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Identification of the radiolytic product of hydrophobic ionic liquid [C₄mim][NTf₂] during removal of Sr²⁺ from aqueous solution†

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SO₃²⁻ is identified as one of the radiolytic products of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]) during the removal of strontium ions (Sr²⁺) from aqueous solution.

The utility of room temperature ionic liquids (RTILs), especially those containing imidazolium cations, for instance 1-butyl-3-methylimidazolium (C₄mim⁺), associated with various inorganic anions such as bis(trifluoromethylsulfonyl)imide ((CF₃SO₂)₂N⁻, or NTf₂⁻), as next generation diluents in traditional liquid–liquid extraction of radioactive nuclei is a well-studied topic that has shown some encouraging results.^{1,2} Such an application, however, demands a comprehensive knowledge of the stability and metal ion extraction of RTILs under radiation conditions. Several investigators have recently focused on the studies of the radiation stability of RTILs. Allen *et al.*, for example, have carried out a preliminary assessment of the α -, β - and γ -radiation effects on the hydrophilic RTILs [C₄mim]NO₃, [C₂mim]Cl and [C₆mim]Cl. It was shown that the tested ILs exhibit radiation-induced darkening and an increase of light absorbance, but less than 1% of the samples undergo radiolysis even exposed to a dose of 400 kGy, suggesting a very high radiation stability for these ILs.³ Moisy and co-workers investigated the radiation stability of the hydrophobic RTILs [C₄mim][PF₆], [C₄mim][NTf₂]⁴ and [N₁₄₄₄][NTf₂],⁵ where [N₁₄₄₄]⁺ is the methyltributylammonium cation. They proposed possible degradation schemes of the RTILs based on the NMR and ESI-MS analyses. Wu *et al.* further investigated in detail γ -radiolysis of neat [C₄mim][PF₆]⁶ and [C₄mim][BF₄]⁷ by spectroscopic methods and differential scanning calorimetry (DSC). Bartels *et al.* determined the yields of hydrogen gas in the irradiated ionic liquids based on imidazolium, pyridinium and phosphonium cations.⁸ The reaction kinetics and the primary effects of radiation

in RTILs were studied using pulse radiolysis techniques^{9–17} and laser photolysis techniques.^{18,19} Recently, we have studied the radiation stability of [C₄mim][PF₆] in the presence of nitric acid²⁰ and decolouration of irradiated [C₄mim][NTf₂].²¹ To assess the influence of γ -radiation on metal ion extraction of RTILs, we also carried out solvent extraction of Sr²⁺ by crown ether using irradiated [C₄mim][PF₆]²² and irradiated [C₄mim][NTf₂].²³ The results showed that H⁺ was formed during irradiation of the ILs, and the radiation-generated H⁺ markedly reduces Sr²⁺ partitioning in the crown ether/ILs extraction phase by competing with Sr²⁺ to interact with the crown ether. All of the above mentioned studies have dealt with the radiation effects on RTILs, including the metal ion extraction of RTILs. To date, the identification of radiolytic products, especially anions, which might be significant for knowledge about the radiolysis of the RTILs, has rarely been reported because of the small quantity and large numbers of the species. By chance in this work, the radiolytic product of a typical RTIL, [C₄mim][NTf₂], is clearly identified during the removal of Sr²⁺ from aqueous solution using irradiated [C₄mim][NTf₂].

The [C₄mim][NTf₂] used in this work was synthesized according to a procedure previously reported^{24,25} and purified by adopting the steps described elsewhere.²⁶ After purification, the water content in the [C₄mim][NTf₂] sample was less than 200 ppm, measured by Karl-Fischer titration, and no impurities were detected by NMR spectrometry analysis. The solution of Sr²⁺ chosen in removal experiment was 0.01 mol L⁻¹ of Sr(NO₃)₂, which is typical for extraction of Sr²⁺ using RTILs-based extraction system.¹

Irradiation of the [C₄mim][NTf₂] was carried out in air atmosphere using ⁶⁰Co source with a total absorbed dose ranging from 50 to 550 kGy. In a typical removal experiment, a 0.5 mL of irradiated [C₄mim][NTf₂] was contacted with a 1.0 mL of Sr(NO₃)₂ aqueous solution for about 30 min in a vibrating mixer followed by centrifugal separation, then the mixture was kept in two phases for different length time to assess the equilibrium dynamics. For comparison purposes, an identical experiment was also conducted using unirradiated [C₄mim][NTf₂]. The removal of Sr²⁺ from the aqueous solution was measured by determining the remnant Sr²⁺ in the aqueous solution using a flame atomic absorption spectrophotometer (AAS). The degree of the removal was calculated as $E_{\text{Sr}} = (C_i - C_f)/C_i$, where C_i and C_f designate the initial and final concentrations of Sr²⁺ in the aqueous phase, respectively.

Fig. 1 shows the results on the removal of Sr²⁺ from the aqueous solution using irradiated [C₄mim][NTf₂] at different doses. As can be seen, almost no Sr²⁺ was removed from the aqueous solution when unirradiated [C₄mim][NTf₂] was used, revealing the low affinity of Sr²⁺ for the RTIL phase. This is consistent with that

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† Electronic supplementary information (ESI) available: Fig. S1 SEM and energy dispersive X-ray spectroscopy (EDS) spectra of the precipitate separated from the interface of irradiated [C₄mim][NTf₂] and aqueous solution of Sr²⁺. The contact time of the two phases is less than 2 weeks (left) and more than 2 months (right), respectively. Fig. S2 ¹H NMR spectra of unirradiated [C₄mim][NTf₂] and irradiated [C₄mim][NTf₂] at 400 kGy after contacting with aqueous solution of Sr²⁺ for 1 month. Fig. S3 FTIR spectra of unirradiated [C₄mim][NTf₂] and irradiated [C₄mim][NTf₂] at 400 kGy after contacting with aqueous solution of Sr²⁺ for 1 month. See DOI: 10.1039/b911026g

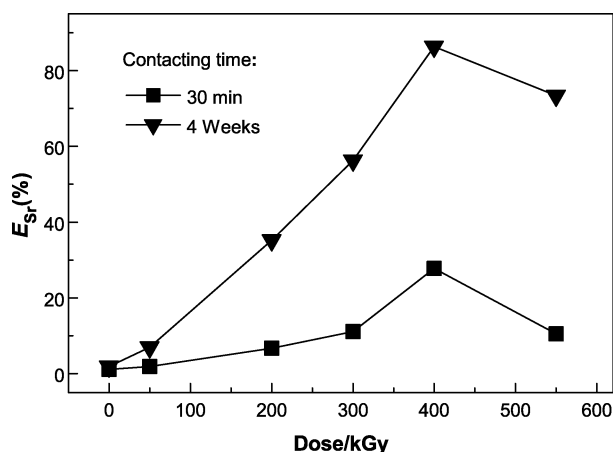


Fig. 1 Influence of dose on E_{Sr} for Sr^{2+} removal from the aqueous solutions by irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$.

on the extraction of Sr^{2+} using $[\text{C}_4\text{mim}][\text{PF}_6]$, in which crown ether was added to improve the affinity of Sr^{2+} for the RTIL phase.^{1,27} When the $[\text{C}_4\text{mim}][\text{NTf}_2]$ was irradiated, however, the removal of Sr^{2+} from the aqueous solution showed an unexpected increase compared to that using unirradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$, and the increase enhanced with increasing dose up to 400 kGy, but dropped at 550 kGy. More interestingly, a further increase of E_{Sr} was observed by prolonging the contact time of aqueous phase and ILs phase. After the contact of 4 weeks, for example, the E_{Sr} of irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 400 kGy is over 80%, which is even comparable with that of $[\text{C}_4\text{mim}][\text{NTf}_2]$ containing crown ether.²³ To assess the equilibrium dynamics, the E_{Sr} of $[\text{C}_4\text{mim}][\text{NTf}_2]$ for different contact time of the two phases was determined as shown in Fig. 2. It is clear that no Sr^{2+} was removed by unirradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ regardless of the contact time of the two phases, while the irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ gave a contact time-dependent removal of Sr^{2+} regardless of the absorbed doses. Besides, the dynamics for the irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 550 kGy seemed to be different from that for the irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ at other doses. The former had not reached equilibrium even after 4 weeks contact of the two phases, while the later tended to equilibrate at about 100 h.

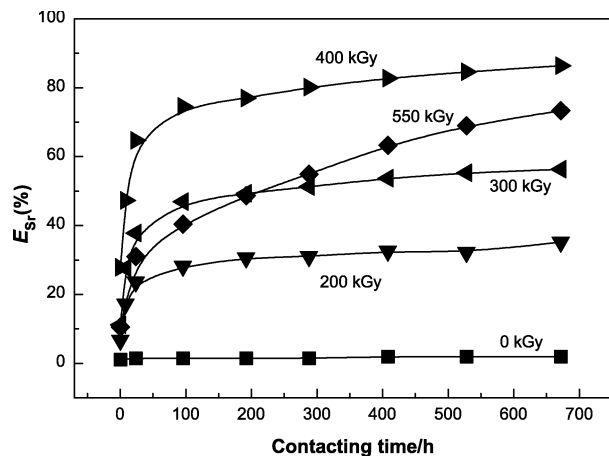


Fig. 2 Dependence of E_{Sr} for Sr^{2+} removal from the aqueous solutions by irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ on contact time of the two phases.

In order to identify why the removal of Sr^{2+} from water can be achieved by irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ without any extractants, the partitioning of Sr^{2+} in ILs phase was determined by AAS. The results, unexpectedly, revealed the absence of Sr^{2+} in $[\text{C}_4\text{mim}][\text{NTf}_2]$ regardless of the absorbed doses. However, a little precipitate was noted on the interface of the water and ILs phase, and the amount of the precipitate increased with increasing dose up to 400 kGy and decreased at 550 kGy, while no insoluble material was observed when unirradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ was used. This is consistent with the removal results of Sr^{2+} as mentioned above, suggesting that the removal of Sr^{2+} using irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ is not by extraction but by precipitation.

After ageing, centrifuging and drying, the precipitate was collected as white powder, and the characterization was performed subsequently. The precipitate shows strip shaped crystal in SEM micrograph (inset in Fig. 3), and the composition was determined to contain C, Sr, S and O elements according to XPS record (Fig. 3). The C element is clearly assigned to adventitious hydrocarbons due to exposure to air, since element analysis of the precipitate revealed the absence of C element. The Sr, S, O elements with atom ratio 1 : 1 : 4 give a chemical formula of SrSO_4 for the precipitate. It is well known that core level binding energy (BE) can be used to identify the specific chemical bonding in materials,²⁸ while some others described chemical bonding effects in a compound by the BE difference.²⁹ Herein, the core level BE and the BE difference for the precipitate in this work were compared with that for SrSO_4 crystal reported previously,³⁰ as shown in Table 1. Both the core level BE value of O 1s, Sr 3d_{5/2}, S 2p_{3/2} and the BE difference ($\Delta(\text{O}-\text{Sr})$) for the precipitate

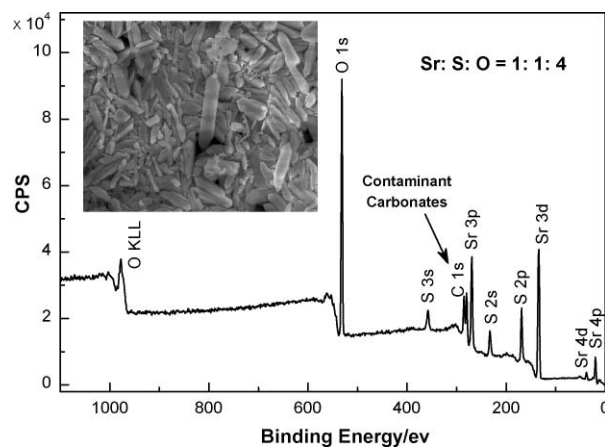


Fig. 3 XPS and SEM (inset) spectra of the precipitate formed during the removal of Sr^{2+} using irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$.

Table 1 Measured core level BE for the precipitate in this work and for SrSO_4 crystal in the reference

Core level	BE/eV	
	The precipitate	SrSO_4 ³⁰
O 1s	531.67	531.60
Sr 3d _{5/2}	133.87	133.85
S 2p _{3/2}	168.67	168.55
$\Delta(\text{O}-\text{Sr})$	397.80	397.75

$\Delta(\text{O}-\text{Sr}) = \text{BE}(\text{O } 1\text{s}) - \text{BE}(\text{Sr } 3\text{d}_{5/2})$.

were perfectly consistent with that for SrSO_4 , confirming that the precipitate in this work is SrSO_4 . Actually, energy dispersive X-ray spectroscopy (EDS) was also used to analysis the component of the precipitate (ESI, Fig. S1).† The results showed that the atom ratio of component in the precipitate changed with the contact time of ILs phase and water. When contacted less than 2 weeks, for example, the value was $\text{Sr} : \text{S} = 1 : 1 : 3$, but when contacted more than 2 months the value changed to $\text{Sr} : \text{S} : \text{O} = 1 : 1 : 4$. Hence, we unambiguously establish that SO_3^{2-} , as one of the radiolytic products of $[\text{C}_4\text{mim}][\text{NTf}_2]$ during removal of Sr^{2+} from aqueous solution, leads to the formation of SrSO_3 precipitate on the interface of the ILs and water, and then SrSO_3 was oxidized to SrSO_4 due to exposure to air.

The radiolysis of ionic liquids based on $[\text{NTf}_2]^-$ anion has been reported in the literature.^{4,5,10–13,17} It is expected that one of initial steps of $[\text{NTf}_2]^-$ anion radiolysis is the loss of F^\bullet , CF^\bullet and $\text{CF}_3\text{SO}_2^\bullet$, forming the remaining radical $\text{NSO}_2^{\bullet-}$, $\text{NSO}_2\text{CF}_3^{\bullet-}$ and $\text{N}(\text{SO}_2\text{CF}_3)\text{SO}_2^{\bullet-}$. Recombination and/or fragmentation of these radicals and that from cation radiolysis lead to various radiolysis species, including sulfonic compounds. Accordingly, the formation of SO_3^{2-} in this study may involve two ways. One way is that sulfonic compounds undergo hydrolysis forming SO_3^{2-} when the irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ contacted with the aqueous solution. Another way is that dissociation of the N–S bonds of some radicals, such as $\text{NSO}_2^{\bullet-}$, lead to the formation of SO_2 gas. SO_2 dissolves into $[\text{C}_4\text{mim}][\text{NTf}_2]$ as reported in the literature,³¹ and then reacts with water to form sulfurous acid (H_2SO_3) upon contact with the aqueous solution. Anyway, SO_3^{2-} is formed during the removal of Sr^{2+} from aqueous solution using irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$, and the amount of SO_3^{2-} , according to the amount of the SrSO_3 or SrSO_4 precipitate, is less than 1 mol% even for an absorbed dose of 400 kGy. This is consistent with the results of NMR and FTIR measurement (ESI, Fig. S2 and Fig. S3),† and that reported by Berthon *et al.*⁴ who found by electrospray ionization mass spectrometry and NMR analysis the presence of nonvolatile radiolysis products of $[\text{C}_4\text{mim}][\text{NTf}_2]$ at concentrations below 1 mol% for a dose exceeding 1200 kGy.

In addition, as mentioned above, the E_{sr} of irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 550 kGy was lower than that at 400 kGy, and the equilibrium dynamics for irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 550 kGy was different from that at other doses (Fig. 2). This is probably due to further radiolysis of the sulfonic compounds and/or SO_2 , and post-irradiation effect of the $[\text{C}_4\text{mim}][\text{NTf}_2]$ at high dose. Investigations on this aspect are still under way in our laboratory.

In summary, we report here the first investigation of the radiolysis of the $[\text{NTf}_2]^-$ anion during removal of Sr^{2+} from aqueous solution using irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$. It was found that while no removal of Sr^{2+} occurred using unirradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$, the irradiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ did remove Sr^{2+} from aqueous solution. Further experiments confirmed that the removal of Sr^{2+} was not by extraction but by precipitation, and the precipitate was identified as SrSO_3 and/or SrSO_4 , depending on the contact time between the IL and the aqueous solution of Sr^{2+} . Accordingly,

SO_3^{2-} is an unambiguous radiolytic product of $[\text{C}_4\text{mim}][\text{NTf}_2]$ and probably all $[\text{NTf}_2]$ -based RTILs during the practical application of separating high level radioactive nuclides from wastewater.

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