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Theoretical study on interactions between ionic liquids and organosulfur compounds

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ABSTRACT

Density functional theory has been used to investigate the interactions between dibenzothiophene, diphenylsulfide, diphenyldisulfide, benzene, tetralin and 1-methyl-3-methylimidazolium methyl sulfate ([MMIM][$MeSO_4$]). The GGA/PW91 functional and DNP basis set were employed to optimize geometries. The interactions between [MMIM][$MeSO_4$] and dibenzothiophene, diphenylsulfide, diphenyldisulfide, benzene, tetralin have been explained by NBO and AIM methods. The most stable gas-phase structure of [MMIM][$MeSO_4$] ion pair indicates that hydrogen bonding interactions between oxygen atoms on [$MeSO_4$] anions and the C2-hydrogen on the imidazolium ring play a dominating role in the formation of ion pair. Additional interactions are found between [$MeSO_4$] anion and the hydrogen atoms on the adjacent methyl chains of [MMIM] cation. The [$MeSO_4$] anion tends to be located near ring C2-proton, suggesting that dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene adsorption on [MMIM][$MeSO_4$] did not change the dominant interactions of [MMIM][$MeSO_4$] pair. The $\pi\cdots\pi$ interactions, $\pi\cdots$C—H interactions and hydrogen bonding interactions occur between [MMIM][$MeSO_4$] and dibenzothiophene, diphenylsulfide, or benzene. The $\pi\cdots$C—H interactions and hydrogen bonding interactions exist between [MMIM][$MeSO_4$] and diphenyldisulfide or tetralin. The order of interaction energies between [MMIM][$MeSO_4$] and molecules is dibenzothiophene > diphenyldisulfide > diphenylsulfide > tetralin > benzene, in agreement with the experimental conclusion.

1. Introduction

Deep desulfurization of diesel fuel has attracted the attention of a growing number of scientists and engineers due to the stringent regulations imposed on the presence of sulfur in fuel. The traditional desulfurization method is catalytic hydrodesulphurization (HDS) using CoMo or NiMo as catalysts, which requires both high temperature and high pressure. HDS was more effective to remove aliphatic sulfur structures such as thiols, thioethers and disulfides than to remove sulfur-containing aromatic compounds. Alternative desulfurization technologies such as adsorption, extraction, and selective oxidation have been proposed. Extractive desulfurization is one of the best methods because the process operation is easy. Wasseerscheid [1] first described that ionic liquids can be utilized as extractant to remove sulfur-containing compounds from the fuels under mild conditions. Lo and co-workers [2] combined the methods of oxidation and extraction, using H_2O_2-acetic acid as the oxidant, and [BMIM][BF_4] and [BMIM][PF_6] as the extractant, this process increases the desulfurization rate by about an order of magnitude relative to that of merely extracting with ionic liquids. Following their studies, the use of ionic liquids as extractants to remove aromatic sulfur compounds in extractive desulfurization has been reported [3]. In 2008, Mochizuki and Sugawara [4] investigated the extraction of thiophenic sulfur from a model fuel using 1-methyl-3-methyl imidazolium methyl sulfate ([MMIM][$MeSO_4$]) at room temperature, it was observed that the extraction yield of dibenzothiophene was higher than that of diphenylsulfide and diphenyldisulfide, dibenzothiophene was efficiently removed regardless of whether benzene or tetralin was used as the solvent. However, the detailed structures and conformations of interactions between [MMIM][$MeSO_4$] and dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene, which are of vital importance to understanding their physical properties, are still unknown. Before solvation in this ionic liquid can be understood, we need to have an awareness of the gas-phase structural properties and interactions between [MMIM][$MeSO_4$] and dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene. Therefore, this work reports on an analysis of structures of [MMIM][$MeSO_4$], [[MMIM] [$MeSO_4$]-dibenzothiophene, [MMIM][$MeSO_4$]-diphenylsulfide, [MMIM][$MeSO_4$]-diphenyldisulfide, [MMIM][$MeSO_4$]-tetralin and [MMIM][$MeSO_4$]-benzene complexes using quantum

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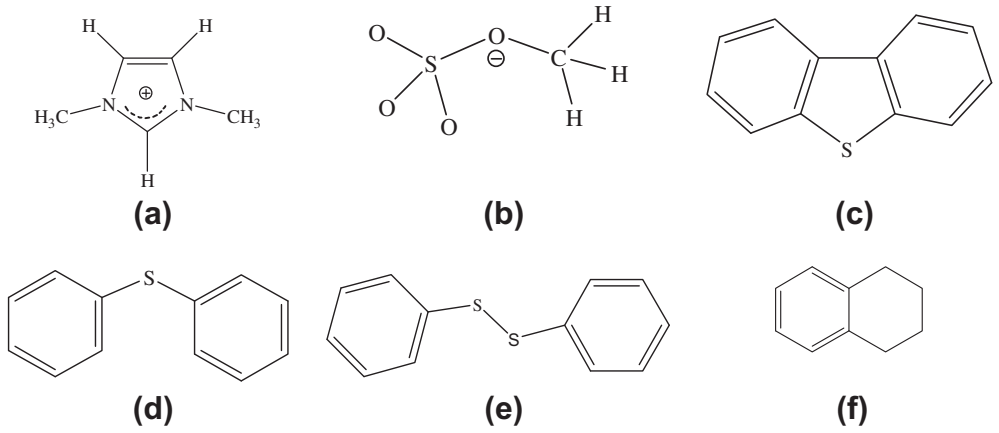

Fig. 1. The structures of (a) 1-methyl-3-methylimidazolium cation, (b) methyl sulfate anion, (c) dibenzothiophene, (d) diphenylsulfide, (e) diphenyldisulfide and (f) tetralin.

chemical calculations. The theoretical results here will help to understand the fundamental interactions between [MMIM][$MeSO_4$] and the five molecules. Recent efforts have been made using theoretical methods to model sulfur-containing compounds extraction by ionic liquids [5–17], but the interactions between [MMIM][$MeSO_4$] pairs and dibenzothiophene, diphenyl sulfide, diphenyldisulfide, tetralin, benzene were not theoretically investigated.

The structures of 1-methyl-3-methylimidazolium cation, methyl sulfate anion, dibenzothiophene, diphenylsulfide, diphenyldisulfide and tetralin were shown in Fig. 1. The interactions between [MMIM][$MeSO_4$] pairs and dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene were compared and electronic and topological properties were computed.

2. Computational methods

The density functional theory (DFT) method has been shown to produce more reliable geometries for hydrogen-bond systems than Hartree–Fock (HF) methods, and has the advantage of a much lower computational cost than the second order Möller–Plesset perturbation MP2 methods. DFT has also been successfully employed to calculate the structural properties of some of the ionic liquids. All geometric optimizations reported here were performed with DMol^3 program package [18,19]. The double numerical basis sets plus polarization functional (DNP) was employed. For the exchange correlation term of the energy functional, the generalized gradient corrected functional GGA and PW91 functional [20] as implemented in the DMol^3 program, were used for all the geometry optimizations. 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 [21]. No restrictions on symmetries were imposed on the initial structures. A frequency analysis was performed on all DFT structures to ensure the absence of imaginary frequency and verify the existence of a true minimum. The NBO analysis was obtained with 6-31++G** basis set to provide information of interactions [22]. 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 $F_{i,j}$ is the off-diagonal NBO Fork matrix element. Atoms in molecules (AIM) analyses were calculated by AIM2000 to provide topological properties [23,24].

DMol^3 uses numerical functions that are far more complete than traditional Gaussian functions, and therefore we expect BSSE contribution to be small [25]. The interaction energies are defined as the differences between the energies of [MMIM][$MeSO_4$]-dibenzothiophene/diphenylsulfide/diphenyldisulfide/tetralin/benzene and the sum of the energies of [MMIM][$MeSO_4$] and dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene.

$$\begin{aligned}\Delta E = -\{&\mathrm{E}([\mathrm{MMIM}][\mathrm{MeSO_4}] - \text{dibenzothiophene/diphenylsulfide} \\ &\text{/diphenyldisulfide/tetralin/benzene}) - [\mathrm{E}([\mathrm{MMIM}][\mathrm{MeSO_4}]) \\ &+ (\text{dibenzothiophene/diphenylsulfide/diphenyldisulfide} \\ &\text{/tetralin/benzene})]\}\end{aligned}$$

3. Results and discussion

3.1. Geometric and electronic properties

In order to investigate the structures of [MMIM][$MeSO_4$], a [$MeSO_4$] anion was added to the corresponding C2—H2, C4—H4, and C5—H5 ring protons of vicinity of imidazolium ring. For comparison, [$MeSO_4$] anions placed in the positions around the methyl side chains of imidazolium ring were taken into consideration. The most stable structure of [MMIM][$MeSO_4$] is shown in Fig. 2a. It can be seen that the most stable structure of [MMIM][$MeSO_4$] has four O···H interactions, the corresponding interacting distances of H2···O3, H61···O3, H61···O1, and H71···O2 are 1.897 Å, 2.750 Å, 2.597 Å, and 2.206 Å. The interacting distances are below or equal to the sum of the Bondi's van der Waals radii (3.55 Å) of carbon (1.52 Å) and hydrogen (1.20 Å) approximately [26]. The shortest distance of H2···O3 suggest that the C2—H2 is involve in the formation of strongest hydrogen bond. Hydrogen bonds also occur between oxygen atoms on [$MeSO_4$] and the C—H on the methyl groups (H61 and H71) of imidazolium ring. It can be seen that a single hydrogen atom (H61) participates in two hydrogen bonds. This type of bonding is called bifurcated hydrogen bonding or three centered hydrogen bonding [27]. The C2—H2 involved strongest hydrogen bond is in agreement with the conclusion of report [28].

The initial structures were designed by placing [$MeSO_4$] anions and dibenzothiophene, diphenylsulfide, diphenyldisulfide, tetralin, benzene around the imidazolium ring, two methyl side chains. The possible π(imidazolium)-π(dibenzothiophene/diphenylsulfide/diphenyldisulfide/tetralin/benzene) interactions were considered with the anion of [$MeSO_4$] arranged in different positions. The most stable structures of [MMIM][$MeSO_4$]-dibenzothiophene, [MMIM]-[$MeSO_4$]-diphenylsulfide, [MMIM][$MeSO_4$]-diphenyldisulfide, [MMIM][$MeSO_4$]-tetralin, [MMIM][$MeSO_4$]-benzene are shown in