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

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ABSTRACT

The extraction of Th(IV) from aqueous phase into the ionic liquids (ILs) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ($C_n$mimNTf$_2$, $n = 2, 4, 6, 8$) 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-$C_n$mimNTf$_2$ 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.

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 convention4epurpos-

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.

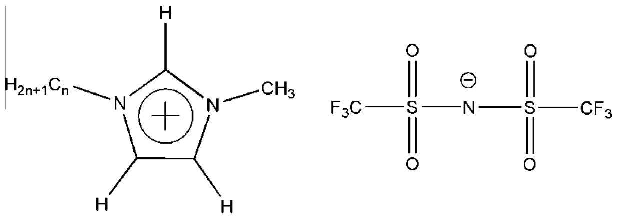
Sc-CO_2 is the most widely used SCF due to its unique properties of moderate critical constants ($P_c = 7.37$ MPa and $T_c = 304.4$ K), chemical inertness, non-flammability and low cost. The application of sc-CO_2 for metal ions extraction from solid or liquid samples can be accomplished by using proper 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 $C_n$mimNTf$_2$ (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

$C_n$mimNTf$_2$ (n = 2, 4, 6, 8, see Scheme 1) were synthesized via metathetical reaction according to the published method [36]. $C_n$mimBr 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 $Th(NO_3)_4 \cdot 6H_2O$ into deionized water. Carbon dioxide (99.95%, Reijiye, Beijing) was used in all the stripping experiments. All other chemicals were of analytical reagent grade.



Scheme 1. Chemical structures of $C_n$mim$^+$ (n = 2, 4, 6, 8), NTf_2^-.

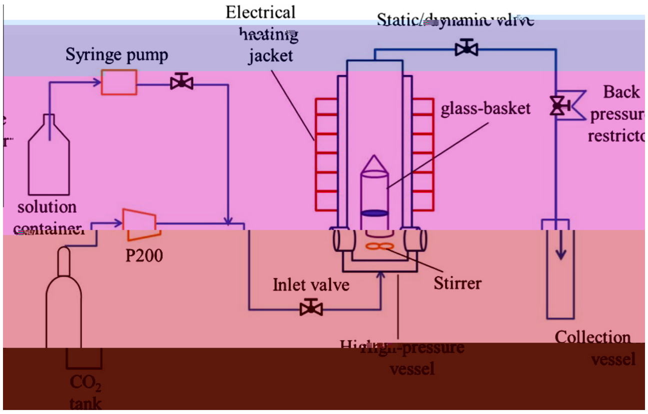
2.2. Methods

The extraction experiments were carried out at room temperature. 0.5 mL of $C_n$mimNTf$_2$ (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 $C_n$mimNTf$_2$ (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 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

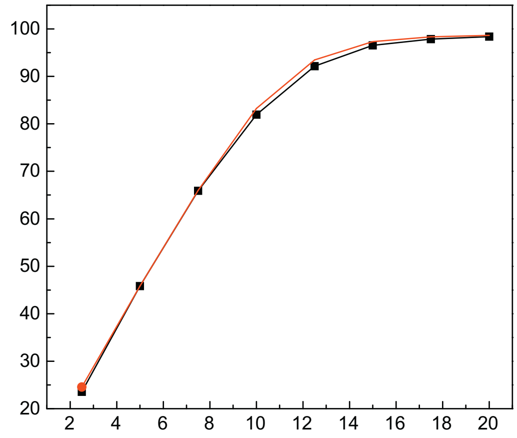
Fig. 1 shows the dependence of the extraction efficiency (*E*) of Th^{4+} on the initial concentration of HTTA in $C_n$mimNTf$_2$. The extraction efficiency increases with an increase in the concentration of HTTA, and reaches nearly 97% when the concentration of HTTA is higher than 12 mmol L^{-1}. The 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



e aqueous phase almost keeps constant at around 5 ± 0.1 mmol L^{-1} with increasing the extraction efficiency of $^{4+}$ from 0% to 98%. Comparing these four extraction systems, e can see that the concentration of NO_3^- has no difference as alkyl chain in the imidazolium cation lengthens from C_2 to This proves that NO_3^- does not participate in the extraction pro- s in all four IL extraction systems. According to the above re- s, there should be a complex of $Th(TTA)_4$ in all four imimNTf$_2$ phases after Th^{4+} is extracted by HTTA from the aque- phase. The extraction may follow a neutral complex mecha- n depicted as:

[redacted]

$$+ 4\mathrm{HTTA}_{(\mathrm{IL})} \rightleftharpoons \mathrm{Th(TTA)}_{4(\mathrm{IL})} + 4\mathrm{H}^{+} \tag{1}$$

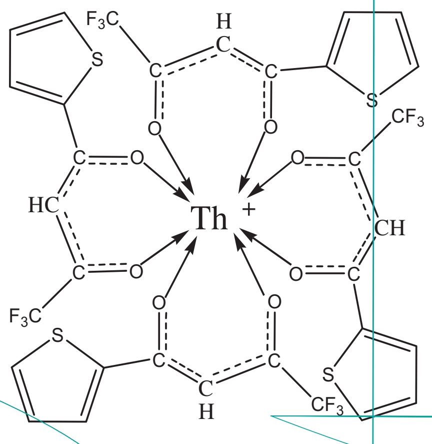
nd the chemical structure of $Th(TTA)_4$ is illustrated in me 3. Based on the neutral complex extraction mechanism, an infer that ILs mainly play a role of solvent in HTTA-$C_n$mim- extraction systems for Th^{4+}. The cation or anion of ILs does not cipate in the extraction process directly. Comparing with the exchange mechanism, the neutral complex mechanism is suf- t to eliminate the possibility of ion exchange of IL. The extrac- of Th^{4+} from aqueous phase by HTTA in $C_n$mimNTf$_2$ is not only ent, but also can eliminate the loss of IL during the extraction ess.

o further confirm the structure of Th^{4+} with TTA^- existing in A-$C_n$mimNTf systems, we employed EXAFS method to deter- e the coordination environment of the inner phase of Th^{4+} n it was extracted by HTTA into $C_n$mimNTf$_2$. The Fourier trans- magnitudes of the EXAFS are shown in Fig. 4. The results of ng the EXAFS data to the single scattering theoretical phase amplitude functions are summarized in Table 1. The Th EXAFS als are dominated by a shell of 8.9 ± 1.5 oxygen atoms directly rdinated to the Th ion at approximately 2.41 ± 0.01 Å, and there o obvious difference in all four IL systems. Contributions from er shells of coordinated atoms are not apparent in each sample. EXAFS measurement shows that the coordination of Th^{4+} is gnificantly different in four different IL systems. Consequently, further proved that the complex is $Th(TTA)_4$ in HTTA-$C_n$mim- $_2$ systems.

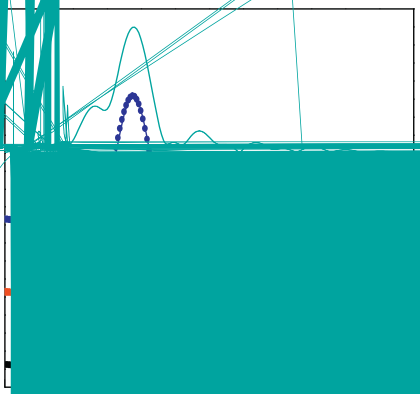
t should be pointed out that, due to the formation of a neutral nplex $Th(TTA)_4$ in the extraction process, losses of IL compo- ts to the aqueous phase can be avoided.

Stripping of Th(IV) by sc-CO$_2$

To find out the optimum stripping condition, we took the C_2- mNTf$_2$ system as an example. In HTTA-C_2mimNTf$_2$ system, sc- $_2$ itself cannot strip Th(IV) from the IL phase due to the low



Scheme 3. Chemical structure of $Th(TTA)_4$.



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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 dis(soluv-523.721ndi)-531.217c-CO

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