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Radiolysis of crown ether/ionic liquid systems: identification of radiolytic products and their effect on the removal of Sr^{2+} from nitric acid†

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The quantitative analysis and identification of the radiolytic products of dicyclohexano-18-crown-6 (DCH18C6), 4',4"(5")-di-tert-butyldicyclohexano-18-crown-6 (DtBuCH18C6) and benzo-18-crown-6 (B18C6) in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C_4mim][NTf_2]) ionic liquid after irradiation were investigated for the first time. It was found that the yield for radiolytic destruction of DCH18C6 and DtBuCH18C6 was less than that of B18C6. The main radiolytic products were identified as substituted crown ethers formed between crown ether and active radicals such as methyl, trifluoromethyl, butyl, and [C_4mim]· radicals generated during the irradiation of crown ether/[C_4mim][NTf_2] system. The radiation effect on the Sr^{2+} partitioning of crown ether/[C_4mim][NTf_2] system shows further that DCH18C6/[C_4mim][NTf_2] and DtBuCH18C6/[C_4mim][NTf_2] still have good extractability for Sr^{2+} after irradiation. The extraction ability of DCH18C6/[C_4mim][NTf_2] and DtBuCH18C6/[C_4mim][NTf_2] system for Sr^{2+} decreased 14.4% and 18.2% even at 500 kGy, respectively.

1. Introduction

^{90}Sr is a major radioactive fission product with a moderate half-life (28.8 a). Due to its high specific activity, it is one of the most dangerous isotopes during the recycling of spent nuclear fuel (SNF), and it contributes a large part of the heat load and radiation in high level liquid waste.[1, 2] The removal of Sr^{2+} from the nitric acid slurries prior to further waste disposal can thus not only greatly reduce the cost of subsequent treatment disposal of SNF, but also be favourable toward the human beings and environment.[3-7] Room-temperature ionic liquids (RTILs) with melting points at or below ambient temperature have received increasing attentions in recent years due to their unique physicochemical properties such as negligible vapour pressure, high chemical and thermal stability, and are considered as potential alternative solvents in the reprocessing of SNF.[8-12] An exceptionally highly efficient extraction of Sr^{2+} from aqueous solution can be achieved using RTILs instead of conventional organic solvents in combination with crown ether.[13-17]

In nuclear applications, extraction systems must be exposed to the strong ionizing conditions generated by radionuclides.[18, 19] The radiation stability of both the solvent and the extracting agent is thus of great importance for the practical application of extraction system and should be assessed carefully in advance. The radiation stability of ionic liquid under irradiation had been widely studied.[20-27] Less than 1% underwent radiolysis when [C_4mim][NTf_2] were exposed to a high absorbed dose even at 550 kGy,[20, 28] and the main radiolytic products of anion of [C_4mim][NTf_2] were identified in our recent work.[25, 26] The extraction of Sr^{2+} by irradiated [C_4mim][NTf_2] in combination with unirradiated DCH18C6 indicated that the decline of distribution ratio was attributed to the radiation-induced hydrogen ions, because hydrogen ions competed with Sr^{2+} to interact with DCH18C6.[29, 30] Shkrob *et al.*[23] employed electron paramagnetic resonance (EPR) spectroscopy to study the formation of crown ether-related radicals in the radiolysis of 18-crown-6-ether/hydrophilic ionic liquid, such as 1-butyl-3-methylimidazolium trifluoromethanesulfonate. 18-crown-6-ether has been found to yield primarily H atoms and the formyl radical. DtBuCH18C6[31] and B18C6[32] have been shown to have strong complexation with Sr^{2+}, and DtBuCH18C6 is considered as a better extractant for extracting Sr^{2+} than DCH18C6,[31] because DtBuCH18C6 is more hydrophobic than DCH18C6 due to the existence of hydrophobic tert-butyl groups. However, the removal of Sr^{2+} by DtBuCH18C6 or B18C6 in ionic liquid has not been reported. Furthermore, due to diversity and complexity of the radiolytic products of crown ethers, radiation effect on DCH18C6, DtBuCH18C6, and B18C6 in hydrophobic ionic liquids is scarcely reported. In fact, the influence of radiation on extractability of crown ether/ionic liquid system from acidic nitrate media is the most important concern before the practical application of crown ether/ionic liquid system.

From an economic perspective, the price of DtBuCH18C6 (*ca.* 160 $\$\cdot g^{-1}$) or B18C6 (*ca.* 50 $\$\cdot g^{-1}$) is much higher than that of DCH18C6 (*ca.* 20 $\$\cdot g^{-1}$). In addition, DtBuCH18C6 is more hydrophobic than DCH18C6. Thus the difference of radiation effect on DCH18C6/ionic liquid, DtBuCH18C6/ionic liquid and B18C6/ionic liquid systems should be compared with carefulness.

Herein, three kinds of extraction systems based on ionic liquid consisting of different crown ethers (DCH18C6, DtBuCH18C6, and B18C6) as extractant and $[C_4mim][NTf_2]$ as diluent were designed for assessment of radiation effect. Ultra-performance liquid chromatography/quadrupole time-of-flight mass spectrometry (UPLC/Q-TOF-MS) and high-resolution electrospray ionization mass spectrometry (ESI-MS) were employed to give a quantitative analysis of crown ether content in $[C_4mim][NTf_2]$ and identify the chemical structures of main radiolytic products of crown ether/$[C_4mim][NTf_2]$ systems, respectively. Sr^{2+} in acidic nitrate media is chosen for assessing radiation effect on the extractability of crown ether/ionic liquid system.

2. Experimental section

2.1 Materials

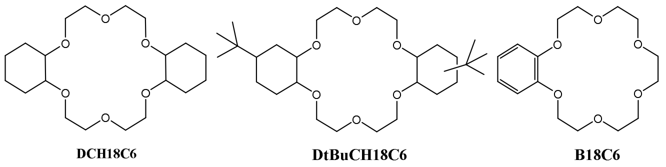


Fig. 1 Chemical structures of DCH18C6, DtBuCH18C6, and B18C6.

$[C_4mim][NTf_2]$ (with a purity > 99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). DCH18C6 (> 98%) and B18C6 (> 97%) were bought from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). DtBuCH18C6 (> 95%) was obtained from Institute of Nuclear and New Energy Technology, Tsinghua University (Fig. 1). All other reagents with analytical-grade were used without further purification.

2.2 Irradiation

Three kinds of crown ethers (DCH18C6, DtBuCH18C6, or B18C6) were dissolved separately in $[C_4mim][NTf_2]$ ionic liquid (0.1 $mol\cdot L^{-1}$). Then the DCH18C6/$[C_4mim][NTf_2]$, B18C6/$[C_4mim][NTf_2]$, and DtBuCH18C6/$[C_4mim][NTf_2]$ solutions were irradiated in air (298 ± 4 K) using ^{60}Co source with an average dose rate of *ca.* 220 $Gy\cdot min^{-1}$ (Institute of Applied Chemistry of Peking University). The absorbed dose under γ-irradiation was traced by Fricke dosimeter.

2.3 Characterization

UPLC/Q-TOF-MS: Irradiated samples were dissolved in 2 mL acetonitrile, and the obtained solution was centrifuged at 12,000 rpm for 10 min. The upper supernatant solution was injected directly in UPLC/Q-TOF-MS instrument by six-way valve (Waters Micromass Q-TOF Premier mass spectrometer, Shanghai Jiao Tong University). UPLC, which equipped with an Acquity UPLC BEH C_{18} column (100 mm × 2.1 mm, i.d.: 1.7 μm; Waters, Milford, USA) and an Acquity UPLC VanGuard pre-column (5 mm × 2.1 mm, i.d.: 1.7 μm; Waters), was carried out at constant temperature of 45 ^{o}C. The injection volume was set at 2 μL, and the flow rate was set at 0.4 $mL\cdot min^{-1}$. Q-TOF-MS condition: de-solvation gas flow 600.0 $L\cdot h^{-1}$; capillary potential 3.0 kV; collision energy 6.0 eV; sampling cone potential 35.0 V; scan range m/z: 100 - 2000. Scan time and inter-scan time were set at 0.3 s and 0.02 s, respectively.

High-resolution ESI-MS: The irradiated crown ether/ionic liquid samples were diluted in pure methanol solution for detection. The mass spectrometry measurements were recorded on a Fourier transform ion cyclotron resonance mass spectrometer equipped with electrospray ionization (ESI) source (Apex IV, Bruker, Switzerland). Capillary voltage: 3000 V; spray shield voltage: -3500 V; drying temperature: 200 °C. High purity nitrogen was used as the nebulizing and drying gases. Mass spectra were recorded in positive ionization mode with a mass range of m/z from 100 to 2000.

Theoretical calculations: Calculations were performed with Gaussian 09 program package using density functional theory (DFT) at the B3LYP level of theory.[33] The 6-311+G* basis set was chosen for all carbon, hydrogen, and oxygen atoms. All structures were confirmed without imaginary frequencies by calculating the frequencies.

2.4 Extraction experiments

The organic phase containing 0.1 $mol\cdot L^{-1}$ crown ether (DCH18C6, DtBuCH18C6, and B18C6) was prepared by dissolving crown ether in $[C_4mim][NTf_2]$. The aqueous phase containing 0.01 or 0.05 $mol\cdot L^{-1}$ Sr^{2+} was obtained by dissolving $Sr(NO_3)_2$ in 3 $mol\cdot L^{-1}$ HNO_3 aqueous solution. The extraction experiments were carried out in air bath (303 ± 1 K) with a rotating speed of 120 $r\cdot min^{-1}$. Afterwards, the samples were centrifuged for 4 min to completely separate two phases. The concentration of Sr^{2+} in aqueous solution diluted with deionized water was measured by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICP-AES, Teledyne Leeman Labs, USA). All measurements were in duplicate with uncertainty within 5%. The extraction efficiencies (E_{Sr}) were calculated by $E_{Sr} = (C_i - C_f)/C_i\times100\%$. The distribution ratios (D_{Sr}) were obtained based on $D_{Sr} = (C_i - C_f)/C_f$, in which C_i and C_f represented the initial and final concentrations of Sr^{2+} in the diluted aqueous solution, respectively.

3. Results and discussion

3.1 Quantitative analysis and identification of radiolytic products.

In order to assess the radiation stability of crown ether/$[C_4mim][NTf_2]$ system, it is necessary to give a quantitative analysis on the change of crown ether content in $[C_4mim][NTf_2]$ after irradiation. Thus the concentration of crown ether in $[C_4mim][NTf_2]$ after irradiation was quantified effectively by UPLC/Q-TOF-MS. As shown in Fig 2, the concentration of three kinds of crown ethers in $[C_4mim][NTf_2]$ decreased with increasing dose, and the radiolysis of DCH18C6, DtBuCH18C6 in $[C_4mim][NTf_2]$ is less than that of B18C6 in $[C_4mim][NTf_2]$. The yield for radiolytic destruction of DCH18C6 and DtBuCH18C6 in $[C_4mim][NTf_2]$ are calculated as *ca.* -0.06 $\mu mol \cdot J^{-1}$ and that of B18C6 in $[C_4mim][NTf_2]$ is near -0.09 $\mu mol \cdot J^{-1}$ (Table 1). Based on above analysis, DCH18C6/$[C_4mim][NTf_2]$ and DtBuCH18C6/$[C_4mim][NTf_2]$ systems show better radiation stability than B18C6/$[C_4mim][NTf_2]$ system.

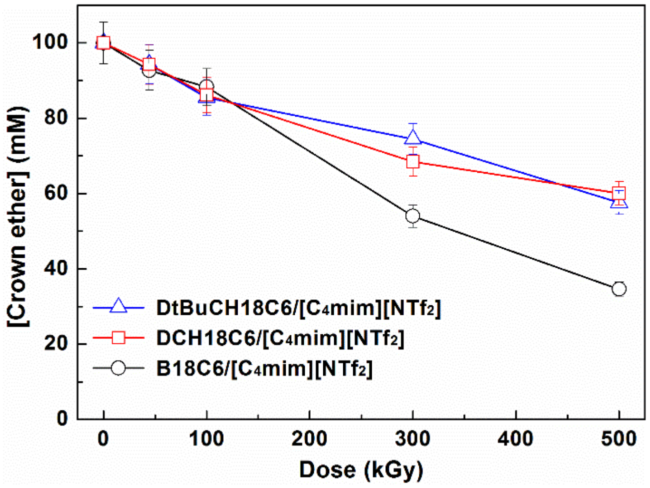


Fig. 2 Influence of dose on the concentration of crown ether of crown ether/$[C_4mim][NTf_2]$ systems.

Table 1. The yield for radiolytic destruction (G_R) of crown ether dissolved in $[C_4mim][NTf_2]$.

Solvent	Solute	[Solute] (M)	G_R ($\mu mol \cdot J^{-1}$)
$[C_4mim][NTf_2]$	DCH18C6	0.10	-0.06 ± 0.01
$[C_4mim][NTf_2]$	DtBuCH18C6	0.10	-0.06 ± 0.01
$[C_4mim][NTf_2]$	B18C6	0.10	-0.09 ± 0.01

The identification of radiolytic products of extraction system is of great importance in understanding the radiolysis of crown ether/$[C_4mim][NTf_2]$ system. It was extremely difficult to separate radiolytic products from crown ether/$[C_4mim][NTf_2]$ extraction system due to diversity and complexity of the radiolytic products, so it was urgent to find an effective approach on identifying the radiolytic products of crown ether/ionic liquid system. Herein, three kinds of crown ethers were dissolved separately in $[C_4mim][NTf_2]$ and irradiated at 500 kGy. The radiolytic products of the crown ether/$[C_4mim][NTf_2]$ system were analysed by high-resolution ESI-MS. Fig. 3 shows the high-resolution ESI-MS spectra of DCH18C6/$[C_4mim][NTf_2]$ system before and after irradiation at 500 kGy. Signals at 558.163, 395.240, 373.258 are observed in the unirradiated sample and attributed to $[[C_4mim][NTf_2]+[C_4mim]]^+$ (theoretical exact m/z is 558.164), $[DCH18C6+Na]^+$ (theoretical exact m/z is 395.240), and $[DCH18C6+H]^+$ (theoretical exact m/z is 373.258), respectively.

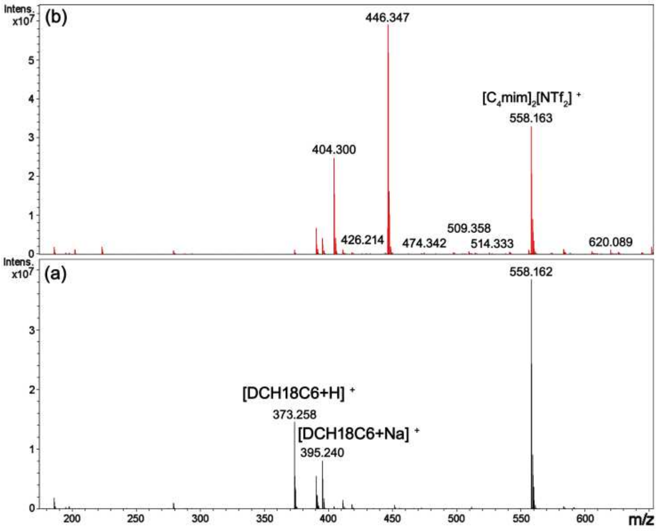


Fig. 3 High-resolution ESI-MS spectra of DCH18C6/$[C_4mim][NTf_2]$ system before (a) and after irradiation at 500 kGy (b).

Table 2. Designation of radiolytic products of crown ether/$[C_4mim][NTf_2]$ system after γ-irradiation.

Solute	Experimental m/z	Designation	Theoretical m/z
DC	514.333	$[DC(-CF_3)-C_4H_9+NH_4]^+$	514.335
	509.358	$[DC-C_4mim]^+$	509.358
	474.342	$[DC(-CHO)-C_4H_9+NH_4]^+$	474.343
	446.347	$[DC-C_4H_9+NH_4]^+$	446.348
	426.214	$[[C_4mim]_2+CF_3SO_2NH]^+$	426.215
	404.300	$[DC-CH_3+NH_4]^+$	404.301
DtBuC	626.459	$[DtBuC(-CF_3)-C_4H_9+NH_4]^+$	626.460
	621.482	$[DtBuC-C_4mim]^+$	621.484
	586.467	$[DtBuC(-CHO)-C_4H_9+NH_4]^+$	586.468
	570.396	$[DtBuC-CF_3+NH_4]^+$	570.398
	558.472	$[DtBuC-C_4H_9+NH_4]^+$	558.473
	516.425	$[DtBuC-CH_3+NH_4]^+$	516.426
	446.346	$[DC-C_4H_9+NH_4]^+$	446.348
	426.214	$[[C_4mim]_2+CF_3SO_2NH]^+$	426.215
	404.301	$[DC-CH_3+NH_4]^+$	404.301
BC	454.240	$[BC(-CF_3)-C_4H_9+NH_4]^+$	454.241
	449.263	$[BC-C_4mim]^+$	449.265
	426.215	$[[C_4mim]_2+CF_3SO_2NH]^+$	426.215
	398.178	$[BC-CF_3+NH_4]^+$	398.178
	386.253	$[BC-C_4H_9+NH_4]^+$	386.254
	344.206	$[BC-CH_3+NH_4]^+$	344.207

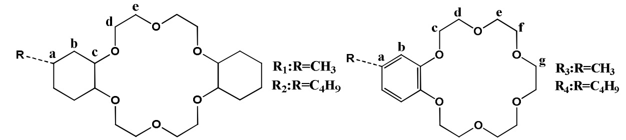
DC, DtBuC, and BC represent DCH18C6, DtBuCH18C6, and B18C6, respectively.

As seen in Fig. 3(b), several new signals, which are assigned to radiolytic products of DCH18C6/$[C_4mim][NTf_2]$

system, are observed with relative high signal intensity at 446.347, 404.300, and with low intensity at 620.089, 514.333, 509.358. Methyl, trifluoromethyl, butyl, and [C_4mim]· radical generated from [C_4mim][NTf_2] under γ-irradiation were reported in previous work.[21, 27] Therefore, the products at m/z = 404.300, 446.347 were suggested to the substitution products [DCH18C6-CH_3+NH_4]$^+$ (theoretical exact m/z is 404.300) and [DCH18C6-C_4H_9+NH_4]$^+$ formed between crown ether and alkyl radicals. A low intensity product at m/z = 509.358 corresponds to [crown ether-[C_4mim]]$^+$ (theoretical exact m/z is 509.356) formed by complexation of DCH18C6 and [C_4mim]· radical. Other products were identified as [[C_4mim]$_2$+CF_3SO_2NH]$^+$,[25] [DCH18C6(-CF_3)-C_4H_9+NH_4]$^+$, [DC18C6(-CHO)-C_4H_9+NH_4]$^+$. For comparison purpose, the DtBuCH18C6/[C_4mim][NTf_2] (Fig. S1), and B18C6/[C_4mim][NTf_2] systems (Fig. S2) were also analysed by high-resolution ESI-MS, and similar radiolytic products were observed in irradiated crown ether/[C_4mim][NTf_2] and shown in Table 2. [DCH18C6-C_4H_9+NH_4]$^+$ with very low intensity was also observed as the radiolytic products of DtBuCH18C6/[C_4mim][NTf_2], which indicated the radiolysis of tert-butyl groups of DtBuCH18C6. These substituted products still keep cavity structure when crown ether is substituted by active radicals generated from the radiolysis of [C_4mim][NTf_2].

For the purpose of ascertaining the chemical structure of the alkyl substituted radiolytic products of crown ether/[C_4mim][NTf_2] system, the energy difference between different substituted radiolytic products was calculated. Geometry optimization of each species at the B3LYP/6-311+G* level of theory and the calculated results are illustrated in Table 3. Compared with the methyl substituted product on cyclohexyl ring of DCH18C6 (R_{1a}), the methyl substituted product on cavity of DCH18C6 (R_{1d}) shows the lowest energy ($\triangle E$ = -6.70 kJ·moL^{-1}), which indicated that the formation of methyl substituted product (R_{1d}) on cavity of DCH18C6 is extremely easier than that on cyclohexyl ring of DCH18C6. The similar results were observed in the butyl substituted radiolytic products. For B18C6, the energy difference of alkyl substituted products between the benzene ring of B18C6 (R_{3a}) and the cavity (R_{3g}) of DCH18C6 is near -2.59 kJ·moL^{-1}. Furthermore, the amount of substituted location of cavity of B18C6 is near 5 times than that of benzene ring of B18C6. Additionally, EPR was employed to study the radical intermediates of crown ethers including DCH18C6[34, 35] and benzo-substituted crown ether[36], and the main radical intermediates were determined mainly on the cavity of crown ethers. Therefore, we can propose that the alkyl substituted products of DCH18C6 and B18C6 are mainly on the cavity of crown ether, and R_{1d}, R_{2d}, R_{2e}, R_{3g}, and R_{4g} are the mainly alkyl substituted radiolytic products of crown ether during irradiation. Consequently, the radiolysis pathways of crown ether/[C_4mim][NTf_2] system were proposed as follows (Fig. 4): (1) Active radicals of [C_4mim][NTf_2], such as hydrogen, methyl, trifluoromethyl, butyl, and [C_4mim]· radicals *etc.* were formed by the interaction between [C_4mim][NTf_2] and γ-photon. (2) Then the generated active radicals reacted with [C_4mim][NTf_2], which led to the formation of substituted [C_4mim]$^+$ compounds in previous reports.[21-24] (3) Meanwhile the crown ethers were also attacked by these active radicals, which led to the formation of substituted crown ether, mainly forming alkyl substituted compounds on the cavity of crown ethers.

Table 3. The energy difference between different alkyl substituted radiolytic products.



$\triangle E = E_i - E_a$ (kJ·moL^{-1})

Num	$\triangle E$	Num	$\triangle E$	Num	$\triangle E$	Num	$\triangle E$
R_{1a}	0.00	R_{2a}	0.00	R_{3a}	0.00	R_{4a}	0.00
R_{1b}	12.09	R_{2b}	7.52	R_{3b}	0.57	R_{4b}	3.77
R_{1c}	3.77	R_{2c}	5.03	R_{3c}	0.28	R_{4c}	1.41
R_{1d}	-6.70	R_{2d}	-6.39	R_{3d}	0.59	R_{4d}	1.12
R_{1e}	-0.21	R_{2e}	-5.08	R_{3e}	-0.58	R_{4e}	7.2
				R_{3f}	0.24	R_{4f}	6.13
				R_{3g}	-2.59	R_{4g}	-0.84

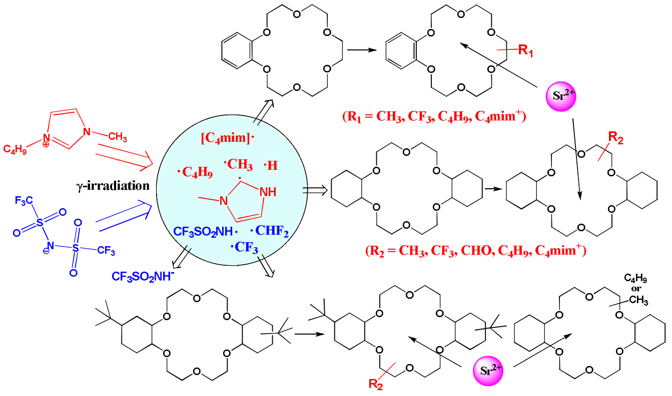


Fig. 4 Proposed simplified radiolysis pathways of crown ether/[C_4mim][NTf_2].

3.2 Radiation effect on extractability of crown ether/[C_4mim][NTf_2] systems.

In order to assess the influence of radiation on extractability of crown ether/[C_4mim][NTf_2] systems, the extractability of Sr^{2+} using irradiated crown ether/[C_4mim][NTf_2] solution was investigated further. The extraction ability of DtBuCH18C6 or B18C6 in ionic liquid for removal of Sr^{2+} has not been reported, and the extraction kinetics reflect the basic properties of crown ether/[C_4mim][NTf_2] extraction system. Therefore, the extraction kinetics of Sr^{2+} by DCH18C6/[C_4mim][NTf_2], DtBuCH18C6/[C_4mim][NTf_2], and B18C6/[C_4mim][NTf_2] system is carried out firstly. During the reprocessing of spent nuclear fuel, the extraction process will be carried out under *ca.* 3 M HNO_3 condition, so the acidity of aqueous phase was chosen at 3 M HNO_3. As shown in Fig. S3, the extraction equilibrium was achieved within *ca.* 15 min for B18C6/[C_4mim][NTf_2] system, *ca.* 30 min for DCH18C6/[C_4mim][NTf_2] system, and *ca.* 60 min for DtBuCH18C6/[C_4mim][NTf_2] system (detailed data in Table

S1). These crown ethers have low solubility in water, and the order of water-solubility of crown ethers is as follows: B18C6 > DCH18C6 > DtBuCH18C6. The transport of the crown ether-Sr complex into the ionic liquid is limited by the miniscule concentration of the crown ethers in the aqueous phase, and the lengths of time needed for equilibration correlate with the hydrophobicities of the crowns. In order to avoid the influence of extraction time, the equilibrium time at 120 min was chosen in the following experiments.

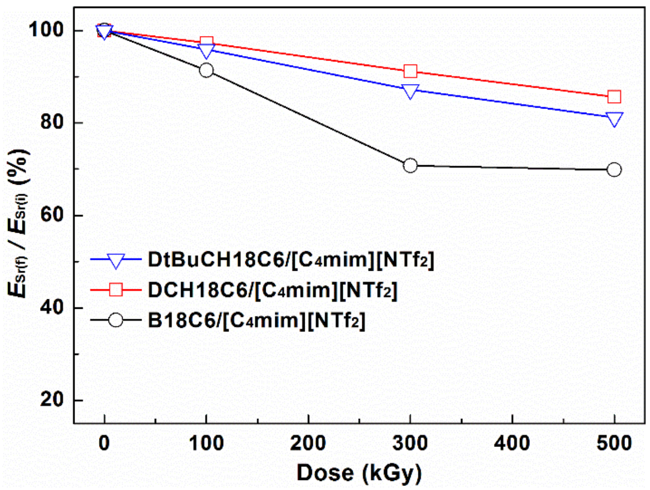


Fig. 5 Influence of dose on Sr^{2+} extraction by crown ether/[C_4mim][NTf_2] systems. $E_{Sr(i)}$ and $E_{Sr(f)}$ represent the extraction efficiency of crown ether/[C_4mim][NTf_2] system before and after irradiation, respectively. ([Crown ether]: 0.10 M; [Sr^{2+}]: 0.01 M; [HNO_3]: 3 M)

Table 4. D_{Sr} and E_{Sr} of crown ether/[C_4mim][NTf_2] system before and after irradiation. ([Crown ether]: 0.1 M; [Sr^{2+}]: 0.01 M; [HNO_3]: 3 M)

Dose (kGy)	DCH18C6 /[C_4mim][NTf_2]		DtBuCH18C6 /[C_4mim][NTf_2]		B18C6 /[C_4mim][NTf_2]	
	D_{Sr}	E_{Sr} (%)	D_{Sr}	E_{Sr} (%)	D_{Sr}	E_{Sr} (%)
0	4.01	79.8	5.77	85.1	3.98	79.8
100	3.47	77.6	4.49	81.6	2.69	72.9
300	2.67	72.7	2.94	74.2	1.30	56.5
500	2.16	68.3	2.24	69.1	1.26	55.7

As shown in Fig. 5, the extraction results show the Sr^{2+} partitioning of DCH18C6/[C_4mim][NTf_2] system decreases with the increase of dose (detailed data in Table 4), because the concentration of DCH18C6 in DCH18C6/[C_4mim][NTf_2] is deduced after irradiation. Compared with B18C6/[C_4mim][NTf_2] system, the decrement of Sr^{2+} partitioning of DCH18C6/[C_4mim][NTf_2] system is less than that of B18C6/[C_4mim][NTf_2] system, indicating that macro-cyclic structure of DCH18C6 is not damaged seriously in the presence of dicyclohexyl groups. This is in accordance with the change of crown ether content in [C_4mim][NTf_2] after irradiation. DCH18C6/[C_4mim][NTf_2] shows slightly better radiation stability than that of DtBuCH18C6/[C_4mim][NTf_2]. For example, the extraction ability of DCH18C6/[C_4mim][NTf_2] system decreases 14.4% at 500 kGy (E_{Sr} deduces from 79.8% to 68.3%), but E_{Sr} of DtBuCH18C6/[C_4mim][NTf_2] system decreases 18.2% at 500 kGy (E_{Sr} deduces from 85.1% to 69.1%) (Table 4). The extraction of Sr^{2+} using 0.05 M Sr^{2+} nitric acidic solution was also evaluated (Fig. S4). The extraction results (detailed data in Table S2) showed similar influence of radiation on Sr^{2+} extraction. Therefore, the order of radiation stability of crown ether/[C_4mim][NTf_2] system is as follows: DCH18C6/[C_4mim][NTf_2] > DtBuCH18C6/[C_4mim][NTf_2] > B18C6/[C_4mim][NTf_2]. Taking the chemical structure of crown ether into consideration, tert-butyl groups of DtBuCH18C6 were slight easily attacked by active radicals, which led to subsequent radiolysis of DtBuCH18C6/[C_4mim][NTf_2], and the radiolytic products of DtBuCH18C6 itself were identified as [DCH18C6-C$(CH_3)_3$+NH_4]$^+$, [DCH18C6-CH_3+NH_4]$^+$ *etc.* The alkyl substituted reactions of B18C6 were mainly on the cavity of B18C6 based on calculated results, so the cavity of B18C6 without the presence of a cyclohexyl group was easily attacked by active radicals, which led to further radiolysis of B18C6 (the radiolysis rate is 65.4%) during irradiation. Therefore, B18C6/[C_4mim][NTf_2] system showed obvious decrement of extraction efficiency. Based on above analysis, the scavenge of methyl, trifluoromethyl, butyl, and [C_4mim]· radicals by adding radical scavenger could be an effective method to avoid the damage of cavity of crown ether molecule, and the radiation stability of crown ether/[C_4mim][NTf_2] system under γ-irradiation would be improved effectively.

Interestingly, the radiolysis loss of crown ether is near 40% for DCH18C6/[C_4mim][NTf_2] system and 42% for DtBuCH18C6/[C_4mim][NTf_2] system at 500 kGy, but the decrement of extraction ability of DCH18C6/[C_4mim][NTf_2] is just 14.2% and that of DtBuCH18C6/[C_4mim][NTf_2] system is 18.2% at 500 kGy. These results suggested that the cavity of crown ether was not damaged seriously during irradiation of crown ether/[C_4mim][NTf_2], which was in accordance with the results of identification of radiolytic products of crown ether/[C_4mim][NTf_2]. Furthermore, these results indicate the substituted radiolytic products of crown ether/[C_4mim][NTf_2] still retain extraction ability for Sr^{2+} even at 500 kGy.

4. Conclusions

In conclusion, the quantitative analysis of crown ether content in [C_4mim][NTf_2] before and after irradiation by UPLC/Q-TOF-MS was carried out successfully, which suggested that DCH18C6 and DtBuCH18C6 in [C_4mim][NTf_2] have better radiation stability than B18C6 in [C_4mim][NTf_2]. The radiolytic products of DCH18C6/[C_4mim][NTf_2], DtBuCH18C6/[C_4mim][NTf_2], and B18C6/[C_4mim][NTf_2] systems were identified by high-resolution ESI-MS and assigned mainly to substituted crown ethers formed between crown ether and active radicals such as methyl, trifluoromethyl, butyl, and [C_4mim]· radicals, which were formed in the irradiation of crown ether/[C_4mim][NTf_2]. The decrease of crown ether content in crown ether/[C_4mim][NTf_2] after irradiation is attributed to the decrease of Sr^{2+} partitioning of crown ether/[C_4mim][NTf_2] system. Radiation effect on the Sr^{2+} partitioning of crown ether/[C_4mim][NTf_2] indicates that the radiation stability of crown ether/[C_4mim][NTf_2] system is as follows: DCH18C6/[C$_4$mim][NTf$_2$] > DtBuCH18C6/[C$_4$mim][NTf$_2$] > B18C6/[C$_4$mim][NTf$_2$]. The extraction ability of DCH18C6/[C$_4$mim][NTf$_2$] and DtBuCH18C6/[C$_4$mim][NTf$_2$] system for Sr^{2+} decreased 14.4% and 18.2% at 500 kGy, respectively. DCH18C6/[C$_4$mim][NTf$_2$] and DtBuCH18C6/[C$_4$mim][NTf$_2$] still show good extractability for Sr^{2+} after irradiation. Therefore, DCH18C6/[C$_4$mim][NTf$_2$] and DtBuCH18C6/[C$_4$mim][NTf$_2$] systems are promising extraction systems for removal of Sr^{2+} in the SNF reprocessing and recycling.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [High-resolution ESI-MS spectra of DtBuCH18C6/[C$_4$mim][NTf$_2$] before and after irradiation at 500 kGy; High-resolution ESI-MS spectra of B18C6/[C$_4$mim][NTf$_2$] before and after irradiation at 500 kGy; Influence of equilibrium time on E_{Sr} of crown ether/[C$_4$mim][NTf$_2$] system; D_{Sr} and E_{Sr} of crown ether/[C$_4$mim][NTf$_2$] system depending on equilibrium time; Influence of dose on Sr^{2+} extraction by crown ether/[C$_4$mim][NTf$_2$] system; D_{Sr} and E_{Sr} of crown ether/[C$_4$mim][NTf$_2$] system before and after irradiation.]. See DOI: 10.1039/b000000x/

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