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

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.