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

Chao Xu, Liyong Yuan, Xinghai Shen* and Maolin Zhai*

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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 mim][NTf$_2$], where [C mim]$^+$ is 1-alkyl-3-methylimidazolium and [NTf$_2$]$^-$ is bis(trifluoromethylsulfonyl)imide. The BPC6/[C 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 mim][NTf$_2$] system involves a dual extraction mechanism, . ., exchange of BPC6·Cs$^+$ complex or Cs$^+$ by [C 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, . ., 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$^+$.[1] The diluents used, however, are usually vaporous 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,[2-4] catalytic[5] and electrochemical[6–8] 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.[9–16] A preliminary study by Dai . demonstrated that

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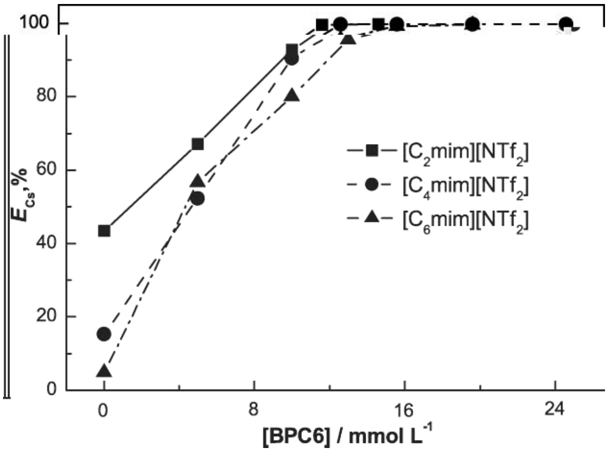


Fig. 2 Relationship between E_{Cs} and the concentration of BPC6 in [C mim][NTf$_2$].

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_{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

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.[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 mim]$^+$ in the aqueous phase before and after extraction. As shown in Fig. 4, there is an obvious increase in the $[C_4mim]^+$ 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 $[C_4mim]^+$ has been exchanged from the ionic liquid phase to the aqueous phase by Cs^+ or $BPC6{\cdot}Cs^+$ complexes.

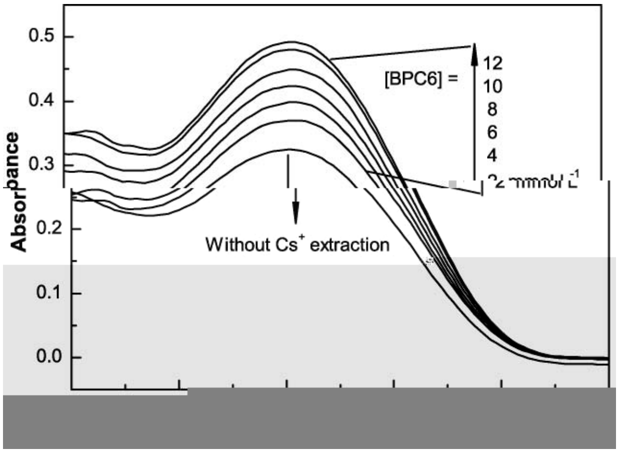
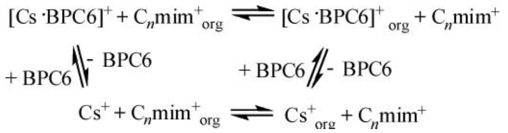


Fig. 4 UV-vis spectra of $[C_4mim]^+$ in the aqueous phase before and after the extraction of Cs^+ with different concentrations of BPC6, $[Cs^+]$ = 10 mmol L^{-1}. The bottom line corresponds to the result of measuring the aqueous phase by direct equilibration of distilled water with pure $[C_4mim][NTf_2]$.

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 mim]$^+$ concentration in the aqueous phase, we confirmed that the extraction of Cs^+ by pure ionic liquids was also achieved by a Cs^+_{aq}–[C mim]$^+_{IL}$ exchange. By using a molecular dynamic simulating method, Wippf . have also shown Cs^+ can transfer from the aqueous phase to the ionic liquid phase by exchanging with [C mim]$^+$.[24] Accordingly, we propose a dual extraction mechanism for extracting Cs^+ by the BPC6/C mimNTf$_2$ system, . ., exchange of $BPC6{\cdot}Cs^+$ complex or Cs^+ by imidazolium ions of ILs. The extraction process can be shown as follows:



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 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 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 $[C_6mim][NTf_2]$ 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/$[C_4mim][NTf_2]$ by solvent extraction of Cs^+ using irradiated $[C_4mim][NTf_2]$ in combination with unirradiated or irradiated BPC6.

Influence of γ-irradiation of $[C_4mim][NTf_2]$ on the extraction of Cs^+. Fig. 5 shows extraction results for $[C_4mim][NTf_2]$ containing 15 mmol L^{-1} BPC6. As can be seen, a very high D_{Cs} of >1000 for unirradiated $[C_4mim][NTf_2]$ 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 $[C_4mim][NTf_2]$ 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 $[C_4mim][NTf_2]$ was even less than 50, a value 20 times lower than that of unirradiated $[C_4mim][NTf_2]$, while the E_{Cs} decreased from 99.9% to 97.9%.

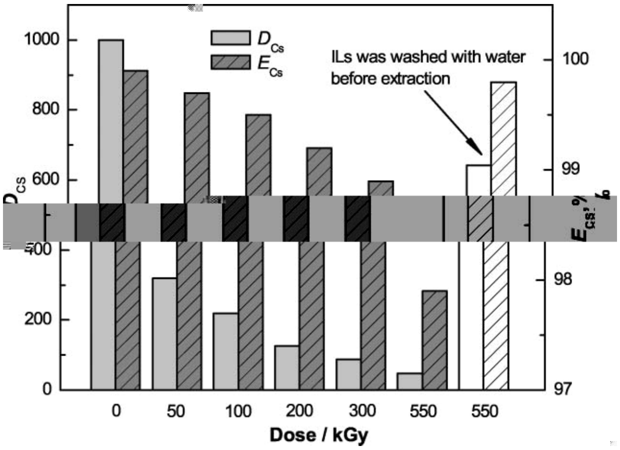


Fig. 5 Influence of dose on Cs^+ extraction from aqueous solutions by irradiated $[C_4mim][NTf_2]$ in combination with BPC6.

We have recently investigated the influence of γ-radiation on $[C_4mim][PF_6]$ and $[C_4mim][NTf_2]$ 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 $[C_4mim][NTf_2]$. The studies of solvent extraction of Cs^+ from nitric acid media by BOBCalixC6[21] and crown ethers[19] 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.1(lso6t)-0.3o oeffect wasss C

Cs$^+$ by BPC6/[C mim][NTf$_2$]. Detailed work on the influences of HNO$_3$ 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 HNO$_3$ when using conventional solvents.

Irradiation experiments show a radiation-suppression effect on the BPC6/[C mim][NTf$_2$] system. However, the suppression can be easily released by a simple water-washing method for irradiated [C mim][NTf$_2$] in combination with unirradiated BPC6. Special attention should be paid to the possible radiolysis of BPC6 in [C mim][NTf$_2$], 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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