Theoretical investigation of the interaction between aromatic sulfur compounds and [BMIM]+[FeCl4]− ionic liquid in desulfurization: A novel charge transfer mechanism

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ABSTRACT

In this work, interaction nature between a group of aromatic sulfur compounds and [BMIM]+[FeCl4]− have been investigated by density functional theory (DFT). A coordination structure is found to be critical to the mechanism of extractive desulfurization. Interaction energy and extractive selectivity follow the order: thiophene (TH) < dibenzothiophene (DBT) ≈ benzothiophene (BT). Alkylation of TH or BT (e.g. 3-methylthiophene, and 3-methylbenzothiophene) leads to a stronger interaction with ionic liquid, but steric hindrance effects of some alkylic derivatives (e.g. 2,7-dimethylbenzothiophene) lead to a weaker interaction with ionic liquid. The mechanism of extractive desulfurization is attributed to the charge transfer effect. During extractive desulfurization, electrons on aromatic sulfur compounds transfer into the Lewis part of ionic liquid, namely, [FeCl4]−. Furthermore, it is better to consider the Lewis acidity of Fe-containing ionic liquid by the whole unit (such as [FeCl4]− and aromatic sulfur compounds (X)) rather than only Fe or S atom.

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1. Introduction

Ionic liquids (ILs) offer high-potential solutions to a broad range of applications. The large number of cations and anions that can be combined to afford low melting salts suggests the feasibility of designing a suitable liquid for specific task [1]. One application of ILs in green chemistry is desulfurization from fuels or aqueous media [2]. It is well known that paraffinic sulfur-containing compounds, including thiols, thioethers, and disulfuids, can be readily removed by the conventional hydrodesulfurization (HDS) process, but aromatic sulfur compounds, such as thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT) and their alkylic derivatives are hardly removed by the HDS process [2]. Recently, tremendous works show that ILs can efficiently remove the aromatic sulfur compounds [3–10] as compared to the conventional HDS process. The flexible combination of cations and anions makes ILs to be easily

functionalized. However, its flexibility also indicates a complexity for designing the so called functionalized ILs without theoretically understanding the interaction nature between ILs and other molecules.

In order to reach a deep understanding of the interaction between aromatic sulfur compounds and ILs, many theoretical works are attempted to disclose the mechanism of extractive desulfurization. Zhang et al. [11] studied the interaction nature between TH and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]+[PF6]−) as well as 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]+[BF4]−). Results have demonstrated that the TH molecule interacts with ILs mainly via electrostatic attraction. However, Wang et al. [12] believed that the hydrogen bond played a crucial role in the extraction of TH for above systems. It was suggested that CH-π interaction was the dominant interaction in N-butylpyrdinium tetrafluoroborate ([BPY]+[BF4]−) ionic liquid for extractive desulfurization (EDS) [13]. However, Wang et al. [14] found that both hydrogen bonding and π–π interactions played an important role between TH, BT, DBT and [BPY]+[BF4]− ionic liquid. Moreover, hydrogen bonding and π–π

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interactions were proposed to be the dominant interactions during the removal of aromatic sulfur compounds in other ILs systems, such as *N*-butylpyridinium nitrate ([BPY]$^+$[NO$_3$]$^-$), [15] 1-methyl-3-methylimidazolium methyl sulfate ([MMIM]$^+$[MeSO$_4$]$^-$), [16] 1-methyl-3-octylimidazolium tetrafluoroborate ([C$_8$MIM]$^+$[BF$_4$]$^-$) [17]. The π–π interaction mechanism has been also widely accepted in experimental fields [18–22]. In summary, theoretical works show different EDS systems may have different mechanisms.

Recently, Fe-containing ILs, a kind of Lewis acidic extractant, have been attracted more attentions due to the high extractive efficiency [23–27]. Ko et al. found that the extractive ability increased with an increasing molar ratio of FeCl$_3$/[imidazolium]Cl [23]. They also suggested that the extractive ability of the Fe-containing ILs depended on the combined effects of Lewis acidity and fluidity. In addition, interaction between ethanethiol and Fe-containing ILs for desulfurization of natural gasoline has been studied by DFT [24]. Results show that the high desulfurization performance is due to a Dewar–Chatt–Duncanson-like mechanism of electron donation–backdonation among ethanethiol and [Fe$_2$Cl$_7$]$^-$ when there is an excess of FeCl$_3$ in the [BMIM]$^+$[FeCl$_4$]$^-$ ionic liquid, while cation has small contribution for this EDS reaction. The superiority of the Lewis acidic ILs over neutral ILs could be also confirmed by the observations of Gao and co-workers [25]. It was suggested that Lewis acid–base interaction involved Fe^{3+} could form π-complexation bonding with aromatic sulfur compounds and thus enhanced the extraction of sulfur species for [BMIM]$^+$[FeCl$_4$]$^-$ IL [25]. The π-complexation concept comes from theoretical results on the solid sorbents, like Ag–Y and Cu–Y zeolites, which can efficiently remove sulfur compounds from transportation fuels [28–30]. Because the chemical environments is unlike the solid sorbents, (*e.g.* coordination number, charge distribution), there may be some unique characteristics existing in metal-based ILs. As far as we know there is no theoretical work to systematically investigate this "π-complexation" interaction with various aromatic sulfur compounds in metal based ILs. In addition, previous works on Fe-containing ionic liquids mainly focused on the function of [Fe$_2$Cl$_7$]$^-$ when there is an excess of FeCl$_3$ [23,24]. Nevertheless, experimental results have shown that Fe-containing ionic liquids also exhibits high extractive performance when there is no excess of FeCl$_3$ [25,26,31,32]. On the other hand, desulfurization mechanism can be also employed to understand the desulfurization selectivity for different aromatic sulfur compounds. As we know, the selectivity between different aromatic sulfur compounds, such as TH, BT, and DBT, have been investigated by experimental researchers [6]. Experimental results have shown the selectivity is DBT(> or ≈)BT > TH [22,26,33]. The selectivity order between DBT and BT mainly depends on the extractants. For example, the selectivity of DBT is higher than BT in 4-dimethylaminopyridinium-based and imidazolium-based phosphoric ILs. However, our experimental results have shown that the selectivity of BT is slightly higher than DBT in Feton-like ILs ([Et$_3$NH]$^+$[FeCl$_4$]$^-$) [26]. To date, there is no systematically theoretical study on the selectivity for removal of aromatic sulfur compounds.

In the present work, EDS mechanism between [BMIM]$^+$[FeCl$_4$]$^-$ and a group of aromatic sulfur compounds, such as TH, BT, DBT and their alkylic derivatives, will be systematically investigated. The organization of this paper is as following: First, all of the structures related to the extraction process will be studied in detail; in the second section, we focus on the relationship between interaction energy and the extractive selectivity; lastly, natural bond orbital (NBO) analysis will be employed to analyze EDS mechanism and a possible extractive mechanism will be proposed. We hope this study can give useful information to design highly efficient ILs for EDS.

2. Computational details

Ionic liquids are a challenge for computational chemistry [34–38]. Commonly used IL consists of inorganic anions and organic cations. Organic cations usually contain alkyl side chains and/or aromatic moieties with significant contribution from dispersion forces to their equilibrium structures and interaction energies [37]. Moreover, the interaction between the cation and anion is influenced significantly by dispersion forces [38,39]. Thus, computational approaches for reliable studies of ILs require not only a proper description of Coulomb and induction forces but also an accurate description of dispersion forces. Recently, Zahn et al. [37] have performed an assessment of density functional theory for ILs. It shows that traditional functional like B3LYP, without an explicit dispersion correction, should be avoided. Hence, they recommend the density functional of the Minnesota family of the M0X type with a diffusion basis set 6–31 + +G**, which can give reliable results for ILs [40]. In the current work, M06-2X density functional with the 6–31 + +G** basis set (while Fe atom is described by LANL2DZ effective core potential) [41] have been employed to study all of the structures and their properties. LANL2DZ effective core potential has been widely used to study the properties and energetics of transition metal based ILs for its good accuracy [23,42,43]. Fe atom in [BMIM]$^+$[FeCl$_4$]$^-$ IL has been demonstrated to be a low-spin state by magnetic susceptibilities experiment [44]. Hence, a low-spin state of Fe atom with S = 1/2 is used in the current system. Furthermore, thermodynamic enthalpy is used in this paper because EDS is usually operated at room temperature and pressure. The corrected temperature and pressure is 298 K and 101 kPa, respectively. The correction scheme is based on the partition function of an idea gas. The thermodynamic enthalpy is the sum of electronic energy (E_0) and thermal correction energy (H_{corr}) where the H_{corr} consists of the contributions for translation, rotation, vibration and electronic motion. Basis set superposition error (BSSE) is believed to be small at the level of M06-2X/6–31 + +G** as discussed in Ref. [37].

On the other hand, the ion pair model of ILs has been widely used to explore the interactions and properties [11,12,23,24,38]. Although ion pair is a simple model for ILs, many properties as well as mechanisms for EDS can be obtained from the ion pair model. Therefore, it is reasonable to construct an ion pair model for this current system, [BMIM]$^+$[FeCl$_4$]$^-$...X (X = TH, BT, DBT and their alkylic derivatives). Fe-containing ILs have been studied by theoretical methods [23,24]. Both of the theoretical models are based on the condition that the molar ratio of FeCl$_3$/[imidazole]Cl is greater than 1 [23,24]. However, our experimental results have shown this system possesses several drawbacks such as difficulties in separation/recovery, environmental hazards, disposal problems *etc.* [31]. On the other hand, experimental results have shown that Fe-containing ionic liquids also exhibited high performance when there is no excess of FeCl$_3$ [25,26]. Therefore, it is believed a [BMIM]$^+$[FeCl$_4$]$^-$ model based on molar ratio 1:1 (FeCl$_3$/BMIMCl) should be reasonable and optimal. In order to better understand the charge, electronic structure, and interaction nature between aromatic sulfur compounds and ILs, NBO analysis has been performed. All the calculations are used the Gaussian 09 suit of programs [45].

The interaction energy between the ion pair and aromatic sulfur compounds is calculated according to the following expression:

$$\Delta H = H_{Complex} - (H_X + H_{ILs})$$

where H_X and H_{ILs} are the individual thermodynamic enthalpy of the aromatic sulfur compounds (X = TH, BT, DBT and their alkylic derivatives) and ILs, respectively. $H_{Complex}$ is the enthalpy of the complex formed by aromatic sulfur compounds and ILs. ΔH is the interaction energy between ILs and aromatic sulfur compounds.

The value of ΔH is usually negative. And more negative of ΔH stands for stronger interaction between them.

3. Results and discussion

3.1. Structure

3.1.1. [BMIM]$^+$[FeCl$_4$]$^-$

Two configurations have been located on the basic structure of [BMIM]$^+$[FeCl$_4$]$^-$ ion pair (see Fig. 1). Structure of Fig. 1a is based on the structure of [EMIM]$^+$[FeCl$_4$]$^-$ from reference, which is re-optimized by M06-2X density functional with 6–31 + +G** basis set (while Fe atom is described by LANL2DZ effective core potential) [23]. The structure of the optimized configuration is some different from the reference. The shortest interaction distance between Cl atom and H atom from imidazolium ring is 2.77 Å while the distance is 2.58 Å from the reference. Source of the difference may come from the involved methods that the M06-2X describes the dispersion interactions more accurate than the hybrid functional B3LYP. It should be noted that only two smallest hydrogen bond distances are listed in Fig. 1. There are also other reasonable hydrogen bond lengths existing in Fig. 1a, which are 2.77 Å (for the left Cl atom), 2.86 Å (for the right Cl atom), respectively. Both two Cl atoms interact with other CH group but not the CH group (. . .N—CH—N. . .) on the imidazolium ring. In another configuration (see Fig. 1b), [FeCl$_4$]$^-$ situates over the imidazolium ring, with a shortest interaction distance of 2.69 Å with H atom. This configuration is more stable than the former by −1.23 kcal/mol. Hence, it is reasonable to use this basic structure to estimate the interaction energy between ILs and aromatic sulfur compounds in the current work.

3.1.2. [BMIM]$^+$[FeCl$_4$]$^-$. . .X

The EDS performance of Fe-containing ILs is believed to be correlated to the Lewis acidity as mentioned above. Previous work reported a π–π interaction and hydrogen bonding model for [EMIM]$^+$[FeCl$_4$]$^-$ interacted with DBT by using the B3LYP density functional (6–31 + G* basis set, while LANL2DZ for Cl and Fe atom). This model has been employed in the current work, and a similar structure of [BMIM]$^+$[FeCl$_4$]$^-$ interacting with DBT is re-optimized (see Fig. 2a). This structure is similar with the structure from Ref. [23,24]. In Fig. 2a, the imidazolium ring is over the plane of DBT molecule which shows a π–π interaction between them. Three shortest hydrogen bonds are similar with the reference values, e.g. Cl^{24}. . .H^{29} (2.63 Å), Cl^{23}. . .H^{41} (2.67 Å), and Cl^{23}. . .H^{17} (2.85 Å). Moreover, it is interesting that a new configuration structure has been found with a coordination model (see Fig. 2b). It can be seen that the interaction comes from the sulfur atom coordinating to FeCl$_4$$^-$. After coordination, the coordination number of Fe atom increases from 4 to 5 while the previous tetrahedral configuration deforms into trigonal bipyramid. Trigonal bipyramid of Fe complexes are well accepted by coordination chemistry [46,47]. The length of the Fe—S bond in the current model is 2.52 Å (Fe^{19}. . .S^{25}) which is a typical length for Fe—S coordination bond [48–51]. It is also known that the coordination type of this interaction is found at an EDS system of FeCl$_3$ plus [EMIM]$^+$[FeCl$_4$]$^-$ [23]. The length of Fe—S bond from reference is 2.58 Å which is longer than the current systems. In order to search more configurations that would be favorable, other conformational space has been explored. Finally, another configuration has been located (Fig. 2c). There is a tilted π–π interaction combined with hydrogen bonding interaction in this configuration. The hydrogen bond lengths are Cl^{20}. . .H^{36} (2.88 Å) and Cl^{20}. . .H^{45} (2.82 Å). Furthermore, interaction energy shows that configuration of Fig. 2b is most stable among these structures (Section 3.2 in details). Therefore, it is believed this

Table 1
Interaction energies between [BMIM]$^+$[FeCl$_4$]$^-$ and aromatic sulfur compounds.

System	Interaction energy (kcal/mol)
[BMIM]$^+$[FeCl$_4$]$^-$. . .TH	−7.26
[BMIM]$^+$[FeCl$_4$]$^-$. . .2-MTH	−7.39
[BMIM]$^+$[FeCl$_4$]$^-$. . .3-MTH	−8.02
[BMIM]$^+$[FeCl$_4$]$^-$. . .3-ETH	−7.77
[BMIM]$^+$[FeCl$_4$]$^-$. . .BT	−10.19
[BMIM]$^+$[FeCl$_4$]$^-$. . .3-MBT	−10.29
[BMIM]$^+$[FeCl$_4$]$^-$. . .2,7-DMBT	−8.28
[BMIM]$^+$[FeCl$_4$]$^-$. . .DBT	−9.94

coordination configuration is critical to the EDS process and all the following calculations are based on this coordination model.

For investigating the interaction energy and comparing the selectivity between [BMIM]$^+$[FeCl$_4$]$^-$ and a series of aromatic sulfur compounds, such as thiophene (TH), 2-methylthiophene (2-MTH), 3-methylthiophene (3-MTH), 3-ethylthiophene (3-ETH), benzothiophene (BT), 3-methylbenzothiophene (3-MBT), 2,7-dimethylbenzothiophene (2,7-DMBT), all the structures of complexes are obtained at the same theoretical level. Because of the similarity of these structures, results show that these aromatic sulfur compounds locate on a similar site (see Fig. 3). Most of the aromatic sulfur compounds (e.g. DBT) can coordinate to Fe atom which leads to coordination number of Fe center increasing from 4 to 5 while the previous tetrahedral configuration deforms into trigonal bipyramid except 2,7-DMBT. All the bond lengths of Fe—S are nearly close to 2.50 Å. For example, the bond lengths for TH, 2-MTH, and 3-ETH are 2.52 Å (Fig. 3a), 2.53 Å (Fig. 3b), and 2.50 Å (Fig. 3c), respectively. The shortest bond length (2.49 Å) occurs on the interaction between BT and [BMIM]$^+$[FeCl$_4$]$^-$ while the longest bond length (2.55 Å) occurs on the interaction between 2,7-DMBT and [BMIM]$^+$[FeCl$_4$]$^-$. We note that 2,7-DMBT tends to form a tetragonal pyramid structure (see Fig. 3g). This can be ascribed to the stereo-hindrance effect that methyl groups of 2,7-DMBT prevent Fe center forming a trigonal bipyramid configuration. For the Fe—S bond lengths in alkylic derivatives of TH, such as 3-MTH (Fig. 3d) and 3-ETH (Fig. 3e), Fe—S bond lengths are shorter as compared to TH complex. While the Fe—S bond length (2.53 Å) of 2-MTH complex is slightly longer than TH complex. 3-MBT complex (Fig. 3f), and 2,7-DMBT complex (Fig. 3g), as the alkylic derivatives of BT, which show longer Fe—S bond lengths than BT complex. The longest Fe—S bond length in 2,7-DMBT complex (2.55 Å) can also be ascribed to the stereo-hindrance effect which the methyl groups prevent the S atom coordinating to Fe atom.

3.2. Interaction energy

From the point of view that the extractive performance is related to the interaction energy between ILs and aromatic sulfur compounds, hence, it is important to investigate the interaction energy between [BMIM]$^+$[FeCl$_4$]$^-$ and aromatic sulfur compounds. In addition, extractive selectivity for different aromatic sulfur compounds is also related to the interaction energy. Table 1 lists the interaction energy between them. It can be seen that the lowest interaction energy is corresponding to the extractive process of TH (−7.26 kcal/mol). Interaction energy between [BMIM]$^+$[FeCl$_4$]$^-$ and its alkylic derivatives of TH (2-MTH, 3-MTH and 3-ETH) is slightly lower than TH. The reason for this slight difference will be discussed in the section of NBO analysis. It also shows that interaction between [BMIM]$^+$[FeCl$_4$]$^-$ and BT as well as its alkylic derivatives (3-MBT, 2,7-DMBT) are stronger than [BMIM]$^+$[FeCl$_4$]$^-$. . .TH system. For example, interaction energy between [BMIM]$^+$[FeCl$_4$]$^-$ and BT is −2.93 kcal/mol lower than TH. These results show higher selectivity to BT and its derivatives. It is interesting to find that 3-MBT promote the interaction energy (−10.29 kcal/mol) while the
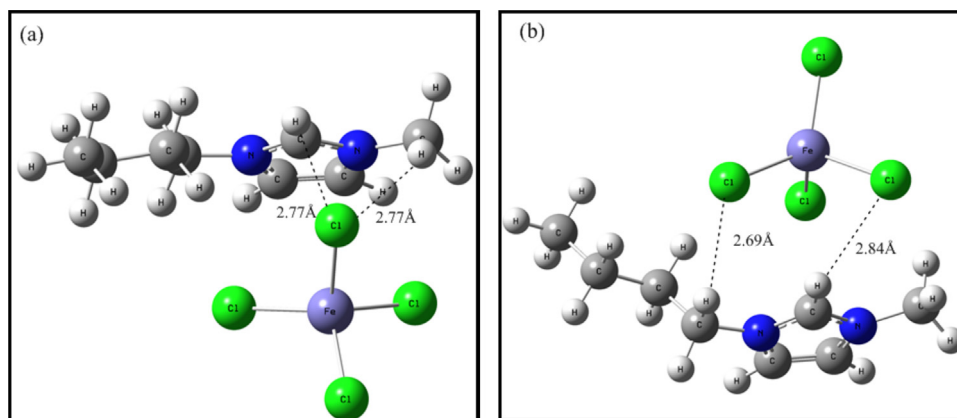
Fig. 1. Two possible configurations of [BMIM]⁺[FeCl₄]⁻ ion pair.

2,7-DMBT decreases the interaction energy into −8.28 kcal/mol. In Fig. 3g, the complex formed by 2,7-DMBT is tetragonal pyramid which is obviously different from other sulfur compounds. This can be ascribed to the steric hindrance effects [4,5,22]. Lastly, the interaction between [BMIM]⁺[FeCl₄]⁻ and DBT has also been calculated, the interaction energy is −9.94 kcal/mol which is slightly higher than BT system. It was reported that the interaction energy between [EMIM]⁺[FeCl₄]⁻ and DBT was −4.50 kcal/mol calculated by B3LYP [23]. In this work, a similar model of [BMIM]⁺[FeCl₄]⁻ based on that configuration is optimized by M06-2X method (see Fig. 2a). The interaction energy between them is −6.33 kcal/mol. The interaction energy of the new configuration (Fig. 2b) based on coordination model is −9.94 kcal/mol which shows this coordination model is stronger than the π−π interaction model by −3.61 kcal/mol. Interaction energy of another π−π interaction configuration (Fig. 2c)

is also 1.01 kcal/mol higher than the coordination configuration (Fig. 2b).

Ko et al. found that when more FeCl₃ were added into the ionic liquids, the extractive performance would improve [23]. In order to understand the higher extractive performance when the molar ratio of FeCl₃/[imidazole]Cl was greater than 1, they proposed a FeCl₃ + [EMIM]⁺[FeCl₄]⁻ model. This model was based on a coordination model. They found this model was more stable than [EMIM]⁺[Fe₂Cl₇]⁻ which demonstrated the coordination model was favorable in EDS process [23]. Moreover, Martinez-Magadan et al. also proposed a FeCl₃ + [BMIM]⁺[FeCl₄]⁻ model to investigate the interaction between ethanethiol and Fe-containing ILs for desulfurization of natural gasoline [24]. Both of their theoretical models were based on the condition that the molar ratio of FeCl₃/[imidazole]Cl was greater than 1. However, our experimental
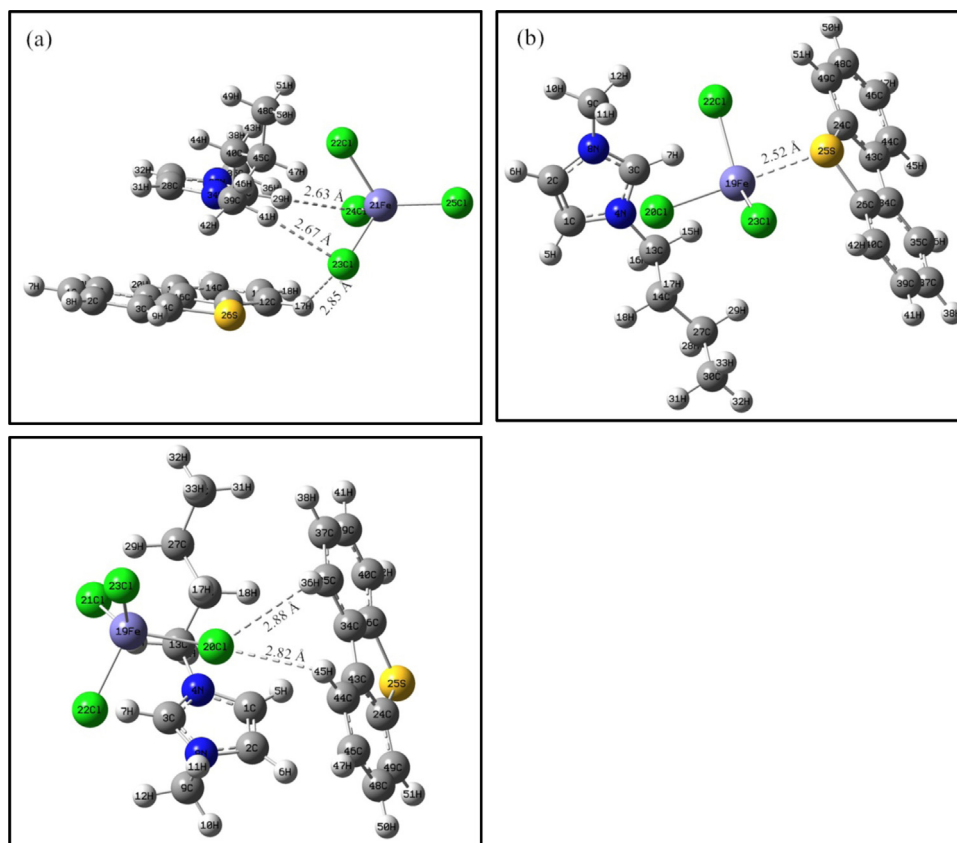

Fig. 2. Three possible configurations of [BMIM]⁺[FeCl₄]⁻ interacting with DBT. All the elements were labeled by symbol and number.
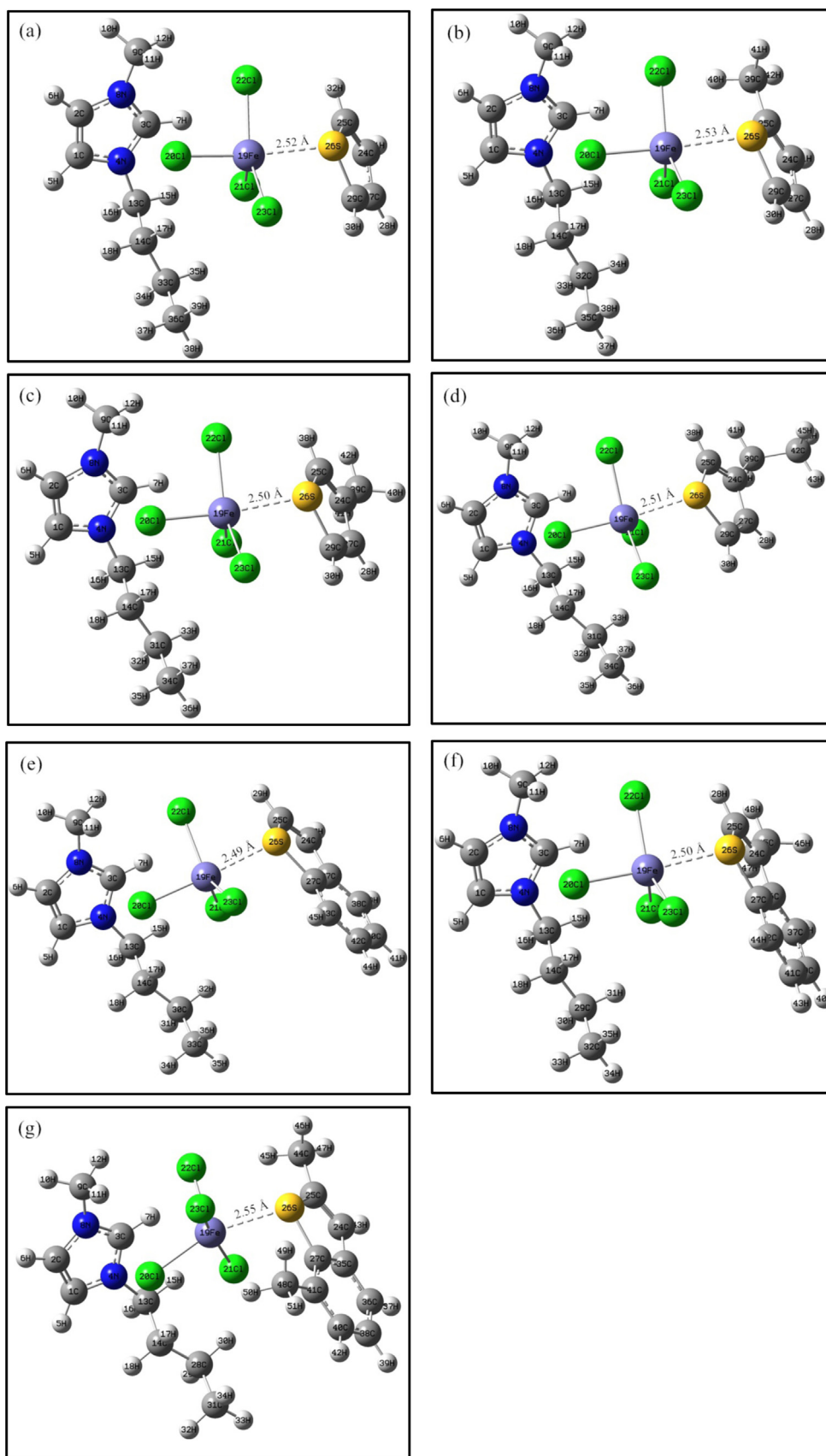
Fig. 3. Coordination type model for series aromatic sulfur compounds. Complex from (a) to (g) are: (a) TH; (b) 2-MTH; (c) 3-MTH; (d) 3-ETH; (e) BT; (f) 3-MBT; (g) 2,7-DMBT.

results have shown this system possessed several drawbacks such as difficulties in separation/recovery, environmental hazards, disposal problems *etc.* [31]. Therefore, it is believed [BMIM]$^+$[FeCl$_4$]$^-$ model based on molar ratio 1:1 should be reasonable and optimal. Besides, experimental results have shown that the presence of acidic H atom or atoms on the imidazolium ring could not promote the interaction between FeCl$_3$–[imidazolium]Cl with DBT through a hydrogen bond [23]. This is difficult to understand by a model based on π–π interaction and hydrogen bonding network model in previous works. The present coordination interaction model is almost hardly affected by the number of hydrogen bonds. This also can be an evidence of the validity for the current model.

Computational results of interaction energy can be summarized as: (a) for TH, BT and DBT, the interaction energies follow the order TH < DBT ≈ BT, thus the extractive selectivity for [BMIM]$^+$[FeCl$_4$]$^-$ follows the order TH < DBT ≈ BT; (b) the alkyl group for TH and BT may improve the interaction energy but the steric hindrance effects should also be considered. In the EDS process, the selectivity of different aromatic sulfur compounds such as TH, BT, and DBT have been investigated by experiments. Experimental results have shown the reactivity order is DBT(> or ≈)BT > TH [22,26,33]. The selectivity order between DBT and BT is mainly depended on the extractants. For example, the selectivity of DBT is higher than BT in 4-dimethylaminopyridinium-based and imidazolium-based phosphoric ILs. However, our previous experimental results have shown that the selectivity of BT is slightly higher than DBT in Feton-like ILs ([Et$_3$NHCl]FeCl$_3$) [26]. Because Fenton-like ILs [Et$_3$NHCl]FeCl$_3$ contains the FeCl$_4$$^-$ anion, this extraction chemical environment is similar with the current system. Hence, our computational results agree well with the experimental results. In most cases alkyl substitution can promote the selectivity, such as 2-MTH, 3-MTH, 3-ETH, and 3-MBT. However, with the steric hindrance effects, some type of alkyl substitution will lower the selectivity (*e.g.* 2,7-DMBT).

In order to understand this coordination interaction with traditional chemical concept, it can be interpreted by hard and soft acids and bases theory (HSAB) [52]. In the field of adsorptive desulfurization with solid sorbents, there are many works focus on the hardness of TH, BT, DBT and Fe(III) cation [53–56]. All of the results show that TH, BT, DBT are soft base while the Fe(III) cation is hard acid. Hence, according to the HSAB theory, the interaction between Fe and S atom may be a weak interaction. Interaction energies between [BMIM]$^+$[FeCl$_4$]$^-$ and aromatic sulfur compounds range from −7.26 kcal/mol to −10.29 kcal/mol in the current work, which show our results are consistent with the HSAB theory. On the other hand, as the Fe(II) cation is a bordline Lewis acid, it is hoped that Fe(II) based ILs will strongly interact with aromatic sulfur compounds by HSAB theory. Therefore, we construct an ion pair model of [BMIM]$^+$[Fe(II)Cl$_3$]$^-$ and calculate its interaction energy with TH (Fig. S1). The calculated interaction energy is −54.33 kcal/mol. Result shows that there is a strong interaction between them, which indicates that [BMIM]$^+$[Fe(II)Cl$_3$]$^-$ can serve as an efficient extractant.

It is found that Fe-containing ILs show higher extractive ability than Al-containing ILs [57]. The reason for the lower extractive ability of Al containing ILs is ascribed to be lack of d orbitals. Hence, it cannot interact with molecule that is high density of aromatic π-electrons [24]. In the current work, the structure of [BMIM]$^+$[AlCl$_4$]$^-$ interacting with TH has been optimized at the same theoretical level (Fig. S2). However, the coordination model of this complex cannot be obtained. This result shows that [AlCl$_4$]$^-$ is lack of coordination ability. Moreover, the interaction energy for this non-coordination model for [BMIM]$^+$[AlCl$_4$]$^-$ interacts with TH is −2.27 kcal/mol which is nearly 5 kcal/mol higher than [BMIM]$^+$[FeCl$_4$]$^-$. This is also an evidence of the importance of coordination interaction during extraction aromatic sulfur compounds with ILs.

3.3. NBO analysis

Because different units may have different functions during EDS, The EDS system can be divided into several units, such as [BMIM]$^+$, [FeCl$_4$]$^-$, aromatic sulfur compounds, Fe atom, and S atom. Before interaction, NBO calculation results show that [FeCl$_4$]$^-$ unit from [BMIM]$^+$[FeCl$_4$]$^-$ is negatively charged by −0.964 while [BMIM]$^+$ is positively charged (0.964). This NBO analysis gives a reasonable value that agrees well with the formula of [BMIM]$^+$[FeCl$_4$]$^-$ and traditional chemical concept. The charge of Fe atom is 0.578. This highly positive charge can be attributed to the back-donation effect from Fe atom to Cl atom. On the other hand, aromatic sulfur compounds are neutral while sulfur atom in the aromatic sulfur compounds is positively charged, for example, 0.460 in TH, 0.432 in BT, and 0.423 in DBT.

The charge distributions for different units after interaction are listed in Table 2. Aromatic sulfur compounds (X) are positively charged (Δe = 0.316–0.382) while [BMIM]$^+$[FeCl$_4$]$^-$ become negatively charged (Δe = −0.316 ∼ −0.382), correspondingly. It directly shows a charge transfer reaction is occurred during the EDS process. It seems that the whole charge for imidazolium ring unit ([BMIM]$^+$) does not change during the interactions (Δe = −0.011 ∼ −0.014). From previous works, it is believed that the extractive ability comes from the Lewis acidity of Fe species [23]. However, the π–π interaction model of ILs. . .DBT as shown in Fig. 2a is not related to a charge transfer mechanism. Because the [BMIM]$^+$[FeCl$_4$]$^-$ ion pair only gains 0.005 electron from DBT molecule. Interestingly, [FeCl$_4$]$^-$ unit gains almost all the electrons from the aromatic sulfur compounds based on the current results which demonstrates its Lewis acidity. For instance, after interacting with TH, [FeCl$_4$]$^-$ is charged by −1.269 which means that 0.305 electron is transferred from the electron donor, namely, TH. Furthermore, [BMIM]$^+$ also gets few electron (Δe = −0.011) from TH which leads to a net charge transfer of 0.316 from TH to the [BMIM]$^+$[FeCl$_4$]$^-$ ion pair. The same results also can be found in BT and DBT systems. Martinez et al. also found that the charge transfer occurred during the interaction between [Fe$_2$Cl$_7$]$^-$ and ethanethiol with mulliken charge population analysis [24]. As the main electron donation comes from the aromatic ring, it is necessary to investigate the effect of alkylic derivation on TH, BT, and DBT because alkyl group can donate its electrons by hyper-conjugation effect. Hence, the alkylic derivatives, (*e.g.* 2-MTH, 3-MTH, 3-ETH, 3-MBT, and 2,7-DMBT) are analyzed by NBO tools. As we can see from Table 2, for TH alkylic derivatives (2-MTH,3-MTH, and 3-ETH), results show that alkyl chain can promote the charge transfer effects. For the benzothiophene alkylic derivatives (3-MBT and 2,7-DMBT), it is found that 3-MBT can promote the electron transfer effect while 2,7-DMBT restrains the electron transfer process. The reason for this restraining effect can be ascribed to the stero-hindrance effect. These two methyl groups prevent S atom coordinating to Fe atom which leads to a longer Fe—S bond length (2.55 Å, see Fig. 3g). As far as we know, experimental results have also shown that some alkylic derivatives of aromatic sulfur compounds are hardly to remove, such as 4,6-DMDBT [22].

In addition, Wiberg bond index (WBI) has been used to evaluate the strength of coordination bond between Fe and S atom. The WBI is calculated as the sum of the quadratic non-diagonal elements of the density matrix between two atoms. In Table 3, the WBI between Fe and S atom for different extraction systems range from 0.413 to 0.458. Results obviously show that there is a coordination bond between Fe and S atom. The strongest bond is in BT complex (0.458) while the WBI of Fe—S bond from DBT complex is 0.447 which is slightly lower than former. As mentioned above, the interaction energy between BT and [BMIM]$^+$[FeCl$_4$]$^-$ is slightly bigger than DBT system. Here, results of WBI are consistent with the interaction energy calculations. Moreover, it can be found that

Table 2
Charge distributions for different units after interaction.

	BMIM⁺		Fe		FeCl₄⁻		S			X[a]
	After	Δe	After	Δe	After	Δe	Before	After	Δe	Δe
ILs…TH	0.953	−0.011	0.382	−0.196	−1.269	−0.305	0.460	0.555	0.095	0.316
ILs…2-MTH	0.952	−0.013	0.401	−0.177	−1.271	−0.307	0.450	0.559	0.109	0.319
ILs…3-MTH	0.953	−0.012	0.387	−0.192	−1.294	−0.330	0.454	0.564	0.110	0.341
ILs…3-ETH	0.953	−0.011	0.391	−0.187	−1.283	−0.319	0.454	0.554	0.100	0.330
ILs…BT	0.952	−0.012	0.392	−0.186	−1.331	−0.367	0.432	0.595	0.163	0.379
ILs…3-MBT	0.953	−0.011	0.413	−0.165	−1.335	−0.370	0.428	0.588	0.160	0.382
ILs…2,7-DMBT	0.951	−0.014	0.402	−0.176	−1.290	−0.326	0.417	0.561	0.144	0.339
ILs…DBT	0.951	−0.013	0.419	−0.159	−1.327	−0.362	0.423	0.603	0.180	0.376

[a] X stands for aromatic sulfur compounds.

Table 3
Wiberg bond index analysis.

	Fe—S
ILs…TH	0.421
ILs…2-MTH	0.424
ILs…3-MTH	0.438
ILs…3-ETH	0.429
ILs…BT	0.458
ILs…3-MBT	0.451
ILs…2,7-DMBT	0.413
ILs…DBT	0.447

alkylic derivatives have different effects on different substrates. For TH, alkyl groups promote the strength of Fe—S bond while negative effect is taken on BT.

For Dewar–Chatt–Duncanson mechanism, there exists both σ bond and π back-donation bond in olefin coordination compounds [58,59]. Martinez-Magadan and coworkers suggested that a Dewar–Chatt–Duncanson-like mechanism was occurred during the enthanethiol EDS process by Fe-containing ILs. Furthermore, the π-complexation concept has been widely accepted in the systems of solid sorbents like Ag–Y and Cu–Y zeolites [28–30]. In the π-complexation mechanism the metal atoms form usual σ bonds with their s-orbitals. In addition, their d-orbitals back-donate electron density to the anti-bonding π-orbitals of the sulfur rings. In a word, both of the Dewar–Chatt–Duncanson mechanism and π-complexation mechanism are based on the σ bond and π back-donation bond. We note that the standard π-complexation structure existing only in a simple model structure consists of only a Cu and Cl atom as sorbents. When the sorbents model become more realistic and complicated, the standard π-complexation structure transforms into a coordination type structure which may be interpreted that π-complexation should need more coordination sites. The optimized π-complexation structure is similar with the current works. In the current work, the "π-complexation" structure also transforms into a coordination type structure during geometry optimization. In order to understand the different mechanism between solid sorbents
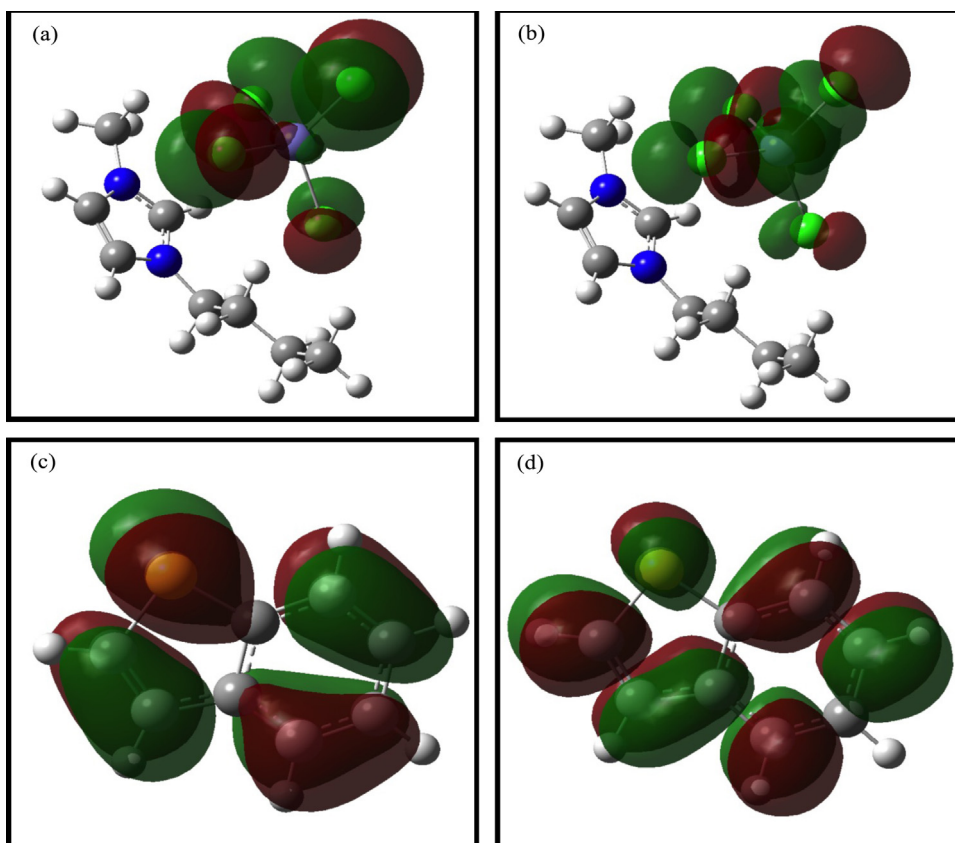

Fig. 4. Frontier orbitals of [BMIM]⁺[FeCl₄]⁻ and BT. (a) and (b) are HOMO, LUMO of [BMIM]⁺[FeCl₄]⁻ while (c) and (d) are HOMO, LUMO of BT.
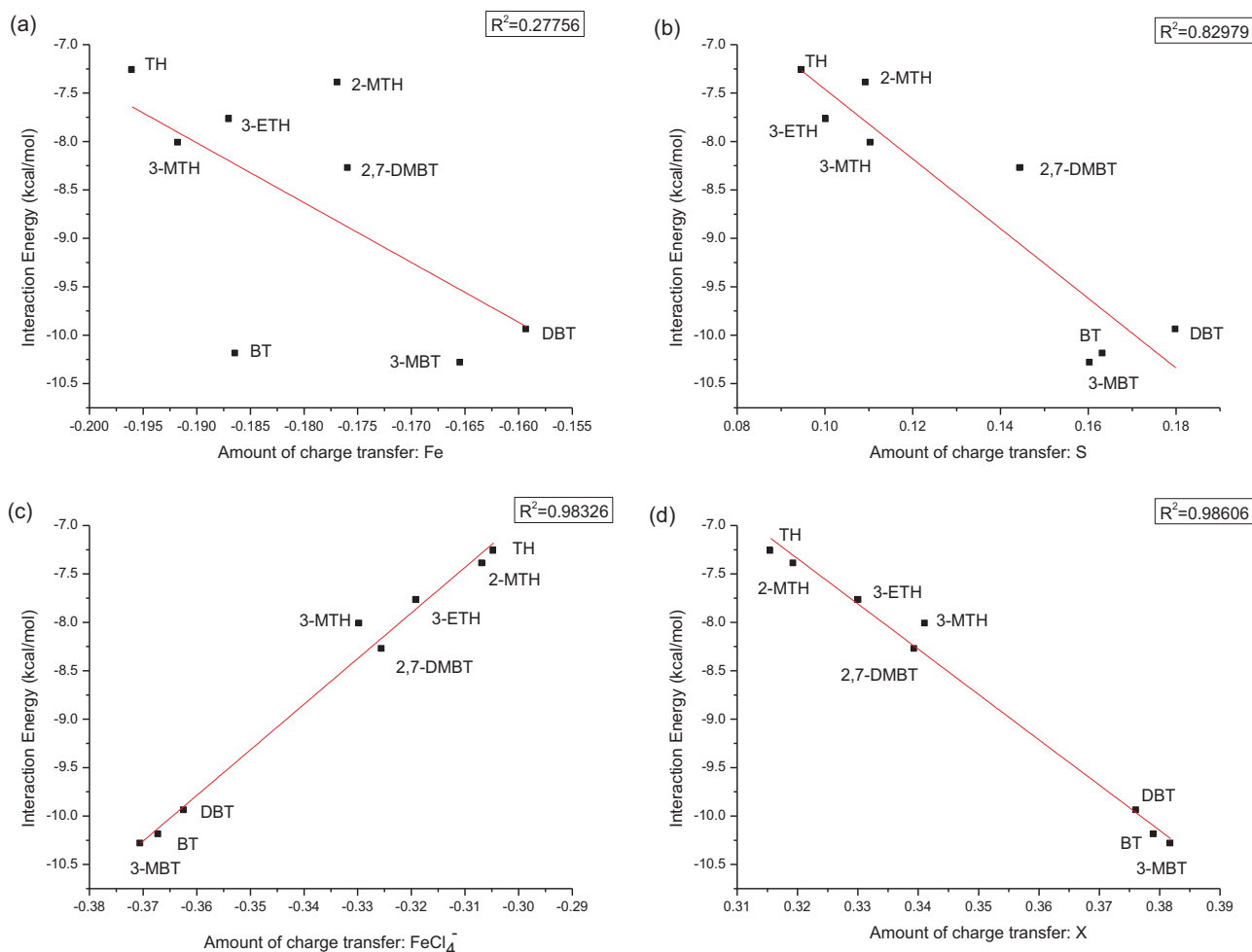
Fig. 5. Relationship diagrams between interaction energy and amount of charge transfer for different units.

Table 4
Electron configuration of Fe atom after interaction.

	After interaction	$\Delta 3d$
ILs...TH	4S(0.35)3d(6.45)	0.10
ILs...2-MTH	4S(0.35)3d(6.43)	0.08
ILs...3-MTH	4S(0.35)3d(6.45)	0.10
ILs...3-ETH	4S(0.35)3d(6.44)	0.09
ILs...BT	4S(0.35)3d(6.44)	0.09
ILs...3-MBT	4S(0.35)3d(6.43)	0.08
ILs...2,7-DMBT	4S(0.35)3d(6.42)	0.07
ILs...DBT	4S(0.35)3d(6.42)	0.07

and liquids extractants, we summarize the electron configuration of Fe atom in different extraction systems (see Table 4). The natural electron configuration of Fe atom before extraction is 4s(0.35)3d(6.35). After interaction, the electron configuration of Fe atom changes into 4s(0.35)3d(6.45) for TH system which shows electron population of 4s orbital does not change and 3d orbitals have gained net electron from TH. The number of electrons of 4s orbital remains the same after interaction which means there is no usual σ bond between Fe and S atom. Moreover, there is no electron back-donation from Fe atom to TH molecule as the number of electrons in 3d orbitals does not decrease. Results show other systems are similar with TH. Hence, this extraction process is not related to a donation and back-donation mechanism for Fe center. It is a charge transfer process that electrons transfer from aromatic sulfur compounds to the Lewis part units, such as Fe atom

or FeCl$_4$$^-$. This is different from solid sorbent systems. The reason for this difference is believed that in solid sorbents the coordination number of transition metal is low. Hence, their d-orbitals can effectively interact with anti-bonding π-orbitals of the sulfur rings. However, in this ILs system, the coordination number of Fe atom is nearly saturated. Therefore, the back-donation is difficult to occur.

As well known, frontier orbitals are useful to interpret interaction between different molecules. The frontier orbitals of [BMIM]$^+$[FeCl$_4$]$^-$ and BT (as an example) are plotted in Fig. 4. According to frontier orbital theory, HOMO is related to the donation ability while LUMO is related to the back-donation ability. In this EDS system, aromatic sulfur compounds is the donor while the Lewis part [BMIM]$^+$[FeCl$_4$]$^-$ is the acceptor. Hence, the shape of HOMO for aromatic sulfur compounds (e.g. BT) and the LUMO for [BMIM]$^+$[FeCl$_4$]$^-$ is vital to this interaction. It can be seen from Fig. 4a that HOMO of [BMIM]$^+$[FeCl$_4$]$^-$ mainly consists of 3p orbitals of Cl atom but not 3d orbital of Fe atom. Hence, it indicates that back-donation is difficult to occur in this system. On the other hand, 3d orbital of Fe indeed contributes to the LUMO of [BMIM]$^+$[FeCl$_4$]$^-$ (Fig. 4b) which leads to a possibility for forming a coordination bond. This analysis agrees well with the above results. Fig. 4c and d are the HOMO and LUMO of BT molecule, respectively. Frontier orbitals of BT are both typical π and π^* orbitals which show the donation and back-donation potentials when interacting with transition metals. On the other hand, A typical interaction energy between Cu–Y zeolite and BT is −22.90 kcal/mol while our result is only −10.19 kcal/mol, which

is also an evidence of lack of back-donation in the current system [28].

3.4. Linear relationship between interaction energy and amount of charge transfer

As mentioned above, the mechanism for extraction aromatic sulfur compounds with $[BMIM]^+[FeCl_4]^-$ is *via* a charge transfer mechanism. What's the quantitative relationship between interaction energy and the amount of charge transfer for series of aromatic sulfur compounds? In order to understand this relationship quantitatively, we have plotted linear relationship diagrams between interaction energy and amount of charge transfer for different units (see Fig. 5). First, the relationship between interaction energy and the amount of charge transfer to Fe atom is plotted (Fig. 5a). Fitting result shows that the linear relationship between interaction energy and amount of charge transfer on Fe unit is not well accepted as the *R*-square coefficient is 0.27756. Linear relationship between interaction energy and amount of charge transfer on S atom unit seems better than Fe atom because the *R*-square coefficient is 0.82979 (Fig. 5b). However, S atom serves as a minor electron donor while the major part of the electron donation comes from the aromatic ring. And therefore, it is not the determined factor for this extraction process. The amount of charge transfer for $[FeCl_4]^-$ and aromatic sulfur compounds (X) units is also linearly fitted (Fig. 5c and d). It can be seen that $[FeCl_4]^-$ and aromatic sulfur compounds (X) units are well fitted as the *R*-square coefficients are 0.98326 and 0.98606, respectively. These results show that the determined factor for this extractive mechanism is related to a whole unit like $[FeCl_4]^-$ and aromatic sulfur compounds (X). As mentioned above, the charge of $[BMIM]^+$ unit almost does not change during the interaction reaction. If the whole ionic liquid molecule $[BMIM]^+[FeCl_4]^-$ is plotted, the amount of charge transfer is the same as the X unit (with opposite sign). Therefore, it is better to consider the Lewis acidity of Fe-containing ionic liquid by the whole anion unit rather than only Fe or S atom unit. This linear relationship is based on a coordination model. It may be useful to understand the mechanism for similar EDS systems and predict the extractive selectivity for different aromatic sulfur compounds.

4. Conclusion

In the current work, interaction between $[BMIM]^+[FeCl_4]^-$ and a group of aromatic sulfur compounds has been systematically studied by DFT. Mechanism for EDS and extractive selectivity have been discussed in detail. Based on the results and discussions we draw the conclusion as following:

(a) A coordination structure has been found to be critical to the process of EDS by using $[BMIM]^+[FeCl_4]^-$ ionic liquid.
(b) Interaction energy and extractive selectivity follow the order: TH < DBT ≈ BT. The alkylic derivatives of TH or BT may improve the interaction energy and extractive selectivity but the steric hindrance effects should also be considered.
(c) NBO results show that the mechanism of this EDS reaction is determined by a charge transfer process. It is better to consider the Lewis acidity of Fe-containing ionic liquids by the whole unit (like $[FeCl_4]^-$ and aromatic sulfur compounds (X)) rather than only the Fe or S atom.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jmgm.2015.03.007

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