Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism and radiation effect†

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The removal of radioactive $^{137}$Cs from nuclear waste is of great importance for both the environment and energy saving. Herein, we report a study on the removal of Cs$^+$ using a calix crown ether bis(2-propyloxy)calix[4]crown-6 (BPC6) in ionic liquids [C$_{4}$mim][NTf$_{2}$], where [C$_{4}$mim]$^+$ is 1-alkyl-3-methylimidazolium and [NTf$_{2}$]$^-\,$ is bis(trifluoromethylsulfonyl)imide. The BPC6/[C$_{4}$mim][NTf$_{2}$] system is highly efficient in removing Cs$^+$ from aqueous solution, even at a low concentration of BPC6. HNO$_3$ and metal ions such as Na$^+$, Al$^{3+}$ in the aqueous phase interfered with the extraction of Cs$^+$ by competitive interaction with BPC6 and/or salting-out effect. UV analysis confirmed that the extraction of Cs$^+$ by the BPC6/[C$_{4}$mim][NTf$_{2}$] system involves a dual extraction mechanism, i.e., via exchange of BPC6-Cs$^+$ complex or Cs$^+$ by [C$_{4}$mim]$^+$. Irradiation of [C$_{4}$mim][NTf$_{2}$] dramatically decreases Cs$^+$ partitioning in the ionic liquid phase by the competitive interaction of radiation-generated H$^+$ with BPC6, while irradiation of BPC6/[C$_{4}$mim][NTf$_{2}$] decreases Cs$^+$ partitioning more markedly due to the radiolysis of BPC6.

Introduction

$^{137}$Cs, as a major radioactive fission product in spent nuclear waste, contributes a large part of the heat load and radiation in high level liquid waste (HLLW). Removal of $^{137}$Cs from HLLW provides several advantages, e.g., reducing waste volume and subsurface storage time, and facilitating handling and transportation. Solvent extraction has been regarded as a potential method to separate Cs$^+$ from aqueous solutions. So far, dicarbollides, crown ethers and calixarenes have been used as extractants for the removal of Cs$^+$.

The diluents used, however, are usually vapporous and toxic organic solvents, which result in a series of subsequent environmental problems. Besides, the extraction capacity is usually limited in these solvents as a result of the difficulty of dissolving the extracted species.

In recent years, room-temperature ionic liquids (RTILs) have received increased attention in a variety of synthetic, catalytic and electrochemical applications due to their potential as "green" and "versatile" solvents. Recent efforts by several investigators have focused on the application of RTILs in separations, in particular, on the utilization of these materials as next generation diluents in liquid–liquid extraction of metal ions. A preliminary study by Dai et al. demonstrated that the distribution ratio of Sr$^{2+}$ ($D_{a}$) can be as high as 10$^4$ using a crown ether as an extractant in RTILs. Of additional interest is that the extraction mechanism with RTILs as diluents usually differs from that with conventional solvents. A cation exchange mechanism has been suggested by Dietz and his coworkers for the extraction of Sr$^{2+}$ by dicyclohexane-18-crown-6 (DCH18C6) in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_{2}$mim][NTf$_{2}$]). While many investigations have been focused on the extraction of Sr$^{2+}$ and other metal ions using RTILs, those on Cs$^+$ are somewhat limited. Several crown ethers have been adopted in ionic liquids to separate Cs$^+$ from the aqueous phase, but the distribution ratio of Cs$^+$ ($D_{a}$) is significantly lower than that of Sr$^{2+}$. Luo et al. were the first to employ a calix crown ether, calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalix6), to extract Cs$^+$ with RTILs as diluents and a large distribution coefficient ($D_{a}$) value was achieved. Also with BOBCalix6 as an extractant, Hussey et al. used tert-ammonium based ionic liquids with wide electrochemical windows to extract Cs$^+$ and the electro-reduction stripping of Cs$^+$ was demonstrated. Sieffert and Wipff reported molecular dynamics studies on the solvation of Cs$^+$ and Cs$^+$-calix[4]-crown-6 complex in RTILs and compared their interfacial behaviors with traditional molecular solvents. These works revealed the vast opportunities of an RTILs-based extraction system for the separation of radioactive $^{137}$Cs from waste water.

Full realization of such a potential, however, demands a comprehensive knowledge of the stability of extractants and RTILs under radiation conditions. Allen et al. have carried out a preliminary assessment of the $\alpha$, $\beta$ and $\gamma$-radiation effects on hydrophilic RTILs [C$_{4}$mim]NO$_3$, [C$_{2}$mim]Cl, and [C$_{6}$mim]Cl. It was shown that the tested ILs exhibit radiation-induced darkening and an increase in light absorbance, but less than 1% of the samples undergo radiolysis even when exposed to a dose of 400 kGy, suggesting very high radiation stability of these ILs. Moisy and
his co-workers investigated the radiation stability of hydrophobic RTILs [C4mim][PF6] and [C4mim][NTf2],26 and [Niim][NTf2],27 where [Niim]⁺ is methyltributylammonium. They proposed a possible degradation mechanism of the RTILs based on the NMR and ESI-MS analysis. Wu et al. further investigated the γ radiolysis of neat [Cnmim][PF6]28 and [Cnmim][BF4]29 in detail by spectroscopic methods and differential scanning calorimetry. Bartels et al. have determined the yields of hydrogen gas in irradiated ionic liquids based on imidazolium, pyridinium, and phosphonium cations.30 Recently, we have studied the radiation stability of [Cnmim][PF6] in the presence of nitric acid31 and decoloration of irradiated [Cnmim][NTf2].32 To assess the influence of γ-radiation on metal ions extraction of RTILs, we also carried out solvent extraction of Sr2⁺ by crown ether using irradiated [Cnmim][PF6]33 and irradiated [Cnmim][NTf2].34 The results showed that H⁺ was formed during irradiation of the RTILs, and the radiation-generated H⁺ markedly reduced Sr2⁺ partitioning in the crown ether/RTILs extraction phase by competing with Sr2⁺ to associate with the crown ether.

To expand the applications of RTIL based extraction systems in separating Cs⁺, we report here a study on the highly efficient extraction of Cs⁺ by using a calix crown ether, bis(2-propyloxy)calix[4]-crown-6 (BPC6, Fig. 1) in ionic liquids [Cnmim][NTf2] (n = 2, 4, 6). A possible mechanism for the extraction of Cs⁺ in BPC6/[Cnmim][NTf2] system was proposed. Further, the influence of γ-irradiation on BPC6/[Cnmim][NTf2] was assessed by solvent extraction of Cs⁺ using irradiated BPC6/RTILs.

Experimental

Materials

All RTILs used in this work were synthesized according to the procedure previously reported35,36 and purified by adopting the steps described elsewhere.37 After purification, the water content in the RTILs samples was less than 200 ppm, measured by Karl-Fischer titration, and no impurities were detected by NMR spectrometry analysis. The extractant BPC6 (>95%) was obtained from INET, Tsinghua University, P.R. China, and was used as received. The synthesis and purification of BPC6 is described elsewhere.38 134Cs in a 1 mol L⁻¹ HCl solution was purchased from Eckert & Ziegler Chemical Co. and used after dilution with deionized water.

All other chemicals were of analytical grade and were used without further purification.

Sample irradiation

Irradiation of the samples was carried out at room temperature using a 60Co source at the Department of Applied Chemistry of Peking University. A sample of 2 ml [Cnmim][NTf2] or BPC6/[Cnmim][NTf2] contained in a glass tube with a plug was subjected to γ-irradiation using a dose rate of 55–65 Gy min⁻¹, up to a maximum dose of 550 kGy. The absorbed dose was traced using a conventional ferrous sulfate dosimeter.

Liquid/liquid extraction

The extraction experiments were conducted using a radioactive tracer method. A 0.5 mL of RTIL with variable BPC6 concentrations was contacted with 0.5 mL of an aqueous solution containing 10 mmol L⁻¹ CsNO₃ and 10 μL ¹³⁴CsCl tracer, followed by vortexing (4 min) and centrifuging (3000 g, 5 min) to ensure that the phases were fully mixed and separated. After phase separation, 100 μL of each phase was removed into 5 ml cuvette for radiometric analysis. Because equal volumes of both phases were removed for analysis, the distribution ratio and extraction efficiency (represented by Dcs and Ecs, respectively) was calculated from the ratio between the γ-count number of the ionic liquid phase and that of the aqueous phase. Each experiment was performed in duplicate and the results agreed to within 5%.

UV analysis

UV-vis spectra of [Cnmim]⁺ were recorded on a Hitachi 3010 UV-vis Spectrometry. The absorption at 211 nm was used to calculate the concentration of [Cnmim]⁺.

Results and discussion

The influence of the concentration of BPC6 in the RTIL phase, and HNO₃ and salts in the aqueous phase on the extraction of Cs⁺ for the new RTILs-based extraction system for removing Cs⁺ were first investigated. Based on these results, an extraction mechanism was proposed.

Influence of BPC6 concentration

Fig. 2 shows the relationship between Ecs and BPC6 concentration in [Cnmim][NTf2]. The relationship between Dcs and BPC6 concentration is given in the ESI†, Fig. S1. Obviously, the Ecs and Dcs strongly depend on the BPC6 concentration, which indicates that the extraction of Cs⁺ is mainly due to the complex interaction between Cs⁺ and BPC6. Under the experimental conditions, i.e., equal volumes with initially 10 mmol L⁻¹ of Cs⁺ in the aqueous phase and 15 mmol L⁻¹ of BPC6 in the ionic liquid phase, Ecs can be more than 99.9% (Dcs > 1000) when [Cnmim][NTf2] and [Cnmim][NTf2] were used. As a comparison, in the work by Luo et al.,38 the largest Dcs was 137 when BOBCalixC6/[Cnmim][NTf2] was used and the initial concentrations of Cs⁺ and BOBCalixC6 were respectively 2.5 and 13.6 mmol L⁻¹. Undoubtedly, the BPC6 in [Cnmim][NTf2] based extraction system shows a much higher extraction ability for Cs⁺ than that by BOBCalixC6.

In addition to the stronger extraction ability for Cs⁺ in an ionic liquid based extraction system, BPC6 also has a better solubility in ionic liquids. For the ionic liquid [Cnmim][NTf2] as an...
example, more than 25 mmol L\(^{-1}\) BPC6 can be soluble in it while for BOBCalixC6 the solubility is no more than 13.6 mmol L\(^{-1}\). Selecting an extractant with a better solubility in the diluent is very important for practical application, because a wide concentration adjustment can be easily conducted according to the need of specific systems.

Besides, as shown in Fig. 2, the alkyl chain length on the imidazolium cation also has an influence on the extraction of Cs\(^{+}\). Generally, \(E_{\text{cs}}\) decreases with increasing the alkyl chain length from ethyl (C\(_2\)) to hexyl (C\(_6\)), indicating that a shorter alkyl chain results in a higher extraction efficiency. This can be rationalized by the higher water content that assists the solvation of extracted species in RTIL, and by the extraction mechanism discussed in the following corresponding section.

### Effects of HNO\(_3\) in the aqueous phase

HNO\(_3\) has a significant impact on the extraction of Cs\(^{+}\) by the BPC6/[C\(_n\)mim][NTf\(_2\)] system. Fig. 3 and ESI†, Fig. S2 show the dependence of \(E_{\text{cs}}\) and \(D_{\text{cs}}\) of BPC6/[C\(_n\)mim][NTf\(_2\)] system on the initial concentration of HNO\(_3\) in the aqueous phase. It is clear that the extraction is more efficient with a low initial concentration of HNO\(_3\) and the highest extraction efficiency is reached under neutral conditions. This agrees well with some previous results using ionic liquids as media for extracting metal ions\(^{19,39,40}\). This observation is much different from that in traditional solvents systems and indicates a different extraction mechanism may be involved. The decrease of \(E_{\text{cs}}\) can be attributed to the competition effect of H\(^{+}\). According to the published work concerning the extraction of Sr\(^{2+}\) by DCH18C6/[C\(_n\)mim][NTf\(_2\)]\(^{19,39}\) the extraction process in the present system may also proceed via a cation exchange mechanism.

Moreover, Fig. 3 shows that the trends for the HNO\(_3\) effect in systems using all three ionic liquids are very similar. From C\(_2\) to C\(_6\) of alkyl chain on the imidazolium ions, the effect of HNO\(_3\) is almost structure-independent.

### Interference of other metal ions

Preliminarily, we have selected two inorganic salts, NaNO\(_3\) and Al(NO\(_3\))\(_3\), to study their effects on the extraction of Cs\(^{+}\) by BPC6/[C\(_n\)mim][NTf\(_2\)]. The sodium ions (Na\(^{+}\)) and aluminium ions (Al\(^{3+}\)) are usually high-content ions in some HLLW and Al(NO\(_3\))\(_3\), is often used as a salting-out reagent.

Table 1 shows the effect of NaNO\(_3\) on the extraction system. From Table 1, it can be found that for [C\(_2\)mim][NTf\(_2\)] and [C\(_n\)mim][NTf\(_2\)] based systems the distribution ratio of Cs\(^{+}\) (\(D_{\text{cs}}\)) is reduced by increasing NaNO\(_3\) concentration. A slightly different effect of NaNO\(_3\) is observed when [C\(_6\)mim][NTf\(_2\)] is used. On this occasion, \(D_{\text{cs}}\) is increased from 130 with no NaNO\(_3\) to 244 with 0.05 mol L\(^{-1}\) NaNO\(_3\), which shows an obvious salting-out effect on the extraction of Cs\(^{+}\). Continued increasing of the concentration of NaNO\(_3\) will bring about a drop of \(D_{\text{cs}}\). On the whole, NaNO\(_3\) mainly shows a competition effect on the extraction of Cs\(^{+}\), which may result from the competitive complexation of Na\(^{+}\) with BPC6.

Although Al(NO\(_3\))\(_3\) is a very strong salting-out reagent, adding 0.1 or 1 mol L\(^{-1}\) Al(NO\(_3\))\(_3\) to the aqueous phase resulted in a decrease of \(D_{\text{cs}}\) for all the three ionic liquid based extraction systems (extraction data not shown here).

Based on above results, except at low concentrations, NaNO\(_3\) shows some salting-out effect on the BPC6/[C\(_n\)mim][NTf\(_2\)]–Cs\(^{+}\) system; NaNO\(_3\) and Al(NO\(_3\))\(_3\) in other systems behave as competition reagents. The competition effect is probably induced by the extraction of Na\(^{+}\) or Al\(^{3+}\) by BPC6. And no evidence indicates that NO\(_3^{-}\) in ionic liquid based extraction systems participates in the extraction process as obviously as they did in conventional solvent extraction systems with a neutral complex mechanism.

<table>
<thead>
<tr>
<th>[NaNO(_3)]/mol L(^{-1})</th>
<th>[C(_2)mim][NTf(_2)]</th>
<th>[C(_n)mim][NTf(_2)]</th>
<th>[C(_6)mim][NTf(_2)]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>&gt; 10(^{3})</td>
<td>&gt; 10(^{3})</td>
<td>130</td>
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<tr>
<td>0.05</td>
<td>268</td>
<td>175</td>
<td>244</td>
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<tr>
<td>0.20</td>
<td>124</td>
<td>107</td>
<td>49</td>
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<td>1.00</td>
<td>29.7</td>
<td>33.6</td>
<td>13.7</td>
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Extraction mechanism

The extraction mechanisms in an ionic liquid based system sometimes differ from that in traditional solvent extraction. Cation exchange or anion exchange mechanisms have been revealed by several investigators.\textsuperscript{12,18,39,40} From the above results, the extraction mechanism for the present systems can be explored. The adding of HNO$_3$ to the aqueous phase decreased the extraction efficiency of Cs$^+$ due to the competition of H$^+$ complexed with BPC6 and no evidence indicates that NO$_3^-$ participated in the extraction process. The competition effect of NaNO$_3$ and Al(NO$_3$)$_3$ also confirms that the extraction of Cs$^+$ may not proceed with a NO$_3^-$-participated neutral complex mechanism. All the results seem to reveal an ion exchange mechanism for the present system.

Herein, UV-vis spectroscopy has been employed to determine the concentration of [C$_n$ mim]$^+$ in the aqueous phase before and after extraction. As shown in Fig. 4, there is an obvious increase in the [C$_4$ mim]$^+$ absorption at 211 nm after the extraction of Cs$^+$, and the increase enhanced linearly with increasing concentration of extracted Cs$^+$ (ESI†, Fig. S3), implying that some [C$_4$ mim]$^+$ has been exchanged from the ionic liquid phase to the aqueous phase by Cs$^+$ or BPC6-Cs$^+$ complexes.

Fig. 4 UV-vis spectra of [C$_4$ mim]$^+$ in the aqueous phase before and after the extraction of Cs$^+$ with different concentrations of BPC6, [Cs$^+$] = 10 mmol L$^{-1}$. The bottom line corresponds to the result of measuring the aqueous phase by direct equilibration of distilled water with pure [C$_4$ mim][NTf$_2$].

Of additional interest is that the pure ionic liquids in the absence of extractants can also extract Cs$^+$ from aqueous solutions, which can be seen from the $E_{Cs}$ values in the absence of BPC6 in Fig. 2. Through the determination of [C$_n$ mim]$^+$ concentration in the aqueous phase, we confirmed that the extraction of Cs$^+$ by pure ionic liquids was also achieved by a Cs$^+$-[C$_n$ mim]$^+$ exchange. By using a molecular dynamic simulating method, Wippf et al. have also shown Cs$^+$ can transfer from the aqueous phase to the ionic liquid phase by exchanging with [C$_n$ mim]$^+$.\textsuperscript{24} Accordingly, we propose a dual extraction mechanism for extracting Cs$^+$ by the BPC6/C$_n$ mimNTf$_2$ system, i.e., via exchange of BPC6-Cs$^+$ complex or Cs$^+$ by imidazolium ions of ILs. The extraction process can be shown as follows:

\[
\text{[Cs·BPC6]$^+$} + \text{C}_n\text{mim}^+_{\text{org}} \rightarrow \text{[Cs·BPC6]$^+$} + \text{[C}_n\text{mim}$^+$}
\]

From the mechanism proposed above, we can have a deeper understanding of the role of ionic liquids in extraction systems. Not only as diluents of the extractant BPC6, but also the ionic liquids themselves participate in the extraction process directly by exchange of [C$_n$ mim]$^+$ with Cs$^+$. In other words, ionic liquids can be regarded as a dual functional media here. It may be deduced that just through this dual function the extraction system in the present work shows a greatly high efficiency of extracting Cs$^+$.

Another point that should be declared here is that the extraction of Cs$^+$ in the present systems may not proceed totally via the dual cation exchange mechanism. NO$_3^-$ may participate in the extraction to some extent, especially with those ionic liquids that have a longer side alkyl chain, reflected by the salting-out effect of NaNO$_3$ on the [C$_6$ mim][NTf$_2$] system.

Radiation effect on the BPC6/RTILs system

As mentioned above, both extractant and RTILs should be robust to a high radiation dose for successful application in the separation of radioactive Cs$^+$. Therefore, we also assessed the radiation stability of BPC6/[C$_4$ mim][NTf$_2$] by solvent extraction of Cs$^+$ using irradiated [C$_4$ mim][NTf$_2$] in combination with unirradiated or irradiated BPC6.

Influence of \(\gamma\)-irradiation of [C$_4$ mim][NTf$_2$] on the extraction of Cs$^+$. Fig. 5 shows extraction results for [C$_4$ mim][NTf$_2$] containing 15 mmol L$^{-1}$ BPC6. As can be seen, a very high $D_{Cs}$ of $>1000$ for unirradiated [C$_4$ mim][NTf$_2$] was obtained. And the removal of Cs$^+$ from aqueous solution was almost complete (\(>99.9\%\)). However, a significant decline of the $D_{Cs}$ was observed when the [C$_4$ mim][NTf$_2$] solvent was irradiated, and the decline enhanced obviously with increasing dose (Fig. 5). After being irradiated at a dose of 550 kGy, for example, the $D_{Cs}$ of [C$_4$ mim][NTf$_2$] was even less than 50, a value 20 times lower than that of unirradiated [C$_4$ mim][NTf$_2$], while the $E_{Cs}$ decreased from 99.9% to 97.9%.

Fig. 5 Influence of dose on Cs$^+$ extraction from aqueous solutions by irradiated [C$_4$ mim][NTf$_2$] in combination with BPC6.
We have recently investigated the influence of γ-radiation on \([C_{4}\text{mim}][\text{PF}_6]\) and \([C_{4}\text{mim}][\text{NTf}_2]\) for extraction of Sr\(^{2+}\). The result showed that the Sr\(^{2+}\) partitioning in DCH18C6/RTILs decreased as the absorbed dose of RTILs increased, and the decreases of Sr\(^{2+}\) partitioning is related to radiation-generated H\(^+\).\(^{33,34}\) It was thought that the radiation-generated H\(^+\) was also the main factor that influences the extraction of Cs\(^+\) by BPC6 in irradiated \([C_{4}\text{mim}][\text{NTf}_2]\). The studies of solvent extraction of Cs\(^+\) from nitric acid media by BOBCalixC6\(^{21}\) and crown ethers\(^{29}\) using RTILs demonstrated that the partitioning of Cs\(^+\) in RTILs decreased as the acidity of aqueous solution increased. A similar acid-effect was also observed for BPC6/[C4mim][NTf2] systems as shown in Fig. 3. When the \([C_{4}\text{mim}][\text{NTf}_2]\) was irradiated, acidic products were generated as proved by NMR spectroscopy and pH measurement.\(^{44}\) And the acidic products were cumulated with increasing dose, leading to the decrease of pH in aqueous solution when the extraction was conducted (ESI, Fig. S4). As a result, the partitioning of Cs\(^+\) in RTILs decreased due to the acid effect. To prove this, the irradiated \([C_{4}\text{mim}][\text{NTf}_2]\) at 550 kGy was washed several times with deionized water before extraction, until a neutral upper aqueous phase was obtained. As expected, the Cs\(^+\) partitioning in \([C_{4}\text{mim}][\text{NTf}_2]\) was recovered with the washed irradiated \([C_{4}\text{mim}][\text{NTf}_2]\). The \(D_{cs}\) of 642 and the complete removal of Cs\(^+\) (99.8%) from the aqueous solution were regained (Fig. 5). Hence, it is unambiguous that H\(^+\) is responsible for the decline of partitioning of Cs\(^+\) in irradiated \([C_{4}\text{mim}][\text{NTf}_2]\) with BPC6 as extractant.

As mentioned above, the extraction of Cs\(^+\) by the BPC6/\(C_{4}\text{mim}\text{NTf}_2\) system involves a dual extraction mechanism, i.e., via exchange of BPC6-Cs\(^+\) complex or Cs\(^+\) by imidazolium ions of RTILs. When H\(^+\) coexists in the extraction system, its hydrate may influence the extraction by competition with Cs\(^+\) as follows:

\[
\begin{align*}
H_2O\cdot\text{BPC6}^+ + C_{4}\text{mim}^{\text{+}}_{\text{org}} &\rightarrow [H_2O\cdot\text{BPC6}]_{\text{org}} + C_{4}\text{mim}^{\text{+}} \\
+ \text{BPC6} &\rightarrow \text{BPC6} + C_{4}\text{mim}^{\text{+}} \\
H_2O + C_{4}\text{mim}^{\text{+}}_{\text{org}} &\rightarrow H_2O^+ + C_{4}\text{mim}^{\text{+}}
\end{align*}
\]

Based on the above discussion, we suggest that the influence of γ-radiation on \([C_{4}\text{mim}][\text{NTf}_2]\) for the extraction of Cs\(^+\) will be diminished by increasing the acidity of the aqueous phase, since the high acidity of the aqueous phase makes the difference in the amount of H\(^+\) formed during the irradiation of \([C_{4}\text{mim}][\text{NTf}_2]\) at different doses insignificant. Investigation on this aspect is still underway in our laboratory.

**Influence of γ-irradiation of BPC6/[C4mim][NTf2] on the extraction of Cs\(^+\).** Fig. 6 shows extraction results for irradiated BPC6/[C4mim][NTf2]. It is clear that the partitioning of Cs\(^+\) in irradiated BPC6/[C4mim][NTf2] greatly decreased compared to that in unirradiated BPC6/[C4mim][NTf2], and the decrement enhanced obviously with increasing dose (Fig. 6). After being irradiated at a dose of 550 kGy, for example, the \(D_{cs}\) of BPC6/[C4mim][NTf2] was even less than 5, a value 200 times lower than that of unirradiated BPC6/[C4mim][NTf2], while the \(E_{cs}\) decreased from 99.9% to 75.0%. The decline is much more significant than that for irradiated \([C_{4}\text{mim}][\text{NTf}_2]\)/unirradiated BPC6 system. To rationalize why the partitioning of Cs\(^+\) in irradiated BPC6/[C4mim][NTf2] decreased, we adopted the same strategy used in irradiated \([C_{4}\text{mim}][\text{NTf}_2]\)/unirradiated BPC6 system. The irradiated BPC6/[C4mim][NTf2] at 550 kGy was washed several times with deionized water before extraction, and the removal of H\(^+\) was confirmed by making sure that a neutral upper aqueous phase was obtained. The extraction results, as seen in Fig. 6, show that the recovery of the Cs\(^+\) partitioning in irradiated BPC6/[C4mim][NTf2] after washing irradiated BPC6/[C4mim][NTf2] was slight, suggesting that the radiolysis-generated H\(^+\) was not the main factor that influenced the extraction of Cs\(^+\) in irradiated BPC6/[C4mim][NTf2]. We infer that BPC6 was subjected to severe radiolysis during the irradiation. It is known that a crown ether such as dicyclohexyl-18-crown-6(DCH18C6) underwent loop opening during irradiation.\(^{41-44}\) BPC6, being similar to crown ether, is a kind of macrocyclic compound with a cavity. Cs\(^+\) entered into the cavity during the extraction, forming a stable complex Cs-C-E\(^{-}\). And the Cs-C-E\(^{-}\) moved into the RTIL phase by cation-exchange as described above. After irradiation, BPC6 was subjected to γ-damage and the loop opened, and Cs\(^+\) could not associate with BPC6 effectively, leading to the decrease of Cs\(^+\) partitioning in BPC6/[C4mim][NTf2]. However, the radiolytic products related to the open-loop were not so easy to identify due to the small amount and large number of the species. Besides, it is clear that the radiolysis of BPC6 is adverse to using BPC6/RTILs for separation of radioactive nuclei, and inhibition of the radiolysis of BPC6 is of great importance for the practical application. The studies on the radiation stability of tributyl phosphate (TBP) suggested that alkene and aromatic compounds obviously inhibit the radiolysis of TBP.\(^{45-48}\) The investigation on the radiolysis of DCH18C6 showed that the presence of template ions such as uranyl nitrate increases the macrocycle stability by promoting fragment recombination.\(^{44}\) The radiation stability of BPC6 may be improved in the presence of Cs\(^+\) (as template ions) or by introducing additives or by using specially-designed RTILs as solvent. Further research on these aspects is required.

**Conclusions**

We have demonstrated that a simple calix-crown ether BPC6, in combination with ionic liquids \([C_{4}\text{mim}][\text{NTf}_2]\), exhibits extremely high extraction ability for Cs\(^+\) in aqueous solutions. A dual exchange mechanism has been proposed for the extraction of...
Cs+ by BPC6/[C, mim][NTf2]. Detailed work on the influences of HNO3 and some metal ions showed that the results were significantly different from those of a conventional solvent extraction system. With the present system, a special low acidity extraction behavior has been revealed, which may provide an alternative way for extraction of Cs+ under low acidity HLLW conditions, avoiding the use of a high concentration of HNO3 when using conventional solvents.

Irradiation experiments show a radiation-suppression effect on the BPC6/[C, mim][NTf2] system. However, the suppression can be easily released by a simple water-washing method for irradiated [C, mim][NTf2] in combination with unirradiated BPC6. Special attention should be paid to the possible radiolysis of BPC6 in [C, mim][NTf2], which resulted in a sharp decrease of extraction efficiency for Cs+. Future work will concentrate on the radiolysis mechanism of calix-crown ether in ionic liquids.

In conclusion, though practical problems may still be present and continue, our systematic work on the extraction of Cs+ by calix-crown ether in ionic liquids has shed some light on the selection of appropriate calix-crown ether/RTILs systems for extraction of Cs+ and give a careful consideration on the likely future utilization of RTILs based extraction system in the treatment of HLLW in nuclear industry.

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Notes and references