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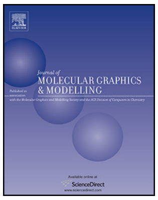

Experiment and DFT studies on radioiodine removal and storage mechanism by imidazolium-based ionic liquid

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ABSTRACT

In order to remove and store radioactive substances effectively, studies on the mechanisms of radioiodine captured by ionic liquids (ILs) with a fixed cation (1-butyl-3-methyl-imidazolium cation [Bmim]+) were carried out in experimental and theoretical methods. Fourier transform infrared attenuated total reflectance (FT-IR ATR) spectra of 2BP8HQ and ultraviolet–visible (UV/vis) spectroscopy were used to investigate the kinetic process of radioiodine removal by ILs in experiment. Corresponding theoretical investigations on the structures and formation mechanisms of ILs, bare anions and complexes as well as hydrogen bonds was carried using density functional theory. The electrostatic potential was used in configuration design and construction. Charge distribution was used to show the variation of atom charge density, Interaction energy and vibration frequency change were performed to explore possible mechanisms on the halogen bond formation between radioiodine molecule and bare anion or anion in ILs when radioiodine captured by ILs. In order to characterize halogen bonds both natural bond orbital analysis and atoms in molecules analysis were performed. Both experimental and computational results showed that radioiodine could be captured by ILs with a 1:1 mol stoichiometry. It was noteworthy that [Bmim][Br], [Bmim][I] and [Bmim][Cl], containing high radioiodine capture efficiency anions, were better candidates in removal and reliable storage of radioiodine for their capture efficiencies of over 80% in 5 h.

1. Introduction

As the accelerated industrialization and exploitations of nuclear energy, nuclear waste such as radioiodine (I_2) would be released to the environment, which is produced from the nuclear weapon manufacture, nuclear energy production and particularly nuclear accident [1]. Radioactive isotopes of iodine including ^{125}I, ^{129}I and ^{131}I (the common iodine isotope without radioactivity is ^{127}I) are generated as byproducts after the fission of uranium, plutonium or tellurium, and then leached into groundwater, soil and atmosphere due to its high vapor pressure [2]. Much attention is coming to be paid to ^{129}I and ^{131}I. ^{129}I with a long half-life (about 1.6×10^7 years) must be entrapped and storage efficiently, otherwise, it is easy to transform into iodine and iodate species when exposed to an aqueous environment [3,4]. ^{131}I possessing a short half-life (about 8.02 days) shows detrimental effect on human metabolic process, and it is believed to trigger thyroid cancer [5–7], thus, people are more looking forward to explore efficiency capture methods.

In the past decades, several radioiodine sorbents and storage materials have been studied such as metal-organic frameworks (MOFs) [8,9], apatites [10,11], zeolite-apatite composites [12], silver-exchanged zeilites [13] AgI-Ag2O-P2O5 glass [14] and chalcogel [15]. However, these materials show various drawbacks, such as the high cost, adverse environmental impact and low capacity for radioiodine removal. Thus, there is still an environmental, economic and effective interest in the development of new materials for the efficiency removal and storage of radioiodine.

Ionic liquids (ILs) are composed of organic cation and organic/inorganic anion, showing a liquid state around the room temperature, which has been proved that radioiodine can be removed by ILs [16,17]. ILs have many unique properties such as high chemical and thermal stability [18], high biodegradation, nonflammability, easy synthesis, negligible vapor pressure [19], wide liquid range temperature and strong dissolution ability for various organic and inorganic materials and they are highly tunable and relative green. ILs have attracted much attention in many fields, such

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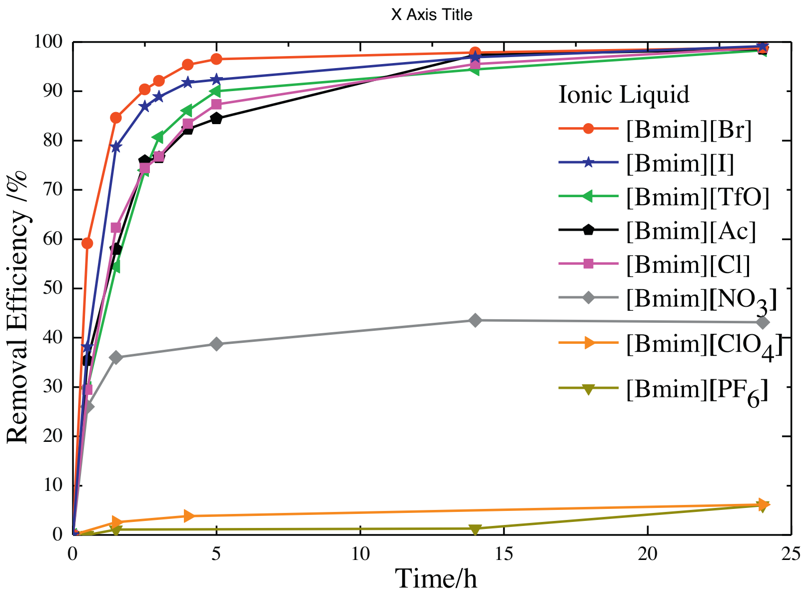

Fig. 1. radioiodine removal kinetics of [Bmim]-based ILs with differrent anions at room temperature (25 °C) [17].

as material synthesis [20], electrochemistry and electronic spectroscopy [21,22] and CO_2 capture [23,24], which is believed that ILs might be solvents of the future.

Very recently, Yan and Mu were interested in exploring the most potentials of ILs in efficient removal and reliable storage of radioiodine [17]. In Mu's previous study, a series of ILs was investigated for removal and storage of radioiodine (I_2) via ultraviolet–visible (UV/vis) spectroscopy, and it has been found that the capability of ILs to hold I_2 is mainly attributed to the halogen-bond accepting ability of the anions [16].

In this paper, a series of [Bmim]-ILs, consisted of 1-butyl-3-methyl-imidazolium cation $[Bmim]^+$ and eight anions ($[Cl]^-$, $[Br]^-$, $[I]^-$, $[Ac]^-$, $[NO_3]^-$, $[ClO_4]^-$, $[PF_6]^-$ and $[TfO]^-$ (trifluoromethanesulfonate)), are chosen as examples to investigate the mechanisms of efficient removal and reliable storage of radioiodine by ILs. In addition, the dimeric complexes formed by I_2 with bare anions and ILs are systematically investigated by both experimental and theoretical methods. The structural features of all studied complexes are obtained and characterized by Fourier transform infrared attenuated total reflectance (FT-IR ATR) spectra of 2BP8HQ, UV/vis spectroscopy and density function theory (DFT). To provide more details about these interactions, the halogen bond nature and proton transfer process are analyzed by the vibrational frequencies changes (VFC), the electrostatic potential (ESP), atomic charges distribution (ACD), atoms in molecules (AIM) analyses and natural bond orbital (NBO) analyses are undertaken. Finally, the calculated results and the experimental findings of corresponding ILs are compared and discussed to explore reaction mechanism between I_2 with ILs.

2. Experimental methods

All the studied ILs (≥99%) mentioned above were supplied by Lanzhou Greenchem ILs, LICP, CAS (Lanzhou, China) or synthesized. Before experiments, the pretreatment of the studied ILs have been carried out according to Mu's methods [17]. Iodine and other basic chemicals were purchased from Sinopharm Chem. Regent Co., Ltd.

To wipe out the influences of the contact area at room temperature without stirring, 100 mg ILs sample and 5 ml iodine/cyclohexane solution (initial concentration of 0.01 mol l^{-1}) were placed into the bottom and the up of the UV cuvette with a volume of 15 ml by ultrasonic oscillation, respectively. UV/vis spectroscopy was used to depicted the supernatant and determine iodine concentration. Furthermore, FT-IR ATR [25] was used to determine the intrinsic electrostatic field of ionic liquids, which the molecular probe had been replaced by acetonitrile. In the following discussion on the complexes of iodine with ILs were carried out with the aid of a comparison of changes of UV/vis spectroscopy characteristic absorption bands after addition of equal molar ILs.

3. Computational methods

All the geometries of studied monomers and complexes are fully optimized at M06-2X/6-31+G (d) level and also characterized as minima by frequency analyses, then geometry optimizations are performed at M06-2X/aug-cc-pVTZ level [26], which pseudopotentials are used to describe the inner core orbital for iodine. Frequency calculations are carried out at the same level to verify the reasonability of the optimized structures. The distribution of atomic charges is investigated using the Merz–Singh–Kollman (MK) scheme [27]. Quantitative analysis of molecular surface and AIM analysis is performed via the Multiwfn 3.3.8 program [28]. NBO analyses are performed to investigate characteristics of halogen bond at M06-2X/aug-cc-pVTZ level. In order to account for the basis set superposition error (BSSE), the procedure is carried out to correct interactions of the studied complexes, which was put forward by Boys and Bernardi [29]. Especially pointed out that DFT calculation is carried out with Gaussian 09 package [30].

4. Results and discussion

4.1. Experimental analysis

4.1.1. Radioiodine kinetic removal analysis

As is shown in Fig. 1 [17], in order to investigate the radioiodine removal and stable storage efficiency by Eight [Bmim]-based ILs, the process of radioiodine kinetic removal is investigated and analyzed. As is shown in Fig. 1, ILs with anions such as $[PF_6]^-$ and