Extraction of Th(IV) from aqueous solution by room-temperature ionic liquids and coupled with supercritical carbon dioxide stripping

Jing Fu, Qingde Chen, Taoxiang Sun, Xinghai Shen *

Beijing National Laboratory for Molecular Sciences (BNLMS), Fundamental Science on Radiochemistry and Radiation Chemistry Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

ABSTRACT

The extraction of Th(IV) from aqueous phase into the ionic liquids (ILs) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ($C_nmimNTf_2$, n = 2, 4, 6, 8) by the β-diketone extractant 2-thenoyltrifluoroacetone (HTTA), and the stripping of Th(IV) from the IL phase using supercritical carbon dioxide (sc-CO_2) were studied. Th(IV) was extracted efficiently by HTTA-$C_nmimNTf_2$ systems. A neutral complex extraction mechanism was proposed via log–log plot analysis method and ion chromatograph (IC) method. The formed neutral complex partitioning in all four IL systems was Th(TTA)$_4$, and the structure was further confirmed by Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). Supercritical CO_2 with ethanol showed good stripping of Th(IV) from the IL phase. The pressure and temperature of CO_2, the volume and polarity of modifiers, and the dynamic extraction time influencing on the stripping efficiency were examined.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In the nuclear industry, thorium is treated as an important substituted nuclear fuel in nuclear reactors [1]. Meanwhile, in the thorium–uranium fuel cycle, a large amount of spent nuclear fuel containing uranium, thorium and various fission products will be generated. Separation and recovery of thorium, uranium, and other valuable metal elements are of great importance due to their limited resources and also for the purpose of reducing their disposal quantum as radioactive wastes [2]. In a conventional solvent extraction process, Th and U are extracted by volatile organic solvents (VOCs) from the aqueous solution employing tri-*n*-butylphosphate (TBP) or 2-thenoyltrifluoroacetone (HTTA) as typical extractants [3,4]. However, a large amount of secondary wastes will be produced, and the organic solvents will be degraded by hydrolysis and radiolysis. Therefore, there is incentive to explore alternative solvents to overcome these drawbacks.

Room temperature ionic liquids (ILs) have been considered as alternative reaction media to replace VOCs in a variety of synthetic, catalytic, electrochemical and separated applications [5–7]. The unique properties of ILs such as nonflammability, high thermal stability, low vapor pressure, wide liquid range, and good radiation stability are important advantages over VOCs used in liquid–liquid extraction [7–9]. Especially, they have been considered as next generation diluents as the replacement of VOCs in the reprocessing of spent nuclear fuel [10–12]. Because of the ionic compositions and the corresponding physicochemical properties and characteristics of ILs, the extraction of metal ions is more efficient in IL systems than in conventional solvent systems, especially for Sr^{2+}, Cs^+, UO_2^{2+}, and lanthanide ions [13–16]. There are some reports about the extraction of Th(IV) using ILs. Zou et al. utilized the primary amine N1923 as extractant in C_8mimPF_6 to extract Th^{4+} efficiently with additional Na_2SO_4 in aqueous phase. A reversed micellar solubilization extraction mechanism was suggested for this system. Therefore, the addition of salt-out agent could promote the extraction efficiency greatly via prompting the solubilization of Th^{4+} into the reversed micelles formed in the IL phase [17]. Shen et al. studied the extraction of Th^{4+} from aqueous phase by diglycolamide in C_nmimPF_6, and obtained the extraction efficiency over 90%. The extraction mechanism in the C_4mimPF_6 and C_6mimPF_6 systems is a cation-exchange mechanism, whereas in the C_8mimPF_6 system, it is changed to a neutral complex one [18]. The extraction mechanism in an IL based system may differ from that in traditional solvent extraction. Cation exchange, anion exchange, or neutral complex mechanisms have been revealed by several investigations [19–21]. The application of ILs in practical extraction of metal ions may be challenged by multiple extraction mechanisms [22].

On the other hand, the above researches on the extraction of Th(IV) are mainly focused on the extraction process, but the stripping process is paid less attention. From the view point of the application, the stripping process is as important as the extraction process. ILs exhibit many advantages towards the extraction of metal ions, whereas the stripping still remains a challenge [7].

* Corresponding author. Tel.: +86 10 62765915; fax: +86 10 62759191.
E-mail address: xshen@pku.edu.cn (X. Shen).

The traditional liquid–liquid stripping has been tried to recover metal ions from the ILs phase [23,24]. However, the cross contamination between two phases and the loss of ILs are the major obstacles. Electrodeposition is another method to recover metal ions from the IL phase [25,26]. But this method is only suitable for highly electropositive elements, and requires the electrochemical window of IL matching with the reduction potential of metal ion. Fortunately, green solvent supercritical fluid (SCF) is discovered to be an efficient medium to overcome the above problems and limitations.

Sc-CO_2 is the most widely used SCF due to its unique properties of moderate critical constants (P_c = 7.37 MPa and T_c = 304.4 K), chemical inertness, non-flammability and low cost. The application of sc-CO_2 for metal ions extraction from solid or liquid samples can be accomplished by using proper chelating agents as extractants. For example, actinides, lanthanides, and transition metals are easily extracted by highly soluble fluorinated β-diketones or organophosphorus reagent in sc-CO_2 [27–29]. As environmentally benign solvents, sc-CO_2 and IL have been utilized together in several applications. The volatile and nonpolar sc-CO_2 with nonvolatile and polar IL forms a different two-phase system. The principle of product recovery by this biphasic system is based on the solubility of sc-CO_2 in the IL, and the insolubility of the IL in sc-CO_2 [30–32]. This provides a feasible method to back extract metal ions from the IL phase by sc-CO_2. Mekki et al. first demonstrated that the stripping of metal complexes of Cu^{2+} and lanthanides (La^{3+} and Eu^{3+}) coordinated with β-diketone extractants from $C_4mimNTf_2$ could be effectively achieved by sc-CO_2 [33,34]. Wai et al. found that UO_2^{2+} could be stripped into sc-CO_2 from TBP-$C_4mimNTf_2$, and formed $UO_2(NO_3)_2(TBP)_2$ complex in sc-CO_2 phase [35]. These reports provide a possible way employing sc-CO_2 to strip metal species from the IL phase, and avoiding the loss and the cross contamination of IL during the stripping process.

To the best of our knowledge, there are few reports in literatures that describe the complete cycle of thorium ions including extraction and back extraction processes with both ILs and sc-CO_2. In the present paper, we are interested in studying on the abilities of HTTA in $C_nmimNTf_2$ (n = 2, 4, 6, 8) for the extraction of Th(IV) from aqueous phase. Meanwhile, the stripping of Th(IV) from the IL phase by sc-CO_2 is investigated.

2. Experimental

2.1. Materials

$C_nmimNTf_2$ (n = 2, 4, 6, 8, see Scheme 1) were synthesized via metathetical reaction according to the published method [36]. C_nmimBr and $LiNTf_2$ were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. HTTA was purchased from J&K Chemical Technology and used as received. Stock solution of Th(IV) was prepared by dissolving $Th(NO_3)_4·6H_2O$ into deionized water. Carbon dioxide (99.95%, Reijiye, Beijing) was used in all the stripping experiments. All other chemicals were of analytical reagent grade.
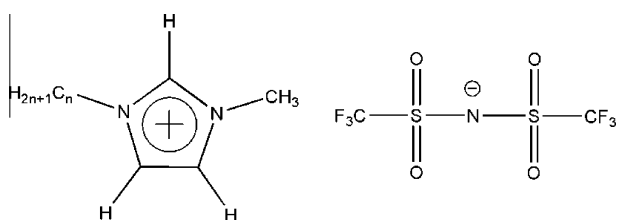
2.2. Methods

The extraction experiments were carried out at room temperature. 0.5 mL of $C_nmimNTf_2$ (n = 2, 4, 6, 8) containing various concentrations of HTTA and 0.5 mL of aqueous solution containing 2.5 mmol L^{-1} of Th^{4+} were added into a plastic centrifuge tube, followed by vigorous shaking for 24 h. Then the mixture was centrifuged (8000 r, 2 min) and the two phases were separated. The concentration of Th^{4+} remained in the aqueous phase was determined by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Leeman, USA). The extraction efficiency of Th^{4+} was calculated from the concentration of Th^{4+} in the aqueous phase before and after extraction, respectively. The relative error in our experiments was less than 5%.

The determination of the concentration of NO_3^- in an aqueous solution was performed on a Dionex model ICS-900 ion chromatograph (IC) with Chromeleon 7.0 software (Dionex Corporation, USA) at room temperature. For the analysis of NO_3^-, an IonPacAS19 analytical column (250 × 4 mm) and an IonPacAG19 guard column (50 × 4 mm) were used. The analytes were eluted by isocratic elution with an aqueous solution of 30 mmol L^{-1} of KOH at a flow rate of 1 mL min^{-1}. The suppressor ASRS-300 was installed for 75 mA electric suppression. The peak of NO_3^- emerged at about 8 min, and the peak area of NO_3^- in the chromatogram linearly depends on the concentration. All experiments were reproducible and the results agreed within 5%.

Samples for Extended X-ray Absorption Fine Structure (EXAFS) measurements were contained in 1 cm path length plexi glass cuvettes. The preparation of the sample was based on 200 mmol L^{-1} of HTTA in $C_nmimNTf_2$ (n = 2, 4, 6, 8) contacting with the aqueous solution of $Th(NO_3)_4$ (50 mmol L^{-1}) in the absence of HNO_3. XAFS experiments were carried out in the transmission mode at the XAFS station of Shanghai Synchrotron Radiation Facility (SSRF), China. Data reduction and analysis were conducted according to standard procedures with pre-edge background removal, edge normalization to a unit step height, conversion to momentum space, and extraction of the EXAFS with a spline function. The data analysis was carried out using the Athena and Artemisinter faces to the IFEFFIT program package [37].

All stripping experiments were performed with a lab supercritical fluid extraction apparatus (100 mL, SEPAREX, France). The apparatus includes the following devices: a liquid-CO_2 tank, a high-pressure piston pump (P200), a modifier syringe pump, a high-pressure extraction vessel, an automatic back pressure regulator, and a collection vessel. The SFE apparatus is illustrated in Scheme 2. All experiments were performed with a stainless-steel high-pressure extraction vessel with electrical heating jacket. The

Scheme 1. Chemical structures of C_nmim^+ (n = 2, 4, 6, 8), NTf_2^-.
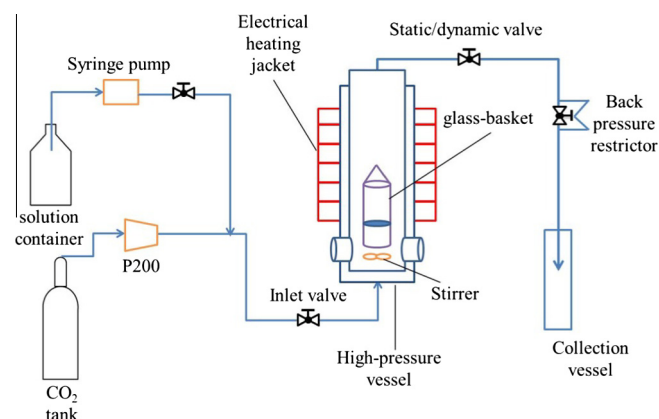
Scheme 2. Apparatus for the stripping of Th(IV) from the IL phase to sc-CO_2.

temperature inside of the high-pressure vessel was controlled by an adjusting thermocouple (±1 K). In the high-pressure extraction vessel, 0.5 mL of $C_n$mimNTf$_2$ containing 2.5 mmol L^{-1} of Th(IV) in a 10 mL glass-basket placed under stirring. All stripping experiments were carried out using dynamic extraction step, in which the sc-CO$_2$ and modifier solution passed continuously through the extraction chamber. The flow rate of CO$_2$ was fixed at 0.2 mL min^{-1}. The stripping efficiency was calculated on the basis of the content of Th(IV) in the initial IL phase and the residue IL phase, which was analyzed by ICP-AES after microwave digestion. The relative error in our experiments was less than 5%.

3. Results and discussion

3.1. Extraction behavior of Th(IV) in RTILs

Fig. 1 shows the dependence of the extraction efficiency (E) of Th^{4+} on the initial concentration of HTTA in $C_n$mimNTf$_2$. The extraction efficiency increases with an increase in the concentration of HTTA, and reaches nearly 97% when the concentration of HTTA is higher than 12 mmol L^{-1}. The length of the alkyl chain in the imidazolium cation of ILs does not influence greatly the extraction efficiency of Th^{4+}.

To assess the partitioning behavior of Th^{4+} in $C_n$mimNTf$_2$ systems, the extraction efficiency of Th^{4+} was measured as a function of the concentration of HNO$_3$ in the aqueous phase. As seen in Fig. 2, HTTA shows high extraction ability of Th^{4+} only at a very low concentration of HNO$_3$ in the aqueous phase. The extraction efficiency of Th^{4+} is reduced by an increase in the concentration of HNO$_3$. As is well known, HTTA is an acidic extractant, thus the existence of H$^+$ in the aqueous phase can restrain its dissociation to reduce the extraction efficiency of Th^{4+}. In addition, the effect of the acid on the extraction efficiency of Th^{4+} varies as the alkyl chain of the ILs lengthens. The influence of HNO$_3$ on the extraction of Th^{4+} by HTTA is greater in the short alkyl chain ILs systems than that in the long alkyl chain ILs systems. When the initial concentration of HNO$_3$ in the aqueous phase is 25 mmol L^{-1}, the extraction efficiency of Th^{4+} is only 6% in the C_2mimNTf$_2$ system, while it is about 30% in the C_8mimNTf$_2$ system.

Generally, cation exchange, anion exchange and neutral complex extraction mechanisms are proposed in the IL extraction system. When the extraction mechanism is the ion-exchange mechanism, the extraction of metal ions is more efficient in the
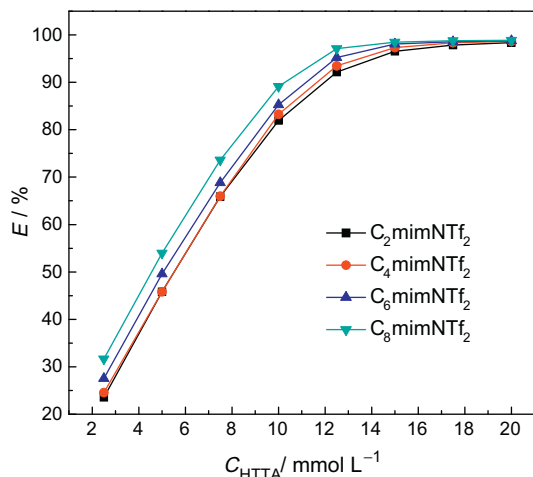
system of a shorter alkyl chain IL [16,24]. However, the result seems opposite in this work. HTTA shows better extraction ability towards Th^{4+} in the C_8mimNTf$_2$ system than in the C_2mimNTf$_2$ system. This is very possibly caused by a different extraction mechanism, which will be discussed in the following section.

To determine the fundamental stoichiometry of the Th^{4+}–TTA$^-$ complex, slope analysis is conducted as a function of the equilibrium concentration of HTTA in the IL phase. A slope close to 4 is obtained in the plot of log D vs. log [HTTA] in $C_n$mimNTf$_2$ systems, where [HTTA] is approximately the initial concentration of HTTA in the IL phase (Fig. 3). This suggests that four HTTA molecules are required to extract one Th^{4+}, indicating that a 4:1 complex is formed. The stoichiometry of the Th^{4+}–TTA$^-$ complex is considered all the same in HTTA-$C_n$mimNTf$_2$ systems and almost independent on the alkyl chain on the imidazolium ion.

To ascertain whether NO$_3^-$ participates in the extraction process or not, the dependence of the concentration of NO$_3^-$ in the aqueous phase on the concentration of the extracted Th^{4+} in the IL phase is investigated. The initial concentration of Th(NO$_3$)$_4$ in the aqueous phase is 2.5 mmol L^{-1}, and the concentration of HTTA in $C_n$mimNTf$_2$ various from 0 to 20 mmol L^{-1}. The concentration of NO$_3^-$ in
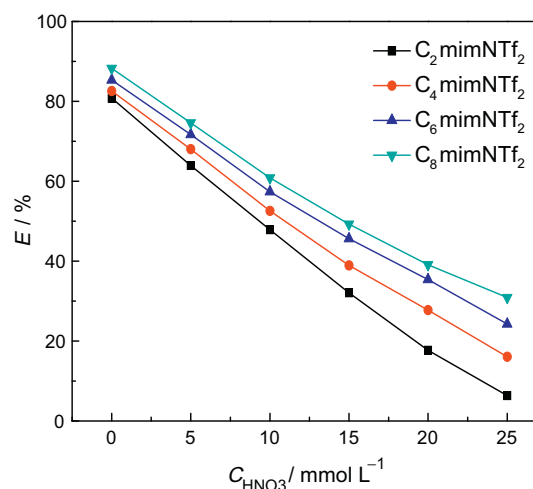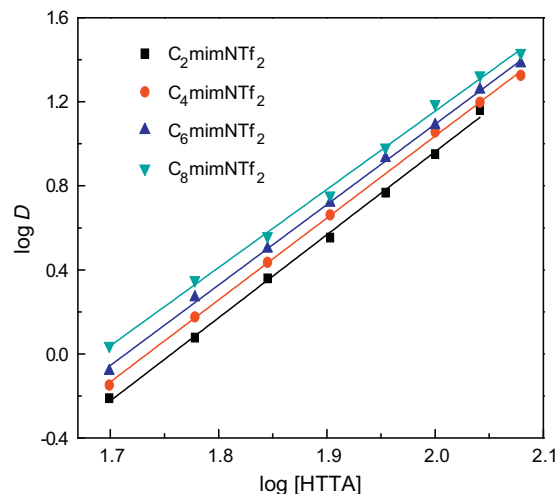

Fig. 2. Dependence of the extraction efficiency of Th^{4+} by HTTA-$C_n$mimNTf$_2$ on the initial HNO$_3$ concentration in the aqueous phase (10 mmol L^{-1} of HTTA and 2.5 mmol L^{-1} of Th^{4+}).

Fig. 1. Dependence of the extraction efficiency of Th^{4+} on the initial concentration of HTTA in $C_n$mimNTf$_2$. The initial concentration of Th^{4+} in the aqueous phase is 2.5 mmol L^{-1}.

Fig. 3. Plots of log D as a function of log [HTTA] in $C_n$mimNTf$_2$ at constant acidity (100 mmol L^{-1} of HNO$_3$ and 2.5 mmol L^{-1} of Th^{4+}).

the aqueous phase almost keeps constant at around 10.5 ± 0.1 mmol L^{-1} with increasing the extraction efficiency of Th^{4+} from 0% to 98%. Comparing these four extraction systems, one can see that the concentration of NO_3^- has no difference as the alkyl chain in the imidazolium cation lengthens from C_2 to C_8. This proves that NO_3^- does not participate in the extraction process in all four IL extraction systems. According to the above results, there should be a complex of $Th(TTA)_4$ in all four $C_n mimNTf_2$ phases after Th^{4+} is extracted by HTTA from the aqueous phase. The extraction may follow a neutral complex mechanism depicted as:

$$Th^{4+} + 4HTTA_{(IL)} \rightleftharpoons Th(TTA)_{4(IL)} + 4H^+ \qquad (1)$$
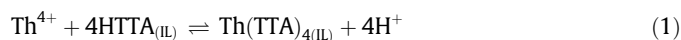
And the chemical structure of $Th(TTA)_4$ is illustrated in Scheme 3. Based on the neutral complex extraction mechanism, we can infer that ILs mainly play a role of solvent in HTTA-$C_n mim$-NTf_2 extraction systems for Th^{4+}. The cation or anion of ILs does not participate in the extraction process directly. Comparing with the ion-exchange mechanism, the neutral complex mechanism is sufficient to eliminate the possibility of ion exchange of IL. The extraction of Th^{4+} from aqueous phase by HTTA in $C_n mimNTf_2$ is not only efficient, but also can eliminate the loss of IL during the extraction process.

To further confirm the structure of Th^{4+} with TTA^- existing in HTTA-$C_n mimNTf$ systems, we employed EXAFS method to determine the coordination environment of the inner phase of Th^{4+} when it was extracted by HTTA into $C_n mimNTf_2$. The Fourier transform magnitudes of the EXAFS are shown in Fig. 4. The results of fitting the EXAFS data to the single scattering theoretical phase and amplitude functions are summarized in Table 1. The Th EXAFS signals are dominated by a shell of 8.9 ± 1.5 oxygen atoms directly coordinated to the Th ion at approximately 2.41 ± 0.01 Å, and there is no obvious difference in all four IL systems. Contributions from other shells of coordinated atoms are not apparent in each sample. The EXAFS measurement shows that the coordination of Th^{4+} is insignificantly different in four different IL systems. Consequently, it is further proved that the complex is $Th(TTA)_4$ in HTTA-$C_n mim$-NTf_2 systems.

It should be pointed out that, due to the formation of a neutral complex $Th(TTA)_4$ in the extraction process, losses of IL components to the aqueous phase can be avoided.

3.2. Stripping of Th(IV) by sc-CO₂

To find out the optimum stripping condition, we took the C_2-$mimNTf_2$ system as an example. In HTTA-$C_2 mimNTf_2$ system, sc-CO_2 itself cannot strip Th(IV) from the IL phase due to the low
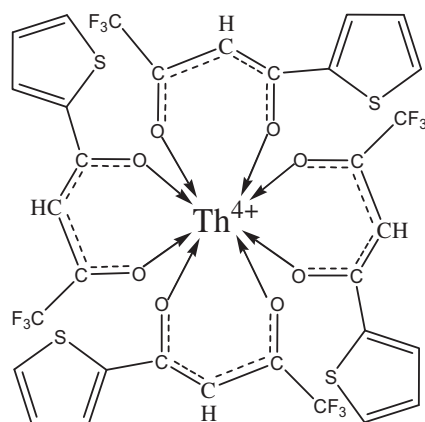
Scheme 3. Chemical structure of $Th(TTA)_4$.

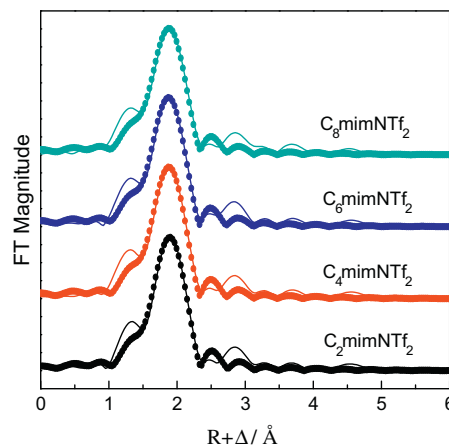**Fig. 4.** The L^3-edge EXAFS (line) and best fit (dots) of Th^{4+} extracted by HTTA in $C_n mimNTf_2$. Fourier transform are not phase shift corrected.

Table 1
Results of coordination number (CN) and Th–O bond length (R) by fitting two shells of the k3 weighted Th L3 edge EXAFS.

IL	CN	R (Å)	σ^2 (10^{-3} Å²)	ΔE (eV)
$C_2 mimNTf_2$	8.9 ± 1.5	2.42 ± 0.02	8.3 ± 2.0	-0.43 ± 1.65
$C_4 mimNTf_2$	8.9 ± 1.5	2.41 ± 0.01	8.3 ± 2.0	-1.59 ± 1.70
$C_6 mimNTf_2$	8.8 ± 1.5	2.41 ± 0.01	8.2 ± 2.0	-2.25 ± 1.74
$C_8 mimNTf_2$	9.0 ± 1.6	2.41 ± 0.01	8.9 ± 2.0	-1.22 ± 1.68

polarity of CO_2. Nevertheless, this limitation could be overcome by adding a small amount of polar solvent as modifier to increase the polarity and solvation power of CO_2. We have selected four conventional organic solvents, i.e., methanol, ethanol, tetrahydrofuran and ethyl acetate, to investigate their effects on the stripping of Th(IV) from $C_2 mimNTf_2$. The stripping efficiency (SE) of Th(IV) is 92% by methanol, 94% by ethanol, 90% by tetrahydrofuran and 88% by ethyl acetate at 20 MPa, 313 K, 0.5 mL min⁻¹ of modifier, 30 min of dynamic extraction time. All these modifiers can improve the stripping ability of sc-CO_2 towards Th(IV) at the same stripping condition. In the following study, we chose ethanol as the representative to systematically investigate the influence of various parameters, i.e., pressure (p), temperature (T), dynamic extraction time (t), and the flow rate of modifier (F) on the stripping efficiency.

The influence of both pressure and temperature on the stripping efficiency of Th(IV) is reported in Table 2. The stripping efficiency of Th(IV) is improved with an increase in pressure at 313 K, 15 min dynamic extraction time, and 0.5 mL min⁻¹ of ethanol. As the pressure increases, the density of CO_2 is increased, and thus the solvability of sc-CO_2 becomes stronger at higher pressure [38]. Therefore, the increasing of the stripping efficiency of Th(IV)

Table 2
The effect of the pressure and temperature on the stripping efficiency of Th(IV) in $C_2 mimNTf_2$ (0.5 mL min⁻¹ of ethanol).

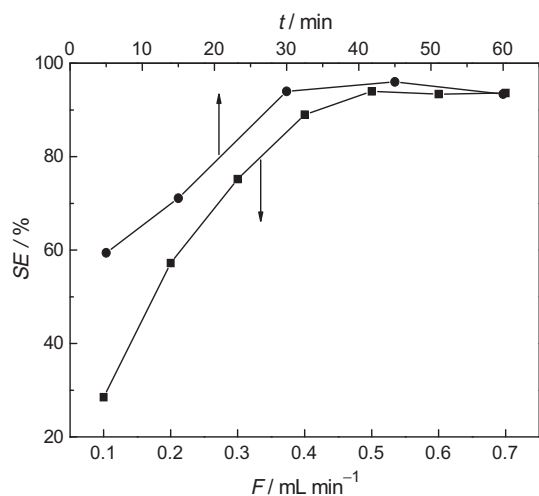| p (MPa)	T (K)	t (min)	SE (%)
10	313	15	34
20	313	15	71
30	313	15	92
20	313	30	94
20	323	30	86
20	333	30	66
20	343	30	58

Fig. 5. Dependence of the stripping efficiency of Th(IV) on the dynamic extraction time (t) at 20 MPa, 313 K, 0.5 mL min^{-1} of ethanol (●), and on the flow rate of ethanol (F) at 20 MPa, 313 K, 30 min of dynamic extraction time (■) in C_2mimNTf$_2$.
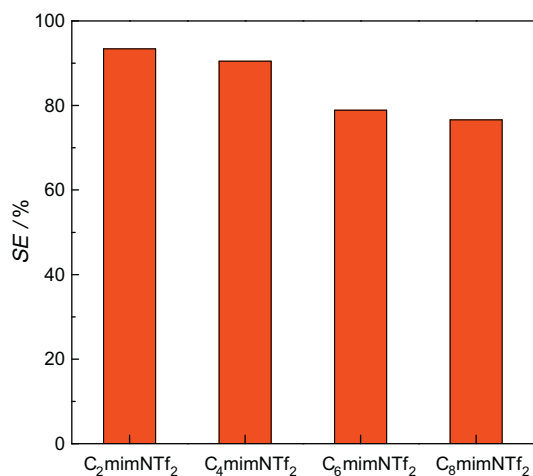

Fig. 6. The stripping efficiency of Th(IV) in $C_n$mimNTf$_2$ at 20 MPa, 313 K, 30 min of dynamic extraction time, and 0.5 mL min^{-1} of ethanol.

could be attributed to an increase in the solubility of Th(TTA)$_4$ with raising the pressure.

The solubility of an analyte in sc-CO$_2$ is also controlled by temperature directly. At higher temperature, an analyte becomes more volatile and the density of sc-CO$_2$ decreases, which must result in a maximum value of extraction efficiency. As shown in Table 2, the stripping efficiency of Th(IV) decreases with increasing temperature at 20 MPa, 30 min of dynamic extraction time, and 0.5 mL min^{-1} of ethanol. This indicates that low temperature is suitable for Th(TTA)$_4$ complex to dissolve into sc-CO$_2$. Besides, HTTA is photosensitive and thermosensitive, and decomposes easily at high temperature. Therefore, the stripping of Th(TTA)$_4$ is more efficient at low temperature than at high temperature.

The effect of the dynamic extraction time on the extraction efficiency is also investigated at five different cases (5 min, 15 min, 30 min, 45 min, and 60 min). The pressure, temperature, and the flow rate of ethanol are maintained at the constant values (20 MPa, 313 K and 0.5 mL min^{-1} of ethanol). Fig. 5 shows that the stripping efficiency of Th(IV) is increased steeply with increasing time. After 30 min, the extraction efficiency changes little.
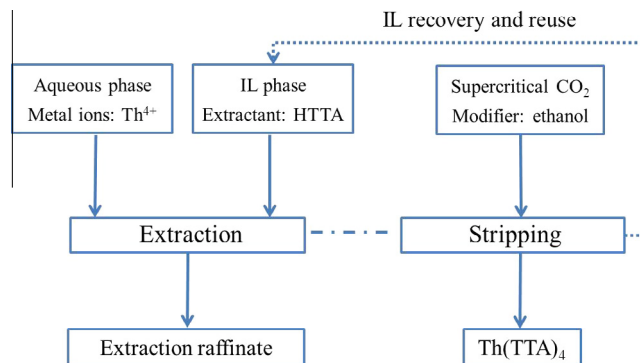
Scheme 4. A diagram showing the extraction–stripping procedure for thorium.

Another main factor on SFE is the amount of modifier in sc-CO$_2$, which significantly influences the stripping efficiency. The effect of the flow rate of modifier on the stripping efficiency is studied at 20 MPa, 313 K, and 30 min. As shown in Fig. 5, the stripping efficiency is increased remarkably at first and then reaches a plateau at 0.5 mL min^{-1} of the flow rate of ethanol. According to above studies about the effects of pressure, temperature, dynamic extraction time, and flow rate of modifier on the stripping efficiency of Th(IV), we conclude that 20 MPa, 313 K, 30 min of dynamic extraction time, and 0.5 mL min^{-1} of ethanol are suitable and economic conditions for stripping Th(IV) from the IL phase, and 94% of Th(IV) can be stripped out.

The stripping efficiency of Th(IV) from all four IL systems at the stripping conditions of 20 MPa, 313 K, 30 min of dynamic extraction, and 0.5 mL min^{-1} of ethanol are shown in Fig. 6. In C_2mimNTf$_2$ and C_4mimNTf$_2$ systems, more than 90% of Th(IV) can be stripped by sc-CO$_2$, while in C_6mimNTf$_2$ and C_8mimNTf$_2$ systems, the stripping efficiency is only 80%. This means that the stripping efficiency of Th(IV) decreases with increasing the alkyl chain length in the imidazolium cation. According to the results in the extraction section, Th(TTA)$_4$ is relatively stable in C_6mimNTf$_2$ and C_8mimNTf$_2$ systems. Therefore, the stripping process using sc-CO$_2$ is more difficult in C_6mimNTf$_2$ and C_8mimNTf$_2$ systems than in other two short alkyl chain IL systems.

According to the above experiments, the procedure of the extraction and stripping for Th(IV) is proposed in Scheme 4. In this procedure, both the extraction based on ILs and the stripping by sc-CO$_2$ for metal elements can reach high efficiency. Meanwhile, losses of IL during both the extraction and the stripping processes can be avoided.

4. Conclusion

The combination of IL and sc-CO$_2$ to extract and strip Th(IV) is established in this paper. Th^{4+} can be efficiently extracted from the aqueous phase with HTTA in $C_n$mimNTf$_2$ (n = 2, 4, 6, 8). The neutral complex mechanism is proposed for the extraction of Th^{4+} by HTTA-$C_n$mimNTf$_2$, that is, Th^{4+} forms a neutral complex with TTA$^-$ (Th(TTA)$_4$). The stripping step is the transfer of Th(IV) from the IL phase to the sc-CO$_2$ phase. Under the specific stripping conditions, Th(IV) can be successfully stripped out from the IL phase. Therefore, in the procedure of extraction and stripping of Th(IV), not only the efficiency reaches high, but also the losses of IL can be avoided.

References

[1] J.S. Herring, P.E. MacDonald, K.D. Weaver, C. Kullberg, Low cost, proliferation resistant, uranium–thorium dioxide fuels for light water reactors, Nucl. Eng. Des. 203 (2001) 65–85.

[2] C.S.K. Raju, M.S. Subramanian, Sequential separation of lanthanides, thorium and uranium using novel solid phase extraction method from high acidic nuclear wastes, J. Hazard. Mater. 145 (2007) 315–322.

[3] J.R. Kumar, J.S. Kim, J.Y. Lee, H.S. Yoon, A brief review on solvent extraction of uranium from acidic solutions, Sep. Purif. Rev. 40 (2011) 77–125.

[4] M.R. Yaftian, A.A. Zamani, S. Rostamnia, Thorium(IV) ion-selective transport through a bulk liquid membrane containing 2-thenoyltrifluoroacetone as extractant-carrier, Sep. Purif. Technol. 49 (2006) 71–75.

[5] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2083.

[6] P. Hapiot, C. Lagrost, Electrochemical reactivity in room-temperature ionic liquids, Chem. Rev. 108 (2008) 2238–2264.

[7] H. Zhao, S.Q. Xia, P.S. Ma, Use of ionic liquids as 'green' solvents for extractions, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.

[8] R.D. Rogers, K.R. Seddon, Ionic liquids – solvents of the future?, Science 302 (2003) 792–793.

[9] D. Han, K.H. Row, Recent applications of ionic liquids in separation technology, Molecules 15 (2010) 2405–2426.

[10] K. Binnemans, Lanthanides and actinides in ionic liquids, Chem. Rev. 107 (2007) 2592–2614.

[11] X.Q. Sun, H.M. Luo, S. Dai, Ionic liquids-based extraction: a promising strategy for the advanced nuclear fuel cycle, Chem. Rev. 112 (2012) 2100–2128.

[12] I. Billard, A. Ouadi, C. Gaillard, Liquid–liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding, Anal. Bioanal. Chem. 400 (2011) 1555–1566.

[13] S. Dai, Y.H. Ju, C.E. Barnes, Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids, J. Chem. Soc.-Dalton Trans. (1999) 1201–1202.

[14] A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, Solvent extraction of U(VI) by task specific ionic liquids bearing phosphoryl groups, Green Chem. 9 (2007) 1160–1162.

[15] S. Panja, P.K. Mohapatra, S.C. Tripathi, P.M. Gandhi, P. Janardan, A highly efficient solvent system containing TODGA in room temperature ionic liquids for actinide extraction, Sep. Purif. Technol. 96 (2012) 289–295.

[16] C. Xu, L.Y. Yuan, X.H. Shen, M.L. Zhai, Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism and radiation effect, Dalton Trans. 39 (2010) 3897–3902.

[17] Y. Zuo, J. Chen, D.Q. Li, Reversed micellar solubilization extraction and separation of thorium(IV) from rare earth(III) by primary amine N1923 in ionic liquid, Sep. Purif. Technol. 63 (2008) 684–690.

[18] Y.L. Shen, S.F. Wang, L. Zhu, J.J. Wang, W.S. Wu, Extraction of Th(IV) from an HNO₃ solution by diglycolamide in ionic liquids, Ind. Eng. Chem. Res. 50 (2011) 13990–13996.

[19] M.P. Jensen, M. Borkowski, I. Laszak, J.V. Beitz, P.G. Rickert, M.L. Dietz, Anion effects in the extraction of lanthanide 2-thenoyltrifluoroacetone complexes into an ionic liquid, Sep. Sci. Technol. 47 (2012) 233–243.

[20] M.L. Dietz, D.C. Stepinski, A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): implications for the "greenness" of RTILs as extraction solvents, Green Chem. 7 (2005) 747–750.

[21] A. Messadi, A. Mohamadou, S. Boudesocque, L. Dupont, E. Guillon, Task-specific ionic liquid with coordinating anion for heavy metal ion extraction: cation exchange versus ion-pair extraction, Sep. Purif. Technol. 107 (2013) 172–178.

[22] M.L. Dietz, J.A. Dzielawa, M.P. Jensen, J.V. Beitz, M. Borkowski, Mechanisms of metal ion transfer into ionic liquids and their implications for the application of ionic liquids as extraction solvents, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids IIIB: Fundamentals, Progress, Challenges and Opportunities: Transformations and Processes, Amer Chemical Soc, Washington, 2005, pp. 2–18.

[23] Y. Zuo, Y. Liu, J. Chen, D.Q. Li, Extraction and recovery of cerium(IV) along with fluorine(I) from bastnasite leaching liquor by DEHEHP in [C(8)mim]PF₆, J. Chem. Technol. Biotechnol. 84 (2009) 949–956.

[24] M. Srncik, D. Kogelnig, A. Stojanovic, W. Korner, R. Krachler, G. Wallner, Uranium extraction from aqueous solutions by ionic liquids, Appl. Radiat. Isot. 67 (2009) 2146–2149.

[25] P.Y. Chen, The assessment of removing strontium and cesium cations from aqueous solutions based on the combined methods of ionic liquid extraction and electrodeposition, Electrochim. Acta 52 (2007) 5484–5492.

[26] P. Giridhar, K.A. Venkatesan, S. Subramaniam, T.G. Srinivasan, P.R.V. Rao, Extraction of uranium(VI) by 1.1 M tri-n-butylphosphate/ionic liquid and the feasibility of recovery by direct electrodeposition from organic phase, J. Alloy. Compd. 448 (2008) 104–108.

[27] C.M. Wai, B. Waller, Dissolution of metal species in supercritical fluids – principles and applications, Ind. Eng. Chem. Res. 39 (2000) 4837–4841.

[28] P. Kumar, A. Pal, M.K. Saxena, K.L. Ramakumar, Supercritical fluid extraction of uranium and thorium from solid matrices, Desalination 232 (2008) 71–79.

[29] W.H. Duan, L.Y. Zhu, S. Jing, Y.J. Zhu, J. Chen, Study on properties of TBP-HNO₃ complex used for direct dissolution of lanthanide and actinide oxides in supercritical fluid CO₂, Chin. J. Chem. 25 (2007) 319–322.

[30] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Green processing using ionic liquids and CO₂, Nature 399 (1999) 28–29.

[31] S.G. Kazarian, B.J. Briscoe, T. Welton, Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO₂ dissolved in two ionic liquids at high pressures, Chem. Commun. (2000) 2047–2048.

[32] S. Keskin, D. Kayrak-Talay, U. Akman, O. Hortacsu, A review of ionic liquids towards supercritical fluid applications, J. Supercrit. Fluids 43 (2007) 150–180.

[33] S. Mekki, C.M. Wai, I. Billard, G. Moutiers, C.H. Yen, J.S. Wang, A. Ouadi, C. Gaillard, P. Hesemann, Cu(II) extraction by supercritical fluid carbon dioxide from a room temperature ionic liquid using fluorinated beta-diketones, Green Chem. 7 (2005) 421–423.

[34] S. Mekkii, C.M. Wai, I. Billard, G. Moutiers, J. Burt, B. Yoon, J.S. Wang, C. Gaillard, A. Ouadi, P. Hesemann, Extraction of lanthanides from aqueous solution by using room-temperature ionic liquid and supercritical carbon dioxide in conjunction, Chem.-Eur. J. 12 (2006) 1760–1766.

[35] J.S. Wang, C.N. Sheaff, B. Yoon, R.S. Addleman, C.M. Wai, Extraction of uranium from aqueous solutions by using ionic liquid and supercritical carbon dioxide in conjunction, Chem.-Eur. J. 15 (2009) 4458–4463.

[36] A. Paul, P.K. Mandal, A. Samanta, How transparent are the imidazolium ionic liquids? A case study with 1-methyl-3-butylimidazolium hexafluorophosphate, [bmim]PF₆, Chem. Phys. Lett. 402 (2005) 375–379.

[37] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat. 12 (2005) 537–541.

[38] W. Wang, H.J. Yang, J.C. Hua, C.Y. Guo, Extraction of metal ions with non-fluorous bipyridine derivatives as chelating ligands in supercritical carbon dioxide, J. Supercrit. Fluids 51 (2009) 181–187.