSC2-TSC1})$, which is 20.87 kcal/mol, 21.34 kcal/mol for [BMIM]⁺[PF₆][−]-thiophene and 20.58 kcal/mol, 21.65 kcal/mol for [BMIM]⁺[BF₄][−]-thiophene. The large $E(2)$ values of 12.38 kcal/mol ($\text{LP}(\text{F3}) \rightarrow \sigma^*(\text{C2-H2})$) in [BMIM]⁺[PF₆][−]-thiophene and 18.88 kcal/mol ($\text{LP}(\text{F3}) \rightarrow \sigma^*(\text{C2-H2})$) in [BMIM]⁺[BF₄][−]-thiophene imply that the dominant interactions between [BMIM]⁺ and [PF₆][−] or [BF₄][−] have not been changed by the interactions between thiophene and cation-anion pairs. Therefore, the C2-proton involved hydrogen bonds are the strongest. On the other hand, interactions occur between thiophene and [PF₆][−] or [BF₄][−] as revealed by the $E(2)$ values of $\text{LP}(\text{F4}) \rightarrow \sigma^*(\text{TSC4-TSH4})$, $\text{LP}(\text{F2}) \rightarrow \sigma^*(\text{TSC4-TSH4})$ in [BMIM]⁺[PF₆][−]-thiophene, $\text{LP}(\text{F4}) \rightarrow \sigma^*(\text{TSC1-TSH1})$, $\text{LP}(\text{F3}) \rightarrow \sigma^*(\text{TSC1-TSH1})$, $\text{LP}(\text{F2}) \rightarrow \sigma^*(\text{TSC2-TSH2})$ in [BMIM]⁺[BF₄][−]-thiophene. It is also exhibited that the CH groups participate and play an important role in the interactions between the CH₃ group of [BMIM]⁺ and thiophene as shown by the interactions of $\pi(\text{TSC4-TSC3}) \rightarrow \sigma^*(\text{C6-H63})$, $\pi(\text{TSC4-TSC3}) \rightarrow \sigma^*(\text{C6-H62})$, $\sigma(\text{S-TSC1}) \rightarrow \text{RY}^*(\text{H61})$, $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{C6-H61})$, $\pi(\text{TSC2-TSC1}) \rightarrow \sigma^*(\text{C6-H61})$ in [BMIM]⁺[PF₆][−]-thiophene, and $\pi(\text{TSC1-TSC2}) \rightarrow \sigma^*(\text{C6-H63})$, $\pi(\text{TSC3-TSC4}) \rightarrow \sigma^*(\text{N3-C6})$, $\pi(\text{TSC3-TSC4}) \rightarrow \sigma^*(\text{C6-H62})$, $\pi^*(\text{TSC1-TSC2}) \rightarrow \sigma^*(\text{C6-H63})$, $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{C6-H63})$ in [BMIM]⁺[BF₄][−]-thiophene. Similar conclusions have been reported previously in 1-alkyl-3-methylimidazolium based ionic liquids and heteroaromatic compounds (nitrogen and sulfur containing heterocycles), and the crystal structures of diastereomeric salts of mandelic acid and its analogs [46,48]. The CH- π interaction is similar to hydrogen-bond in nature, and has been evidenced by ab initio calculations and NMR experiments [49,50]. Based on the calculations, the HOMO (highest occupied molecular orbital) of both [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene are mainly derived from the HOMO of thiophene spreading over its ring, while the LUMO (lowest unoccupied molecular orbital) of both [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene is composed of delocalized orbitals of imidazolium rings.

4.2. Topological properties of interactions

The interactions can be successfully investigated by means of topological properties of electron density distribution $\rho(r)$ which were analyzed by AIM2000. According to Bader's topological AIM theory [51], the chemical bonds can be illustrated in terms of the total electronic density $\rho(r)$ and its corresponding Laplacian,

$\nabla^2 \rho(r)$. It has been proposed that the great differences in the topological features of the electron density reflect the profound interactions between cations and anions [52,53]. Rozas et al. found that the bifurcated hydrogen bonds are energetically weaker than the typical hydrogen bonds according to the AIM theory [42]. The electron density is shared by two H...Y contacts showing two H...Y bond paths. In terms of the criterion of hydrogen bonding ($\rho_{\text{BCP}} = 0.002\text{--}0.035$ a.u., $\nabla^2_{\text{BCP}} = 0.024\text{--}0.139$ a.u.) [54], there are nine hydrogen bonds in [BMIM]⁺[PF₆][−]-thiophene and ten hydrogen bonds in [BMIM]⁺[BF₄][−]-thiophene. The Laplacian ∇^2_{BCP} of the bond critical points is positive, demonstrating a nature of closed shell interactions. The large values of electronic density and Laplacian of F3...H2 in [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene are consistent with the short distance of their hydrogen bonds, showing a close relationship between the topological properties of the charge density and the internuclear distances of the hydrogen-bonded systems [53]. The different topological properties of ring critical points in isolated [BMIM]⁺, isolated thiophene, [BMIM]⁺[PF₆][−]-thiophene, and [BMIM]⁺[BF₄][−]-thiophene reflect the interactions between [BMIM]⁺, thiophene, and [PF₆][−] or [BF₄][−]. The interactions between the C-H bond and thiophene ring in [BMIM]⁺[PF₆][−]-thiophene and [BMIM]⁺[BF₄][−]-thiophene are proved by their topological properties, including the S...H61 bond critical point ($\rho = 0.00602$, $\nabla^2 = 0.02116$), TSC1...H61 bond critical point ($\rho = 0.00597$, $\nabla^2 = 0.01918$), thiophene ring...H61 cage critical point ($\rho = 0.00415$, $\nabla^2 = 0.01681$) in [BMIM]⁺[PF₆][−]-thiophene, S...H63 bond critical point ($\rho = 0.00756$, $\nabla^2 = 0.02565$), TSC3...H62 bond critical point ($\rho = 0.00466$, $\nabla^2 = 0.01445$), and H62-H63-TS cage critical point ($\rho = 0.00439$, $\nabla^2 = 0.01762$) in [BMIM]⁺[BF₄][−]-thiophene. Formation of bifurcated hydrogen bonds are proposed since the hydrogen atoms are involved in a double interactions with the fluorine atoms from [PF₆][−] or [BF₄][−]. The topological properties of various F-H bonds also confirmed the above conclusions considering the F1...H71 bond critical point ($\rho = 0.00720$, $\nabla^2 = 0.03292$), F2...H71 ($\rho = 0.00985$, $\nabla^2 = 0.03880$), F1-H71-F2 ring critical point ($\rho = 0.00641$, $\nabla^2 = 0.03276$), F2...H2 bond critical point ($\rho = 0.01333$, $\nabla^2 = 0.05398$), F3...H2 ($\rho = 0.02517$, $\nabla^2 = 0.07712$), F2-H2-F3 ring critical point ($\rho = 0.01249$, $\nabla^2 = 0.05915$) in [BMIM]⁺[PF₆][−]-thiophene, F2...H2 bond critical point ($\rho = 0.01199$, $\nabla^2 = 0.05574$), F3...H2 bond critical point ($\rho = 0.03038$, $\nabla^2 = 0.09333$), and F2-H2-F3 ring critical point ($\rho = 0.01155$, $\nabla^2 = 0.05935$) in [BMIM]⁺[BF₄][−]-thiophene. It should be noted that the H2 involved bifurcated hydrogen bond is pronouncedly stronger than the H71 involved one in [BMIM]⁺[PF₆][−]-thiophene in terms of the electron density of bond critical points and the short F...H distances.

AIM theory can not only localize the critical points nature of interactions, but also describe the strength of interactions (especially of hydrogen bonds) with the electron density [42,55]. An exponential dependence on $d(\text{H} \cdots \text{O})$ is observed for the values of the second derivatives of ρ at the BCPs of hydrogen bonds, which are provided by the three eigenvalues of $\lambda_1(\text{BCP})$, $\lambda_2(\text{BCP})$, and $\lambda_3(\text{BCP})$ of the Hessian matrix [56,57]. Relationships between the distances of $d(\text{F} \cdots \text{H})$ and their corresponding $\ln(\rho_b)$ have been established. Fig. 3 displays the plots of the distances of $d(\text{F} \cdots \text{H})$ versus their corresponding $\ln(\rho_b)$. The linear correlation coefficients of $[\text{BMIM}]^+[\text{PF}_6]^-$ -thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ -thiophene are 0.996 and 0.995, respectively, exhibiting the dependence of the hydrogen bonding strength on their distances. The topological parameters derived from AIM theory may be applied to estimate the hydrogen bond strength.

5. Conclusions

Density functional theory has been carried out to calculate the interactions between thiophene and $[\text{BMIM}]^+[\text{PF}_6]^-$ or $[\text{BMIM}]^+[\text{BF}_4]^-$. The electronic and topological properties of the most stable $[\text{BMIM}]^+[\text{PF}_6]^-$ -thiophene and $[\text{BMIM}]^+[\text{BF}_4]^-$ -thiophene were obtained by means of NBO and AIM analyses. It is found that the cation-anion-thiophene interactions give rise to changes of hybridization and occupancy in terms of the σ , π occupancy and linear combination of NAOs of isolated $[\text{BMIM}]^+$, isolated thiophene, $[\text{BMIM}]^+[\text{PF}_6]^-$ -thiophene, and $[\text{BMIM}]^+[\text{BF}_4]^-$ -thiophene. The C2-proton involving in the formation of hydrogen bonds play an important role in the $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$. The dominant interactions of the C2–H2 \cdots F hydrogen bonds between $[\text{BMIM}]^+$ and $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ were not altered by the adsorption of thiophene on the $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$. Therefore, it is of significant importance to investigate the interactions between thiophene and the cation-anion pairs of $[\text{BMIM}]^+[\text{PF}_6]^-$ or $[\text{BMIM}]^+[\text{BF}_4]^-$. The C–H($[\text{BMIM}]^+$) $\cdots\pi$ (thiophene) hydrogen bonds play a very distinct part in the interactions between $[\text{BMIM}]^+$ and thiophene. Similarly, the H(thiophene) \cdots F($[\text{PF}_6]^-$ or $[\text{BF}_4]^-$) hydrogen bonds are also crucial interactions between thiophene and anions, giving rise to strong adsorption of thiophene on $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$. Linear relationships have been established between the distances of $d(\text{F} \cdots \text{H})$ and corresponding $\ln(\rho_b)$.

Acknowledgments

The authors gratefully acknowledge financial support from the Natural Science Foundation of China (51103179, 20706060) and the Important Project of Science and Technology in Developing Great Oil & Gas Field and Coal Bed Gas (2011ZX05051).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jmkgm.2012.03.005](https://doi.org/10.1016/j.jmkgm.2012.03.005).

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