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ARTICLE

Extraction mechanism and γ-radiation effect on the removal of Eu³⁺ by a novel BTPhen/[Cₙmim][NTf₂] system in the presence of nitric acid

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The extraction mechanism of 2,9-bis (5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (BTPhen) in combination with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ionic liquids ([Cₙmim][NTf₂], n = 2, 4, 8) in the presence of nitric acid is studied by using Eu³⁺, which has similar properties with trivalent actinides. The dominant complex compound forming between BTPhen and Eu changes from [Eu(BTPhen)₂(NO₃)]²⁺ to [Eu(BTPhen)(NO₃)₃] gradually with the increase of [HNO₃] or the length of alkyl chain in the [Cₙmim]⁺, indicating that the main extraction mechanism of BTPhen/[Cₙmim][NTf₂] varies from cation exchange mechanism to neutral species mechanism. The irradiation of BTPhen in solid state has no effect on the extraction of Eu³⁺. The abnormally enhanced removal of Eu³⁺ was observed in irradiated BTPhen/[C₂mim][NTf₂] system at 0.1 M nitric acid, and it was attributed to the formation of precipitation between Eu³⁺ and trace radiolytic products of [C₂mim][NTf₂], which could be recovered by water wash before extraction. The extraction of Eu³⁺ was slightly changed for the irradiated BTPhen/[C₂mim][NTf₂] system at 1 M nitric acid, demonstrating good radiation stability of this novel extraction system.

1. Introduction

During the reprocessing of spent nuclear fuel (SNF), PUREX process has been widely used to separate U and Pu, but few minor actinides (MA, mainly Am and Cm), which are responsible for high-level and long-term radiotoxicity of SNF, still exist in the outflow water solution of PUREX process.[1, 2] It is necessary to remove them before further safe disposal of SNF. MA transmutation by fast neutron, leading to residues with less radiotoxicity and shorter half-life nuclides, has been anticipated to be an effective method. However, prior to all processing it still requires another necessary step to separate them from lanthanides (Ln) which greatly exist in SNF and have higher neutron capture section than MA.[3-5] However, the separation of MA-Ln is a huge challenge due to their similar chemical properties.

In the past decades, tridentate 2,6-bis(1,2,4-triazine-3-yl)pyridine (BTP, Fig. 1(a)) and quadridentate 6,6'-bis(1,2,4-triazine-3-yl)-2,2'-bipyridine (BTBP, Fig. 1(b)), two main series of N-donor heteropolycyclic ligands have been widely investigated and proved to be effective in the MA-Ln separation.[5-8] Some research suggested that their high selectivity is due to their relatively softer N-donor atoms and unusual orbital interactions.[5, 8] Moreover, compared with previously reported BTBPs, structurally modified BTBP ligand,

2,9-bis (5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-1,10-phenanthroline (BTPhen, Fig. 1(c)), which has been recently synthesized, is reported to have higher separation factor and faster extraction kinetic in traditional extraction process for Am-Eu partition.[9]
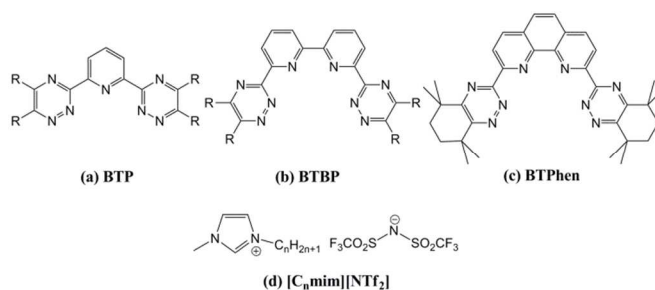

Fig. 1 Chemical structures of BTP (a), BTBP (b), BTPhen (c) and [Cₙmim][NTf₂] (d).

Studies show that the extraction capacity of BTBPs reduces significantly under high doses γ-radiation, even though BTBP is consisted of relatively stable CyMe₄-substituted ligands,[10] and diluent plays a pivotal role in radiolysis of BTBPs.[11] Some active species such as free radicals could be easily produced in the volatile organic diluents (e.g. 1-octanol) under radiation. H-abstraction reaction on ligand molecules induced by free radicals could lead to some subsequent radiolysis of BTBPs.[11]

As a consequence, the extractants would lose their extractability and selectivity. In order to apply BTPhen to the separation of MA-Ln in practical system, the evaluation of radiation stability of BTPhen is necessary, and more stable extraction system is required.

Room temperature ionic liquids (RTILs) have been considered as alternative medias to replace traditional organic diluents in the reprocessing of SNF,[12, 13] because of a number of unique properties such as non-volatility, good solubility, along with chemical stability, *etc* in them.[14, 15] Among these properties, the environmental protection and the potential in reducing the critical accident are the most admirable features concerning a safety media used in the reprocessing of SNF.[16-18] In addition, RTILs combining with other extractants, which show excellent extraction performance, have been studied in the separation of some radionuclides (*e.g.* Sr, Cs, An).[19-21] However, up to now there has been no study on BTPhen/ionic liquid extraction system. Herein, we expect to design a new extraction system in which BTPhen as extractant and $[C_nmim][NTf_2]$ (Fig. 1(d)) as diluent. Since Am is known for its radiotoxicity and the difficulty in handling, while Eu^{3+} has similar properties with trivalent actinides, Eu^{3+} has been widely used on behalf of the trivalent Ln and An in the spent nuclear fuel.[22-24] Therefore, Eu^{3+} is chosen to evaluate the extractability and the γ-radiation stability of BTPhen/$[C_nmim][NTf_2]$ system in this work.

2. Materials and methods

2.1. Materials.

$[C_nmim][NTf_2]$ (n = 2, 4, 8 stands for ethyl-, butyl-, octyl-, respectively; with a purity > 99%) were purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected using ^1H NMR spectrometry, and the residual water amounts less than 400 ppm in the $[C_nmim][NTf_2]$ were determined by Karl-Fischer titration before irradiation. These compounds were used as received prior to irradiation. BTPhen was synthesized and purified according to the literature with a satisfactory purity (> 95%).[9] All other solvents were analytical-grade reagent and used without further purification.

2.2. Extraction of Eu^{3+}.

The aqueous phase (1.0 mL) with various nitric acid concentrations and 1 mM $Eu(NO_3)_3$ was mixed with the organic phase (0.5 mL) containing 10 mM BTPhen. Then the mixtures were oscillated in a constant temperature incubator shaker at 323 ± 1 K with a rotating speed at 200 rpm for a certain period. The obtained mixtures were centrifuged for phase separation and the aqueous phase was analysed by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICP-AES) (Teledyne Leeman 85 Labs, USA) to determine the concentration of Eu^{3+}. The distribution ratio (D_{Eu}) and the extraction efficiency (E_{Eu}) are calculated from Eqn (1) and Eqn (2), respectively. The "[Eu]" represents the concentration of

Eu^{3+}, and the subscript "org/aq" is short for organic phase/aqueous phase, while the "i/f" represents the initial/final concentration before/after extraction.

$$D_{Eu} = \frac{[Eu]_{org}}{[Eu]_{aq}} = \frac{[Eu]_{aq.i} - [Eu]_{aq.f}}{[Eu]_{aq.f}} \times \frac{V_{aq}}{V_{org}} \quad (1)$$

$$E_{Eu} = \frac{[Eu]_{aq.i} - [Eu]_{aq.f}}{[Eu]_{aq.i}} \times 100\% \quad (2)$$

2.3. Irradiation.

Irradiation of solid BTPhen, $[C_2mim][NTf_2]$, BTPhen/$[C_2mim][NTf_2]$ and BTPhen/1-octanol solution was carried out separately at room temperature in air using a ^{60}Co source with a dose rate of *ca.* 300 Gy·min^{-1} (Institute of Applied Chemistry of Peking University). Plastic tubes were chosen as the container during irradiation to avoid the reaction between container and acidic radiolytic products.[25] The absorbed dose was measured with Fricke dosimeter.

2.4. Characterization.

NMR experiments were recorded on a Bruker AV-500 instrument. (1) The determination of the concentration of ionic liquid in water: the solubility equilibrium of $[C_2mim]^+$ in water was achieved by contacting 0.5 mL $[C_2mim][NTf_2]$ with 3 mL deuterium oxide (D_2O) containing 1 mM Eu^{3+} and different concentrations of HNO_3 for 30 seconds. The aqueous phase was partitioned and then mixed with equal volume of sodium acetate/D_2O solution at 50 mM. The mixture was analysed by ^1H NMR and the concentration of $[C_2mim]^+$ was calculated from Eqn (3), where the "$[C_2mim^+]$" and "$[CH_3COO^-]$" are the concentrations of $[C_2mim]^+$ and CH_3COO^-, respectively. The "$A_{[C2mim]}+$" and "$A_{CH3COO}-$" are the integrals of the methyl in the $[C_2mim]^+$ and CH_3COO^-, respectively.

$$[C_2mim^+] = [CH_3COO^-] \times \frac{A_{[C2mim]^+}}{A_{CH3COO^-}} \quad (3)$$

(2) Solid BTPhen samples irradiated at different doses were dissolved into deuterated chloroform ($CDCl_3$) separately and the chemical shift scale was calibrated with tetramethylsilane at 0 ppm for ^1H NMR. (3) The determination of the water soluble radiolytic products of $[C_2mim][NTf_2]$: the separation of water-soluble radiolytic products from $[C_2mim][NTf_2]$ was conducted by contacting 0.5 mL irradiated sample with 0.5 mL D_2O for about 10 min in a vibrating mixer, followed by centrifuging to ensure that the phases were fully mixed and separated. The aqueous phase obtained by washing the irradiated sample was analysed by ^{19}F NMR and the chemical shift scale was calibrated with C_6F_6 (-162.73 ppm according to the reference [17]).

Micro Fourier transform Infrared spectroscopies (Micro-FTIR) of solid BTPhen at different doses were recorded on a Thermo Scientific Micro Fourier transform infrared spectrometry.

X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos

Analytical using monochromatic Al Kα radiation and low energy electron flooding for charge compensation. The binding energies (BE) were calibrated using C1s hydrocarbon peak at 284.80 eV.

3. Results and discussion

3.1. Extraction of Eu^{3+} in BTPhen/[C$_2$mim][NTf$_2$] system.

The extraction kinetics of BTPhen/[C$_2$mim][NTf$_2$] system was first investigated at 0.1 M HNO$_3$. The E_{Eu} increases rapidly and reaches a flat with a value exceeding 95% after an hour (Fig. S1). The result indicates that the extraction equilibrium at 0.1 M HNO$_3$ could be achieved in an hour and the Eu^{3+} could be almost completely extracted into organic phase after two hours. In order to study the effect of nitric acid concentration and the chemical structures of [C$_n$mim][NTf$_2$] on the extraction property of the extraction systems, [C$_n$mim][NTf$_2$] with different alkyl lengths in the cations were selected as the diluents. Extraction experiment is carried out at different initial nitric acid concentrations (abbreviated as [HNO$_3$]) ranging from 0.01 M to 3 M. For purpose of comparison, two hours oscillation time was chosen for all extraction samples.
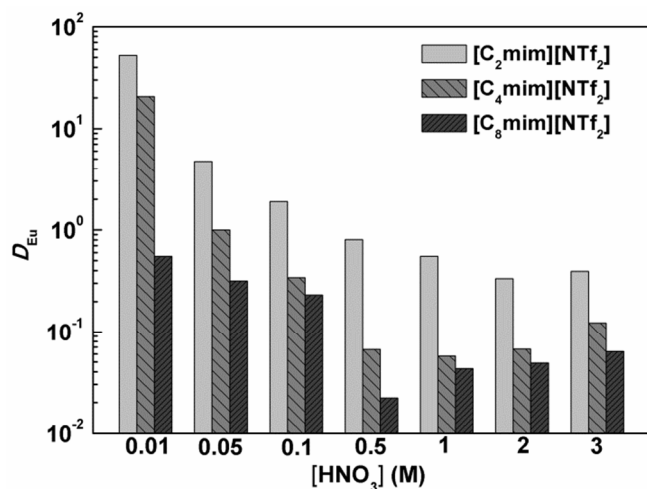

Fig. 2 Influence of the initial nitric acid concentration on D_{Eu} of [C$_n$mim][NTf$_2$].

As shown in Fig. 2 (data refer to Table S1), the D_{Eu} of BTPhen/[C$_2$mim][NTf$_2$] system declines from 52 (0.01 M HNO$_3$) to the minimum of 0.33 (2 M HNO$_3$), and then slightly rises to 0.40 (3 M HNO$_3$) with the [HNO$_3$] increasing. The variations of D_{Eu} with the [HNO$_3$] in [C$_4$mim][NTf$_2$] and [C$_8$mim][NTf$_2$] are similar to those in [C$_2$mim][NTf$_2$]. This phenomenon is also observed in extraction systems applying RTILs for other radionuclides (e.g. actinides, Sr, Cs).[21, 26, 27] However, when traditional solvents in which better extraction results are usually obtained at high acidities are employed, this phenomenon is not common.[28] That the variations of D_{Eu} of BTPhen/[C$_n$mim][NTf$_2$] systems with the [HNO$_3$] increase indicates a tendency which is similar to the "boomerang curves" previously described by Billard et al,[29] who proposed an extraction model that unified three possible basic

mechanisms: cation exchange, anion exchange, and neutral complex extraction. These mechanisms are normally synergic during the extraction, whereas the dominant one depends on conditions. The boomerang curves reveal an interesting phenomenon that an extraction system employing RTILs perform well at neutral or low acidity. The extractability declines to a bottom level with the acidity increasing and then slowly rises again in a region of rather high acidity.
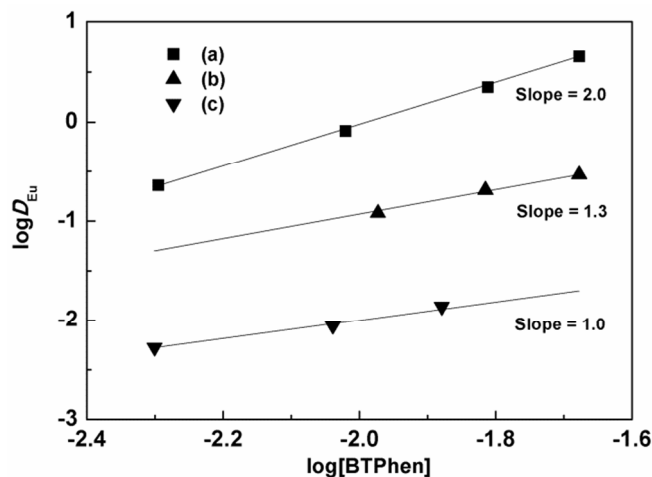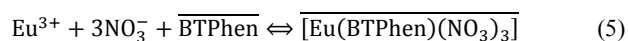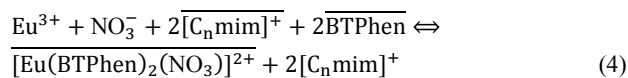

Fig. 3 Variations in logD_{Eu} as a function of log[BTPhen] in [C$_2$mim][NTf$_2$]. Initial nitric acid concentration: 0.1 M (a), 1 M (b), 3 M (c).

In order to reveal the extraction mechanism of BTPhen/[C$_n$mim][NTf$_2$] system, the relationship of logD_{Eu} against log[BTPhen] in [C$_2$mim][NTf$_2$] is measured with the previous method[30] and shown in Fig. 3. The fitted slope value is reduced from 2.0 (0.1 M HNO$_3$) to 1.0 (3 M HNO$_3$). This result indicates the molar ratio between BTPhen and Eu of complexes changes from 2 : 1 to 1 : 1 gradually with the [HNO$_3$] increasing. Two kinds of complexes formed between BTPhen and Eu^{3+}, namely [Eu(BTPhen)$_2$(NO$_3$)]$^{2+}$ (2 : 1 complex) and [Eu(BTPhen)(NO$_3$)$_3$] (1 : 1 complex), have been reported to be formed in traditional diluents based on previous report.[24] Consequently, the complexes between BTPhen and Eu^{3+} formed in [C$_2$mim][NTf$_2$] are in accordance to the previous report.[30] Considering the difference in the chemical structures of two complexes, the cation exchange mechanism for [Eu(BTPhen)$_2$(NO$_3$)]$^{2+}$ and the neutral complex mechanism for [Eu(BTPhen)(NO$_3$)$_3$] in the presence of [C$_n$mim][NTf$_2$] are proposed as Eqn (4) and Eqn (5), respectively. In the equations, overlines represent that the covered species are in the RTILs phase, while the uncovered species are in the aqueous phase. In addition, Eu^{3+} cannot be extracted by pure [C$_n$mim][NTf$_2$] in the presence of nitric acid, and thus anion exchange mechanism does not exist in this situation without BTPhen.

$$Eu^{3+} + NO_3^- + 2\overline{[C_n mim]^+} + 2\overline{BTPhen} \Leftrightarrow$$
$$\overline{[Eu(BTPhen)_2(NO_3)]^{2+}} + 2[C_n mim]^+ \quad (4)$$

$$Eu^{3+} + 3NO_3^- + \overline{BTPhen} \Leftrightarrow \overline{[Eu(BTPhen)(NO_3)_3]} \quad (5)$$
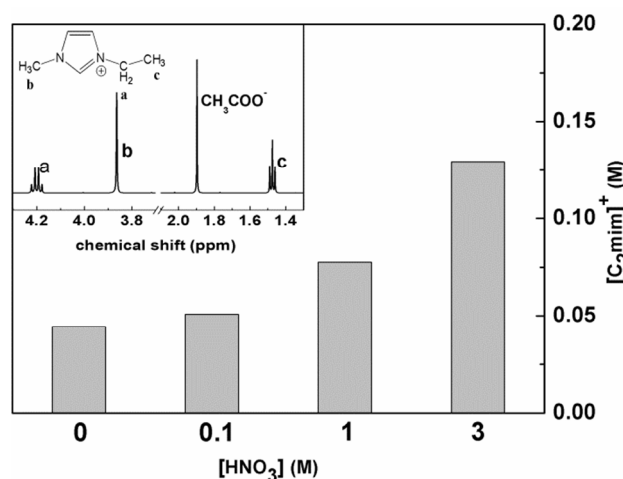
Fig. 4 The water-solubility of $[C_2mim]^+$ at different acidities. Inset: ^{1}H NMR spectrum of the mixture solution of $[C_2mim]^+$ and sodium acetate.

Although both of the cation exchange and neutral complex extraction mechanisms are present during the extraction, each contribution depends on the extraction conditions, especially the $[HNO_3]$. According to the slope values displayed in Fig. 3, the dominant mechanism varies from cation exchange mechanism to neutral complex mechanism with the $[HNO_3]$ increasing. The proportion of cation exchange mechanism is restrained by the nitric acid, while the proportion of neutral complex mechanism is enhanced simultaneously. The influence of $[HNO_3]$ on the water-solubility of $[C_2mim]^+$ is evaluated by ^{1}H NMR. The solubility equilibrium between $[C_2mim][NTf_2]$ and aqueous phase is established rapidly through vibrating mixer. As shown in the Fig. 4, the solubility of $[C_2mim]^+$ evidently increases with the $[HNO_3]$ increasing which is possibly due to the cation exchange between $[C_2mim]^+$ and H^+. These results indicate that the solubility equilibrium between $[C_2mim]^+$ and aqueous phase will be established firstly during the extraction, and the concentration of $[C_2mim]^+$ is positively related to the $[HNO_3]$. According to Eqn (4), higher concentration of $[C_2mim]^+$ in aqueous phase makes the cation exchange between $[Eu(BTPhen)_2(NO_3)]^{2+}$ and $[C_2mim]^+$ less favourable. Therefore, the contribution of the cation exchange mechanism to the extraction of Eu^{3+} is restrained significantly with the $[HNO_3]$ increasing. Although the contribution of the neutral complex mechanism to the extraction of Eu^{3+} would be improved with the concentration of NO_3^- increasing, the effect is not significant until the $[HNO_3]$ is great enough, which is similar to that in traditional solvents.[9] As a result, the D_{Eu} decreases obviously to a minimum and then slightly rises again (Fig. 2).

Moreover, the influence of the chemical structure of $[C_nmim][NTf_2]$ on the Eu^{3+} partitioning is also shown in Fig. 2. At controlling nitric acid concentrations, especially the low concentrations, the D_{Eu} decreases with the length of alkyl chain of $[C_nmim]^+$ changing from 2 to 8. Fig. 5 displays the $logD_{Eu}$-$log[BTPhen]$ curves in three kinds of $[C_nmim][NTf_2]$. The slope value gradually decreases with the length of alkyl chain

increasing, indicating the restraining of the cation exchange mechanism. Thus, longer alkyl chain is less favourable to the cation exchange, due to higher hydrophobicity of the corresponding $[C_nmim]^+$. Furthermore, longer alkyl chain of $[C_nmim]^+$ leads to higher viscosity (η) of RTILs ($\eta_{[C2mim][NTf2]}$ < $\eta_{[C4mim][NTf2]}$ < $\eta_{[C8mim][NTf2]}$), which is impeditive to both of the cation exchange and the neutral complex extraction.[31] Therefore, in the same condition, the D_{Eu} decreases with the length of alkyl chain increasing and the $BTPhen/[C_2mim][NTf_2]$ system shows the best extraction performance of Eu^{3+}. Thus, shorter alkyl chain of $[C_nmim][NTf_2]$ or lower $[HNO_3]$ are favourable for the effective extraction of Eu^{3+} in $BTPhen/[C_nmim][NTf_2]$ systems. Combined with $[C_2mim][NTf_2]$, BTPhen could provide satisfactory extraction of Eu^{3+} at low $[HNO_3]$ (0.01 M ~ 0.1 M HNO_3). Additionally, the D_{Eu} of BTPhen/1-octanol system was measured under the same conditions for comparison (data refer to Table S2). BTPhen/1-octanol system achieves the highest D_{Eu} (2.56) at 3 M HNO_3. $BTPhen/[C_nmim][NTf_2]$ system achieved the highest D_{Eu} (52) at 0.01 M HNO_3 when $[C_2mim][NTf_2]$ is used. Thus the diluent has obvious different influence on Eu3+ extraction in the presence of nitric acid.
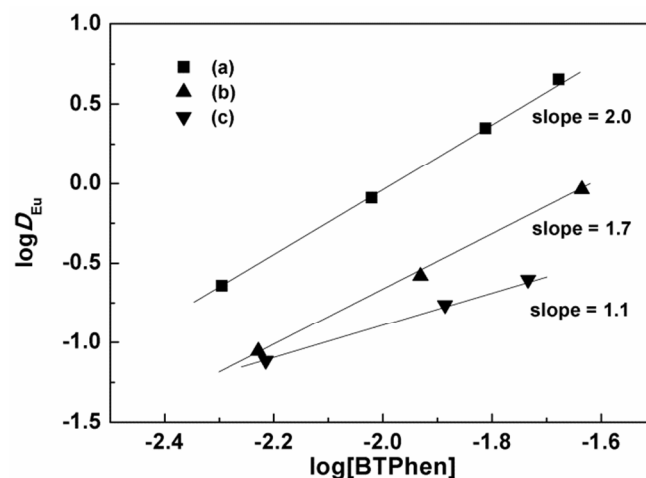

Fig. 5 Variations in $logD_{Eu}$ as a function of $log[BTPhen]$ in $[C_2mim][NTf_2]$ (a), $[C_4mim][NTf_2]$ (b), $[C_8mim][NTf_2]$ (c). Initial nitric acid concentration: 0.1 M.

3.2. Radiation effect on BTPhen/$[C_2mim][NTf_2]$ system.

The influence of γ-radiation on the extraction of Eu^{3+} by $BTPhen/[C_2mim][NTf_2]$ system at 0.1 M HNO_3 is shown in Fig. 6(a). The D_{Eu} of the irradiated $BTPhen/[C_2mim][NTf_2]$ system evidently rises with dose increasing in the presence of 0.1 M HNO_3. Such tendency is neither reported nor explicable. The irradiated samples were washed with water before extraction. The consequent D_{Eu} is shown in Fig. 6(b) and almost be constant to that in the unirradiated $BTPhen/[C_2mim][NTf_2]$. Therefore, the abnormal increase of Eu^{3+} partitioning of irradiated $BTPhen/[C_2mim][NTf_2]$ was attributed to some water-soluble radiolytic product. Moreover, it was observed that the influence of γ-radiation on the extraction of Eu^{3+} in $BTPhen/[C_2mim][NTf_2]$ system could be eliminated by

enhancing the concentration of HNO_3 during the extraction. At 1 M HNO_3, the D_{Eu} of irradiated BTPhen/[C_2mim][NTf_2] system changes slightly with the increase of dose (Fig. 6(c)). The above results indicate that BTPhen/[C_2mim][NTf_2] system has high radiation stability.
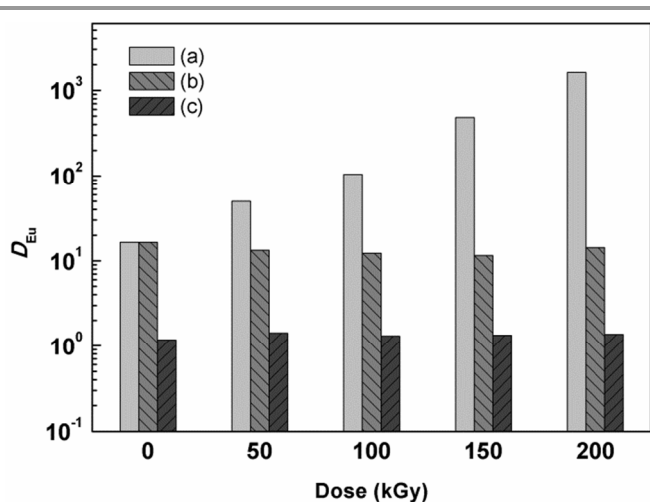

Fig. 6 Influence of γ-radiation on the D_{Eu} in BTPhen/[C_2mim][NTf_2] system. Oscillation time: an hour. Initial nitric acid concentration: 0.1 M (a), 0.1 M (samples were washed by water before extraction) (b), 1 M (c).

In order to further access the radiation stability of BTPhen/[C_2mim][NTf_2], the irradiated BTPhen in solid state was also studied by ^{1}H NMR (Fig. S2) and Micro-FTIR (Fig. S3). Both ^{1}H NMR and Micro-FTIR spectra of the irradiated samples display slightly change compared with those of the unirradiated samples. Thus BTPhen has satisfactory radiation stability in the solid state due to its relatively stable alkyl side chains and aromatic structure which can dissipate the energy during the irradiation. Furthermore, when the irradiated BTPhen was dissolved in [C_2mim][NTf_2], the irradiation of BTPhen has no obvious effect on the D_{Eu} (the results are omitted since they are similar with Fig. 6(b) and Fig. 6(c) at 0.1 M and 1 M HNO_3, respectively). However, when BTPhen was dissolved in 1-octanol, the irradiation effect on the extractability of BTPhen/1-octanol system was significant. The D_{Eu} of BTPhen/1-octanol system decreases rapidly with the dose increasing (Fig. S4). According to previous research,[11] traditional solvents are easy to decompose and produce active radicals during irradiation. Those radicals can induce serious radiolysis of extractants, which lead to the decrease of extractability. Although BTPhen has great radiation stability in solid state, its extractability is reduced significantly by radiation when it is dissolved in 1-octanol. Apparently, the traditional solvent that easily produces active species during irradiation (*e.g.* 1-octanol) is very unfavourable for the radiation stability of BTPhen. On the contrary, RTILs are more stable than traditional solvents during irradiation.[18] Due to the high viscosity of RTILs, the diffusion rate and activity of radicals produced from solvent are reduced, and the possibility of radiolysis of extractant decreased further.[32, 33] Thus the

radiolysis of BTPhen in [$C_n$mim][NTf_2] is much lower than that in traditional solvents.
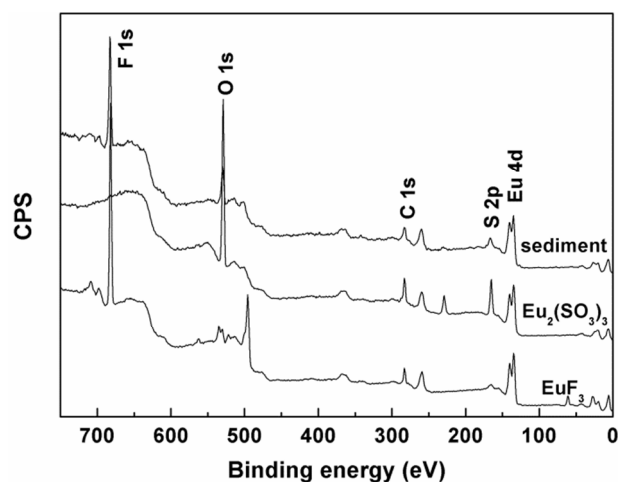

Fig. 7 XPS spectra of the sediment, $Eu_2(SO_3)_3$ and EuF_3.

Based on the washing-off effect, the increase of D_{Eu} is attributed to some water-soluble radiolytic products of the extraction system. In order to elucidate the composition of water-soluble radiolytic products, the removal of Eu^{3+} by irradiated [C_2mim][NTf_2] alone was measured at 0.1 M HNO_3. The removal of Eu^{3+} increases with the increase of dose for the irradiated [C_2mim][NTf_2], which has similar relationship with that for the irradiated BTPhen/[C_2mim][NTf_2] system. Since the unirradiated [C_2mim][NTf_2] cannot extract Eu^{3+} and the irradiated BTPhen slightly affects the extraction of Eu^{3+}, these results indicate that the water-soluble radiolytic products are derived from irradiated [C_2mim][NTf_2]. We find that when the concentration of Eu^{3+} is enhanced to 50 mM, visible white sediment is observed at the interface between irradiated [C_2mim][NTf_2] and the 50 mM Eu^{3+} solution. The solubility of this sediment is gradually dissolved with the acidity increasing, and the sediment is completely dissolved in 1 M HNO_3. This phenomenon indicates that the white sediment is responsible for the abnormal increase of Eu^{3+} partitioning of the irradiated BTPhen/[C_2mim][NTf_2] system at 0.1 M HNO_3.

Based on ^{19}F NMR analysis of irradiated [C_2mim][NTf_2] (Fig. S5), several dominant radiolytic products (HF, CF_3SOOH, CF_3SOONH_2, *etc.*) are identified based on our previous work. [25] A third-phase was observed when the concentration of Eu^{3+} was enhanced to 50 mM. After a separation procedure from the mixture of 50 mM Eu^{3+} solution and irradiated [C_2mim][NTf_2], white powder sediment was obtained and analysed by XPS. The composition of the sediment was determined to contain C, F, O, S and Eu elements according to the analysis of XPS pattern (Fig. 7). The C element is assigned to hydrocarbons which are used for calibration. The BE of elements can be used to identify the specific chemical bonding in different compounds,[34] so the core level BE and the BE difference for the obtained sediment are compared with that for $Eu_2(SO_3)_3$ crystal and EuF_3 crystal (Table S3). The sediment shows strong signal of F element, and a chemical formula of EuF_3 for the sediment is confirmed by

the atom ratio of F : Eu which equals to 2.98 : 1. Apparently, EuF_3 is the main species in sediment. Additionally, SO_3^{2-} has been identified as one of the radiolytic products of $[C_4mim][NTf_2]$ under γ-irradiation,[35] so SO_3^{2-} could be formed during the irradiation of $[C_2mim][NTf_2]$ and precipitated with Eu^{3+} as well. It is found that O and S elements have weak signal in XPS spectrum and can be assigned to $Eu_2(SO_3)_3$, but they are not main components of the sediment (less than 10%). Therefore, the precipitation between Eu^{3+} and radiolytic products of $[C_nmim][NTf_2]$ (F^- and SO_3^{2-}) leads to the decrease of Eu^{3+} concentration in water phase. Additionally, the amount of radiolytic products in $[C_nmim][NTf_2]$ is very low based on our previous analysis,[25] so BTPhen/$[C_2mim][NTf_2]$ system has good radiation stability during the extraction of Eu^{3+}.

4. Conclusions

The extraction performance and radiation stability of BTPhen/$[C_2mim][NTf_2]$ system during the removal of Eu^{3+} from HNO_3 solution were reported for the first time. The BTPhen/$[C_2mim][NTf_2]$ system shows the excellent extraction ability of Eu^{3+} at $[HNO_3] \leq 0.1$ M. The molar ratio of complexes between BTPhen and Eu^{3+} changes from 2 : 1 to 1 : 1 gradually, indicating that the dominant extraction mechanism varies from cation exchange mechanism to neutral species mechanism with the $[HNO_3]$ or the length of alkyl chain in the $[C_nmim]^+$ increasing. Although the precipitation between Eu^{3+} and radiolytic products of $[C_2mim][NTf_2]$ (F^- and SO_3^{2-}) leads to the increment in removal of Eu^{3+} for the irradiated BTPhen/$[C_2mim][NTf_2]$ system at $[HNO_3] \leq 0.1$ M, the influence of radiolytic products of $[C_2mim][NTf_2]$ can be easily avoided by enhancing the acidity during extraction or washing the irradiated samples with water before extraction. γ-radiation has no obvious effect on the extraction performance of BTPhen/$[C_2mim][NTf_2]$ system in the presence of 1 M nitric acid. Therefore, the BTPhen/$[C_2mim][NTf_2]$ system shows excellent extraction capacity and high radiation stability.

Acknowledgements

Notes and references

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