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The Absorption Mode of H_2S on Ionic Liquids: A DFT Study

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Abstract

Over the last two decades, the ability to efficiently absorb, store, and convert H2S, with or without the use of ionic liquids, while simultaneously minimizing energy costs and over-potential, has become increasingly significant in the field of chemical research. The ab initio Density Functional Theory (DFT) methods have proven to be a powerful tool for calculating the absorption, adsorption, and reduced rates of chemical species in a variety of phases, including water, vacuum, and Room Temperature Ionic Liquids (RTILs). This happens due to their relative ease of application and computational efficiency. On the other hand, DFT has a number of constraints that impair the accuracy and dependability of its predictions. This is the context in which the current work was carried out to investigate the absorption of H2S in ionic liquids utilizing DFT theory and developing accurate computational techniques. According to our findings, ionic liquids (ILs) were found to physically absorb H_2S, with the hydrogen bond acting as the driving force behind this process. Overall, the purpose is to provide information that may be applied to developing and implementing new concepts.

Keywords: Density functional calculations, ionic liquids, absorption of H_2S, interaction energy, binding energy, computational protocol.

Introduction

Hydrogen sulfide (H_2S) is the most prevalent sulfur component in natural gas. Natural gas can contain up to 28 percent hydrogen sulfide gas. Hydrogen sulfide must be eliminated from industrial gas and oil streams due to its toxicity and corrosive property (Syed et al., 2006). Industrial removal of H_2S and CO_2 can be carried out using aqueous solutions of monoethanolamine, diethanolamine, *N*-methyldiethanolamine, and diisopropanolamine (Sakhaeinia et al., 2010). However, disadvantages of commercial use of alkanolamine solutions include: loss of alkanolamine and water into gas stream during desorption, oxidative degradation of alkanolamines to form corrosive by-products and high heat capacity of the solvent water, and large enthalpy of reaction between acid gases and alkanolamines, requiring high energy consumption during the desorption (Dhar, 2019).

Many active researchers in the fields of gas sweetening and gas separation are now looking into using new chemical compounds known as room temperature ionic liquids (RTILs) (Dhar and Fahim, 2016). RTILs are a class of organic compounds that are comprised of positive ions (cations) and an inorganic or organic anion, such as $[Cl]^-$, $[BF_4]^-$, $[PF_6]^-$, or $[AlCl_4]^-$, which are liquid (below

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boiling point of water) (Dhar, 2014). RTILs have a low vapor pressure and possess excellent thermal and electrochemical stability due to Coulombic attraction between their ions. Since 1995, these compounds have gained popularity as solvent media for reaction synthesis, supercritical CO_2 extraction, gas separation and purification, and electrochemical reduction of CO_2 in Pt, Ag, or Au electrodes (Dhar and Cavallotti, 2014). To remove acid gases (CO_2 and H_2S) from gas sweetening processes more efficiently, many researchers propose amine-functionalized task-specific ionic liquids, instead of alkanolamine solutions. An in-depth understanding of the solubility of gases and the rate of solubility at various experimental temperatures and pressures is critical in evaluating the suitability of ionic liquids for wider applications in the commercial purification of natural gas in various treatment facilities (Dhar, 2014).

Computational methods have long been used to investigate the absorption of H_2S on various types of ionic liquids (ILs), including 1-ethyl-3-methylimidazolium cation ([EMIM] $^{(+)}$), and chlorine anion ([Cl])$^-$. H_2S absorptions in ionic liquids (ILs), such as 1-methyl -3-methylimidazolium cation ([MMIM])$^+$ with five different sets of anions, were also investigated.

Methodology

Experimental Methods

A wide range of ionic liquids will be subjected to simulations in the presence of H_2S to examine this gas's absorption process. The Polarized Continuum Model (PCM) will be utilized to model both the vacuum and solution simulations. The complexes, reactants, and products were analyzed using the density functional theory (DFT) to establish their minimal energy structures, interaction energies, binding energies, and preferred interaction locations (Pople et al., 1992). Using the B3LYP hybrid function, quantum mechanical calculations will be carried out (Raghavachari, 2000). All simulations will be done using the Gaussian 09 quantum chemistry software suite program, which will be utilized to derive the minimal energy cluster architectures. Water was employed as a solvent in the simulations, and the implicit PCM model was used to model it. In the SMD model, a solute molecule's quantum mechanical charge density interacts with a continuum description of the solvent. "SMD" stands for "solute electron density," which indicates that the electron density is utilized instead of atomic charges to describe the model's parameters. The solute-solvent boundaries are not explicitly represented by the term "continuum" but rather by a dielectric medium with high surface tension. The SMD model was used to estimate the energy released by cavitation and other non-polar processes. The frequency calculations will test all the most minor energy constructions for the stability test. The graphical sketches in this study were created using the Molden 4.4 visualization tool (Schaftenaar and Noordik, 2000).

Results and discussion

Absorption of H_2S in ionic liquids: Energetic Analysis

In this study, we first like to explain the energy structures of the ILs-H_2S system that have been computed, and then we will discuss the absorption of H_2S by ILs. We have introduced the liquid phase and computed the minimum energy structure of the monomer with H_2S. It is intended to assist an understanding of the peculiarities of ionic liquid structures and their absorption processes. This is represented in Tables 1 and 2, which demonstrate the structures of the anionic pair, the structures of various cations, anions, and H_2S, as well as their related interactions and binding energies.

Table 1: Optimized structures and some key distances

H_2S in ionic liquid	**H-Cl distance (Å)**	**C-F distance (Å)**	**Interaction energies (kcal/mol)**
EMIMCl	2.4	4.4	-6.7
MMIMCl	2.5	5.2	-5.5
$MMIMBF_4$	--	2.9	-6.4
$MMIMPF_6$	--	3.8	-5.2

The calculation was performed at the B3LYP/6-31 + g(d, p) level of theory. Relevant distances between H-Cl and C-F atoms have been reported in angstrom (indicated with arrows). The relative energies were reported in kcal/mol. The energies were not corrected for ZPE.

Table 2 shows the interaction energy structures of different s ion pairs, 1,3-dimethylimidazolium cation with $AlCl_4$ anion, i.e., ion pair MMIM-$AlCl_4$ with H_2S are less stable compared to the other four anions.

Table 2: Interaction Energy of H_2S in RTIL'S

Ionic liquids (cations)	**Ionic liquids (anions)**	**Absorption of H_2S (interaction energy) kcal/mol**
1,3-dimethylimidazolium	BF_4	-6.7
1,3-dimethylimidazolium	$AlCl_4$	-3.7
1,3-dimethylimidazolium	Cl	-5.5
1,3-dimethylimidazolium	Br	-6.9
1,3-dimethylimidazolium	PF_6	-5.6

Although the ion pair and H_2S absorption processes appear to be similar to our experimental data, there is a subtle difference between the two. Because of this, a more precise estimate based on this benchmark is required to examine further the processes involved in this system.

In general, a molecule's free volume (Vf) has a linear relationship with the volume of the molecule (VM). The greater the volume of these IL complexes, the greater the solubility of H_2S in the water solution. This is another important finding for increasing the solubility of hydrogen sulfide in ionic liquids.

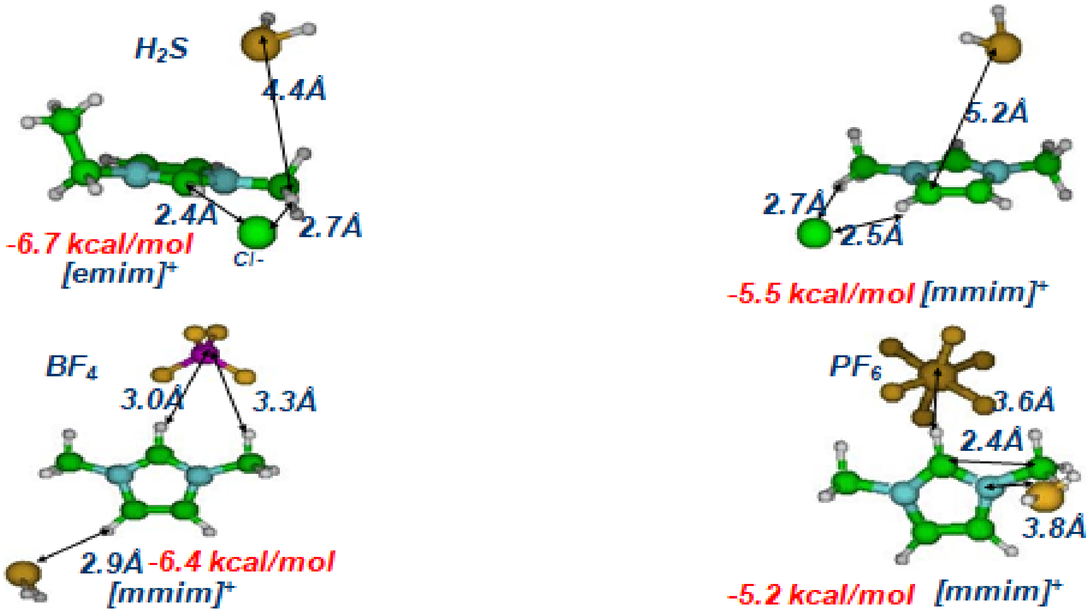

Figure 1: Favored interaction site of H_2S in different RTIL'S (optimized ion pair monomer minimum energy structure in liquid phase).

The structure of 1-ethyl-3-methylimidazolium chloride [EMIM][CL]-H_2S, dimethylimidazolium chloride [MMIMCL]–H_2S, dimethylimidazoliumtetrafluoroborate [MMIMBF4]-H_2S and hexafluorophosphate based ionic liquid MMIMPF6 –H_2S in liquid phase are reported in Figure (1). The structures are stable and fully optimized. The MMIMPF6-H_2S systems are less stable in comparison to the liquid phase energy content than other sets of ionic liquids. The minimum energy structure is the most stable, where H_2S is located near the methyl group in [MMIM][BF_4] IL.

We have conducted statistical research and have discovered that ionic liquids with low molecular weights and compact structures typically possess higher selectivity. Low temperature and pressure are highly advantageous for increasing the separation performance in the absorption of H_2S (Wang, 2018) in investigating the selectivity of ionic liquids in natural gas sweetening.

Although implicit models are generally considered unsuitable for studying the structures of ionic liquids, however, they are considered reasonably appropriate in this case because the absorption of H_2S is performed using a 1: 5 IL-to-water ratio, indicating that each ion pair will be surrounded by a significant number of water molecules, more than enough to complete the first solvation shell, as demonstrated by the results.

Conclusion

Even though RTILs were, at first, appeared technologically in the early 1980s, these processes are still not fully understood. H_2S absorption or adsorption, for example, are complex processes involving many fundamental atomic processes. The purpose of our work is to begin with an investigation of the atomic steps, and in fact, we believe that a fundamental understanding of the chemical phenomena occurring in the gas or liquid phase and on the surface is the only way to have a correct picture of the macroscopic process. To achieve this goal, quantum chemistry was used in this work to investigate H_2S absorption in ionic liquids. The current study demonstrates that RTIL is an excellent candidate for H_2S absorption. The theoretical calculations of the four sets of ionic liquids structure and the H_2S absorption processes have been discussed. The preferred interaction sites and binding energy of the ILs were calculated. The simulations of H_2S absorption in [MMIM][BF_4] ionic liquid revealed that the absorption process is slightly exothermic. Multiple minimum energy structures for the absorbed H_2S molecules were discovered, which differ slightly in calculated interaction energies. According to the results of the comparison, the solubility of H_2S in [EMIM][CL] is more significant than that in [MMIM][PF6].

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