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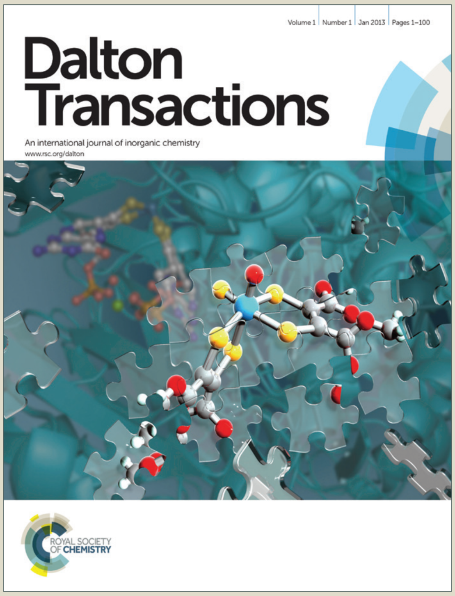

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α-Radiolysis of ionic liquid irradiated with helium ion beam and the influence of radiolytic products on Dy^{3+} extraction†

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Helium ion (He^+) beam produced by a heavy ion linear accelerator was used to simulate the α-rays for studying radiation effect on 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid ($[C_4mim][NTf_2]$). The water-soluble radiolytic products of $[C_4mim][NTf_2]$ under He^+ beam irradiation were analysed, and found that they were similar to those by γ-rays irradiation, but their amount was much less than that by γ-rays irradiation, which was attributed to the recombination of $[C_4mim][NTf_2]$ radical cations in track by high linear energy transfer (LET) radiations of He^+ beam. The extracting behaviour of Dy^{3+} using irradiated $[C_4mim][NTf_2]$ in combination with alkylated bis-triazinyl-pyridine (CA-BTP) was assessed, and found that the influence of He^+ beam on the extraction was less than that of γ-rays irradiation. In addition, radiolytic products have different influence on Dy^{3+} extraction at different doses, Dy^{3+} partitioning decreases at 50 kGy due to the protonation of CA-BTP and the inhibition of cation exchange mechanism by radiation-formed hydrogen ions. The abnormal increase of Dy^{3+} partitioning at 100 kGy is mainly attributed to the precipitation formed between Dy^{3+} and radiolytic products (F^- and SO_3^{2-}).

1. Introduction

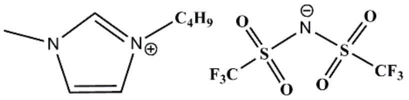
The room-temperature ionic liquids (RTILs) are novel solvents and have too many potential applications in wide areas. It has been demonstrated that RTILs can be considered as promising solvents for the extraction of radioactive isotopes from the spent nuclear fuel (SNF).[1-3] During the practical application of liquid-liquid extraction, RTILs must be exposed to very complicated environment, such as salinity, acidity, temperature, and radiation (α, β, γ-irradiation) field, *etc*.[4-6] Therefore, studies on the radiation effect of RTILs and their extraction for metal ions are of great importance in the assessment of application feasibility in the reprocessing of SNF. A highly efficient extraction of Sr^{2+} from aqueous solution can be achieved using RTILs in combination with crown ether.[7, 8] However, Sr^{2+} partitioning from water to irradiated $[C_4mim][NTf_2]$ decreased obviously with dose increasing.[9-11] Similar results were found during the extraction of Cs^+ using RTILs in combination with calixarene.[12] The decline of distribution ratio was attributed to the formation of hydrogen ions in the irradiation of RTILs, because hydrogen ions competed with metal ions to interact with extracting agents. In addition, the main radiolytic products of $[C_4mim][NTf_2]$ under γ-irradiation have been identified.[11, 13] In order to widen the application of RTILs in the reprocessing of SNF, RTILs are considered as solvents for the extraction of transplutonium elements,[14-16] which are responsible for the majority of long-lived and high-level radiotoxicity.[17-19] After their removal from SNF, these elements can be either used in radioactive sources or transmuted by neutron bombardment to short-lived radionuclides. The separation of transplutonium elements, especially for minor actinides-lanthanides (MA-Ln), is a huge challenge, because these elements have very similar chemical properties. Moreover, most of long-lived minor actinides elements are α-decay resources. Extracting agents and solvents will be used under high level α-ray condition, which increases the difficulty of investigation on the α-radiolysis of extraction system in common lab.

There were some reports about the radiation effects of RTILs under γ-irradiation,[20-24] but that about the radiolytic behaviour of RTILs under α-rays was scarcely mentioned. Pioneering research was carried out by Allen *et al*.[4] They noted that less than 1% of RTILs underwent radiolysis when exposed to a dose of 400 kGy under α-irradiation. No more information is provided for the following research, so it is urgent circumstance to investigate the radiation behaviour of RTILs under α-irradiation. There are tremendous difficulties to study the radiation effect of ionic liquid compounds under α-irradiation, because α radioactive source is very dangerous to human beings when it enters the body. In addition, when α radioactive element was put into ionic liquid sample, it is extremely difficult to separate α radioactive source from the liquid sample due to its radioactivity.

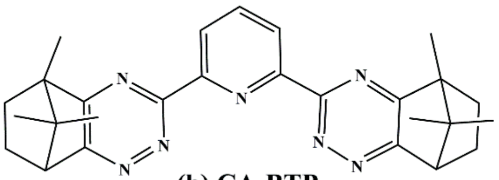
The aim of the present work is to investigate the radiation effect of extraction system based on RTILs under He^+ irradiation, and special irradiation equipment was designed for He^+ irradiation. The designed irradiation equipment was used to investigate the α-radiation effect of RTILs with He^+ beam provided by a 4.5 MV heavy ion linear accelerator. There are some different characteristics between α-rays and He^+ beam, such as, electric charge and energy, but the He^+ beam is the optimal replacement for investigating the α-radiation effect of extraction system. Dysprosium ion (Dy^{3+}) has similar chemical proprieties with MA-Ln, [25-27] thus Dy^{3+} is chosen for assessing the extracting behaviour of He^+ irradiated $[C_4mim][NTf_2]$ (Fig.1(a)) in combination with alkylated bis-triazinyl-pyridine (CA-BTP, Fig. 1(b)). CA-BTP has good stability, high solubility, reasonably fast extraction kinetics, and the ability to separate actinides(III) and lanthanides(III). [28-31] γ-radiolysis of RTILs is also studied to compare the LET effect. Some encouraging, though unreported results of the experiment were achieved.

2. Experimental section

2.1. Materials. $[C_4mim][NTf_2]$ (≥ 99%) was obtained from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). The water content in the $[C_4mim][NTf_2]$ ionic liquids was less than 350 ppm, and no impurities were detected by NMR spectrometry. CA-BTP (≥ 95%) was synthesized according to the reference.[19, 28] These compounds were used as received. All other solvents were analytical-grade reagent and used without further purification.



(a) $[C_4mim][NTf_2]$



(b) CA-BTP

Fig. 1 The chemical structure of $[C_4mim][NTf_2]$ (a) and CA-BTP (b).

2.2. Irradiation. The container (diameter 10 mm × length 30 mm) for the irradiation of ionic liquid using He^+ beam was made by stainless steel (Fig. 2). The ionic liquid samples were irradiated in air (298 ± 2 K) with 2.5 MeV He^+ beam. The projected range of He^+ beam implant into ionic liquids was simulated by SRIM (stopping and range of ions into matter) 2012 Monte Carlo code. 2.115 MeV energy of He^+ beam was absorbed by 5 μm titanium foil during the irradiation, then 0.385 MeV He^+ beam was implanted in $[C_4mim][NTf_2]$ ionic liquid mostly at length 2.9 ~ 3.1 μm according to the results of Monte Carlo simulations (Fig. S1), so the perforated He^+ should be totally absorbed by ionic liquid. It was also found that irradiated ionic liquid could mixed quickly with other ionic liquid, thus the absorbed dose of $[C_4mim][NTf_2]$ was calculated by the following equation:

$$D_{RTILs} = 10^6(E_i\text{-}E_a)\cdot C_{He}\cdot \rho_{RTILs}^{-1}\cdot V_{RTILs}^{-1},$$

where D_{RTILs} is the absorbed dose of sample (kGy), E_i is the incident energy of He^+ ions (MeV), E_a the absorbed energy by titanium foil (MeV), C_{He} accumulated charge of He^+ (C), ρ_{RTILs} is the density of $[C_4mim][NTf_2]$ (1.43 g·mL^{-1}), V_{RTILs} is the volume of $[C_4mim][NTf_2]$ (2.5 mL). The temperature of sample did not increase during the irradiation. The irradiated samples were characterized by various spectroscopic methods and used as solvent for extraction experiment.

For comparison purpose, the irradiation of $[C_4mim][NTf_2]$ ionic liquid under γ-rays in air (298 ± 4 K) was carried out using ^{60}Co source with a dose rate of ca. 250 Gy·min^{-1}. The absorbed dose under γ-irradiation was determined by Fricke dosimeter.

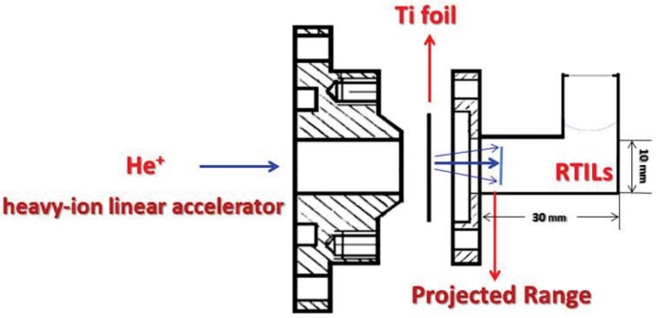


Fig. 2 The equipment for the irradiation of ionic liquid using He^+ beam.

2.3. Characterization.

UV-vis The ionic liquid samples before and after irradiation were dissolved in acetonitrile (V_{RTILs} : $V_{acetonitrile}$ = 30 μL : 10 mL) and their ultraviolet visible spectroscopies (UV-vis) were recorded on a Hitachi 3010 UV-vis spectrophotometer.

Micro-FTIR The aqueous phase from the wash of irradiated sample was dropped onto a slide and dried at 40 °C for 30 min, and then the residual compounds on the slide were analysed by a Thermo Scientific Micro Fourier transform infrared spectrometer (Micro-FTIR).

^{1}H and ^{19}F NMR NMR experiments were carried out with a Bruker AV-500. Samples were diluted in dimethyl sulfoxide-d6 (DMSO-d6) and the chemical shift scale was calibrated with tetramethylsilane at 0 ppm for ^{1}H NMR. The aqueous phase from the wash of 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 previous literature. [22]

XPS analysis The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical. The binding energies were calibrated using C1s hydrocarbon peak at 284.80 eV.

2.4. Extraction experiment

The extraction solution (0.5 mL) contained 20 mmol·L^{-1} CA-BTP was prepared by dissolving the extracting agent CA-BTP in [C_4mim][NTf_2], and the aqueous solution (0.5 mL) contained 2 mmol·L^{-1} Dy^{3+} was prepared by dissolving $Dy(NO_3)_3$ in water. The extraction experiments were oscillated in a constant temperature incubator shaker which maintained a thermostated air bath at 50 ^{o}C with a rotating speed of 150 r·min^{-1}, then were centrifuged for 10 min to ensure that two phases were completely separated. After phase separation, the aqueous solution was diluted with deionized water, and then the concentration of Dy^{3+} in the diluted aqueous solution was measured by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICP-AES) (Teledyne Leeman Labs, USA). The calculation of extraction efficiencies was based on $E_{Dy} = (C_i - C_f)/C_i$ and distribution ratios were calculated as $D_{Dy} = (C_i - C_f)/C_f$, where C_i and C_f designate the initial and final concentrations of Dy^{3+} in the diluted solution, respectively.

3. Results and discussion

3.1. The radiolytic behaviour of ionic liquid under He^+ beam.

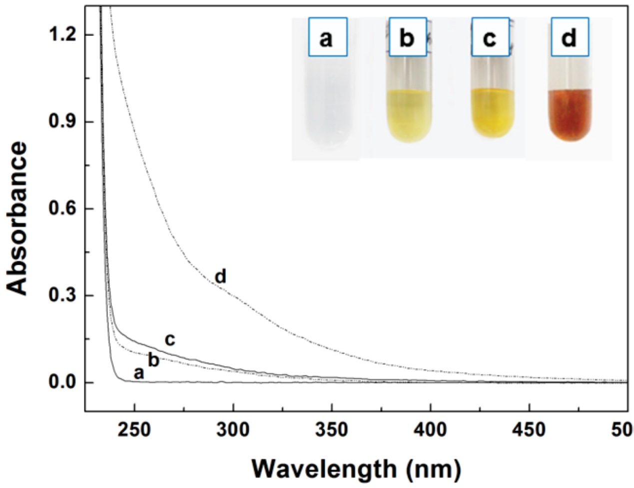


Fig. 3 UV–Vis spectra of [C_4mim][NTf_2] after He^+ irradiation at different doses. Insert shows the colour change of irradiated ionic liquid [C_4mim][NTf_2]. (a) 0 kGy, (b) 50 kGy, (c) 100 kGy, (d) 500 kGy.

The colour of samples showed considerable darkening following He^+ irradiation, but the samples were still transparent after He^+ irradiation (see the insert in Fig. 3). With the increase of dose, the colour of [C_4mim][NTf_2] changed from colourless to gamboge, and no insoluble material was observed in the irradiated sample. The UV-vis spectra of [C_4mim][NTf_2] after He^+ irradiation were presented in Fig.3. Compared with unirradiated [C_4mim][NTf_2], a new absorption band at 230 ~ 400 nm corresponding to coloured radiolytic products was found in the irradiated samples and the absorption band enhanced with dose increasing (Fig. 3). Berthon *et al.* pointed out that the coloured radiolytic products came from the radiolysis of alkylimidazolium cation. [32] The above result indicated that the radiolysis of ionic liquid increased with dose increasing. Compared with the results of [C_4mim][NTf_2] under γ-rays, it can be found that the radiolysis of [C_4mim][NTf_2] under He^+ beam was less than that under γ-irradiation (Fig. S2). However, the intensity of absorbance band at 285 nm for γ-irradiated sample is nearly 5 times higher than that of under He^+ beam irradiation, while the intensities of the band at 325 - 400 nm are about 1.4 times higher than that with He^+ beam irradiation. These results indicated that the species shown absorbance bands at 285 nm and at 325 - 400 nm are definitely different. Allen *et al.* suggested that conjugated alkenes were possible radiolytic products of alkylimidazolium cation under γ-irradiation.[4] It was found that the absorbance band at 285 nm decreased obviously after the treatment of ozone,[33] thus the absorbance band at 285 nm was attributed to the absorbance of conjugated alkenes. Berthon *et al.* suggested that recombination of primary radiolytic products lead to various polymeric or aggregated species,[32] so absorbance band at 325 - 400 nm is mainly assigned to the absorbance of various polymeric or aggregated species. Sugo *et. al* mentioned that the degradation of N, N, N', N'-tetraoctyldiglycolamide (TODGA) in n-dodecane by He^+ beam irradiation was less than that by γ-irradiation, which suggested that the degradation of TODGA was decreased due to the recombination of n-dodecane radical cations in track by He^{2+} beam radiation. [34] Therefore, the decrease of the amount of coloured radiolytic products is attributed to the recombination of [C_4mim][NTf_2] radical cations. There are few chance for them to react with [C_4mim][NTf_2] molecule.

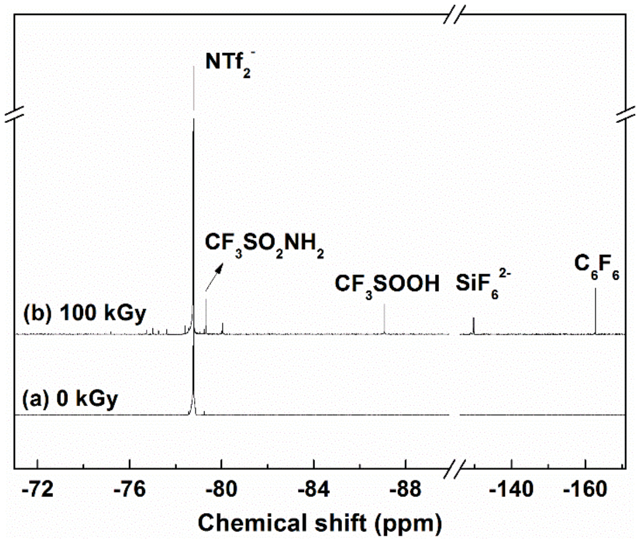


Fig. 4 ^{19}F NMR spectra of He^+ irradiated [C_4mim][NTf_2]. (The aqueous phase from the washing of unirradiated sample (a) and He^+ irradiated sample (b)).

The ^1H NMR spectra of irradiated samples are shown in Fig. S3. Two new weak peaks at 10.9, 10.1 ppm are observed in the irradiated sample and assigned to hydrogen ions of acid radiolytic products. In order to identify the chemical structure of radiolytic products, the irradiated sample was washed by deuterium oxide ($V_{RTILs} : V_{D2O} = 1:1$). Then the aqueous phase was analysed by Micro-FTIR and ^{19}F NMR. The absorption bands at 3300 - 3600 cm^{-1} and 1600 - 1700 cm^{-1} corresponding to the vibration of valence for OH groups, and absorption band at 960 cm^{-1} attributing to NH_2 group were found in Micro-FTIR spectra (Fig. S4). As shown in Fig. 4, the ^{19}F NMR of irradiated sample shows three new peaks at -79.34, -87.09 and -129.80 ppm. According to our previous work,[13] these peaks were assigned to CF_3SOOH, $CF_3SO_2NH_2$, HF formed by the degradation of NTf_2^- anions. Compared with the amount of radiolytic products of $[C_4mim][NTf_2]$ under γ-irradiation, that under He^+ beam was less (Fig. S5), which also attributes to the recombination of $[C_4mim][NTf_2]$ radical cations in track by He^+ beam radiation. [34] This is a big additional difference between low LET radiation (γ-rays) and high LET radiation (α-rays).

According to the calculation of LET,[35, 36] the LET value is proportional to the z^2, where z is the charge, so the effect of charge of He ion will affect the LET value, for He^+, the LET value is quarter that of He^{2+}. On the other hand, LET is inversely proportional to the energy of ions. The LET value of 0.4 MeV He^+ is close to that of 1.5 MeV He^{2+}. It was reported that the radiolysis yield of Fe^{3+} in a Fricke solution increased with increasing He^{2+} energy.[37, 38] Compared with γ radiation, however, the radiolysis yields of Fe^{3+} with 6.7 MeV He^{2+} radiation ($G(Fe^{3+}) = 5.7$)[38] is much less than that with γ-radiation ($G(Fe^{3+}) = 15.5$)[39]. Influence of He^{2+} energy on radiolysis of ionic liquid should be similar to the radiolysis of Fe^{3+} in a Fricke solution. Similarly, when ionic liquid was irradiated by α-radiation (ca. 5 MeV), the radiolysis yield of ionic liquid should be also lower than that with γ-radiation. The influence of He^{2+} energy on the radiolysis of ionic liquid will be investigated in detail in our following work.

3.2. The influence of radiolytic products on the extraction of Dy^{3+}

In order to investigate the influence of radiolytic products on Dy^{3+} extraction, the kinetics of extraction of Dy^{3+} from aqueous solution into $[C_4mim][NTf_2]$ was obtained firstly. The observation of relatively fast kinetics is shown in Fig. S6, a very high D_{Dy} at 445 is achieved and the E_{Dy} exceeds 99.5% after an hour, so the equilibrium time at an hour is chosen for the following experiments. Interestingly, in 0.1 mol·L^{-1} HNO_3 solution, the E_{Dy} was no more than 30% after 4 hours (just 5% at 1 mol·L^{-1} HNO_3), which indicated that CA-BTP was an extremely sensitive extractant for acidity, due to the protonation of extractant[29] and the inhibition of cation exchange mechanism by hydrogen ions. When $[C_4mim][NTf_2]$ was used as extracting diluent, the cation exchange is dominant extraction mechanism.[10, 40]

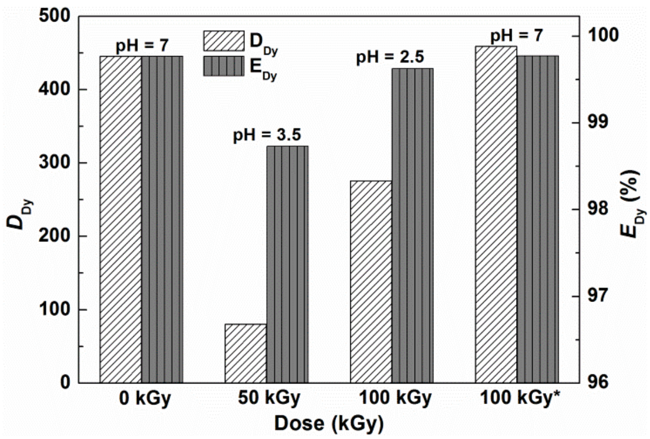


Fig. 5 Influence of dose on Dy^{3+} extraction from aqueous solution by He^+ irradiated $[C_4mim][NTf_2]$ in combination with CA-BTP.*The irradiated sample was washed by water for 4 times before extraction experiment. The pH of the aqueous phases after extraction was provided.

As shown in Fig. 5, in irradiated $[C_4mim][NTf_2]$, Dy^{3+} partitioning evidently reduces at 50 kGy, but an abnormal increase of Dy^{3+} partitioning is observed at 100 kGy. Some water-insoluble compounds were observed at the interface between irradiated $[C_4mim][NTf_2]$ and the aqueous solution. After the irradiated $[C_4mim][NTf_2]$ was washed by water for 4 times, a nearly full recovery of Dy^{3+} partitioning was obtained. These results suggested that both the decrease of Dy^{3+} partitioning at 50 kGy and increase of Dy^{3+} partitioning at 100 kGy were ascribed to the influence of water-soluble radiolytic products. The decrease of Dy^{3+} partitioning at 50 kGy was mainly attributed to the protonation of CA-BTP and the inhibition of cation exchange mechanism by radiation-formed H^+, so the acidity had an obvious negative impact on the extraction of Dy^{3+}. It was well-known that the acidity of irradiated samples enhanced with dose increasing based on the previous literature,[13] but an abnormal increase of Dy^{3+} partitioning appeared at 100 kGy, which was mainly attributed to the precipitation formed between Dy^{3+} and radiolytic products (F^- and SO_3^{2-}). After the water-soluble radiolytic products (F^- and SO_3^{2-}) of $[C_4mim][NTf_2]$ irradiated by He^+ beam was washed with water, Dy^{3+} partitioning was almost recovered. Similar results were obtained when $[C_4mim][NTf_2]$ was irradiated by γ-rays (Fig. S7). The decrease of Dy^{3+} partitioning under γ-irradiation is more obvious than that of under He^+ beam, so this result also demonstrates that the radiolysis of $[C_4mim][NTf_2]$ under γ-irradiation is more serious than that under He^+ beam. However, the Dy^{3+} partitioning was not fully recovered when the γ-irradiated $[C_4mim][NTf_2]$ was washed by water. The above result indicated that the extraction of Dy^{3+} was influenced by coloured radiolytic products, whose amount was nearly 5 times higher than that of under He^+ beam based on UV-vis analysis (Fig. S2). In our previous work, it has been found that the water-insoluble coloured radiolytic products of $[C_4mim][NTf_2]$ under γ-irradiation has influence on Sr^{2+} extraction.[13] The amount of water-insoluble coloured radiolytic products under He^+ beam is much less than that under γ-irradiation, so the influence of extraction of Dy^{3+} by He^+ beam irradiation is much less than that of by γ-rays irradiation.

The sediment, which was formed at the interface between Dy^{3+} solution and $[C_4mim][NTf_2]$ irradiated by He^+ beam or γ-rays, was analysed by XPS. The composition of sediment was determined to contain F, O, S and Dy elements according to XPS record (Fig. 6). The binding energies (BE) of elements can be used to identify the specific chemical bonding in different compounds. According to the XPS results (Table 1), the main component of sediment was confirmed as DyF_3, and the sediment contained $Dy_2(SO_3)_3$ nearly 10%. The extraction of Dy^{3+} under different conditions is still under way.

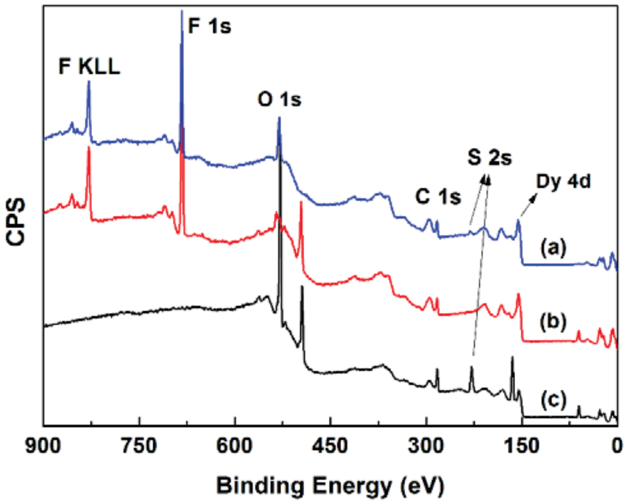


Fig. 6 XPS spectra of the sediment (a), DyF_3 (b) and $Dy_2(SO_3)_3$ (c).

Table. 1 Measured core level BE for the sediment, DyF_3 and $Dy_2(SO_3)_3$

Core level	BE (eV)		
	The sediment	DyF_3	$Dy_2(SO_3)_3$
F 1s	684.62	684.32	—
O 1s	531.71	—	531.07
S 2s	232.22	—	231.00
Dy 4d	153.85	153.74	153.72

4. Conclusions

We reported α-radiation effect on ionic liquids using He^+ beam for the first time. The amount of coloured radiolytic products of $[C_4mim][NTf_2]$ under He^+ beam was much less than that of under γ-irradiation. The confirmative water-soluble radiolytic products (CF_3SOOH, $CF_3SO_2NH_2$, HF, SO_3^{2-}) of $[C_4mim][NTf_2]$ under He^+ beam were identified, and their amount is less than that of under γ-irradiation due to the recombination of $[C_4mim][NTf_2]$ radical cations. The extracting behaviour of Dy^{3+} using irradiated $[C_4mim][NTf_2]$ in combination with CA-BTP further indicated that the influence of He^+ beam on the extraction is smaller than that of γ-irradiation. In addition, radiolytic products have different influences on Dy^{3+} extraction at different doses. Dy^{3+} partitioning decreases at 50 kGy due to the protonation of CA-BTP and the inhibition of cation exchange mechanism by radiation-formed H^+, and an abnormal increase of Dy^{3+} partitioning at 100 kGy is mainly attributed to the precipitation formed between Dy^{3+} and radiolytic products (F^- and SO_3^{2-}). This work promises to provide a new method for assessing the feasibility of RTILs as alternative medium for the separations of MA-Ln from SNF.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [The relationship between the energy of ions source and the penetrated depth of He^+ beams in titanium foil. UV–Vis spectra of $[C_4mim][NTf_2]$ before (a) and after irradiation of He^+ beam (b), γ-rays (c). ^1H NMR spectra of $[C_4mim][NTf_2]$ before (a) and after irradiation at 100 kGy by He^+ beam (b). Micro-FTIR spectra of unirradiated and irradiated $[C_4mim][NTf_2]$. ^{19}F NMR spectra of unirradiated and irradiated $[C_4mim][NTf_2]$. Influence of time on Dy ^{III} extraction from aqueous solution by unirradiated $[C_4mim][NTf_2]$ in combination with CA-BTP. Influence of dose on Dy ^{III} extraction from aqueous solution by γ-irradiated $[C_4mim][NTf_2]$ in combination with CA-BTP.]. See DOI: 10.1039/b000000x/

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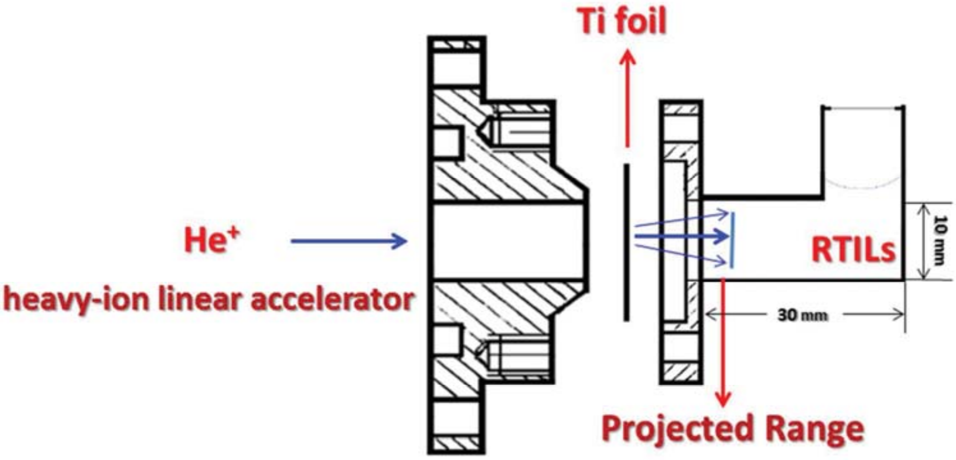

The equipment for the irradiation of ionic liquid using He+ beam.
210x111mm (96 x 96 DPI)