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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.

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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

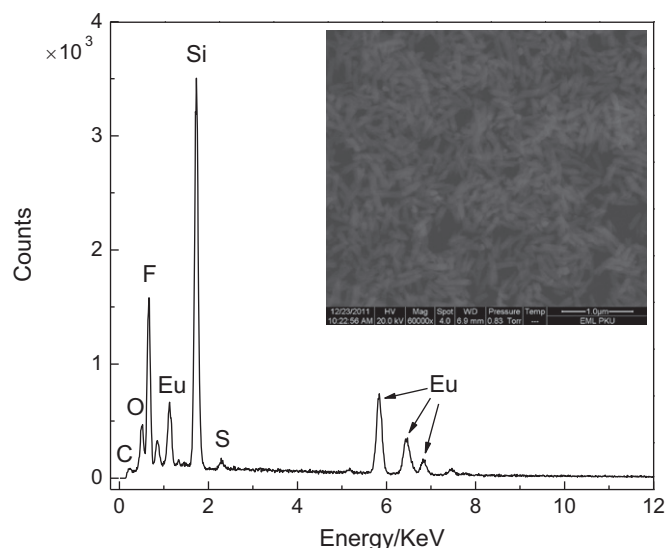


Fig. 1. EDS spectra and SEM (inset) of the precipitate formed at the interface between the aqueous phase and the IL phase during the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ using the irradiated $\text{C}_4\text{mimNTf}_2$.

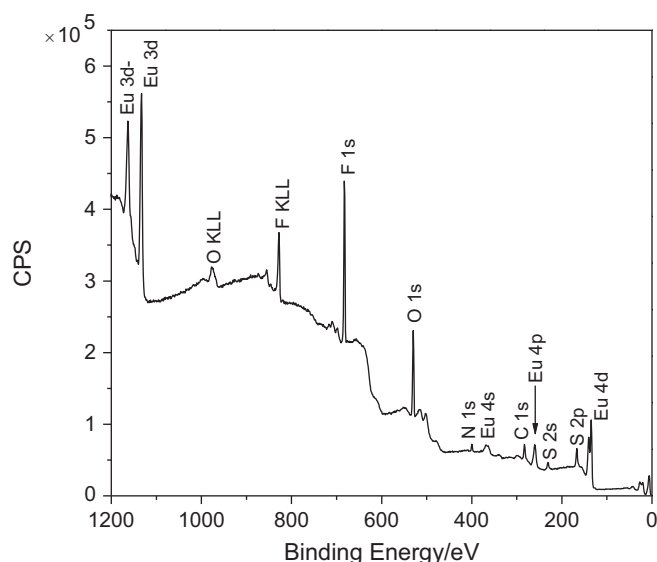


Fig. 2. XPS spectra of the precipitate formed at the interface between the aqueous phase and the IL phase during the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ using the irradiated $\text{C}_4\text{mimNTf}_2$.

was determined to contain Eu, F, S, and O elements according to EDS (Fig. 1) and XPS records (Fig. 2). The C element in EDS and XPS is assigned to adventitious hydrocarbons due to exposure to air. The EDS spectrum and EA analysis show no N element in the precipitate whereas there is a small peak belonging to N 1 s in XPS spectrum, which may be also due to exposure to air.

The values of core level binding energy (BE) in XPS were used to identify the specific chemical bonding in the precipitate. The BE value of S $2p_{3/2}$ at 169.1 eV is consistent with the standard BE value of sulfate compound. The values of O 1 s at 531.8 eV and F 1 s at 685.0 eV are consistent with those of $\text{Eu}_2(\text{SO}_4)_3$ and EuF_3 , respectively, in the literature (Alliot et al., 2006; Kawamoto et al., 1998; Konishi et al., 1996; Vercaemst et al., 1995; Zhong et al., 2009). These results indicate that the precipitate is a mixture of $\text{Eu}_2(\text{SO}_4)_3$ and EuF_3 , which is also suggested by the analysis of the atom ratio in the XPS record. The precipitate comprises over 80 mol% of EuF_3 and less than 20 mol% of $\text{Eu}_2(\text{SO}_4)_3$. We also analyzed the precipitate by PXRD and found that the main peaks are consistent with those of the standard EuF_3 (see Fig. 3).

The analysis of the precipitate formed at the water–IL interface in the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ using irradiated $\text{C}_4\text{mimNTf}_2$ indicates that F^- and SO_4^{2-} are the radiolytic products of $\text{C}_4\text{mimNTf}_2$. Because only the anion NTf_2^- in ILs has F and S elements, one can conclude that both F^- and SO_4^{2-} are generated from the radiation degradation of NTf_2^- . SO_4^{2-} as one of the radiolytic products of NTf_2^- is consistent with our previous report (Yuan et al., 2009b). On the other hand, we herein provide a direct evidence that F^- is also one of the radiolytic products of NTf_2^- , as proposed previously in the literature (Shkrob et al., 2011b).

3.2. Radiation effect on the extraction of UO_2^{2+}

TBP– $\text{C}_4\text{mimNTf}_2$ system was selected to examine the effect of the radiation degradation of IL on the extraction of UO_2^{2+} . Since both SO_4^{2-} and F^- are the radiolytic products of $\text{C}_4\text{mimNTf}_2$, we first detected the influence of H_2SO_4 and HF on the extraction of UO_2^{2+} by TBP in unirradiated $\text{C}_4\text{mimNTf}_2$. To eliminate the effect of the variation of the concentration of H^+ on extraction, 1 mol dm^{-3} of HNO_3 was added. Fig. 4a shows that both SO_4^{2-} and F^- in aqueous phase decrease the extraction efficiency of UO_2^{2+} by TBP in $\text{C}_4\text{mimNTf}_2$. The efficiency decreases to 14%

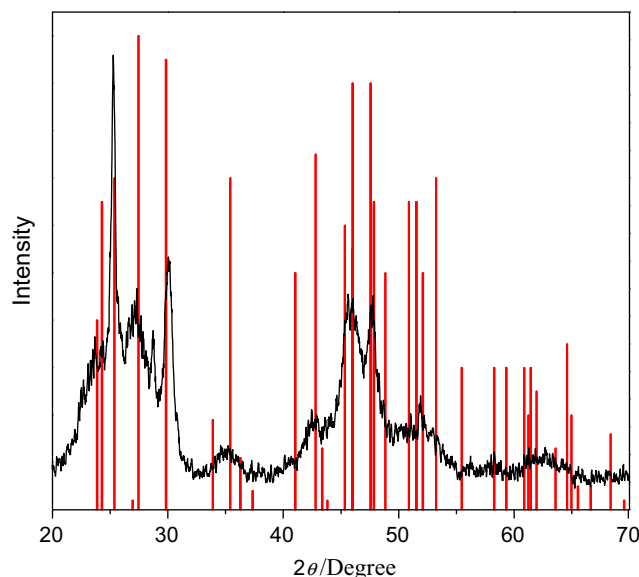


Fig. 3. PXRD spectrum of the precipitate formed at the interface between the aqueous phase and the IL phase during the separation of $\text{UO}_2^{2+}/\text{Eu}^{3+}$ using the irradiated $\text{C}_4\text{mimNTf}_2$, compared with the standard data of EuF_3 (Orthorhombic, $\text{Pnma}(62)$, Cell = $6.62 \times 7.015 \times 4.396 < 90 \times 90 \times 90 >$).

upon the addition of 100 mmol dm^{-3} of H_2SO_4 and no UO_2^{2+} is extracted in the presence of 100 mmol dm^{-3} of HF in the aqueous phase.

The extraction of UO_2^{2+} by TBP in irradiated $\text{C}_4\text{mimNTf}_2$ was subsequently examined. Since H^+ is also one of the radiolytic products of $\text{C}_4\text{mimNTf}_2$ (Yuan et al., 2008, 2009a), 1 mol dm^{-3} of HNO_3 was added once again. A significant reduction was found in the extraction efficiency with increasing dose (Fig. 4b). Combining the effect of H_2SO_4 and HF on the extraction, one can conclude that: (i) the radiation degradation of $\text{C}_4\text{mimNTf}_2$ generates some products including F^- and SO_4^{2-} with strong complexing ability with UO_2^{2+} and (ii) the complex of F^- or SO_4^{2-} with UO_2^{2+} is hardly extracted into the IL phase.

Our results show that the radiation degradation of ILs generates some products, such as F^- and SO_4^{2-} , and affects the extraction of UO_2^{2+} . The extraction efficiency of UO_2^{2+} decreases as dose increased. Fortunately, the absorbed dose of the extraction system is actually less than 10 kGy in one circle of the reprocessing of spent nuclear fuel (Chen and Wang, 2011), and there is very little effect on the extraction of UO_2^{2+} by TBP– $\text{C}_4\text{mimNTf}_2$ after 10 kGy irradiation, according to the above results. From practical aspect, ILs are still potentially applicable in the reprocessing of spent nuclear fuel.

3.3. EXAFS investigation

To further confirm that the complex of UO_2^{2+} with SO_4^{2-} or F^- favors existing in the aqueous phase but not in the IL phase, and to detect whether the irradiation of ILs can generate products affecting the coordination of UO_2^{2+} in the IL phase, we employed EXAFS method to determine the changes in the coordination environment of the UO_2^{2+} inner sphere after it was extracted by TBP– $\text{C}_4\text{mimNTf}_2$ and TBP-irradiated $\text{C}_4\text{mimNTf}_2$ from aqueous solution in the absence of HNO_3 . The Fourier transform magnitudes of the EXAFS are shown in Fig. 5, and the results of fitting the EXAFS data to the single scattering theoretical phase and amplitude functions are summarized in Table 1. In the $\text{C}_4\text{mimNTf}_2$ sample, the axial uranyl oxygen distance is $1.763 \pm 0.006 \text{ \AA}$, consisting with the results in the literature (Billard et al., 2007; Gaillard et al., 2005; Sornein et al., 2009; Visser et al., 2003).

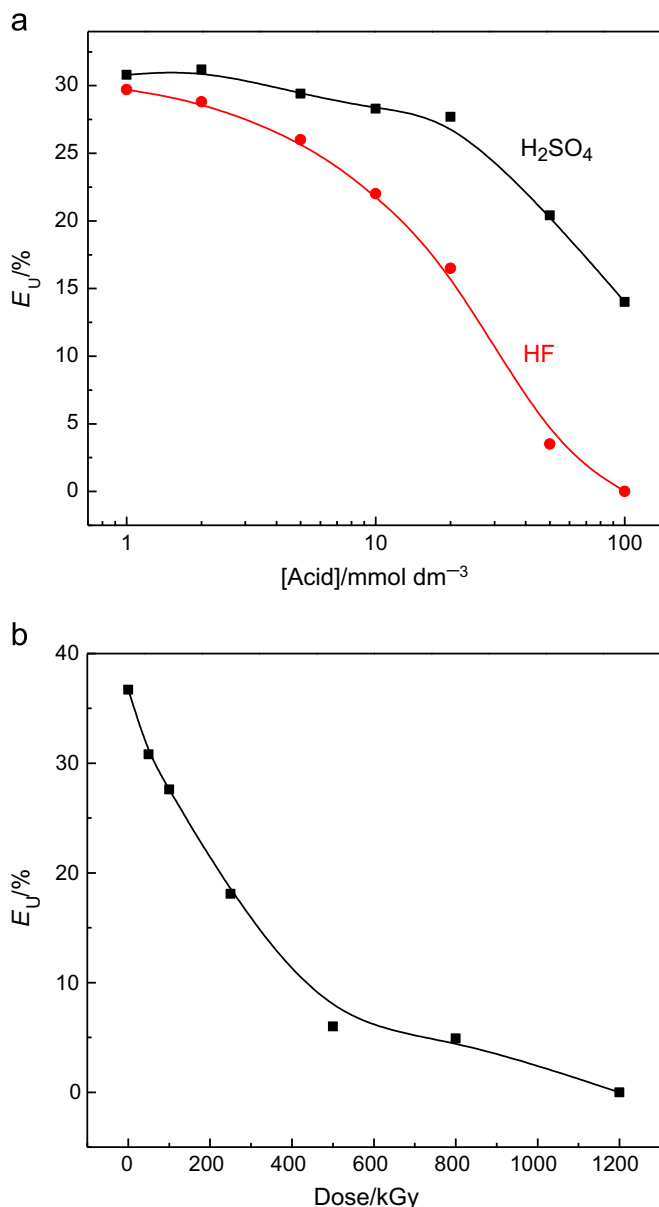


Fig. 4. Variation of the extraction efficiency of UO_2^{2+} by 1.1 mol dm^{-3} of TBP: (a) in $\text{C}_4\text{mimNTf}_2$ system upon the addition of H_2SO_4 and HF and (b) in irradiated $\text{C}_4\text{mimNTf}_2$ system as dose increased. The initial concentration of HNO_3 in aqueous phase is 1 mol dm^{-3} and the initial concentration of UO_2^{2+} is 0.01 mol dm^{-3} .

Only a single equatorial U–O bond distance at $2.39 \pm 0.01 \text{ \AA}$ was observed. The average number of oxygen atoms that equatorially coordinated to U is approximately 4.7 ± 0.9 . The EXAFS measurement of UO_2^{2+} extracted by TBP in irradiated $\text{C}_4\text{mimNTf}_2$ shows no big difference from that in $\text{C}_4\text{mimNTf}_2$ without irradiation (Table 1) and the number of coordinated equatorial oxygen atoms is 4.3 ± 1.0 .

The EXAFS measurement shows that the usage of irradiated $\text{C}_4\text{mimNTf}_2$ insignificantly influences the coordination of UO_2^{2+} in the IL phase. However, the specific coordination of UO_2^{2+} in the IL phase is still unclear based on the EXAFS results. The log–log plot method was subsequently carried out to determine the number of TBP molecules coordinating to UO_2^{2+} in the IL phase.

A slope of 3.8 was found in the plot of $\log D_U$ against $\log [\text{TBP}]$ (Fig. 6), where $[\text{TBP}]$ is the initial concentration of TBP in the IL phase. Within the uncertainty of the observation in EXAFS

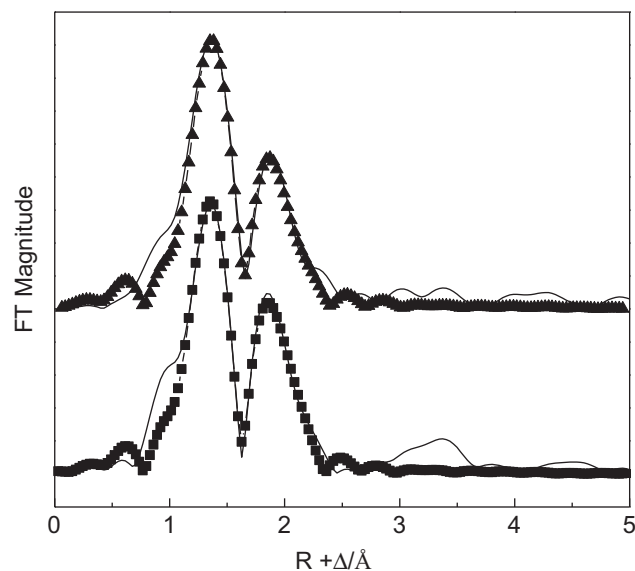


Fig. 5. U L3-edge EXAFS (line) and best fit (dots) of UO_2^{2+} extracted by TBP in $\text{C}_4\text{mimNTf}_2$ (bottom) and irradiated $\text{C}_4\text{mimNTf}_2$ (top). Fourier transform are not phase shift corrected.

Table 1

Results of fitting two shells of the k^3 weighted U L3 edge EXAFS.

	CN	$R/(\text{\AA})$	$\sigma^2 /(\text{\AA}^2)$	$\Delta E/(\text{eV})$
$\text{C}_4\text{mimNTf}_2$				
U=O(yl)	2 ^a	1.763 ± 0.006	0.0022 ± 0.0004	4.6 ± 1.5
U–O(eq)	4.7 ± 0.9	2.39 ± 0.01	0.0065 ± 0.0017	
Irradiated $\text{C}_4\text{mimNTf}_2$				
U=O(yl)	2 ^a	1.769 ± 0.006	0.0022 ± 0.0004	6.6 ± 1.5
U–O(eq)	4.3 ± 1.0	2.40 ± 0.01	0.0076 ± 0.0020	

^a Fixed parameter.

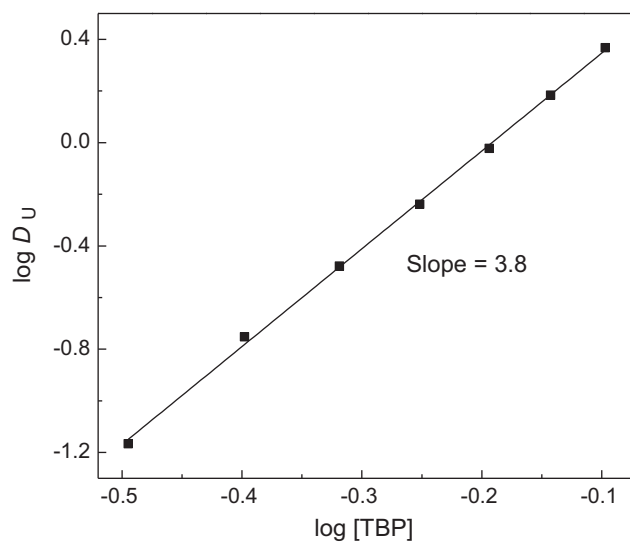
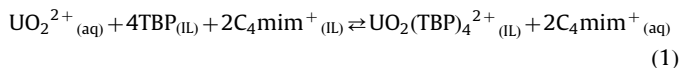


Fig. 6. Log–log plot of D_U as a function of the initial concentration of TBP in the IL phase ($[\text{TBP}]$) without the addition of HNO_3 in aqueous phase. The initial concentration of UO_2^{2+} in the aqueous phase is 0.01 mol dm^{-3} . The initial concentration of TBP is much higher than that of UO_2^{2+} , so that it is used instead of the equilibrated concentration of TBP after extraction.

measurements, there should be a complex of $\text{UO}_2(\text{TBP})_4^{2+}$ in the $\text{C}_4\text{mimNTf}_2$ phase after UO_2^{2+} is extracted by TBP from neutral aqueous solution, and the extraction may follow a cation

exchange mechanism as depicted below:



This mechanism is different from the results of the previous reports in which HNO_3 existed in aqueous phase. At 3 mol dm^{-3} of HNO_3 in the aqueous phase, two TBP molecules complex with UO_2^{2+} in the IL phase, and one more TBP molecule complexes with UO_2^{2+} as the concentration of HNO_3 decreases to 0.01 mol dm^{-3} (Bell and Ikeda, 2011; Dietz and Stepinski, 2008). In the absence of HNO_3 , there are four TBP molecules complexing with UO_2^{2+} , according to this work. On the other hand, $\text{UO}_2(\text{TBP})_4^{2+}$ is still very likely the predominant species in the irradiated $\text{C}_4\text{mimNTf}_2$ based on the EXAFS results. Notably, based on the oxygen coordination numbers derived from the EXAFS measurements, we cannot exclude the coordination of UO_2^{2+} with other molecules such as H_2O , which was also indicated by Visser et al. (2003). Thus, further investigation is necessary in the future study.

4. Conclusion

Both F^- and SO_4^{2-} were identified as the radiolytic products of the IL $\text{C}_4\text{mimNTf}_2$. The existence of F^- and SO_4^{2-} led to a reduction in the extraction efficiency of UO_2^{2+} but showed insignificant influence on the coordination environment of UO_2^{2+} in the IL phase. According to the measurements of EXAFS and the result of the log–log plot of D_U as a function of [TBP], a complex of $\text{UO}_2(\text{TBP})_4^{2+}$ is suggested in the IL phase during the extraction of UO_2^{2+} from aqueous phase in the absence of nitric acid. Our work will be helpful for the practical application of ILs as diluents in the reprocessing of spent nuclear fuel.

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