Influence of FeCl₃ on radiation stability of ionic liquid BmimCl

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This study investigates the effect FeCl₃ on the radiation stability of the ionic liquid, 1-butyl-3-methylimidazolium chloride (BmimCl) over a wide dose range of 0 to 1000 kGy under γ -ray radiation. The ionic liquid species, BmimFeCl₄, was formed by adding FeCl₃ into BmimCl. The results showed that the presence of FeCl₄[−] significantly improved the radiation resistance of BmimCl, wherein the effect was more pronounced at higher FeCl₄[−] content. Meanwhile, under irradiation, Fe(II) was generated from Fe(III), which was reduced by solvated electron. In addition, the concentration of Fe(II) increased with low level of absorbed dose, but leveled off at higher doses. Moreover, the radiation yield of the solvated electrons of BmimCl was further estimated at approximately 0.358±0.01 $\mu\text{mol/J}$ in BmimCl-7 mol% FeCl₃ system.

radiation, ionic liquid, FeCl₃, BmimFeCl₄, solvated electron

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Ionic liquids (ILs) have low melting points and extremely low volatility; thus, they have potential applications as substitutes for volatile organic or aqueous systems and as possible alternatives to high temperature molten salts in non-aqueous reprocessing [1,2]. Recently, ILs have attracted a great deal attention in the extraction of fission products from spent nuclear fuel because of their high radiation stability and simple separation-reprocessing [3–5]. When applied for nuclear fuel cycle, ILs must withstand high dose of α , β , and γ radiation. Therefore, understanding the radiolytic behavior of ionic liquids and improving their radiation resistance is necessary. Several groups have focused their interests on the radiation stability of ILs [6,7]. Allen et al. [7] have investigated the radiation stability of 1,3-dialkylimidazolium nitrate/chloride ionic liquids, which are more stable than the mixtures of tributylphosphate and odorless kerosene under similar irradiation conditions. The radiation stability of some imidazolium-based ionic liquids, such as

BmimPF₆, BmimTf₂N, and BmimBF₄, has been discussed in our previous study [8,9]. Yuan et al. [10–12] further confirmed the decomposition species of cation [C₄mim]⁺ and anions by EMI-MS and titration analysis. All the studies have indicated that the radiolysis of imidazolium-based ionic liquids can be similar, although the mechanism of improving the radiation stability of ionic liquids remains unclear.

As a water-soluble ionic liquid, some imidazolium-based ionic liquids, such as, [Bmim]Cl, [Emim]AlCl₄, and [Emim]BF₄, cannot be used to extract radioactive species from the aqueous solution; this type of ionic liquids may be used directly to dissolve UO₂ and PuO₂ at elevated temperatures in a dry process [13,14]. Harmon et al. [13] have found that the minimum critical concentration of plutonium in ionic liquids increased by at least one order of magnitude over the aqueous system. Moreover, the concentration can react with FeCl₃ to form a new ionic liquid ([Bmim][FeCl₄]), allowing the investigation of oxidative-reduction processes upon irradiation by measuring the yield of Fe(II). Sitze et al. [15]

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have studied the properties of ionic liquids containing FeCl_3 . FeCl_4^- was found in excess of BmimCl via Raman scattering analysis. On the contrary, when FeCl_3 was in excess, Fe_2Cl_7^- appeared, and the amount increased with increasing FeCl_3 . Considering that Fe(III) can react rapidly with solvated electron to form Fe(II), the solvated electron will disappear completely in a very short time scale at high Fe(III) concentrations. In our group, Huang et al. [16] have found a significant improvement in the radiation resistance of BmimCl after the addition of FeCl_3 . Given that the highest dose is up to 600 kGy and the effect of the single FeCl_3 concentration (5 mol%) was investigated, the higher dose and different concentrations may supply more information about the radiation stability of ionic liquids. In this study, the behavior of BmimCl samples in molar fractions of $x(\text{FeCl}_3) = 0.03, 0.05$, and 0.07 , respectively, exposed to doses up to 1000 kGy, were further compared. The radiation resistance of BmimCl and the effect of FeCl_3 concentration were also investigated in detail. Moreover, the irradiated ionic liquids were analyzed by thermal analysis and various spectroscopic methods.

1 Materials and methods

1.1 Materials

The ionic liquid, BmimCl (99%), was purchased from Shyflx Corp.; the water content was less than 0.5%. Anhydrous FeCl_2 (99.5%) was obtained from J&K Scientific Ltd. Analytical grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) were purchased from SCRC (Shanghai, China). All chemicals were used without further purification. Three kinds of ionic liquids were prepared by mixing BmimCl with different concentrations of FeCl_3 (3 mol%, 5 mol%, 7 mol%). BmimCl and FeCl_3 -containing ionic liquids were then placed in a vacuum desiccator and heated at 70°C for 24 h to remove volatile impurities prior to irradiation. The water content of all samples, measured by ZKF-1 Karl-Fisher titration, was less than 0.05%. Water was freshly deionized and distilled before use.

1.2 Irradiation and measurement

BmimCl and FeCl_3 -containing ionic liquids were transferred to the glass ampoules in a nitrogen atmosphere. The samples were subsequently irradiated to a dose of 0 to 1000 kGy, with a dose rate of 72 Gy/min, at room temperature in a ^{60}Co γ source at Shanghai Institute of Applied Physics.

The samples were characterized by thermal analysis (TG209 F3 analyzer NETZSCH Corp.). UV-Vis absorption spectra analysis (UV-3900 spectrophotometer) was carried out to measure the sample before and after irradiation. $\text{NH}_3 \cdot \text{H}_2\text{O}$ was adopted to deposit the samples after irradiation to observe the reduction species. The samples were diluted with deionized water in a ratio of 1/400 to 1/8000 to

determine the concentration of Fe(II) after irradiation, and $\text{K}_3\text{Fe}(\text{CN})_6$ was added to converse Fe(II) into a Prussian blue complex, which has typical absorption at 700 nm.

2 Results and discussion

2.1 Thermal characterization of BmimFeCl₄

The addition of FeCl_3 to the colorless BmimCl ionic liquid resulted in a dark yellow solution. Sitze et al. [15] and Huang et al. [16] previously prepared these ionic liquids by mixing FeCl_3 with 1-butyl-3-methylimidazolium chloride (BmimCl). When BmimCl is in excess, FeCl_4^- is present via the following reaction:

TG analysis was carried out to compare the thermal stability of BmimCl and BmimFeCl₄. Figure 1(a) shows the TG and DTG curves of BmimCl, in which the BmimCl was stable up to 220°C . The main weight loss was observed at 275°C because of the decomposition of the $[\text{Bmim}]^+$ cation. However, two peaks were observed at 275 and 373°C for the BmimCl-7 mol% FeCl_3 sample (Figure 1(b)). The former was similar to BmimCl and the latter can be assigned to the thermal decomposition of the cation in BmimFeCl₄. This observation is in good agreement with the report by He et al. [17], who revealed that the FeCl_3 -containing ionic liquid is not a single liquid but an ionic compound. The decomposition temperature of BmimFeCl₄ was 350°C . In our study, the onset decomposition temperature was about 346°C , and the residual mass at this temperature was 11.8%, close to the mass percentage of BmimFeCl₄ in the sample (12.0%).

2.2 UV-Vis spectra analysis of BmimCl

Figure 2 shows the dose dependence of the UV-Vis absorption of BmimCl. The irradiated BmimCl showed obvious absorption in the range of 250 to 600 nm, and the intensity increased with the dose. This increase was mainly due to the formation of long-lived dimeric radical cations and their polymerization products [18,19]. A distinct absorption peak appeared at 290 nm; the peak absorbance increased linearly with the dose (inset in Figure 2).

2.3 UV-Vis analysis of FeCl_3 -containing ionic liquids

Figure 3 shows the UV spectra of BmimCl-3 mol% FeCl_3 and BmimCl-7 mol% FeCl_3 . For the 3 mol% FeCl_3 -containing ionic liquid, a broad absorption was observed from 250 to 600 nm. Compared with neat BmimCl, the range decreased from 250 to 600 nm as the molar ratio of FeCl_3 increased. The distinct absorption peak shifted from 290 nm in neat BmimCl (see Figure 2) to 285 nm in 3 mol% FeCl_3 -containing BmimCl, and then to 280 nm in 7 mol% FeCl_3 -containing BmimCl.

Figure 1 Thermogravimetric analysis of the ionic liquids (heating rate: 10°C/min at N₂ atmosphere). (a) BmimCl; (b) BmimCl-7 mol% FeCl₃, inset: the peak between 300 and 450°C.

Figure 2 UV-Vis spectra of BmimCl before and after irradiation with doses of 0, 100, 200, 300, 500, 700, and 900 kGy, respectively. Inset: the variation of BmimCl absorbance at $\lambda_{\max} = 290$ nm versus dose.

Figure 4 shows the absorbance of FeCl₃-containing ionic liquids versus the absorbed dose over 100 to 1000 kGy at 285 nm. The absorbance increased continuously as the dose

Figure 3 UV-Vis spectra of FeCl₃-containing ionic liquids before and after irradiation with doses of 0, 100, 200, 300, 500, 700, and 900 kGy. (a) BmimCl-3 mol% FeCl₃; (b) BmimCl-7 mol% FeCl₃. Inset: the absorbance variation of BmimCl at $\lambda_{\max}$ versus dose.

Figure 4 Absorbance of FeCl₃-containing ionic liquids as a function of dose at 285 nm.

increased. At any dose, the absorbance of irradiated sample gradually decreased with increasing concentration of FeCl₃. For example, at 300 kGy, the absorbance of FeCl₃-containing ionic liquids (3 mol%, 5 mol%, 7 mol%) was 0.117, 0.114, 0.089, respectively, whereas that of neat BmimCl ionic liquid was 0.611. According to these values, the radiolysis degree of FeCl₃-containing ionic liquids can be de-

duced as 17.1%, 16.6%, and 13.0%, and the consumption of Fe(III) was 42.1%, 28.0%, and 22.7%, respectively, from the change of Fe(II) concentration. From the 3 mol% FeCl₃-containing sample, the absorbance increased with increasing dose, but increased linearly when the dose was above 400 kGy and the R^2 was equal to 0.997. In this case, all of the FeCl₃ was assumed to have been reduced to Fe(II). The increase in the absorbance was due to the radiolysis of BmimCl. These results indicated that the presence of FeCl₃ improved the radiation resistance of BmimCl.

During γ radiation, solvated electrons are produced in two paths. One is the ionizing radiation of [Bmim]⁺; the other is the electron detachment of a chloride anion, which has no net contribution to the reduction of Fe(III). The radiation yield of the solvated electrons of BmimCl was approximately 0.217 ± 0.01 $\mu\text{mol/J}$. Jonah et al. [20] measured the rate constant of Fe(III) with hydrated electron ($k = 6.0 \times 10^{10}$ L/(mol s)), which was higher than that of [Bmim]⁺. The rate constant of Fe(III) with the solvent electron was possibly much higher in ionic liquid. Our data suggest that the Fe(III) ion is highly reactive with the solvated electron and competition reactions occur in this system. Therefore, the concentration of [Bmim]⁺ radical decreased after the addition of FeCl₃, further decreasing the formation of long-lived dimeric radical cations. The more the concentration of Fe(III) is, the weaker the radiolysis of [Bmim]⁺.

2.4 Determination of Fe(II) concentration

Solvated electrons, which are active species, are usually generated when ionic liquids are irradiated by γ -ray. Wishart et al. [21] investigated the solvated electron formed in methyltributylammonium bis(trifluoromethylsulfonyl) imide by pulse radiolysis. The radiation chemical yield of the solvated electrons was 0.07 $\mu\text{mol/J}$. For imidazolium-based ionic liquid, [Bmim]⁺ can be reduced by hydrated electrons (e_{aq}^-) rapidly ($k = 1.9 \times 10^{10}$ L/(mol s)) [22], leading to the radiolysis of [Bmim]⁺. Thus, scavenging solvated electrons may be helpful in improving the radiation resistance of irradiated ionic liquids.

Different amounts of FeCl₃ were added to BmimCl to form a BmimCl-FeCl₃ mixture (with 3 mol%, 5 mol%, and 7 mol% of FeCl₃) to observe the radiation protection effect of FeCl₃. The color of the samples changed after irradiation, as shown in Figure 5. At a lower dose, the color turned shallow, indicating that the Fe(III) concentration decreased after irradiation. At higher doses, the color turned darker, and the color of the BmimCl-3 mol% FeCl₃ sample was darker than that of BmimCl-7% FeCl₃ sample. Thus, [Bmim]⁺ possibly began to decompose at higher doses, as described by previous studies [11]. The color change also indicated that the radiolysis degree of [Bmim]⁺ in the BmimCl-3 mol% FeCl₃ sample was higher than that in the BmimCl-7 mol% FeCl₃ sample. The phenomena of color changes were consistent with our previous study [16], which

Figure 5 Color change of FeCl₃-containing ionic liquids at different doses. (a) BmimCl-3 mol% FeCl₃; (b) BmimCl-5 mol% FeCl₃; (c) BmimCl-7 mol% FeCl₃.

showed that the FeCl₃-containing ionic liquid has higher radiation stability than neat [Bmim]Cl, and Fe(III) was assumed to have been reduced by solvated electrons. In the current study, the deposition method was adopted to observe the reduction species using the NH₃·H₂O solution. When NH₃·H₂O was added to the samples after radiation, dark green deposition was first observed, which turned to yellow sharply when exposed to air. In an alkaline solution, Fe(II) easily forms Fe(OH)₂ deposition, which is unstable in air. Therefore, we determined that Fe(III) was deduced to Fe(II).

K₃Fe(CN)₆ was added to the samples to further check the content of Fe(II); the color immediately turned blue. Figure 6 shows the Fe(II) concentration versus the dose of up to 1000 kGy for FeCl₃-containing ionic liquids, wherein the

Figure 6 Fe(II) concentration as a function of dose for BmimCl-FeCl₃.

concentration of Fe(II) increased with the dose. Fe(II) concentration in the 3 mol% FeCl₃-containing ionic liquid (~0.20 mol/L) and 5 mol% FeCl₃-containing ionic liquid (~0.33 mol/L) reached the maximum at the dose of 400 and 700 kGy, respectively. However, Fe(II) concentration in the 7 mol% FeCl₃-containing ionic liquid (~0.46 mol/L) increased continuously with the dose of up to 1000 kGy. Therefore, this data was used to estimate the radiation chemical yield of Fe(II). Fitting the data from Fe(II) concentration in 7 mol% FeCl₃-containing ionic liquid, the slope would be achieved: $k = 4.08 \times 10^{-4}$ mol/(L kGy). In addition, the ρ of the ionic liquid was 1.14 g/mL, thus, the estimated result was 0.358 ± 0.01 μ mol/J, which is considered to be the radiation yield of the BmimCl electrons. This value is higher than the G-value measured by Huang et al. [17] (0.217 ± 0.01 μ mol/J). This difference was probably due to the difference of Fe(III) concentration. At higher Fe(III) concentration, the solvated electrons produced from [Bmim]⁺ cation by irradiation can be totally captured by Fe(III). Electrons can also be scavenged by Fe(III) before alvation, leading to a higher G-value of Fe(II). In addition, the highest dose in this study was 1000 kGy, much higher than the 400 kGy in Huang's report. Higher dose ensures sufficient source of solvated electron to reduce Fe(III). The value obtained in this study was higher than the radiolytic disappearance yield of the cations of the ionic liquid BmimNTf₂ (0.28 ± 0.02 μ mol/J) measured by ESI-MS [23].

Precipitation experiments were carried using NH₃·H₂O to further confirm the formation of Fe(II). The phenomena are shown in Figure 7. After centrifugation, dark green precipitates were observed at the bottom (Figure 7(c)). When the precipitate was exposed to air, it turned to yellow rapidly, which was proven as Fe(OH)₂ because it can be oxidized quickly to Fe(OH)₃ by oxygen. The supernatant color became shallow as the concentration of FeCl₃ increased, implying that FeCl₃ can restrain the radiolysis of [Bmim]⁺ to some extent.

3 Conclusion

In the present study, the radiolytic products were confirmed during the γ -ray irradiation of BmimCl, and increased linearly with dose, as measured by UV-Vis spectroscopy. The addition of FeCl₃ to the ionic liquid BmimCl significantly

Figure 7 Photographs of the irradiated BmimCl and FeCl₃-containing BmimCl at 900 kGy dissolved in (a) H₂O; (b) NH₃·H₂O; and (c) first dissolved in NH₃·H₂O, and then centrifuged at 3000 r/min for 5 min.

improved the radiation resistance of BmimCl by reacting with the solvated electrons. During irradiation, Fe(III) was reduced to Fe(II), and the concentration of Fe(II) increased with dose, until all the Fe(III) was reduced. Moreover, the radiation chemical yield of Fe(II) was estimated at approximately 0.358 ± 0.01 μ mol/J in the BmimCl-7 mol% FeCl₃ system. The radiolysis degree of BmimCl decreased with increasing Fe(III) concentration. Higher concentration showed better protection effect, which was explained as the lower yield of [Bmim][•] radical because of the higher concentration of Fe(III). When all the FeCl₃ was reduced to Fe(II), the radiolysis of FeCl₃-containing ionic liquids increased linearly. This finding implies that, in the real case where ionic liquid is used for the extraction of radioactive metal species, radiation emission of radioactive species will cause damage to the ionic liquids. However, the scavenging of solvated electron by metal ion will simultaneously prevent ionic liquids from radiolysis. Therefore, more consideration should be taken into the radiation resistance of other metallic ions in various ionic liquids media.

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