



Theoretical and experimental investigation on the capture of H₂S in a series of ionic liquids



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ABSTRACT

H₂S absorptions in ionic liquids (ILs), including tetramethyl guanidinelactate (TMGL), 4-bis(2-hydroxypropyl)-1,1,3,3-tetramethyl guanidinium tetrafluoroborate ([TMGHPO₂][BF₄]) and 1-butyl-3-methylimidazolium cation ([BMIM]⁺) with the anions chloride ([Cl]⁻), tetrafluoroborate ([BF₄]⁻), hexafluorophosphate ([PF₆]⁻), triflate ([TfO]⁻), bis-(trifluoromethyl) sulfonylimide ([Tf₂N]⁻), were studied in experiment and computational methods. [TMGHPO₂][BF₄] showed the best H₂S absorption capacity among the seven ILs. Density functional theory (DFT) calculations were applied to reveal the absorption mechanisms. Interaction energy results were consistent with absorptivities (molar ratio of H₂S in IL) measured in experiment. As the best candidate absorbent, [TMGHPO₂][BF₄] was chosen as an example to characterize the hydrogen bonds and orbital interactions between H₂S and [TMGHPO₂][BF₄] in atoms in molecules (AIM) and natural bond orbital (NBO) methods, respectively. IR spectrums obtained in both experimental and computational method were used to characterize the features of absorption process. The results indicated that H₂S was physically absorbed by ILs, in which hydrogen bond was the driving force.

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1. Introduction

Hydrogen sulfide (H₂S) is usually produced with methane, other synthetic gas and hydrodesulfurization process of crude oil, which is a highly toxic and corrosive gases [1]. Aqueous alkanolamine solutions is a kind of widely used industrial solvent, which can remove H₂S from industrial natural gas, refinery tail gas and synthesis gas. However, in the process, the loss of alkanolamine volatilization of and the water transfer to the vapor will form the corrosive degradation and byproducts which has many disadvantages and makes the process economically expensive [2].

In recent years, ionic liquids (ILs) have been widely used to study CO₂ capture [2,3], due to the unique properties, such as the minimal volatile, design properties, thermal stability and liquid form in a wide temperature range [4]. IL is a promising candidate absorbent for the gas separation [5–10]. Besides, ILs were also employed to study harmful gas capture [11–17].

A few years ago, people began to focus on the absorption of H₂S in ILs [18–22]. Jou and Mather [18] first determined H₂S solubility in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) under the conditions of temperatures range of 298.15–403.15 K and pressures up to 9.6 MPa. Pomelli et al. [19] reported the solubility of H₂S in [BMIM]-based ILs with different anions. Morsi et al. [20] published the solubility and transfer coefficient of H₂S in ammonium-based ILs. Jaliliet al. [21–26] measured and provided H₂S solubility at various temperature and pressure. Huang [27] given that dual Lewis base fictionalizations of ILs had highly efficient and selective capture of H₂S. Wang [28] reported oxidative absorption of H₂S by iron-containing ILs.

In this paper, the absorptions of H₂S in the chosen ILs are studied in both experimental and computational method, including tetramethyl guanidinelactate (TMGL), 4-bis(2-hydroxypropyl)-1,1,3,3-tetramethyl guanidinium tetrafluoroborate ([TMGHPO₂][BF₄]) and [BMIM] based ILs with different anions, including chloride ([Cl]⁻), tetrafluoroborate ([BF₄]⁻), hexafluorophosphate ([PF₆]⁻), triflate ([TfO]⁻), bis-(trifluoromethyl) sulfonylimide ([Tf₂N]⁻). The hydrogen bonds between H₂S and ILs are investigated by the vibrational frequency analyses (VFA), natural bond orbital (NBO) and atom in molecule (AIM) methods.

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2. Experiments

2.1. Materials

High-purity H₂S (purity 99.7%) was purchased from Zibo Anze Standard Gas Co. Ltd. (Zibo, China). The [BMIM][Cl], [BMIM][PF₆], [BMIM][BF₄], [BMIM][TfO] and [BMIM][Tf₂N] were purchased from Lanzhou (Lanzhou, China) Center for Green Chemistry with the purity of 99% and water mass fractions less than 10⁻³ (g/g), respectively. 1,1,3,3-tetramethylguanidine (TMG, 99%), propylene oxide (99%), ethanol (99%), toluene (99.8%), fluoroboric acid (50 wt.% solution in water) were purchased from Air Liquide. The TMGL [12] and [TMGHPO₂][BF₄] [13] were synthesized and purified before absorption process. To remove traces of volatile compounds, the ILs were kept in a vacuum (about 10⁻⁶ bar) at 343 K for 24 h prior.

2.2. Synthesis of TMGL and [TMGHPO₂][BF₄]

To synthesize TMGL, TMG dissolved in ethanol was added into a flask in a water bath of 25 °C under mechanical stirring. Then, the solution consisting of lactic acid and ethanol was added into the flask. The mole ratio of TMG and lactic acid was 1:1. The reaction process was allowed to proceed for 2.5 h. After the evaporation of solvent under vacuum, the residue was obtained, which was further treated with active carbon and washed by ethanol. The colorless product was obtained after ethanol was evaporated under vacuum.

The solution of TMG in toluene was added into a flask in a water bath of 25 °C under mechanical stirring. Then, propylene oxide was slowly dropped into the flask, in which the mole ratio of TMG and propylene oxide was 1:1. The reaction process was allowed to proceed for 36 h, where after fluoroboric acid was slowly added to the solution in an ice bath under mechanical stirring. The mixture was heated (70 °C) to remove solvent under reduced pressure, and the residue ([TMGHPO][BF₄]) was dry under high vacuum (0.1 kPa). Then, an additional equivalent propylene oxide was used to react with [TMGHPO][BF₄] and the future treatments were similar with the steps mentioned above. A colorless product ([TMGHPO₂][BF₄]) was obtained. The ¹H-NMR spectrum of TMGL and [TMGHPO₂][BF₄] are given Figs. S1 and S2 (Electronic Supporting information) to ensure lack of critical impurities.

2.3. Apparatus and measurements

H₂S absorptivity was measured by applying isochoric saturation technique [29]. It is worth mentioning that absorptivity in this work refers to molar ratio of H₂S in IL. The apparatus used for H₂S absorption measurements is schematically represented in Fig. 1. The apparatus was composed of a H₂S cylinder, pressure regulators, magnetic stirrers with heating, oil bath, and glass container filled with IL and off-gas absorption by NaOH solution. The low-pressure gauge had an uncertainty of approximately (0.001 bar) in the experimental pressure range. For a typical experiment, the desired amount of IL was loaded in the glass container (the weight was m₁, about 5 g) using an electronic balance (Sartorius BS224S, uncertainty of 0.001 g), and the air in the system was eliminated by the vacuum pump. Then H₂S was charged into the glass container from the cylinder, and the liquid phase was stirred. The system was considered to have reached equilibrium if the pressure of the system had been unchanged over time for 2 h. Then the pressure of the system was recorded, and the glass container filled with IL was weighed (the weight was m₂). Thus, the absorption of H₂S in a given IL was determined by the shifted quality of the glass container (m₂-m₁). To verify the validation of the apparatus, we determined the absorption of CO₂ in a chloride and urea mixture with this apparatus, and the results were consistent with ref. [30].

To support the computational results, an attenuated total reflection fourier transform infrared (FT-IR ATR) spectra of 2BP8HQ were registered using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm⁻¹; number of scans: 250; resolution: 1 cm⁻¹) to study the variations of IR spectrum of [TMGHPO₂][BF₄] before and after H₂S absorption.

3. Computational methods

In recent years, density functional theory (DFT) method has been widely used since it is a cost-effective and reliable method for calculation chemistry. The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation function combined with the 6-311++G(d,p) basis set are widely applied in theoretical studies of ionic liquids [16,31]. B3LYP method has been confirmed that it can supply reliable interaction energies, in which electron correlation is well considered. Polarizable functions and diffuse functions are used for all atoms in the 6-311++G(d,p) basis set, which is important for the description of hydrogen bonding interactions. The interaction energy (ΔE) considering the basis set superposition errors (BSSE) correction using the counterpoise (CP) method is estimated [32]. The vibrational frequency studies of H₂S, ILs and the complexes have also been performed at the same level. To account for errors due to the neglecting electron correlation and the basis set incompleteness, considering B3LYP systematic errors with a scaling factor of 0.983 up to 1700 cm⁻¹ and 0.958 for greater than 1700 cm⁻¹ [33,34]. What is more, to better understand the nature of the intermolecular H-bonding interactions in the H₂S, different ILs and complexes, natural bond orbital (NBO) and atoms in molecule (AIM) have also been carried out at the same level. All computations are carried out by using Gaussian 09 program package [35].

4. Results and discussion

4.1. Experimental absorptivity of H₂S

Absorptivity of H₂S in the seven ILs is determined by using isochoric saturation technique (Fig. 1), which was depicted in Fig. 2a. Table S1 (Electronic Supporting information) shows the molar ratio of H₂S in seven ILs at 30 °C. It can be seen that [TMGHPO₂][BF₄] is the best candidate for H₂S absorption, due to the high molar ratio of 0.502. However, the absorptivity of H₂S in the other six ILs does not exceed 0.38. The absorptivity order of H₂S in seven ILs is: [TMGHPO₂][BF₄] > [BMIM][Tf₂N] > [BMIM][TfO] > [BMIM][Cl] > [BMIM][BF₄] > [BMIM][PF₆] > TMGL.

4.2. Analysis of geometries and interaction energies

In order to gain the possible interaction modes between H₂S and seven kinds of ILs, the electrostatic potential surfaces of them have been calculated at B3LYP/6-311++G(d,p) level. As shown in Fig. S3, the favorable sites (more negative charges and red area) for proton attack in anion are concentrated on the regions around chloride, oxygen atoms in carbonyl and fluorine atoms in tetrafluoroborate or hexafluorophosphate. The most possible interaction sites can be observed, such as the regions near the chloride, oxygen atom and fluorine atoms (more positive charges and blue area). It can be seen that these atoms are easy to form hydrogen bonds. For cation, the highly positive regions (deep blue) are mainly concentrated on around C–H in [BMIM]⁺, hydrogen atom of amine group of TMGL and the hydrogen atoms of hydroxyl group of [TMGHPO₂]⁺. Commonly, the regions with larger positive charge densities are easier to form hydrogen bonds. With the above analysis, the large area of positive charge density in cation and the area of negative charge density are easy to form hydrogen bonds. Thus the reason-

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