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Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Identification of F^- and SO_4^{2-} as the radiolytic products of the ionic liquid $C_4mimNTf_2$ and their effect on the extraction of UO_2^{2+}

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HIGHLIGHTS

- ▶ The anions F^- and SO_4^{2-} were identified as the radiolytic products of $C_4mimNTf_2$.
- ▶ Utilization of irradiated $C_4mimNTf_2$ reduced the extraction efficiency of UO_2^{2+} .
- ▶ Uranyl ion with four TBP molecules is predominant during the extraction.

ARTICLE INFO

Article history:

Received 29 September 2012

Accepted 19 October 2012

Available online 29 October 2012

Keywords:

Ionic liquid
Radiolytic product
Radiation effect
Extraction
Uranyl ion

ABSTRACT

A precipitate was found at the interface between the aqueous phase and the ionic liquid (IL) phase during the separation of UO_2^{2+}/Eu^{3+} using irradiated IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ($C_4mimNTf_2$), and was analyzed by SEM, EDS, XPS and PXRD. The anions F^- and SO_4^{2-} were identified as the radiolytic products of $C_4mimNTf_2$. The radiation effect on the extraction of UO_2^{2+} from aqueous solution by tri-n-butyl phosphate (TBP) in $C_4mimNTf_2$ was studied. For the presence of F^- and SO_4^{2-} , the utilization of irradiated $C_4mimNTf_2$ as diluent reduced the extraction efficiency of UO_2^{2+} . The EXAFS measurement showed that the degradation of $C_4mimNTf_2$ insignificantly influenced the coordination environment of UO_2^{2+} in the IL phase. Furthermore, it was suggested that the complex of uranyl ion with four TBP molecules is predominant during the extraction of UO_2^{2+} by TBP in $C_4mimNTf_2$ from aqueous solution in the absence of nitric acid. This work gives a further assessment for the application of ILs in the processing of spent nuclear fuel.

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1. Introduction

Room temperature ionic liquids (ILs) have been considered as alternative solvents for synthetic, catalytic, electrochemical and separation sciences because of their unique properties such as low vapor pressure, solvating properties and thermal stability (Armand et al., 2009; Hallett and Welton, 2011; Huddleston et al., 1998; Zhao et al., 2002). Especially, they have been considered as next generation diluents as the replacement of volatile organic compounds (VOCs) in the reprocessing of spent nuclear fuel (Dai et al., 1999; Sun et al., 2012; Visser and Rogers, 2003).

Because of the ionic compositions and the corresponding physicochemical properties and characteristics of ILs, the ionic species (metal ions and metal-extractant complex) are much more favored as thermodynamically solvated in ILs than in

conventional solvent, thus the extraction of metal ions is more efficient in IL systems than that in conventional solvent systems (Dai et al., 1999; Dietz and Dzielawa, 2001; Xu et al., 2010). Besides the high extraction efficiency, however, the application of ILs as next generation diluents in the reprocessing of spent nuclear fuel need to satisfy many other requirements, one of which is the radiation stability. For ILs in the reprocessing of spent nuclear fuel would encounter high radiation fields, the application of ILs demands a comprehensive understanding of the radiation stability of ILs. Allen et al. (2002) gave a preliminary assessment of the radiation stability of imidazolium based hydrophilic ILs and their results suggested a high radiation stability for ILs. Qi et al. (2007, 2008) investigated in detail the γ -radiolysis of C_4mimBF_4 and C_4mimPF_6 by spectroscopic methods and differential scanning calorimetry, where C_4mim^+ is 1-butyl-3-methylimidazolium. Recently, Shkrob et al. (2011a, 2011b) identified fragmentation pathways for imidazolium cations and constituent anions in imidazolium, ammonium, and phosphonium ILs using electron paramagnetic resonance (EPR) spectroscopy.

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While both the IL cations and anions were examined of their possible degradation, the radiolysis of the hydrophobic anion bis(trifluoromethylsulfonyl)imides (NTf_2^-) has attracted more attention (Behar et al., 2002; Berthon et al., 2006; Bosse et al., 2008; Grodkowski and Neta, 2002a, 2002b; Grodkowski et al., 2003; Shkrob et al., 2007, 2011b), for the NTf_2^- based ILs were extensively investigated in the extraction of metal ions. It was reported that one of the initial steps of NTf_2^- anion radiolysis is the loss of $\bullet\text{F}$, $\bullet\text{CF}_3$ and $\bullet\text{CF}_3\text{SO}_2$, forming the remaining radical $\bullet\text{NSO}_2^-$, $\bullet\text{NTf}^-$, $\bullet\text{SO}_2\text{NTf}^-$ (Berthon et al., 2006; Bosse et al., 2008). We previously found that SO_4^{2-} (oxidized from SO_3^{2-} by air) is one of the radiolytic products of $\text{C}_4\text{mimNTf}_2$ (Yuan et al., 2009b). Recently, Shkrob et al. (2011b) identified the radical $\bullet\text{CF}_2\text{SO}_2\text{NTf}^-$ from EPR spectra, which was attributed to dissociative electron attachment to the anion NTf_2^- , albeit with a small yield (comparable to the yield of the $\bullet\text{CF}_3$ radical). F^- was proposed as one of the possible products of the reaction, but it has not been confirmed so far.

The research on the radiolysis of ILs will be very helpful to the assessment of ILs in the reprocessing of spent nuclear fuel. Furthermore, the effect of ILs radiolysis on the extraction of metal ions also needs investigation. It was found that irradiation of imidazolium based ILs produced hydronium that competes with Sr^{2+} in complexing with crown ether, although the extraction efficiency could be restored by washing the irradiated ILs with water (Yuan et al., 2008, 2009a). As the radiolytic products of NTf_2^- , SO_3^{2-} and SO_4^{2-} are formed, which precipitate with Sr^{2+} at the water–IL interface (Yuan et al., 2009b). These studies are of great importance for the assessment of the application of ILs in the reprocessing of spent nuclear fuel. However, research on the radiation effect on extraction was scarce in the literature.

Our research group has recently focused on the selective extraction of UO_2^{2+} in the presence of other metal ions as well as the radiation effect on the extraction. Using the irradiated $\text{C}_4\text{mimNTf}_2$ as solvent in the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ by TBP, a precipitate was found at the interface between the aqueous phase and the IL phase. Because no precipitate was found using unirradiated ILs, the precipitate must be originated from the radiolysis of ILs. Therefore, it is interesting to characterize the precipitate and analyze the radiolytic products of $\text{C}_4\text{mimNTf}_2$. Furthermore, it should be very important to examine the radiation effect on the extraction of UO_2^{2+} by TBP– $\text{C}_4\text{mimNTf}_2$.

2. Experimental

2.1. Materials

$\text{C}_4\text{mimNTf}_2$ was synthesized via metathetical reaction from C_4mimBr and LiNTf_2 (Bonhote et al., 1996). Both C_4mimBr and LiNTf_2 were purchased from Lanzhou Institute of Chemical Physics, China. TBP (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

2.2. Methods

Irradiation of $\text{C}_4\text{mimNTf}_2$ was carried out using ^{60}Co source with a total absorbed dose ranging from 50 to 1200 kGy. Energy dispersive X-ray spectroscopy (EDS) was performed on a QUANTA 200FEG scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra imaging photoelectron spectrometer. Powder X-ray diffraction (PXRD) data were measured on a DMAX-2400 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

In a typical extraction experiment, 0.5 mL of $\text{C}_4\text{mimNTf}_2$ containing 1.1 mol dm^{-3} of TBP and 0.5 mL of aqueous solution

containing 0.01 mol dm^{-3} of $\text{UO}_2(\text{NO}_3)_2$ were added into a plastic centrifuge tube, followed by vibrating for 24 h. The temperature was controlled at 298.2 K. Then the mixture was centrifuged for 2 min at 10,000 r/min and the two phases were separated. The concentration of UO_2^{2+} remained in the aqueous phase was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Leeman, Australia). The extraction efficiency was calculated as $E = (C_i - C_f)/C_i$ and the distribution ratio was calculated as $D = (C_i - C_f)/C_f$, where C_i and C_f designate the initial and final concentrations of UO_2^{2+} in the aqueous phase, respectively.

Samples for extended X-ray absorption fine structure (EXAFS) measurements were put in 1 cm pathlength plexiglass cuvettes. The preparation of the sample was based on 1.1 mol dm^{-3} of TBP in $\text{C}_4\text{mimNTf}_2$ or in irradiated $\text{C}_4\text{mimNTf}_2$ (1000 kGy) contacting with aqueous uranyl nitrite (0.1 mol dm^{-3}) in the absence of nitric acid. Sample prepared at high concentration of HNO_3 (1 mol dm^{-3}) in the aqueous phase was unsuitable for EXAFS experiments because the concentration of UO_2^{2+} in the IL phase after extraction was very low at high concentration of nitric acid (Dietz and Stepinski, 2008). XAFS experiments were carried out in the transmission mode at the XAFS station of Shanghai Synchrotron Radiation Facility (SSRF), China. Data reduction and analysis were conducted according to standard procedures with pre-edge background removal, edge normalization to a unit step height, conversion to momentum space, and extraction of the EXAFS with a spline function. The data analysis was carried out using the Athena and Artemis interfaces to the IFEFFIT program package (Ravel and Newville, 2005). Only single scattering paths were considered.

3. Results and discussion

3.1. Radiolytic products analysis

During the investigation on the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ by TBP in irradiated $\text{C}_4\text{mimNTf}_2$ (over 200 kGy), we found a precipitate at the interface between the aqueous phase and the IL phase. The precipitate was collected, washed with water, vacuum dried, and characterized by SEM, EDS, XPS, PXRD, and EA.

The precipitate shows rod-like crystal with a length less than 500 nm in SEM micrograph (see Fig. 1, inset), and the composition

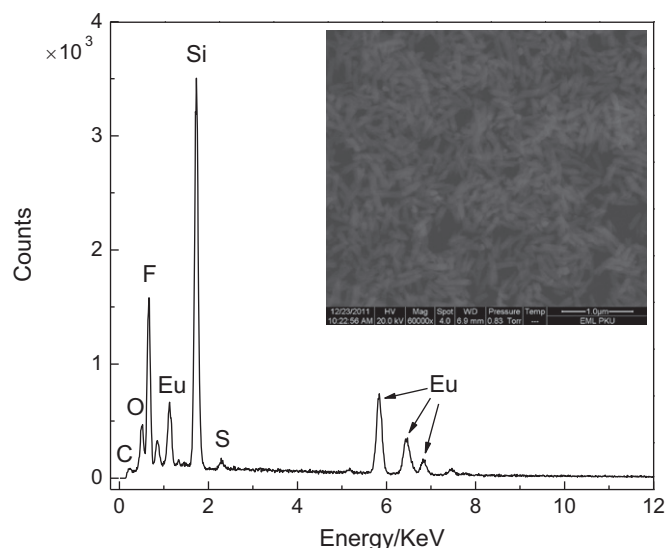


Fig. 1. EDS spectra and SEM (inset) of the precipitate formed at the interface between the aqueous phase and the IL phase during the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ using the irradiated $\text{C}_4\text{mimNTf}_2$.

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