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ARTICLE TYPE

Investigation of ionic liquids for efficient removal and reliable storage of radioactive iodine: a halogen-bonding case

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A series of ionic liquids (ILs) were investigated for removal and storage of radioactive iodine (I_2) waste released by nuclear power plants. The I_2 removal efficiency of ILs was dependent upon the anion species while cation species seemed to have little influence. Particularly, the I_2 removal efficiency of [Bmim][Br] was higher than 96% in 5 hours. The nitrogen gas sweeping tests showed that [Bmim][Br] holds I_2 tightly, and the leak of I_2 from it was negligible under daily life conditions. Spectroscopy studies indicated high removal efficiencies and storage reliability of ILs were attributed to halogen bonding (XB).

The importance of efficient removal and reliable storage of radioactive nuclear wastes is reminded by the recent accident at Fukushima Dai-ichi Nuclear Power Plant in 2011,[1] since the Chernobyl disaster of last century. Radioactive isotopes of iodine ($^{125/129/131}I$) are produced as by-products during the fission of uranium and plutonium, and exposure to these isotopes is believed to boost thyroid cancer.[2, 3] Thus, these isotopes need to be efficiently removed from environment, and be reliably stored, especially for ^{129}I, due to its long half-life (~10^7 years). Until now, many materials, such as activated carbon,[4] porous organics[5, 6] and zeolite-likes,[5, 7-10] have been used to remove iodine. However, these materials still bear some drawbacks, such as low removal efficiency, high cost and difficulty in preparation, and lack of potential in reliable storage in long period of time due to low affinity to iodine. Hence, novel materials for removal of iodine are still of environmental and economical interests.

Recently, increasing attention has been paid to ionic liquids (ILs), especially those with 1-butyl-3-methyl-imidazolium cation ([Bmim]), due to their peculiar properties such as high polarity, negligible vapour pressure, wide liquid range, and tunability by varying cationic or anionic species, etc. ILs are entirely composed of ions and recognized as a future solvent.[11] In the last decades, ILs have been used in the separation process,[12] catalytic reactions,[13] and energy-related applications.[14]

In this study, we demonstrated the potentials of ILs in efficient removal and reliable storage of radioactive iodine. A series of [Bmim]-ILs were chosen as removal and storage agents, followed the other two ILs for comparison (Fig. 1). As described in literature,[7] the I_2 removal efficiency of ILs were investigated by using solutions of I_2 in cyclohexane and analyzed by Ultraviolet–visible (UV/vis) spectroscopy. The potential of ILs in reliable storage of iodine was estimated by the remained mass of iodine after vigorous nitrogen gas sweeping. At last, spectroscopy studies were applied to explain the abilities of ILs in removal and storage of iodine.

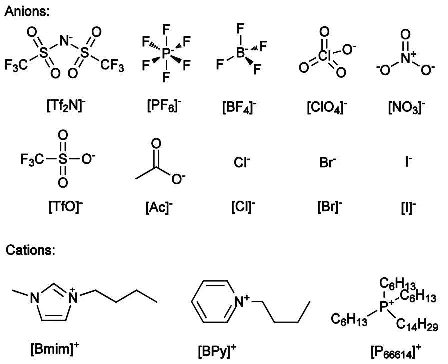

Fig. 1 Structures and abbreviations of the cations and the anions being investigated.

The I_2 kinetic removal was analyzed with the frequently used [Bmim]-based ILs for investigating the effect of anions. Six out of eleven chosen ILs exhibit excellent capability of I_2 removal, and reached capacity of > 80% in 5 hours (Fig. 2 and Fig. S1b). This time scale is much smaller than that reported for the capture of I_2 by amorphous molecular organic solids.[5] ILs with an anion of $[Tf_2N]^-$, $[PF_6]^-$, $[ClO_4]^-$ and $[BF_4]^-$ have poor I_2 removal efficiency, which is only 3, 5.5, 6 and 7%, respectively, after 24 hours. It suggests that I_2 might be just absorbed on the surface of these ILs layer other than into the interior. Higher values are observed with $[NO_3]^-$, $[Ac]^-$, $[Cl]^-$, $[TfO]^-$, $[I]^-$ and $[Br]^-$, which allow a removal efficiency in 5 hours, of 39, 84, 87, 90, 92 and 96%, respectively. At the time of 5 hours, the removal efficiency using $[NO_3]^-$, comes right in the middle between the highest and lowest. After 5 hours, all ILs reach to the equilibrium. The latter five ILs reach maximum efficiency around 98% ~ 99% after 24 hours. Considering an overall error in weighing, dissolution and transfer, of ±1%, it indicates that I_2 is completely removed by these ILs in one day (Figure S1c). It takes only 5 hours for [Bmim][Br] to remove 96% of I_2 from stock solution, while, to accomplish this goal, it takes 48 hours for the best metal-organic framework (MOF) in a very recent study.[7] Since the ILs used in this study are liquid, it's fairly anticipated that less time would be taken to reach maximum efficiency with stirring.

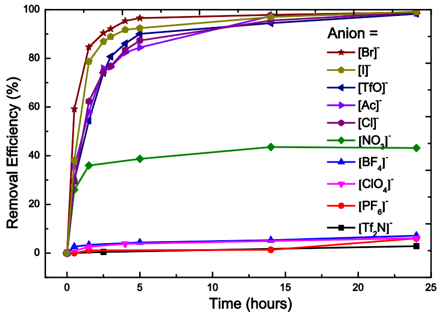

Fig. 2 Iodine (I_2) removal kinetics of [Bmim]-based ILs with different anions at room temperature (volume of I_2 in cyclohexane = 5 ml, concentration = 0.01 mol L^{-1}, amount of ILs = 0.1 g).

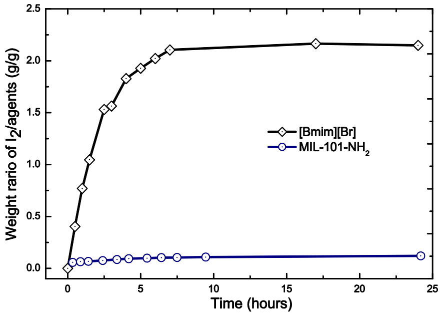

Fig. 3 Iodine (I_2) removal kinetics of different agents: TOP, [Bmim][Br] at room temperature, volume of I_2 in cyclohexane solution = 100 ml, concentration =0.01 mol L^{-1}, amount of ILs = 0.1 g; BOTTOM, metal-organic framework (data retrieved from reference 7), MIL-101-NH_2 (the best one in that study) at room temperature, volume of I_2 in cyclohexane solution = 5 ml, concentration =0.01 mol L^{-1}, amount of MIL-101-NH_2 = 0.1 g.

Nevertheless, ILs with an anion of [Br] has highest capture efficiency (Fig. 2, top and Fig. S1b), except that [P_{66614}][Br] might form strong complexes with I_2, and that complexes are soluble in cyclohexane, so the removal efficiency cannot be measured (Fig. S1d, left). Surprisingly, [Bmim][Br] has stronger removal ability than [Bmim][I] although iodides are well known for increasing iodine solubility in water. The I_2 removal kinetics of [BPy][Br] is nearly identical to [Bmim][Br], indicating that the removal capability of ILs is not influenced by the cation.

To further explore the applicability of ILs in iodine sorption on an industrial scale, the experiment of I_2 removal from 100 ml initial I_2 in cyclohexane solution (C_0 = 0.01 mol/L) by 0.10 g [Bmim][Br] was carried out (Fig. 3). Over a period time of 7 hours, more than 82% of I_2 is removed, which means that the removal capacity is more than 2.1 g I_2 per 1 g [Bmim][Br] or 1.9 mole/mole. This capacity has never been achieved before, which makes [Bmim][Br] the superb iodine removal agent. It is undoubtedly that [Bmim][Br] has greater potential in cleaning up iodine waste than the best MOF in a recent study. [7]

Besides the I_2 removal, it is very important to keep the radioactive iodine tight in container within relatively small space since I_2 is highly volatile (Fig. S3, first from right). Thereby, nitrogen sweeping was carried out to examine the ability of the ILs to hold volatile iodine in a relatively long period of time. A criterion was introduced to evaluate the strength of ILs for holding iodine: the less loss in mass of iodine during nitrogen sweeping means higher storage reliability, since nitrogen sweeping has been applied in clearing out weakly binded residues and thus purification of ILs.[15]

Although I_2 can be well dissolved in a wide range of organic solvents, these solvents are not fit for storing iodine because organic solvents are flammable, toxic, and highly volatile. In contrast, ILs are non-flammable and non-volatile. The nitrogen sweeping in thermal gravimetric analysis (TGA) was aimed to mimic the evaporation process of iodine by air flow in real world. The temperature was set at 30 ℃, and the enhanced nitrogen gas flow was set at 40 ml/min in a sample chamber with a volume of ~20 ml, which accelerated the experiments in order to observe the differences during appropriate time span. Prior to I_2-dissolved samples, the ILs were put under the scrutiny of TGA to let impurities effects be cleared out. The mass loss after 10 hours is negligible for [Bmim][Br] and [Bmim][ClO_4], respectively (Fig. S2). Since no reaction exists between iodine and these ILs, it is reasonable to attribute the lost mass to iodine evaporation (Fig. 4). The results show that 99.9% of iodine dissolved in [Bmim][ClO_4] evaporated after 10 hours, while only 11% of that in [Bmim][Br] was lost under same conditions. For comparison, a tiny solid iodine particle with a diameter of ~1 mm and powdered iodine samples show a mass loss of 46 and 69%, respectively under same sweeping. Although there is still a considerable leak of iodine from [Bmim][Br], the total mass of leaked iodine is very small (around 0.3 mg), compared to that of solid iodine (> 15 mg) under the strong nitrogen fluid. In fact, the leak from [Bmim][Br] is negligible under daily life conditions (Fig. S3). Thus, [Bmim][Br] can be seen as a reliable storage medium for radioactive iodine.

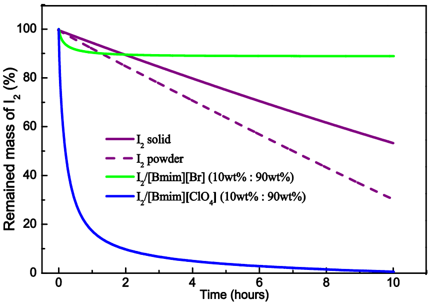

Fig. 4 TGA curve of evaporation of iodine (I_2) under nitrogen (N_2) gas sweeping (amount of sample ~ 30 mg, N_2 flow = 40 ml min^{-1}, temperature = 30 ℃): the percentage of remained mass of I_2 in ILs was calculated as 100% minus lost mass of TGA curve divided by original mass of I_2.

So far, the applicability of ILs with anion of [TfO]$^-$, [Ac]$^-$, [Cl]$^-$, [Br]$^-$, and [I]$^-$ in removal and storage of iodine has been proven. Why are these ILs suitable for removal and storage of I_2? What kind of interactions binds iodine molecules so firmly to these ILs?

Spectroscopy studies were applied to provide further information about the interactions between iodine and ILs (Fig. 5 and Fig. 6). Given that the electron shell of element iodine is easy to be polarized, it is fairly assumed that the iodine is polarized by intrinsic electric field (IE) of ILs and has a high polarity. If the assumption is true, there would be a positive correlation between the strength of IE and capability of ILs to hold iodine. FT-IR spectroscopy was applied to measure IE of ILs,[16, 17] the basis of which was the vibrational Stark effect.[18] Our experimental results show that IE strength of ILs with various anions in following order: $[Tf_2N]^- < [PF_6]^- < [TfO]^- < [ClO_4]^- \sim [BF_4]^- < [NO_3]^- < [I]^- < [Br]^- < [Ac]^- < [Cl]^-$ (Fig. 5). These results are consistent with literature.[16, 17]

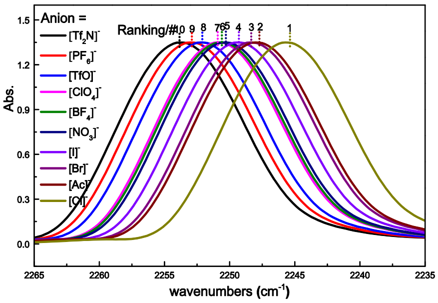

Fig. 5 Normalized FT-IR absorption spectra of $\nu_{C\equiv N}$ in [Bmim]-based ILs (IE strength ranking, from left to right: $[Tf_2N]^-$, $[PF_6]^-$, $[TfO]^-$, $[ClO_4]^-$, $[BF_4]^-$, $[NO_3]^-$, $[I]^-$, $[Br]^-$, $[Ac]^-$, $[Cl]^-$, respectively).

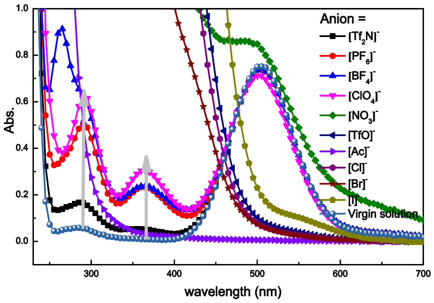

Fig. 6 UV/vis spectroscopy of iodine (I_2) in dichloromethane solution (0.8 mmol L^{-1}) after addition of equivalent mol of ionic liquids (ILs).

While Fig. 2 shows that the I_2 removal efficiency of [Bmim]-based ILs with various anions follows the order: $[Tf_2N]^- < [PF_6]^- < [ClO_4]^- \sim [BF_4]^- < [NO_3]^- < [Ac]^- < [Cl]^- \sim [TfO]^- < [I]^- < [Br]^-$. This is similar to the IE order, except when anion is $[TfO]^-$, $[I]^-$ or $[Br]^-$. Hence, on one hand, a positive correlation does exist between IE and removal efficiency; on the other hand, there must be some other effects to explain exceptions.

In the last two decades, increasing studies are focused on halogen bonding (XB),[19-25] which is considered as a counterpart of hydrogen bonding (HB) in hydrophobic environment. The XB has been defined as interaction involving halogens as electron acceptors, and demonstrated as the general scheme D…X-Y, in which X is the halogen atoms, D is any electron donor, and Y is any other atoms like carbon, halogen, and nitrogen, and so on. XB has been proven to be both reliable and effective in understanding and rationally designing self-assembly processes. Experimental and computational studies have confirmed the attractive nature and directionality of interaction between halogen atoms and electronegative species (halide anions, O and N atoms).[26]

Herein, it can be anticipated that $[TfO]^-$, $[Ac]^-$, $[Cl]^-$, $[Br]^-$, and $[I]^-$ might form complexes with iodine molecules due to XB, which increases the strength of holding iodine. Aimed at proving the existence of such complexes, UV/vis spectroscopy experiment was carried out (Fig. 6). UV/vis method was useful in determined the XB binding constants.[27] The original solution was iodine in dichloromethane (C_i = 0.8 mM). After addition of equal molar ILs, absorption spectra of iodine change in different ways. For anions of $[Tf_2N]^-$, $[PF_6]^-$, $[BF_4]^-$ and $[ClO_4]^-$, enhanced absorption peaks arise at 365 and 290 nm (grey arrow), and the absorption intensity increase in the following order: $[Tf_2N]^- < [PF_6]^- < [BF_4]^- < [ClO_4]^-$, which is exactly the same as IE strength order and removal efficiency order. Therefore, These changes can be attributed to induction effects by these anions with high polarity. Polarized specie arises apart from I_2 of neutral status. The characteristic adsorption band at 509 nm of I_2 was totally wiped out by addition of ILs with any anion of $[TfO]^-$, $[Ac]^-$, $[Cl]^-$, $[Br]^-$, and $[I]^-$, which suggests that new species other than polarized or neutral iodine were produced.

Moreover, a very recent study has explicitly proven the strong XB interaction between I_2 and $[X]^-$ (X = Cl, Br, I.) and the existence of resulted $I_2/[X]^-$ complexes.[28] And Taylor's work showed that the association constants for XB interactions of XB donors and $[X]^-$ decrease as following: $[Cl]^- > [Br]^- > [I]^-$.[23] However, $[Cl]^-$ among forms strong HB with C2-H of imidazole ring,[29] which weaken its XB accepting ability. So, for [Bmim][X], the XB acceptor' ability of $[X]^-$ follows the order as $[Br]^- > [I]^- > [Cl]^-$, which is consistent with the removal efficiency order. And $[Ac]^-$ seems to form weaker XB than $[TfO]^-$, which results in narrower adsorption band of $[Ac]^-$ (Fig. 6). This might be because of the cooperative structure in $[Ac]^-$, which alleviates the density of electron cloud around the oxygen atom, since the halogen bonded structures are mainly electrostatically driven.[30] $[NO_3]^-$ seems to be the tipping point with a partial deformation of absorption band (Fig. 6, green line), which indicates there is still a part of iodine remains as neutral molecules aside from XB bonded ones. This is consistent with the modest I_2 removal efficiency of [Bmim]$[NO_3]$ (Fig. 2).

All in all, given combination of IE and XB evidences, a picture can be drawn like this: both XB and IE contribute to the capability of ILs in I_2 removal and storage, but XB is the main contributor, which can drag the I_2 molecules into interior of ILs and results in excellent performance (Fig. 7). Thereby, it's easy to understand that IL with $[Br]^-$ stands out of these anions as the best I_2 removal and storage agent.

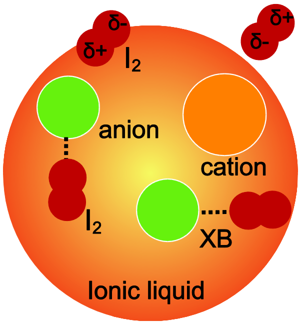

Fig. 7 A cartoon representing that iodine molecules (I_2) existing interior and surface of ionic liquids (ILs) layer.

Conclusions

In summary, we particularly demonstrated the potentials of [Bmim]-based ILs in efficient removal and reliable storage of I_2. Results show that ILs with any anion of $[TfO]^-$, $[Ac]^-$, $[Cl]^-$, $[Br]^-$, and $[I]^-$ are excellent candidates for these applications. The capability of ILs of holding I_2 is mainly related to the halogen bonding acceptor's ability of anions, while intrinsic electric field can weakly bind the I_2 molecules when there is no halogen bonding acceptor.

Experimental section

Materials. All the ILs (≥ 99%) in Table S1 were purchased from Lanzhou Greenchem ILs, LICP, CAS, China. They were pretreated according to literature.[31] Iodine (I_2) and other basic chemicals (≥ 99.5%) were purchased from Sinopharm Chem. Regent Co. Ltd, and used as received. The nitrogen gas (≥99.999%) used in TGA was purchased from Beiwen Special Gases Factory, Beijing, China.

Iodine removal experiments. 100 mg of anhydrous ILs sample was evenly distributed at the bottom of identical vials with a volume of 15 ml, by ultrasonic oscillation in order to wipe out the influences of contact area, followed by addition of 5 ml of I_2 in cyclohexane solution (initial concentration C_0 = 0.01 mol L^{-1}) at room temperature without stirring. Then, UV/vis spectroscopy was applied to characterize the supernatant and determine the iodine concentration, and details are given in ESI (section 'Removal experiments').

Nitrogen sweeping experiments. The potential of ILs in reliable storage of iodine was estimated by the remained mass of iodine after vigorous nitrogen gas sweeping by Thermal-Gravity-Analysis (TGA), mimicking the leak of I_2 from storage medium. TGA was carried out with a TA Instruments Q50-TG thermal analyser (Sample weight ~30 mg, t =10 h and T = 30 ℃, nitrogen gas flow = 40 mL/min).

Spectroscopy studies on iodine-ILs interactions. The intrinsic electrostatic field of ILs was determined through Fourier Transform Infrared Spectroscopy (FT-IR),[16, 17] but the molecular probe was replaced by acetonitrile. The existence of iodine-ILs complexes are depicted in changes of UV/vis spectroscopy characteristic absorption bands after addition of equal molar ILs

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Notes and references

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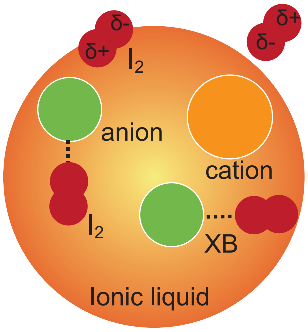
Ionic liquids could be used for removal of radioactive iodine waste released from nuclear power plants by halogen bonding (XB).



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