

## Stripping of uranium from an ionic liquid medium by TOPO-modified supercritical carbon dioxide

Jing Fu, Qingde Chen & 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, China

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$\text{UO}_2^{2+}$ , which is extracted from the aqueous phase into the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $\text{C}_2\text{mimNTf}_2$ ) ionic liquid phase with octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), can be stripped by supercritical  $\text{CO}_2$ . Trioctylphosphine oxide (TOPO), the modifier added to the supercritical  $\text{CO}_2$  phase, enhances the stripping efficiency by up to 99%.

$\text{UO}_2^{2+}$ , supercritical  $\text{CO}_2$ , stripping, CMPO, ionic liquids

### 1 Introduction

Nowadays, room temperature ionic liquids (ILs) have been considered as the next generation diluents to replace volatile organic compounds (VOCs) in the reprocessing of spent nuclear fuel, especially with respect to actinides and fission products separation [1–3]. In the nuclear industry, tributylphosphate (TBP) is an excellent extractant for uranium in the present commercial PUREX process using kerosene as the diluent. TBP has also been used in the IL system [4,5], but must not be the only choice. Actually, some other extractants, such as octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), diglycolamide, and the so-called “task-specific ILs” bearing phosphoryl groups, which act as both organic solvent and extractant, have been used in the IL system for extracting  $\text{UO}_2^{2+}$  [6–8]. CMPO is a highly effective actinide extractant, which shows superior extraction ability and selectivity for lanthanide and actinide ions in the ILs medium to that in the traditional organic diluents [9–11]. Our research group found that more than 99% of  $\text{UO}_2^{2+}$  ( $0.01 \text{ mol L}^{-1}$ ) can be extracted from the aqueous

phase into  $\text{C}_n\text{mimNTf}_2$  ( $n = 2, 4$ ) by merely  $0.04 \text{ mol L}^{-1}$  of CMPO. Besides, the extraction selectivity of  $\text{UO}_2^{2+}$  from the aqueous phase containing  $\text{Zr}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Cs}^+$ , etc., by CMPO in the  $\text{C}_n\text{mimNTf}_2$  ( $n = 2, 4$ ) is also better than that by TBP in the  $\text{C}_4\text{mimNTf}_2$  [12].

Some IL-based extraction systems exhibit superior extraction efficiency and enhanced selectivity. However, the stripping still remains a challenge [13]. From the application of ILs in the nuclear industry’s viewpoint, a complete cycle including the extraction and stripping steps is necessary to be developed, in which the stripping process is as important as the extraction process. The traditional liquid-liquid stripping method has been tried to recover metal ions from the IL phase.  $\text{UO}_2^{2+}$  can be stripped using the aqueous solution with guanidine carbonate from the CMPO- $\text{C}_n\text{mimNTf}_2$  phase, but the cross-contamination between two phases and the loss of ILs into the aqueous phase cannot be ignored [14]. Electrodeposition is another method to recover the metal ions from the IL phase. This method requires the electrochemical window of IL matching with the reduction potential of the metal ion [15]. Recently, our research group [16] has deposited uranium from the CMPO- $\text{C}_4\text{mimNTf}_2$  system, but the efficiency is only 1.7%. Supercritical  $\text{CO}_2$  (sc- $\text{CO}_2$ ) is considered as a clean solvent because

\*Corresponding author (email: xshen@pku.edu.cn)

CO<sub>2</sub> can be recycled while generating almost no wastes. Owing to the unique solubility properties between sc-CO<sub>2</sub> and ILs, that is, the solubility of sc-CO<sub>2</sub> in IL and the insolubility of IL in sc-CO<sub>2</sub> [17–19], a feasible method to strip metal ions from the IL phase by sc-CO<sub>2</sub> has been provided. Mekki *et al.* [20,21] first demonstrated that the stripping of metal complexes of Cu<sup>2+</sup> and lanthanides (La<sup>3+</sup> and Eu<sup>3+</sup>) coordinated with β-diketone extractants from C<sub>4</sub>mimNTf<sub>2</sub> could be effectively achieved by sc-CO<sub>2</sub>. Wai *et al.* [22] found that UO<sub>2</sub><sup>2+</sup> can be stripped from the TBP-C<sub>4</sub>mimNTf<sub>2</sub> system by sc-CO<sub>2</sub>, in which the complex UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> is formed. Recently, our research group achieved the complete cycle including 2-thenoyltrifluoroacetone (HTTA)-C<sub>n</sub>mimNTf<sub>2</sub>-based extraction of Th<sup>4+</sup> from the aqueous phase and its stripping by sc-CO<sub>2</sub> from the IL phase. Both processes can reach high efficiency and avoid the loss of ILs and the cross-contamination [23].

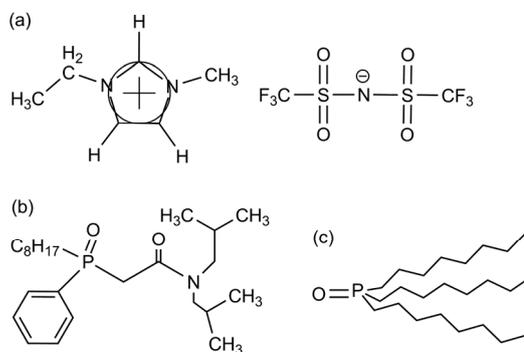
UO<sub>2</sub><sup>2+</sup> in the aqueous phase can be effectively extracted by C<sub>2</sub>mimNTf<sub>2</sub> with CMPO. The fundamental stoichiometry of the UO<sub>2</sub><sup>2+</sup>-CMPO complex in the IL phase is most likely 1:3 [16]. To the best of our knowledge, although CMPO as the extractant in C<sub>2</sub>mimNTf<sub>2</sub> performs excellently for UO<sub>2</sub><sup>2+</sup> extraction, there have been no effective methods so far to strip uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> system with high stripping efficiency, no cross-contamination, and no losses of ILs, as well as the recycle of the IL phase with the extractant. Sc-CO<sub>2</sub> extraction technology has been performed to strip metal ions from the IL phase effectively with or without the modifier (e.g., ethanol or methanol) [20–23]. But the saturated solubility of CMPO in neat sc-CO<sub>2</sub> is only 0.089 mol L<sup>-1</sup> at 60 °C, 20 MPa [24]. Hence, the complex UO<sub>2</sub><sup>2+</sup>-CMPO is hard to dissolve in sc-CO<sub>2</sub>. Only using sc-CO<sub>2</sub> itself or employing ethanol or acetonitrile as the modifier does not strip the complex UO<sub>2</sub><sup>2+</sup>-CMPO out from the IL phase. Therefore, in this paper, we developed an approach to strip the uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> system by sc-CO<sub>2</sub> with a competitive extractant as the modifier. According to the literature, TBP can extract uranium from the aqueous phase or solid matrices into the sc-CO<sub>2</sub> phase [25,26]. However, it does not work to strip uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> phase by sc-CO<sub>2</sub> with TBP as the modifier. Fortunately, we found that the organophosphorus reagent trioctylphosphine oxide (TOPO) as the modifier is effective for the stripping of uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> phase in this work. Meanwhile, the influences of the factors such as pressure, temperature, dynamic stripping time, and the flow rate of modifier on the stripping efficiency of uranium by sc-CO<sub>2</sub> were investigated systematically.

## 2 Experimental

The synthesis of C<sub>2</sub>mimNTf<sub>2</sub> was based on the method in the literature [27]. The analytical grade reagents CMPO

(97%, Strem Chemicals) and trioctylphosphine oxide (TOPO, 99%, Aldrich) were used as received. The chemical structures of C<sub>2</sub>mimNTf<sub>2</sub>, CMPO, and TOPO are shown in Scheme 1. The stripping samples were obtained after extracting UO<sub>2</sub><sup>2+</sup> from the aqueous phase by CMPO-C<sub>2</sub>mimNTf<sub>2</sub>. The concentration of UO<sub>2</sub><sup>2+</sup> was 0.004 mol L<sup>-1</sup> in the C<sub>2</sub>mimNTf<sub>2</sub> phase, which presented a light yellow resulting from the characteristic of the complex of UO<sub>2</sub><sup>2+</sup> with CMPO. All stripping experiments were performed in a lab supercritical fluid extraction apparatus (100 mL, SEPAREX, France), the method of which was described elsewhere [23]. CO<sub>2</sub> (99.95%, Reijiye, China) was used in all experiments. 0.5 mL C<sub>2</sub>mimNTf<sub>2</sub> solution containing 0.004 mol L<sup>-1</sup> of uranium was added in a 10-mL glass-basket, which was fixed in the high-pressure extraction vessel with strong stirring. The stripping process was allowed to take place under dynamic extraction condition, in which the sc-CO<sub>2</sub> and the modifier solution passed continuously through the extraction chamber. The flow rate of CO<sub>2</sub> was fixed at 0.2 g min<sup>-1</sup>, and the modifier was the 0.05 mol L<sup>-1</sup> of TOPO-acetonitrile solution. When the stripping modus operandi was complete, the system was allowed to slowly depressurize and the IL sample was then removed from the cell and analyzed. The stripping efficiency was calculated based on the contents of UO<sub>2</sub><sup>2+</sup> in the initial and the residue IL phases, which were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Leeman, USA) after microwave digestion. The mass spectra of the stripping product and the IL phases were measured with electrospray ionization (ESI/MS) on a Fourier transform ion cyclotron resonance mass spectrometer, APEX IV (Bruker, Germany).

After the stripping experiment, the extraction of UO<sub>2</sub><sup>2+</sup> from the aqueous phase by the recovered IL phase was studied. 0.5 mL of the recovered C<sub>2</sub>mimNTf<sub>2</sub> without addition of new CMPO and 0.5 mL of the aqueous solution containing 0.004 mol L<sup>-1</sup> of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> 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 extraction efficiency



**Scheme 1** Molecular structures of C<sub>2</sub>mimNTf<sub>2</sub> (a), CMPO (b), and TOPO (c).

was calculated based on the contents of  $\text{UO}_2^{2+}$  in the initial and the residual aqueous phases, which were analyzed by ICP-AES.

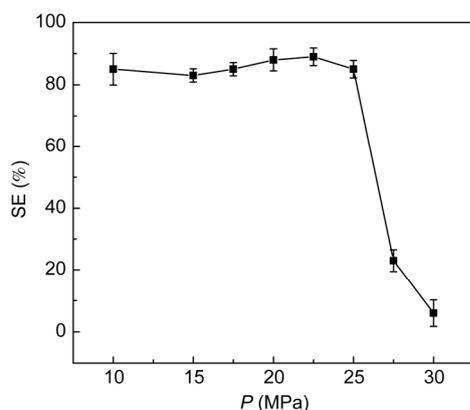
### 3 Results and discussion

#### 3.1 Effect of pressure

The influence of pressure on the stripping efficiency of uranium is shown in Figure 1. The stripping efficiency of uranium increased slightly with an increase in the pressure. However, when the pressure was higher than 25 MPa, the stripping efficiency of uranium reduced dramatically. In general, as the pressure increases, the density of  $\text{CO}_2$  is increased. Thus, the solvability of  $\text{sc-CO}_2$  becomes stronger at higher pressure [28]. However, at a higher density of  $\text{CO}_2$ , the interaction between the fluid and the matrix becomes weaker, resulting from the decrease of diffusion coefficient [29]. In our experiments, we found that after the stripping modus operandi completed, significant volume of acetonitrile dissolved in the IL phase when the experimental pressure was below 25 MPa, but the dissolution of acetonitrile was insignificant when the experimental pressure was higher than 25 MPa. This phenomenon indicates that when the pressure is below 25 MPa, the solubility of TOPO-acetonitrile is good in both  $\text{sc-CO}_2$  phase and the IL phase. Hence, the modified  $\text{sc-CO}_2$  phase interacts with the IL phase sufficiently. However, as the pressure increases, the solubility of the TOPO-acetonitrile in the  $\text{sc-CO}_2$  is higher than that in the IL phase. Thus, most of the modifier is brought out by  $\text{sc-CO}_2$  without interacting with the IL phase adequately, leading to a marked decrease of the stripping efficiency when the pressure is higher than 25 MPa.

#### 3.2 Effect of temperature

The stripping efficiency of uranium from  $\text{C}_2\text{mimNTf}_2$  was

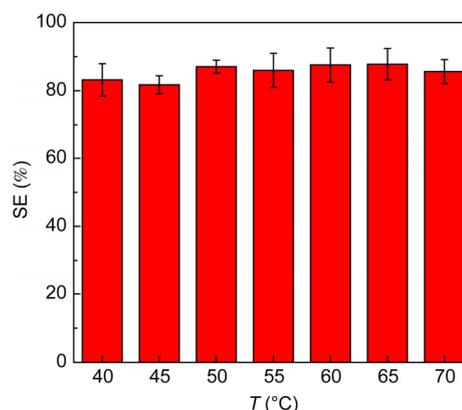


**Figure 1** The influence of pressure on the stripping efficiency of uranium from  $\text{C}_2\text{mimNTf}_2$  at 40 °C, 15 min of the dynamic stripping time, and 0.3  $\text{mL min}^{-1}$  of the modifier.

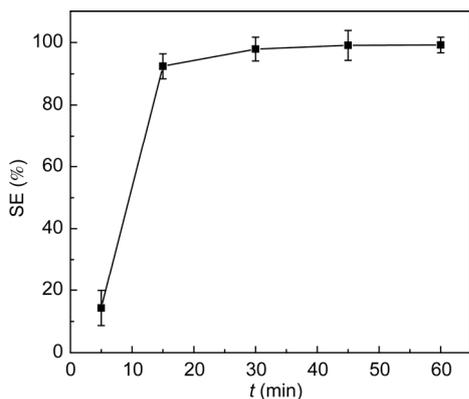
studied at different temperatures. Figure 2 shows that as the temperature increases, the stripping efficiency of uranium almost remains the same. This result indicates that the temperature has no significant effect on the stripping of uranium. Similar trends were also reported in the literature, in which the temperature did not affect notably on the extraction of Pd(II), Bi(III), Mn(II), Au(III), Pt(IV), and Re(VII) from the solid matrix by  $\text{sc-CO}_2$ -containing Cyanex 301 as a ligand [29,30]. However, in the HTTA- $\text{C}_2\text{mimNTf}_2$  system, the stripping efficiency of Th(IV) by  $\text{sc-CO}_2$  decreases as the temperature increases, mainly because of the photosensitiveness and heat-sensitivity of HTTA [23]. In general, as the temperature increases, the density of  $\text{sc-CO}_2$  decreases and the solvability of  $\text{sc-CO}_2$  reduces. However, the extractant, metal complexes, and the modifier in the systems become more soluble in  $\text{sc-CO}_2$  with an increase in temperature [29,31]. Therefore, the effect of temperature on the extraction efficiency of metal ions varies in different systems. For the system in this work, the effect of temperature is not significant, and uranium can be stripped from  $\text{C}_2\text{mimNTf}_2$  with high efficiency in a relatively wide temperature range.

#### 3.3 Effect of dynamic stripping time and flow rate of modifier

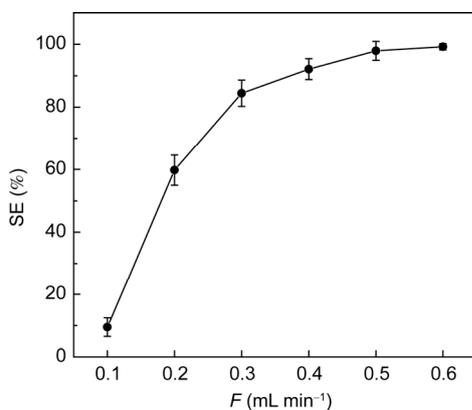
The effect of the dynamic stripping time on the stripping efficiency is shown in Figure 3. At 15 min of the dynamic stripping time, the stripping efficiency is already higher than 90%, which suggests that the complex of uranium readily transports from the IL phase into the  $\text{sc-CO}_2$  phase. After 30 min, the stripping efficiency changes a little. The flow rate of the modifier, which corresponds to the amount of the modifier added in the  $\text{sc-CO}_2$  phase, is another main factor influencing the stripping efficiency. From Figure 4, we can find that the stripping efficiency increases remarkably at first and then reaches a plateau at 0.5  $\text{mL min}^{-1}$  of the flow rate of the modifier.



**Figure 2** The effect of temperature on the stripping efficiency of uranium from  $\text{C}_2\text{mimNTf}_2$  at 20 MPa, 15 min of the dynamic stripping time, and 0.3  $\text{mL min}^{-1}$  of the modifier.



**Figure 3** Dependence of the stripping efficiency of uranium on the dynamic stripping time at 20 MPa, 40 °C, and 0.5 mL min<sup>-1</sup> of the modifier in C<sub>2</sub>mimNTf<sub>2</sub>.



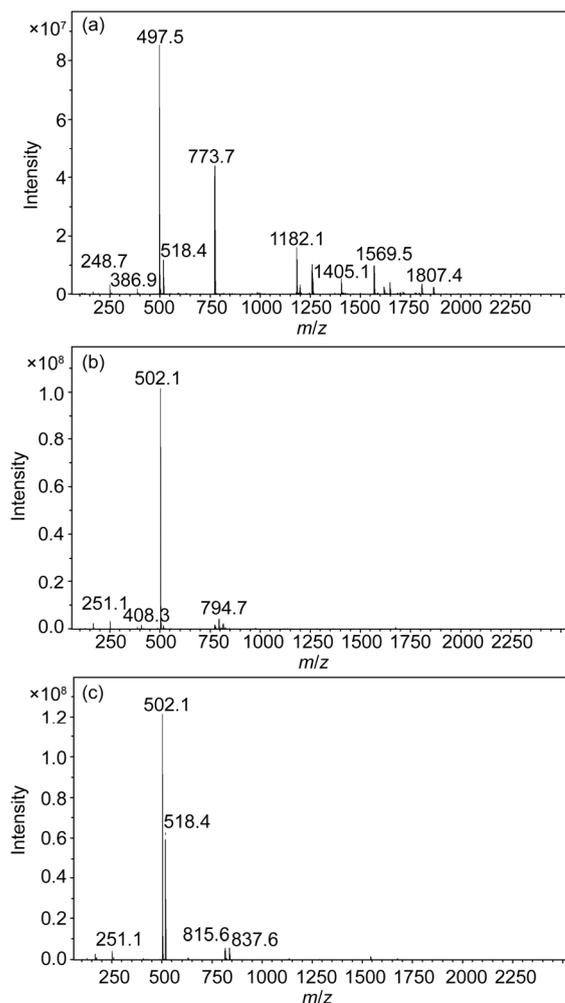
**Figure 4** The effect of the flow rate of the modifier on the stripping efficiency of uranium at 20 MPa, 40 °C, and 30 min of dynamic stripping time from C<sub>2</sub>mimNTf<sub>2</sub>.

### 3.4 Stripping mechanism

The uranium can be effectively transferred from the IL phase into the sc-CO<sub>2</sub> phase with TOPO-acetonitrile solution as the modifier. Acetonitrile as a co-solvent can increase the polarity of CO<sub>2</sub> to enhance the solubility of the complexes of uranium in the modified sc-CO<sub>2</sub>. The stripping efficiency of uranium from the C<sub>2</sub>mimNTf<sub>2</sub> phase can reach over 99%, and about 5% of IL is lost during the stripping experiment under the following condition: 40 °C, 20 MPa, 30 min dynamic stripping, and 0.5 mL min<sup>-1</sup> of the modifier.

We investigated the stripping product and the recovered IL phase by ESI/MS (Figure 5(a, b)). The compositions of the fragments and their corresponding complexes are listed in Table 1. The ESI spectrum of the original IL phase before stripping (Figure 5(c)) is shown as the reference. Because the concentration of uranium in the IL phase is only 0.004 mol L<sup>-1</sup>, the signals of the uranium complexes are too weak to be detected.

Cationic complexes [UO<sub>2</sub>(TOPO)<sub>2</sub>NO<sub>3</sub>NTf<sub>2</sub>·H<sub>3</sub>O]<sup>+</sup>, [UO<sub>2</sub>-



**Figure 5** Positive ESI spectra of the stripping product (a), the recovered IL phase (b), and the original IL phase (c).

(TOPO)<sub>3</sub>NO<sub>3</sub>NTf<sub>2</sub>·2H<sub>2</sub>O-H]<sup>+</sup>, [UO<sub>2</sub>(CMPO)<sub>2</sub>NO<sub>3</sub>·2H<sub>2</sub>O]<sup>+</sup>, and [UO<sub>2</sub>(CMPO)<sub>2</sub>(TOPO)NO<sub>3</sub>·2H<sub>2</sub>O]<sup>+</sup> are observed in the ESI spectrum of the stripping product (Figure 5(a)), which indicates that various kinds of the complexes of UO<sub>2</sub><sup>2+</sup> are formed in the stripping process. TOPO not only competes with CMPO to associate with UO<sub>2</sub><sup>2+</sup>, but also strips UO<sub>2</sub><sup>2+</sup> with CMPO synergistically. According to the above results, one can infer that the affinity of UO<sub>2</sub><sup>2+</sup> with TOPO is larger than that with CMPO, and the complexes of UO<sub>2</sub><sup>2+</sup> associating with TOPO become more soluble in sc-CO<sub>2</sub>. Therefore, with TOPO as the modifier, sc-CO<sub>2</sub> can strip uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> system effectively.

The cationic complexes [C<sub>2</sub>mim-CMPO]<sup>+</sup>, [C<sub>2</sub>mim-TOPO]<sup>+</sup>, and [TOPO-H-TOPO]<sup>+</sup> demonstrate the existence of the extractant CMPO and TOPO in the stripping product. For TOPO, most of them can be easily brought out by sc-CO<sub>2</sub> with acetonitrile, and for CMPO, part of them can be brought out by modified sc-CO<sub>2</sub> as well. Thus, there are signals of CMPO and TOPO in the ESI spectrum (Figure 5(a)). The cationic complexes containing C<sub>2</sub>mim<sup>+</sup> and NTf<sub>2</sub><sup>-</sup>

**Table 1** The compositions of the fragments and their corresponding complexes of the stripping product, the recovered IL phase, and the original IL phase

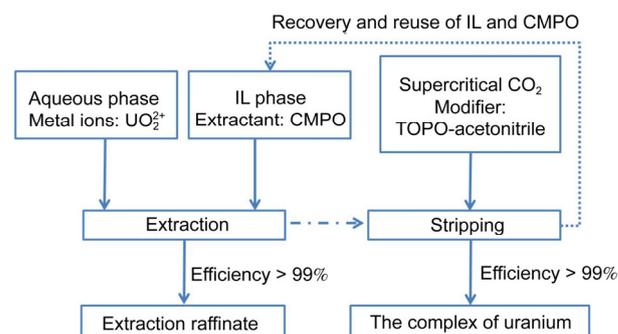
<i>m/z</i>	Cationic complex
The stripping product	
248.7	$[\text{C}_2\text{mim}-\text{TOPO}-\text{H}]^{2+}$
386.9	$[\text{TOPO}-2\text{H}-\text{TOPO}]^{2+}$
497.5	$[\text{C}_2\text{mim}-\text{TOPO}]^+$
518.4	$[\text{C}_2\text{mim}-\text{CMPO}]^+$
773.7	$[\text{TOPO}-\text{H}-\text{TOPO}]^+$
1182.1	$[\text{UO}_2(\text{CMPO})_2\text{NO}_3 \cdot 2\text{H}_2\text{O}]^+$
1405.1	$[\text{UO}_2(\text{TOPO})_2\text{NO}_3\text{NTf}_2 \cdot \text{H}_3\text{O}]^+$
1569.5	$[\text{UO}_2(\text{CMPO})_2(\text{TOPO})\text{NO}_3 \cdot 2\text{H}_2\text{O}]^+$
1807.4	$[\text{UO}_2(\text{TOPO})_3\text{NO}_3\text{NTf}_2 \cdot 2\text{H}_2\text{O}-\text{H}]^+$
The recovered IL phase	
251.1	$[\text{C}_2\text{mim}-\text{NTf}_2-\text{C}_2\text{mim}-\text{H}]^{2+}$
408.3	$[\text{CMPO}-\text{H}]^+$
502.1	$[\text{C}_2\text{mim}-\text{NTf}_2-\text{C}_2\text{mim}]^+$
794.7	$[\text{CMPO}-\text{H}-\text{TOPO}]^+$
The original IL phase	
251.1	$[\text{C}_2\text{mim}-\text{NTf}_2-\text{C}_2\text{mim}-\text{H}]^{2+}$
502.1	$[\text{C}_2\text{mim}-\text{NTf}_2-\text{C}_2\text{mim}]^+$
518.4	$[\text{C}_2\text{mim}-\text{CMPO}]^+$
815.6	$[\text{CMPO}-\text{H}-\text{CMPO}]^+$
837.6	$[\text{CMPO}-\text{Na}-\text{CMPO}]^+$

are observed in the stripping product (Figure 5(a)), which means that the IL is brought out partly by sc-CO<sub>2</sub> with TOPO-acetonitrile. According to the literature, the dissolving capacity of sc-CO<sub>2</sub> for IL can be enhanced significantly, when the sc-CO<sub>2</sub> phase contains some components such as the reactants and polar organic solvents acting as co-solvents [19]. The effect of a co-solvent on the solubility of the ILs in sc-CO<sub>2</sub> mainly depends on its polarity and concentration in sc-CO<sub>2</sub> [32,33]. Therefore, the loss of the IL could be further reduced if the stripping conditions are further optimized.

In the ESI spectrum of the recovered IL phase (Figure 5(b)), the signals of the cationic complexes  $[\text{C}_2\text{mim}-\text{NTf}_2-\text{C}_2\text{mim}]^+$  are observed, which are consistent with those in the ESI spectrum of the original IL phase (Figure 5(c)). The cationic complexes  $[\text{CMPO}-\text{H}]^+$  and  $[\text{CMPO}-\text{H}-\text{TOPO}]^+$  exist in the recovered IL phase. This indicates that some CMPO still exist in the IL phase after stripping. Meanwhile, part of TOPO also remains in the recovered IL phase.

After the stripping experiment, the recovered IL phase was used directly as the extraction phase to extract UO<sub>2</sub><sup>2+</sup> from the aqueous phase again. The concentration of UO<sub>2</sub><sup>2+</sup> remaining in the aqueous phase was less than 1%, which means that the extraction efficiency of UO<sub>2</sub><sup>2+</sup> was greater than 99% by the recovered IL phase.

As mentioned above, TOPO can strip uranium from the IL phase effectively by sc-CO<sub>2</sub> with acetonitrile and the stripping efficiency of uranium reaches over 99%. Combined with our previous work about the extraction of UO<sub>2</sub><sup>2+</sup>

**Scheme 2** A diagram showing the extraction-stripping procedure for uranium.

by CMPO-C<sub>n</sub>mimNTf<sub>2</sub> [12,14], a complete cycle including extraction and stripping processes for UO<sub>2</sub><sup>2+</sup> with both an IL and sc-CO<sub>2</sub> can be established. The whole process is illustrated in Scheme 2. Highly efficient stripping of uranium from the CMPO-C<sub>2</sub>mimNTf<sub>2</sub> system is achieved in this work. In future studies, we will optimize stripping conditions to minimize the loss of the IL and CMPO, and try to eliminate the residual of TOPO in the recovered IL phase.

## 4 Conclusions

The stripping of uranium from the IL phase using the modified sc-CO<sub>2</sub> has been studied. It is found that TOPO is an efficient modifier to facilitate the stripping of uranium from the IL phase and over 99% of uranium could be successfully stripped off using it. The present work demonstrates the feasibility of using sc-CO<sub>2</sub> to strip and promises a highly efficient extraction-stripping cycle for ionic liquids-based uranyl recovery process.

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