

Fluoride ion yield and absorption spectral analysis of irradiated imidazolium-based room-temperature ionic liquids

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ABSTRACT

The radiation chemical yields of F ions ($G(F^-)$ values) were measured for a group of imidazolium-based room-temperature ionic liquids following ^{60}Co gamma ray irradiation. The $G(F^-)$ values of ionic liquids: hexafluorophosphate, bis[(trifluoromethyl)sulfonyl]imide, trifluoromethanesulfonate and tetrafluoroborate anions associated with 1-butyl-3-methylimidazolium cations were determined to be 0.227, 0.136, 0.101 and $0.008 \mu\text{mol J}^{-1}$, respectively. The $G(F^-)$ value is dependent on the F–X (X=B, P, etc.) bond energy and the anion structure and can be considered as an indicator of the radiation stability of fluorine-containing ionic liquids. In addition, as confirmed by UV–Vis absorption measurement, the radiolytic products with strong photoabsorption and color darkening depend on the structures of both the cation and the anion.

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1. Introduction

Room temperature ionic liquid (RTIL) has received much attention due to its low melting point, extremely low vapor pressure and good stability under oxidative and reductive conditions (Berg et al., 2005; Binnemans, 2005; Handy, 2005; Sowmiah et al., 2009). Potential applications of RTILs in the extraction of fission products from spent nuclear fuel and in the uranium enrichment process have been considered. Harmon et al. (2001) found that the minimum critical concentrations of uranium and plutonium in RTILs are much lower than in aqueous solutions. Fields et al. (1998) reported a method of dissolving uranium oxide directly in ionic liquids. Compared to the prevalent method of aqueous reprocessing, the dry reprocessing of spent nuclear fuel could not only reduce the loss of ionic liquids during solvent extraction but also contribute to ionic liquid recycling by using supercritical gaseous CO_2 (Alfassi et al., 2003). A number of recent publications relate to the recovery of metal species such as uranium, europium, samarium and palladium from spent nuclear fuels by electrorefining, taking the advantage of specific properties of RTILs, including their good conductivity and wide electrochemical window (Bhatt et al., 2005; Giridhar et al., 2006a, 2006b; Pitner et al., 2003).

In the traditional nuclear fuel separation processes (UREX or PUREX), tributyl phosphate and odorless kerosene (TBP/OK; extraction solvents) undergo radiolytic degradation and absorb

substantial damage. Hence, the application of RTILs in nuclear spent fuel recycling requires a comprehensive knowledge of their stability and chemical reactions under irradiation conditions. Baston et al. (2002) and Allen et al. (2002) found that imidazolium-based ionic liquids have substantially greater radiation stability than TBP/OK. The gamma irradiation of 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF₆) and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([Bmim]Tf₂N) showed no obvious changes in their physical properties (Berthon et al., 2006). Analyses of radical species of ionic liquids were carried out by magnetic resonance spectroscopy (Shkrob et al., 2007). Zhai and co-workers have studied the radiation-induced darkening and the further decoloration of ionic liquids [Bmim]Tf₂N (Yuan et al., 2009a) and [Bmim]PF₆ (Yuan et al., 2009c), and the influence of the dose on the imidazolium-based ionic liquids during the extraction of metal ions (Yuan et al., 2008, 2009b, 2009d).

Imidazolium-based ionic liquids with commonly used anions, such as Tf₂N[−], PF₆[−], BF₄[−] (tetrafluoroborate) and TfO[−] (trifluoromethanesulfonate), have relatively low H₂ yields under radiation conditions (Le Rouzo et al., 2009). At the same time, Tarabek et al. (2009) also investigated the radiation yields of H₂ for a series of ionic liquids and concluded that the $G(\text{H}_2)$ values of the imidazolium- and pyridinium-based ionic liquids were much lower than that of the phosphonium-based ones.

We have previously investigated the radiation stability of some imidazolium-based ionic liquids (Qi et al., 2007, 2008) and found that ionic liquids containing fluorine atoms in their anions release fluorinated products upon gamma irradiation. It has also been confirmed that the irradiation of [Bmim]PF₆ leads to the formation

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of HF (Yuan et al., 2008). These fluorides and acids impose higher requirements on the containers and treatments in practical use with ionic liquids under radiation conditions, so it is very important to assess the fluoride ion yields of ionic liquids.

In this work, the radiation yields of F^- of four different imidazolium-based ionic liquids containing fluorine were first determined using the fluoride ion selective electrode (F-ISE). The ionic liquids consisted of four commonly used anions: Tf_2N^- , TfO^- , PF_6^- and BF_4^- , associated with the $Bmim^+$ cation. Based on the UV–Vis absorption spectra, the radiolysis products of cations at different doses were quantitatively examined.

2. Experimental

2.1. Materials

The ionic liquids [Bmim] Tf_2N (99%), [Bmim] PF_6 (99%), [Bmim] BF_4 (99%), [Bmim] TfO (99%), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim] BF_4) (99%) and 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim] BF_4) (99%) were purchased from Shyflx Corp. Ionic liquids with BF_4^- and TfO^- are hydrophilic, while those with PF_6^- and Tf_2N^- are hydrophobic. The water content, measured by ZKF-1 Karl-Fisher titration, was less than 0.08 wt%. Analytical grade NaOH, NaF, NaCl, sodium citrate, glacial acetic acid and dimethyl formamide (DMF) were purchased from SCRC (Shanghai, China). All the samples were prepared in a vacuum desiccator and heated at 70 °C for 24 h to remove the volatile impurities prior to irradiation. Water was freshly deionized and distilled before use.

Standard NaF aqueous solution (F^- 100 $\mu g\ ml^{-1}$) and total ion strength adjustment buffer (TISAB; 57 ml glacial acetic acid, 58 g NaCl, 12 g sodium citrate and the proper amount of NaOH in a 1 L volumetric flask, diluted with water and pH \approx 5.5) were prepared and stored in polyethylene (PE) containers before measurement.

2.2. Sample irradiation

Ionic liquid samples were sealed in polypropylene (PP) ampoules and bubbled with N_2 for at least 15 min before irradiation. The samples were then irradiated with a dose of 100–600 kGy ($25\text{--}30\ Gy\ min^{-1}$) at room temperature in a ^{60}Co source at the Shanghai Institute of Applied Physics. The absorbed dose was monitored using a conventional potassium dichromate dosimeter.

2.3. Sample analysis

The yields of F^- produced via radiolysis of ionic liquids were determined by employing a PHSJ-4A digital ionic strength meter and PF-1F-ISE (Precision & Scientific Instrument Corp., Shanghai). The electrodes constructed from single-crystal sections of rare earth fluorides respond to fluoride ion activity over more than five orders of magnitude and show a high selectivity for fluoride over other common anions (Frant and Ross, 1966). For the fluoride ion selective electrode measurements, the standard calibration curve was obtained by adding standard NaF aqueous solution to untreated water solutions. All calibrations and determinations of fluoride concentrations in irradiated ionic liquid were carried out at ambient temperature.

The UV–Vis absorption spectra were obtained from a UV-3010 spectrophotometer (Hitachi) with a cuvette of 1 cm path length, and the irradiated specimens were diluted with water and DMF in a ratio of 1/300.

3. Results and discussion

All samples of ionic liquids in this experiment darkened after irradiation and the degree of darkening was found to be an increasing function of the dose, as in previous works (Qi et al., 2007, 2008; Yuan et al., 2009a). Furthermore, [Bmim] PF_6 has the highest degree of darkening under identical irradiation conditions, and [Bmim] Tf_2N has the lowest. Moreover, there were pungent fumes (containing toxic and corrosive HF) released by these irradiated ionic liquid samples containing fluorine in the anions. Therefore, special care and suitable experimental containers (such as PE or other corrosion-resistant materials) should be used when handling F-containing ionic liquids, as insisted by Swatloski et al. (2003).

3.1. Radiation yields of F^-

Different concentrations of NaF in the range of 0–10 $\mu g\ ml^{-1}$ were applied to obtain a standard calibration curve. The correlation coefficient of the linear fitting curve is 0.9999, as indicated in the inset of Fig. 1. Each sample was measured three times to obtain a mean value. As shown in Fig. 1, the correlation coefficient of the cumulative fluoride ion concentration is linearly proportional to the dose for [Bmim] Tf_2N and other ionic liquids up to 600 kGy.

Fig. 2 shows the yield of F^- as a function of the dose for four different ionic liquids. The radiation yields of F^- calculated from the slopes of the fitting curves are listed in Table 1. Because the concentration of F ion (ca. 1–2 $\mu g\ ml^{-1}$) in the gaseous products was almost independent of the dose, its contribution was neglected and assumed to have little influence on the final result.

As shown in Fig. 2, the four ionic liquids have completely different yields of F^- , and the difference between [Bmim] PF_6 ($0.227\ \mu mol\ J^{-1}$) and [Bmim] BF_4 ($0.008\ \mu mol\ J^{-1}$) is about one order of magnitude. The radiation chemical yields of F^- ions measured in this work are slightly lower than the radiolytic disappearance yields of the cations of [Bmim] Tf_2N ($-0.28\ \mu mol/J$) and [MeBu $_3N$] Tf_2N ($-0.38\ \mu mol/J$), measured by ESI-MS (Bosse et al., 2008; Le Rouzo et al., 2009). As for the anions, the dissociation of the S–C and C–F bonds of Tf_2N^- / TfO^- or the N–S bond of Tf_2N^- takes place. The dissociation of chemical bonds leads to the formation of many radical species such as F^\bullet , $^\bullet CF_3$, $CF_3SO_2^\bullet$,

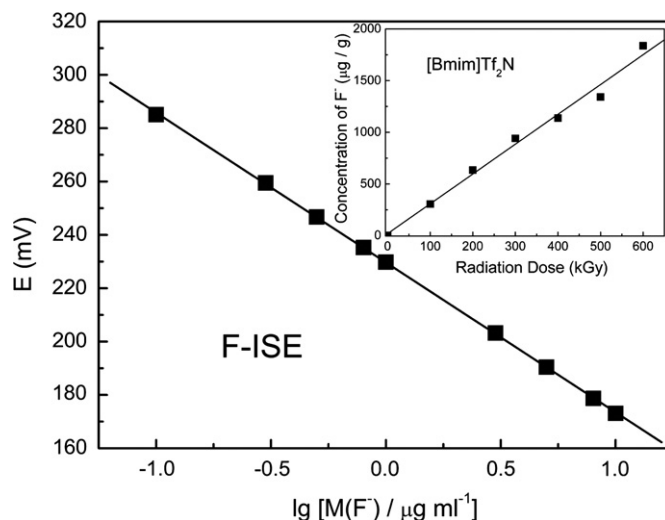


Fig. 1. Standard calibration curve of fluoride ion concentration (M_{F^-}) in $\mu g\ ml^{-1}$ vs. electrode response (E) in millivolts of known amount of NaF solution in a TISAB background. Inset shows the linear plot of cumulative fluoride ion concentration ($\mu g\ g^{-1}$) vs. cumulative radiation dose (kGy) obtained after irradiation of [Bmim] Tf_2N .

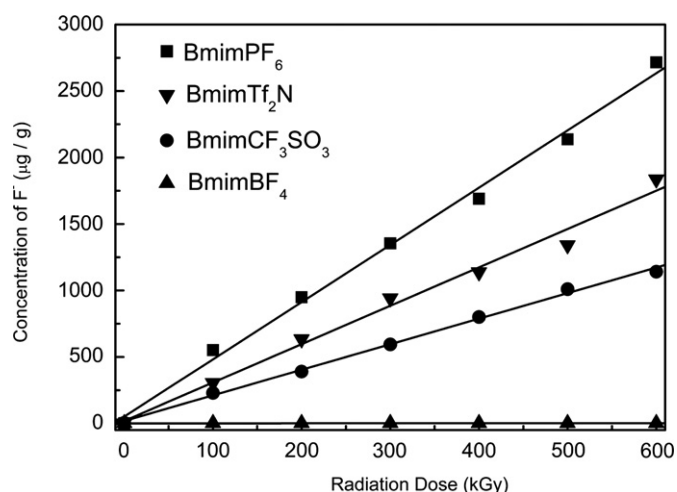


Fig. 2. Concentration of fluoride ion ($\mu\text{g g}^{-1}$) contained in irradiation ionic liquids explored to different radiation dose (kGy).

Table 1

Radiation yields of fluorine ion and corresponding anions.

RTIL	$G(\text{F}^-)$ ($\mu\text{mol J}^{-1}$)	$G(\text{anion})$ ($\mu\text{mol J}^{-1}$) ^a
[Bmim]PF ₆	0.227	−0.18
[Bmim]Tf ₂ N	0.136	−0.22
[Bmim]TfO	0.101	−0.18
[Bmim]BF ₄	0.008	−0.10

^a Le Rouzo et al. (2009).

$\text{CF}_3\text{SO}_2\text{N}^+\cdot$. Some reactions may occur among these radicals during the irradiation, forming a variety of radiolytic products. Therefore, the radiation yields of F^- (or F^\cdot) are lower than the disappearance yields of the Tf_2N^- and TfO^- anions. However, for PF_6^- , the dissociation of the P–F bond leads to double or triple formation of F^\cdot , more than the disappearance of anions. For BF_4^- , the radical BF_4^\cdot seems to be the main product and the radiation chemical yield of F^- is extremely low.

Moreover, this difference in the $G(\text{F}^-)$ values of different anions might also be due to the difference in the F–X (X=B, P, etc.) bond energy. The energy of the B–F bond ($> 640 \text{ kJ mol}^{-1}$; Dibeler and Liston, 1968; Sana et al., 1992) is much higher than that of P–F (ca. 520 kJ mol^{-1} ; Greenhal and Weinberg, 1967), so the $G(\text{F}^-)$ value of [Bmim]PF₆ is higher than that of [Bmim]BF₄. Although the energy of the C–F chemical bond (ca. 540 kJ mol^{-1}) (Lemal, 2004) is very close to that of P–F, the C–S bond (ca. 200 kJ mol^{-1} ; Cullen et al., 1970) of anions seems to be more easily dissociated, and the generation of $\cdot\text{CF}_3$ from the radiolysis of Tf_2N^- and TfO^- is probably more likely than that of F^\cdot . Moreover, the F^- yield of [Bmim]Tf₂N is higher than that of [Bmim]TfO because the Tf_2N^- anion has two $-\text{CF}_3$ groups while the TfO^- has only one. As a result of the influence of the chemical bond energy, the radiation chemical yields of F^- for the four ionic liquids are ordered as follows: [Bmim]PF₆ > [Bmim]Tf₂N > [Bmim]TfO > [Bmim]BF₄. It is worth noting that even the ionic liquid [Bmim]Tf₂N, which is widely investigated due to its excellent physical properties (Bonhote et al., 1996; Huddleston et al., 2001; Oldham et al., 2002; Tokuda et al., 2004) and its efficient extraction capability of metal ions (Nakashima et al., 2005), has a substantially high F^- yield ($0.136 \mu\text{mol J}^{-1}$), which is much higher than the hydrogen gas yield of most imidazolium ionic liquids (Tarabek et al., 2009).

3.2. UV–Vis spectrum

As mentioned above, the color darkening and irritant gas emission indicate that the gamma irradiation could cause significant damage to the chemical structures of ionic liquids. The UV–Vis spectra of the radiolytic products of a series of irradiated [Bmim]BF₄ samples are shown in Fig. 3. A new absorption band at 250–500 nm is observed for irradiated [Bmim]BF₄, with an absorption maximum (λ_{max}) of 285 nm.

The inset of Fig. 3 shows that the intensity of this absorption band increases linearly in the dose range of 0–500 kGy. The color change may be due to the formation of colored products via the further radical-promoted oligomerization of imidazolium or imidazole units (Berthon et al., 2006; Chandrasekhar et al., 2008). The UV–Vis spectra indicate that the amount of colored products generated from the radiolysis of [Bmim]⁺ cation depends on the dose absorbed.

In order to confirm the components of the radiolytic products of imidazolium ionic liquids, a comparative experiment was implemented employing three imidazolium ionic liquids with different alkyl groups in their cations under the same irradiation conditions. Fig. 4 shows the absorption spectra of irradiated ionic liquids containing different alkyl imidazolium cations (butyl for [Bmim]⁺, hexyl for [Hmim]⁺ and octyl for [Omim]⁺) but the same inorganic anions BF_4^- . It is clearly observed that the absorption bands for these three ionic liquids are similar in the UV region around 285–290 nm. The λ_{max} has a red-shift when the number of carbon atoms of alkyl groups is increased. This observation is consistent with the report of Zhai (Yuan et al., 2009a), who found that the absorption peak in the UV spectra of irradiated ionic liquids was affected by the length of the alkyl chain on the imidazolium cation as well as the structure of the anions. Based on the shift in the value of λ_{max} and with the increase in alkyl chain length of cations, we believe that the absorption band at 250–500 nm is due to the products via the radiolysis of organic cations. Also, as shown in Fig. 4, the alkyl chain length of imidazolium cations affects the position of the absorption peak as well as the intensity in the UV absorption spectrum. Longer alkyl chains in imidazolium cations correspond to weaker absorption peaks. This indicates that imidazolium ionic liquids with longer alkyls group might have higher radiation stabilities.

Similarly, the color darkening and increased spectral absorption also occurred in the hydrophobic ionic liquids. Fig. 5 shows the UV

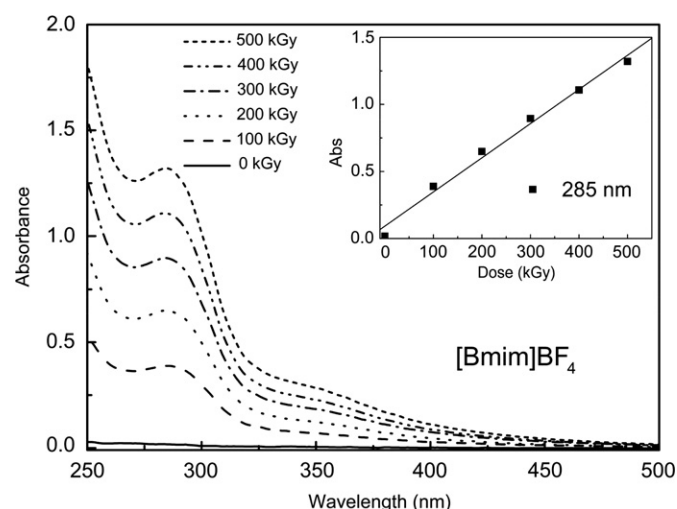


Fig. 3. UV–Vis spectra of [Bmim]BF₄ before and after gamma irradiation at different radiation dose under nitrogen atmosphere. Inset shows the dependence of light absorbance of irradiated [Bmim]BF₄ on absorbed dose at 285 nm.

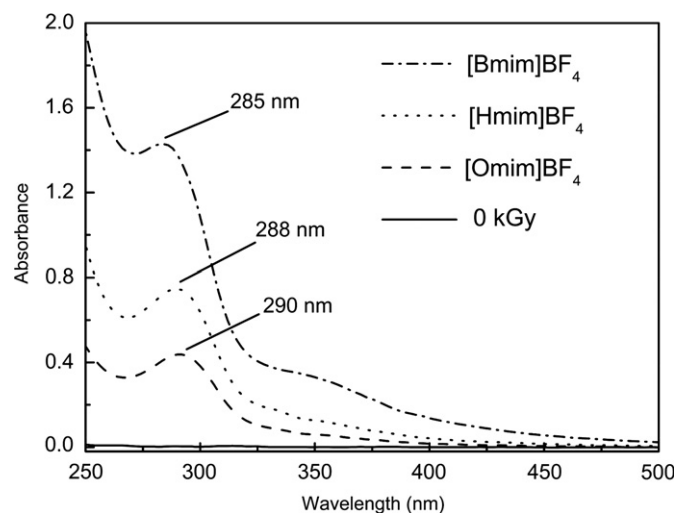


Fig. 4. UV-Vis spectra of [Bmim]BF₄, [Hmim]BF₄, and [Omim]BF₄ after gamma irradiation at 600 kGy and neat specimens of them (overlapped at solid line of 0 kGy) under nitrogen atmosphere.

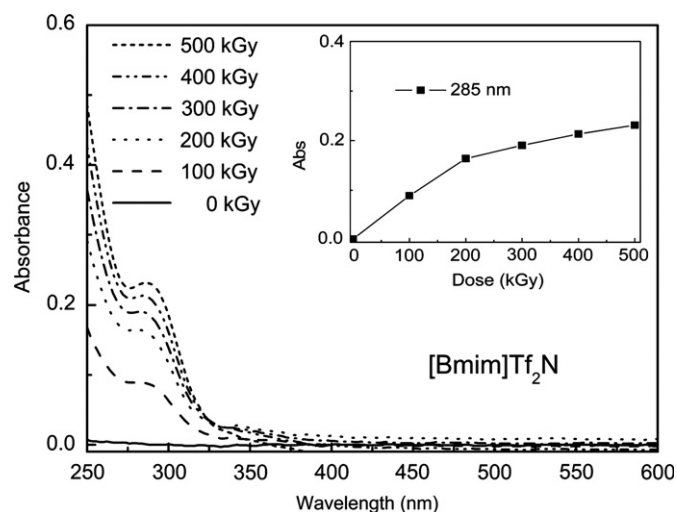


Fig. 5. UV-Vis spectra of [Bmim]Tf₂N before and after gamma irradiation at different radiation dose under nitrogen atmosphere. Inset shows the dependence of light absorbance of irradiated [Bmim]Tf₂N on absorbed dose at 285 nm.

spectra of the hydrophobic [Bmim]Tf₂N after irradiation; the absorption peak at 285 nm indicates a detectable solubility of the irradiated samples in water. Compared with [Bmim]BF₄, the absorption at 250–400 nm exhibits a lower value and does not increase linearly with the dose. As the dose is increased to 200 kGy and higher, the absorption increases very slowly (inset of Fig. 5). It is possible that the radiolytic products have a limited solubility in water and are close to saturation for the irradiated samples above 200 kGy. This implies that the dissolution of radiolytic products in water could separate them from the irradiated hydrophobic ionic liquids, which may be a good pretreatment method for the recycling of ionic liquid in the process of nuclear fuel separation.

4. Conclusion

Several imidazolium ionic liquids with different anions have been investigated under irradiation conditions. These ionic liquids with common anions contain F atoms, which could be released in gaseous or ionic forms upon radiation. We measured the F ion yield

of four ionic liquids with different anions and surmise that this yield mostly depends on the energy of the F–X bonds and the structure of the anions. It was also found that the intensities of new absorption peaks of the irradiated ionic liquids increased with the dose and were influenced by the chemical structure of both cations and anions, while the wavelengths of the absorption peaks are totally dependent on the cations of the ionic liquids. This indicates that different imidazolium cations have different radiolysis products and different levels of radiation stability. In addition, the radiolysis products of hydrophobic ionic liquids also have limited solubility in water, which suggests that water could be a good solvent for the recycling of some hydrophobic ionic liquids in nuclear fuel extraction.

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