

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

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Received February 11, 2014; accepted March 20, 2014; published online September 15, 2014

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 CO_2 . Trioctylphosphine oxide (TOPO), the modifier added to the supercritical CO_2 phase, enhances the stripping efficiency by up to 99%.

UO_2^{2+} , supercritical 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 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 UO_2^{2+} (0.01 mol L^{-1}) can be extracted from the aqueous

phase into $\text{C}_n\text{mimNTf}_2$ ($n = 2, 4$) by merely 0.04 mol L^{-1} of CMPO. Besides, the extraction selectivity of UO_2^{2+} from the aqueous phase containing Zr^{2+} , Eu^{3+} , 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. 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 CO_2 (sc- CO_2) is considered as a clean solvent because

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CO₂ can be recycled while generating almost no wastes. Owing to the unique solubility properties between sc-CO₂ and ILs, that is, the solubility of sc-CO₂ in IL and the insolubility of IL in sc-CO₂ [17–19], a feasible method to strip metal ions from the IL phase by sc-CO₂ has been provided. Mekki *et al.* [20,21] first demonstrated that the stripping of metal complexes of Cu²⁺ and lanthanides (La³⁺ and Eu³⁺) coordinated with β -diketone extractants from C₄mimNTf₂ could be effectively achieved by sc-CO₂. Wai *et al.* [22] found that UO₂²⁺ can be stripped from the TBP-C₄mimNTf₂ system by sc-CO₂, in which the complex UO₂(NO₃)₂(TBP)₂ is formed. Recently, our research group achieved the complete cycle including 2-thenoyltrifluoroacetone (HTTA)-C_nmimNTf₂-based extraction of Th⁴⁺ from the aqueous phase and its stripping by sc-CO₂ from the IL phase. Both processes can reach high efficiency and avoid the loss of ILs and the cross-contamination [23].

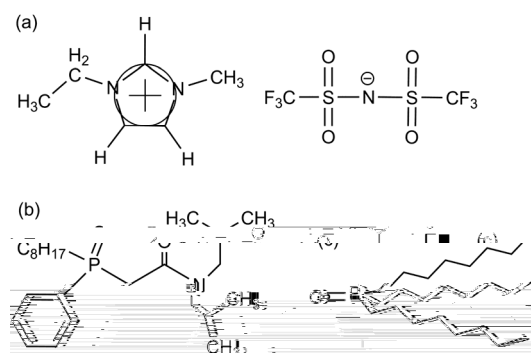
UO₂²⁺ in the aqueous phase can be effectively extracted by C₂mimNTf₂ with CMPO. The fundamental stoichiometry of the UO₂²⁺-CMPO complex in the IL phase is most likely 1:3 [16]. To the best of our knowledge, although CMPO as the extractant in C₂mimNTf₂ performs excellently for UO₂²⁺ extraction, there have been no effective methods so far to strip uranium from the CMPO-C₂mimNTf₂ 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-CO₂ 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-CO₂ is only 0.089 mol L⁻¹ at 60 °C, 20 MPa [24]. Hence, the complex UO₂²⁺-CMPO is hard to dissolve in sc-CO₂. Only using sc-CO₂ itself or employing ethanol or acetonitrile as the modifier does not strip the complex UO₂²⁺-CMPO out from the IL phase. Therefore, in this paper, we developed an approach to strip the uranium from the CMPO-C₂mimNTf₂ system by sc-CO₂ 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-CO₂ phase [25,26]. However, it does not work to strip uranium from the CMPO-C₂mimNTf₂ phase by sc-CO₂ 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-C₂mimNTf₂ 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-CO₂ were investigated systematically.

2 Experimental

The synthesis of C₂mimNTf₂ 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 C₂mimNTf₂, CMPO, and TOPO are shown in Scheme 1. The stripping samples were obtained after extracting UO₂²⁺ from the aqueous phase by CMPO-C₂mimNTf₂. The concentration of UO₂²⁺ was 0.004 mol L⁻¹ in the C₂mimNTf₂ phase, which presented a light yellow resulting from the characteristic of the complex of UO₂²⁺ 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]. CO₂ (99.95%, Reijiye, China) was used in all experiments. 0.5 mL C₂mimNTf₂ solution containing 0.004 mol L⁻¹ 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-CO₂ and the modifier solution passed continuously through the extraction chamber. The flow rate of CO₂ was fixed at 0.2 g min⁻¹, and the modifier was the 0.05 mol L⁻¹ of TOPO-acetonitrile solution. When the stripping modulus 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 UO₂²⁺ 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 UO₂²⁺ from the aqueous phase by the recovered IL phase was studied. 0.5 mL of the recovered C₂mimNTf₂ without addition of new CMPO and 0.5 mL of the aqueous solution containing 0.004 mol L⁻¹ of UO₂(NO₃)₂ 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 C₂mimNTf₂ (a), CMPO (b), and TOPO (c).

was calculated based on the contents of 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 CO_2 is increased. Thus, the solvability of sc-CO_2 becomes stronger at higher pressure [28]. However, at a higher density of 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 modulus 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 sc-CO_2 phase and the IL phase. Hence, the modified sc-CO_2 phase interacts with the IL phase sufficiently. However, as the pressure increases, the solubility of the TOPO-acetonitrile in the sc-CO_2 is higher than that in the IL phase. Thus, most of the modifier is brought out by 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

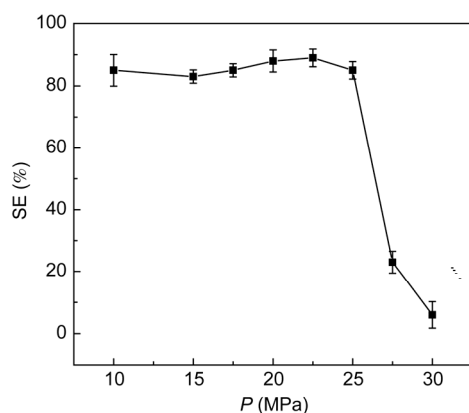


Figure 1 The influence of pressure on the stripping efficiency of uranium from $\text{C}_2\text{mimNTf}_2$ at 40 °C, 15 min of the dynamic stripping time, and 0.3 mL min^{-1} of the modifier.

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 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 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 sc-CO_2 decreases and the solvability of sc-CO_2 reduces. However, the extractant, metal complexes, and the modifier in the systems become more soluble in 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 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 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 mL min^{-1} of the flow rate of the modifier.

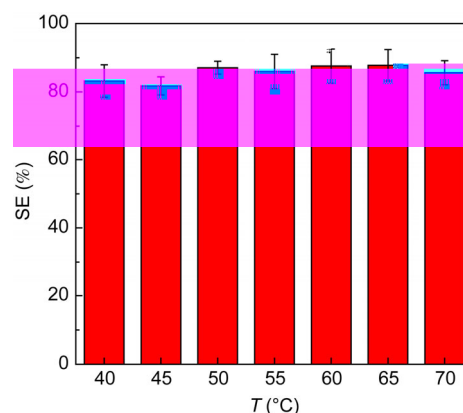


Figure 2 The effect of temperature on the stripping efficiency of uranium from $\text{C}_2\text{mimNTf}_2$ at 20 MPa, 15 min of the dynamic stripping time, and 0.3 mL min^{-1} of the modifier.

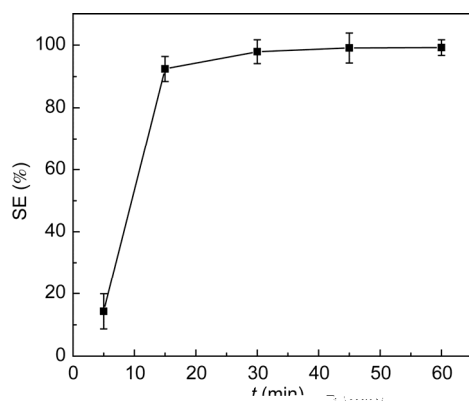


Figure 3 Dependence of the stripping efficiency of uranium on the dynamic stripping time at 20 MPa, 40 °C, and 0.5 mL min⁻¹ of the modifier in C₂mimNTf₂.

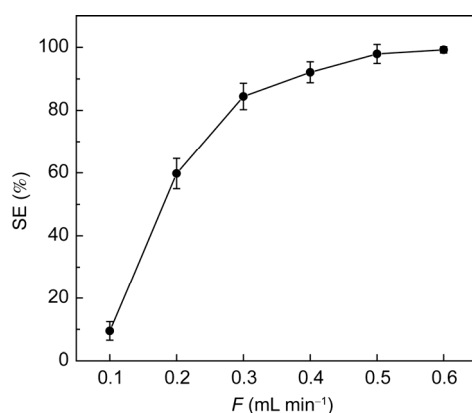


Figure 4 The effect of the flow rate of the modifier on the stripping efficiency of uranium at 20 MPa, 40 °C, and 30 min of dynamic stripping time from C₂mimNTf₂.

3.4 Stripping mechanism

The uranium can be effectively transferred from the IL phase into the sc-CO₂ phase with TOPO-acetonitrile solution as the modifier. Acetonitrile as a co-solvent can increase the polarity of CO₂ to enhance the solubility of the complexes of uranium in the modified sc-CO₂. The stripping efficiency of uranium from the C₂mimNTf₂ 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⁻¹ 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⁻¹, the signals of the uranium complexes are too weak to be detected.

Cationic complexes [UO₂(TOPO)₂NO₃NTf₂·H₃O]⁺, [UO₂-

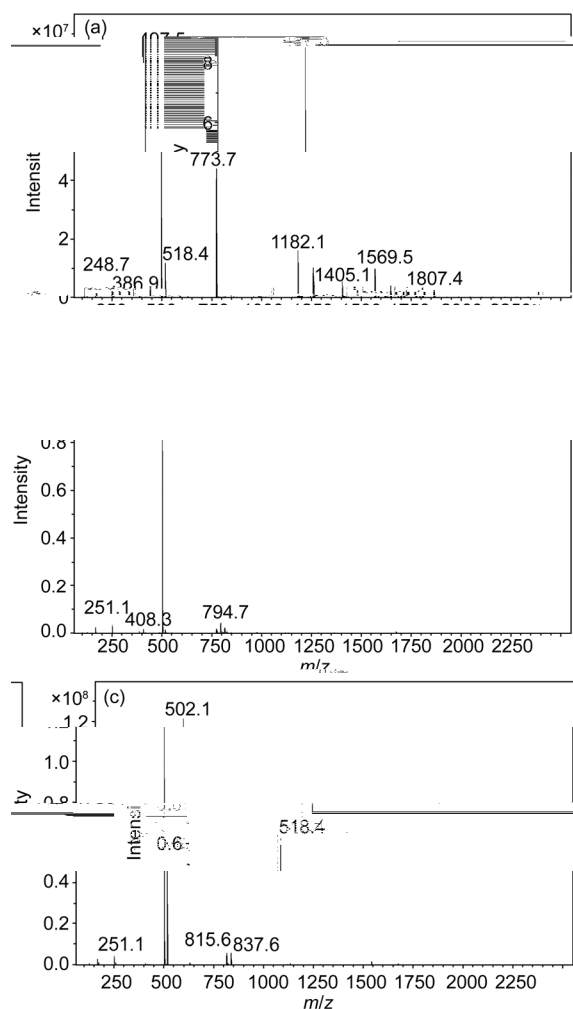


Figure 5 Positive ESI spectra of the stripping product (a), the recovered IL phase (b), and the original IL phase (c).

(TOPO)₃NO₃NTf₂·2H₂O-H]⁺, [UO₂(CMPO)₂NO₃·2H₂O]⁺, and [UO₂(CMPO)₂(TOPO)NO₃·2H₂O]⁺ are observed in the ESI spectrum of the stripping product (Figure 5(a)), which indicates that various kinds of the complexes of UO₂²⁺ are formed in the stripping process. TOPO not only competes with CMPO to associate with UO₂²⁺, but also strips UO₂²⁺ with CMPO synergistically. According to the above results, one can infer that the affinity of UO₂²⁺ with TOPO is larger than that with CMPO, and the complexes of UO₂²⁺ associating with TOPO become more soluble in sc-CO₂. Therefore, with TOPO as the modifier, sc-CO₂ can strip uranium from the CMPO-C₂mimNTf₂ system effectively.

The cationic complexes [C₂mim-CMPO]⁺, [C₂mim-TOPO]⁺, and [TOPO-H-TOPO]⁺ 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-CO₂ with acetonitrile, and for CMPO, part of them can be brought out by modified sc-CO₂ as well. Thus, there are signals of CMPO and TOPO in the ESI spectrum (Figure 5(a)). The cationic complexes containing C₂mim⁺ and NTf₂⁻

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

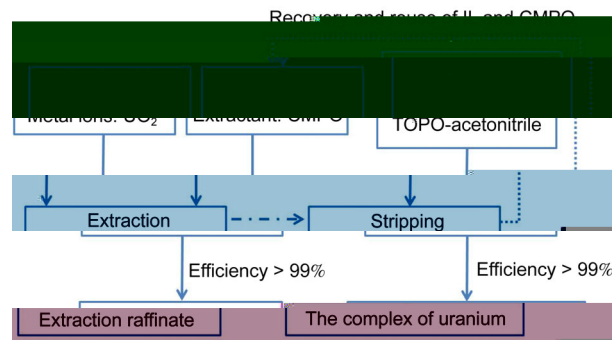
<i>m/z</i>	Cationic complex
The stripping product	
248.7	[C ₂ mim-TOPO-H] ²⁺
386.9	[TOPO-2H-TOPO] ²⁺
497.5	[C ₂ mim-TOPO] ⁺
518.4	[C ₂ mim-CMPO] ⁺
773.7	[TOPO-H-TOPO] ⁺
1182.1	[UO ₂ (CMPO) ₂ NO ₃ ·2H ₂ O] ⁺
1405.1	[UO ₂ (TOPO) ₂ NO ₃ NTf ₂ ·H ₃ O] ⁺
1569.5	[UO ₂ (CMPO) ₂ (TOPO)NO ₃ ·2H ₂ O] ⁺
1807.4	[UO ₂ (TOPO) ₃ NO ₃ NTf ₂ ·2H ₂ O-H] ⁺
The recovered IL phase	
251.1	[C ₂ mim-NTf ₂ -C ₂ mim-H] ²⁺
408.3	[CMPO-H] ⁺
502.1	[C ₂ mim-NTf ₂ -C ₂ mim] ⁺
794.7	[CMPO-H-TOPO] ⁺
The original IL phase	
251.1	[C ₂ mim-NTf ₂ -C ₂ mim-H] ²⁺
502.1	[C ₂ mim-NTf ₂ -C ₂ mim] ⁺
518.4	[C ₂ mim-CMPO] ⁺
815.6	[CMPO-H-CMPO] ⁺
837.6	[CMPO-Na-CMPO] ⁺

are observed in the stripping product (Figure 5(a)), which means that the IL is brought out partly by sc-CO₂ with TOPO-acetonitrile. According to the literature, the dissolving capacity of sc-CO₂ for IL can be enhanced significantly, when the sc-CO₂ 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-CO₂ mainly depends on its polarity and concentration in sc-CO₂ [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 [C₂mim-NTf₂-C₂mim]⁺ are observed, which are consistent with those in the ESI spectrum of the original IL phase (Figure 5(c)). The cationic complexes [CMPO-H]⁺ and [CMPO-H-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 UO₂²⁺ from the aqueous phase again. The concentration of UO₂²⁺ remaining in the aqueous phase was less than 1%, which means that the extraction efficiency of UO₂²⁺ was greater than 99% by the recovered IL phase.

As mentioned above, TOPO can strip uranium from the IL phase effectively by sc-CO₂ with acetonitrile and the stripping efficiency of uranium reaches over 99%. Combined with our previous work about the extraction of UO₂²⁺



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

by CMPO-C_nmimNTf₂ [12,14], a complete cycle including extraction and stripping processes for UO₂²⁺ with both an IL and sc-CO₂ can be established. The whole process is illustrated in Scheme 2. Highly efficient stripping of uranium from the CMPO-C₂mimNTf₂ 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-CO₂ 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-CO₂ to strip and promises a highly efficient extraction-stripping cycle for ionic liquids-based uranyl recovery process.

This work was supported by the National Natural Science Foundation of China (91226112).

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