γ-ray induced radiolysis of [C2mim][NTf2] and its effects on Dy3+ extraction Postprint

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Abstract

The water-soluble radiolytic products of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid ([C2mim][NTf2]) under γ-radiation, such as CF3SOOH, CF3SO2NH2, HF, and H2SO3, were identified by using 1H NMR, 19F NMR, and ion chromicography. The extraction behavior of Dy3+ using irradiated [C2mim][NTf2] in combination with 2,6-di(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine (isobutyl-BTP) was studied and the abnormal increase of Dy3+ partitioning after irradiation is mainly attributed to the precipitation formed between Dy3+ and radiolytic products of [C2mim][NTf2] (F- and SO32-). Washing irradiated [C2mim][NTf2] with water provides a simple method for ionic liquid recycling.

Full Text

Preamble

γ-Ray Induced Radiolysis of [C2mim][NTf2] and its Effects on Dy^{3+} Extraction

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Abstract: The water-soluble radiolytic products of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid ([C2mim][NTf2]) under γ-radiation, such as CF3SOOH, CF3SO2NH2, HF, and H2SO3, were identified using ^{1}H NMR, ^{19}F NMR, and ion chromatography. The extraction behavior of Dy^{3+} using irradiated [C2mim][NTf2] in combination with 2,6-di(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine (isobutyl-BTP) was studied, and the abnormal increase in Dy^{3+} partitioning after irradiation is mainly attributed to the precipitation formed between Dy^{3+} and radiolytic products of [C2mim][NTf2] (F^- and $SO_3{}^{2-}$). Washing irradiated [C2mim][NTf2] with water provides a simple method for ionic liquid recycling.

Keywords: γ-Radiation, [C2mim][NTf2], Isobutyl-BTP, Radiolytic product, Dy^{3+} extraction
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Introduction

Minor actinides-lanthanides (MA-Ln) separation represents a significant challenge due to their similar chemical properties [1–3]. Bistriazinylpyridines (BTPs), as heterocyclic nitrogen donor ligands, exhibit attractive selectivity for minor actinides compared to lanthanides, making them excellent candidates for MA-Ln separation [4–6]. Kolarik et al. reported that 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in kerosene/2-ethylhexanol extracted Am^{3+} with a distribution ratio of 23 from an aqueous phase [7]. Trumm et al. demonstrated that a 50 mmol/L BTP solution in kerosene/1-octanol extracted Am^{3+} from 1 mol/L HNO_3 with an Am/Eu separation factor of approximately 100 [8]. However, the combination of BTPs with traditional solvents introduces new problems related to radiation resistance. For example, a 0.005 mmol/L C5-BTBP solution in cyclohexanone exhibited about an 80% decrease in the Am^{3+} distribution ratio at 17 kGy [9]. It was also reported that an absorbed dose of 100 kGy resulted in 80% decomposition of BTPs in n-octanol [10]. The reaction between BTPs and diluent radicals was thought to be responsible for this degradation, which subsequently caused the decrease in metal ion partitioning.

Room temperature ionic liquids (RTILs) have been extensively studied for potential applications in spent nuclear fuel reprocessing due to their unique properties, including non-volatility, good solubility, and chemical stability [11–13]. Dai et al. first reported that the solvation environment offered by RTILs could enhance the extraction efficiency of metal ions from aqueous solutions [18]. Moreover, RTILs have demonstrated notable radiation resistance under γ-radiation [19–24]. Berthon et al. noted that less than 1% of RTILs underwent radiolysis when exposed to a dose of 1200 kGy [25]. In our previous work, the main radiolytic products of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C4mim][NTf2]) were definitively identified through various spectroscopic methods, which greatly advanced radiolysis research on ionic liquids [26, 27]. The overall concentration of non-volatile acidic radiolysis products was less than 1% for [C4mim][NTf2], even at 500 kGy. However, [C2mim][NTf2] is considered a better solvent than [C4mim][NTf2] for MA-Ln separation due to its larger dissolving capacity and favorable liquidity [28, 29].

Accordingly, it is necessary to evaluate the radiation stability of [C2mim][NTf2] and the extraction ability of extractants in combination with [C2mim][NTf2] under γ-radiation. In this paper, an extraction system consisting of isobutyl-BTP (Fig. 1) as extractant and [C2mim][NTf2] as diluent was designed in our laboratory. The radiation effect on the extraction behavior of the diluent [C2mim][NTf2] was primarily investigated. Dy^{3+} is a non-redox-active trivalent ion with properties similar to trivalent actinides; thus, Dy^{3+} was chosen to assess the extractability and radiation stability of the isobutyl-BTP/[C2mim][NTf2] system.

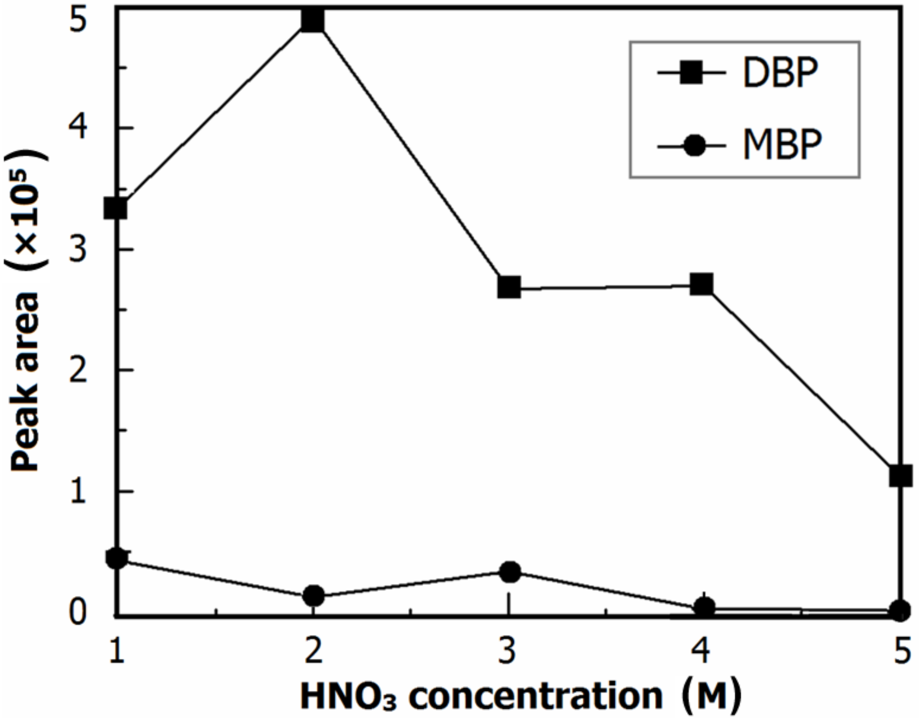

Figure 1: Figure 1

Experimental Section

A. Materials

[C2mim][NTf2] (purity > 99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected by ^{1}H NMR spectrometry. The isobutyl-BTP ($>$ 95%) was synthesized according to [30]. All other solvents were analytical-grade reagents and used without further purification.

B. Irradiation

The irradiation of [C2mim][NTf2] was carried out in air at (298 ± 4) K using a ^{60}Co source with an average dose rate of approximately 240 Gy/min (Institute of Applied Chemistry, Peking University). The absorbed dose was measured using a Fricke dosimeter.

C. Extraction of Dy^{3+}

The organic phase (0.5 mL) contained 20 mmol/L of isobutyl-BTP dissolved in [C2mim][NTf2], and the aqueous phase (0.5 mL) contained 8 mmol/L of Dy^{3+}. The extraction experiments were conducted in a constant temperature incubator shaker maintained at 25 °C with a rotating speed of 120 rpm, followed by centrifugation for 2 min to ensure complete phase separation. After phase separation, the aqueous solution was diluted with deionized water and the concentration of Dy^{3+} in the diluted aqueous solution was measured using a Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICPS-7510, SHIMADZU, JPN). The distribution ratios (D_{Dy}) were calculated by D_{Dy} = (C_i - C_f)/C_f and the extraction efficiencies (E_{Dy}) were calculated based on E_{Dy} = (C_i - C_f)/C_i, where C_i and C_f designate the initial and final concentrations of Dy^{3+} in the diluted aqueous solution, respectively.

D. Characterization

Micro-FTIR. Micro Fourier transform infrared spectra were recorded on a Thermo Scientific Micro Fourier transform infrared spectrometer.

^{1}H and ^{19}F NMR. NMR experiments were carried out with a Bruker AV-500. The chemical shift scale was calibrated with tetramethylsilane at 0 ppm for ^{1}H NMR and NTf_2^- at -78.87 ppm for ^{19}F NMR, respectively.

Ion chromatography analysis. The water-soluble products from the irradiated samples were analyzed using a MIC ion chromatography (IC) System (Metrohm Swiss). A Metrosep A SUPP 5-250 column (4 mm × 250 mm) was used for quantitative analysis of the radiolytic products of [C2mim][NTf2] ionic liquids. The 819 IC conductivity detector was applied and the injection volume was set at 10 µL. The eluent was 3.2 mmol/L Na_2CO_3/1.0 mmol/L $NaHCO_3$ solution at a constant flow rate of 0.7 mL/min. The operating back pressure was 11.6 MPa.

XPS analysis. The X-ray photoelectron spectra (XPS) of the samples were recorded by an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation and low energy electron flooding for charge compensation.

Results and Discussion

A. Identification of Water-Soluble Radiolytic Products of [C2mim][NTf2] Under γ-Radiation

The water-washed sample of irradiated [C2mim][NTf2] was analyzed by Micro-FTIR based on previous work [26]. As illustrated in Fig. 2 [FIGURE:2], the Micro-FTIR spectrum of the irradiated sample changes obviously compared with that of the unirradiated sample. The absorption band at 1136 cm^{-1} (1350 cm^{-1}), corresponding to the vibration of the C−F bonds (S−−O) of NTf_2^-, decreases significantly after γ-radiation. This indicates that C−F and S−−O bonds were broken during irradiation. In addition, OH groups (NH_2 groups) are observed at 1655 cm^{-1} and 3450 cm^{-1} (960 cm^{-1}) in Fig. 2b. These results indicate that radiolytic products containing OH and NH_2 groups were formed after irradiation. These results are similar to those of [C4mim][NTf2] during irradiation [26] because [C2mim][NTf2] has analogous anions (NTf_2^-) with [C4mim][NTf2]. Hence, the observed results in Micro-FTIR are mainly attributed to the radiolysis of [NTf2] anions.

^{1}H NMR and ^{19}F NMR were employed to identify the radiolytic products of [C2mim][NTf2] after irradiation. As shown in Fig. 3 [FIGURE:3], no discernible changes were observed in the ^{1}H NMR at 500 kGy, suggesting that the non-volatile radiolysis products of [C2mim][NTf2] do not exceed 1%. However, the water peak broadened and shifted toward the low field after irradiation. This is consistent with information reported by Yuan et al., who found that the change in water peak shape was attributed to acidic radiolytic products [28]. Therefore, acidic radiolytic products were formed during the irradiation of [C2mim][NTf2].

The ^{19}F NMR spectra of [C2mim][NTf2] before and after irradiation are shown in Fig. 4 [FIGURE:4]. A single peak at −78.78 ppm, which is assigned to NTf_2^-, was observed. Similar to the radiolysis of [C4mim][NTf2] [26], several fluorine-containing compounds in irradiated [C2mim][NTf2] have been identified as CF_3SOONH_2 (−79.33 ppm), CF_3SOOH (−87.08 ppm), HF (−164.55 ppm), and SiF_2^- (−129.56 ppm) [26]. However, a new radiolytic product, which was not observed in irradiated [C4mim][NTf2], appears at −76.75 ppm. The difference in alkyl chain between C_2mim^+ and C_4mim^+ leads to the formation of different radiolytic products.

B. Quantitative Analysis of Trace Water-Soluble Radiolytic Products of [C2mim][NTf2] Under γ-Irradiation

Ion chromatography was employed to provide quantitative analysis of these water-soluble radiolytic products (HF, CF_3SOOH, and H_2SO_3), with experimental details given in a previous paper [26]. As indicated in Fig. 5 [FIGURE:5], the amounts of radiolytic products increased obviously with increasing dose. For instance, the concentration of F^- increased from 0.030 mol/L at 100 kGy to 0.087 mol/L at 500 kGy. The G values of HF, CF_3SOOH, and H_2SO_3 were calculated as 0.22 µmol/J, 0.035 µmol/J, and 0.029 µmol/J, respectively. Compared with the G values of acidic radiolytic products of [C4mim][NTf2] (Table 1), the radiolysis of [C2mim][NTf2] is close to that of [C4mim][NTf2]. The quantitative study using ion chromatography indicated that the overall concentration of nonvolatile acidic radiolysis products was less than 1% for [C2mim][NTf2] even at 500 kGy, demonstrating that [C2mim][NTf2] still exhibits excellent radiation stability under γ-irradiation.

TABLE 1. Radiation chemical yields of acidic radiolytic products of [C2mim][NTf2] and [C4mim][NTf2] RTILs

RTIL	$G(F^-)$ (µmol/J)	$G(CF_3SOO^-)$ (µmol/J)	$G(SO_3{}^{2-})$ (µmol/J)
[C2mim][NTf2]	0.22	0.035	0.029
[C4mim][NTf2]	0.20	0.030	0.025

Data obtained from Ref. [26].

C. The Influence of Acidic Radiolytic Products of [C2mim][NTf2] on the Extraction of Dy^{3+}

The influence of dose on Dy^{3+} extraction is shown in Fig. 6 [FIGURE:6]. An abnormal increase in Dy^{3+} partitioning is observed when irradiated [C2mim][NTf2] is used as extracting solvent. Some water-insoluble compounds were observed at the interface between irradiated [C2mim][NTf2] and the aqueous solution. After the irradiated [C2mim][NTf2] was washed with deionized water three times, Dy^{3+} partitioning recovered to the unirradiated level. These results suggest that the abnormal increase in D_{Dy} in irradiated [C2mim][NTf2] is ascribed to the influence of water-soluble radiolytic products. Based on our previous work [27], Dy^{3+} precipitates with the radiolytic products generated from the ionic liquid (F^- and $SO_3{}^{2-}$), resulting in the increase of Dy^{3+} partitioning in irradiated [C2mim][NTf2].

After centrifuging, washing, and drying, the white sediment was obtained and analyzed by XPS. The binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV. The composition of the sediment was determined to consist of F, O, S, and Dy elements according to the XPS spectrum (Fig. 7 [FIGURE:7]), indicating that the main components of the sediment are DyF_3 and $Dy_2(SO_3)_3$. Similar results have been reported in the α-radiolysis of [C4mim][NTf2] ionic liquid irradiated with a helium ion beam [27]. Consequently, the increase in Dy^{3+} partitioning in irradiated [C2mim][NTf2] is due to precipitation between the water-soluble radiolytic products of [C2mim][NTf2] and Dy^{3+}.

Conclusion

The main water-soluble radiolytic products of [C2mim][NTf2] (CF_3SOOH, $CF_3SO_2NH_2$, HF, and H_2SO_3) under γ-irradiation were systematically investigated using micro-FTIR, ^1H NMR, ^{19}F NMR, and ion chromatography. The radiolytic products of [C2mim][NTf2] are similar to those of [C4mim][NTf2] because the two ionic liquids have similar chemical structures and the same anion. The radiolytic behavior of [C2mim][NTf2] changes slightly compared to [C4mim][NTf2] due to differences in alkyl chain length. The extraction behavior of Dy^{3+} using irradiated [C2mim][NTf2] in combination with isobutyl-BTP showed an abnormal increase in Dy^{3+} partitioning due to precipitation between the acidic radiolytic products of the anion with Dy^{3+}. Water-washing is a very effective and simple method to avoid the influence of radiolytic products of [C2mim][NTf2]. This work provides an assessment of the feasibility of [C2mim][NTf2] as an alternative medium for the separation of MA-Ln from spent nuclear fuel.

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