



# Improvement of the cloud point extraction of uranyl ions by the addition of ionic liquids



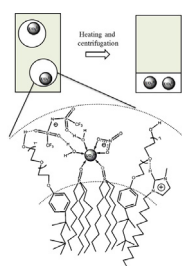
Song Gao, Taoxiang Sun, Qingde Chen, Xinghai Shen\*

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

## HIGHLIGHTS

- $C_{11}mimNTf_2$  improves cloud point extraction of  $UO_2^{2+}$  with neutral extractant.
- The extraction efficiency keeps high at both nearly neutral and acidic condition.
- The addition of  $C_4mimNTf_2$  increases the separation factor of  $UO_2^{2+}$  and  $La^{3+}$ .
- The interaction of the IL anion with micelle induces the synergistic effect.
- TOPO,  $NTf_2^-$  and  $NO_3^-$  establish a soft template for  $UO_2^{2+}$  in the micelle.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 27 April 2013  
Received in revised form 22 August 2013  
Accepted 8 October 2013  
Available online 16 October 2013

### Keywords:

Uranium  
Cloud point extraction  
Ionic liquids

## ABSTRACT

The cloud point extraction (CPE) of uranyl ions by different kinds of extractants in Triton X-114 (TX-114) micellar solution was investigated upon the addition of ionic liquids (ILs) with various anions, i.e., bromide ( $Br^-$ ), tetrafluoroborate ( $BF_4^-$ ), hexafluorophosphate ( $PF_6^-$ ) and bis[(trifluoromethyl)sulfonyl]imide ( $NTf_2^-$ ). A significant increase of the extraction efficiency was found on the addition of  $NTf_2^-$  based ILs when using neutral extractant tri-octylphosphine oxide (TOPO), and the extraction efficiency kept high at both nearly neutral and high acidity. However, the CPE with acidic extractants, e.g., bis(2-ethylhexyl) phosphoric acid (HDEHP) and 8-hydroxyquinoline (8-HQ) which are only effective at nearly neutral condition, was not improved by ILs. The results of zeta potential and  $^{19}F$  NMR measurements indicated that the anion  $NTf_2^-$  penetrated into the TX-114 micelles and was enriched in the surfactant-rich phase during the CPE process. Meanwhile,  $NTf_2^-$  may act as a counterion in the CPE of  $UO_2^{2+}$  by TOPO. Furthermore, the addition of IL increased the separation factor of  $UO_2^{2+}$  and  $La^{3+}$ , which implied that in the micelle TOPO,  $NTf_2^-$  and  $NO_3^-$  established a soft template for  $UO_2^{2+}$ . Therefore, the combination of CPE and IL provided a supramolecular recognition to concentrate  $UO_2^{2+}$  efficiently and selectively.

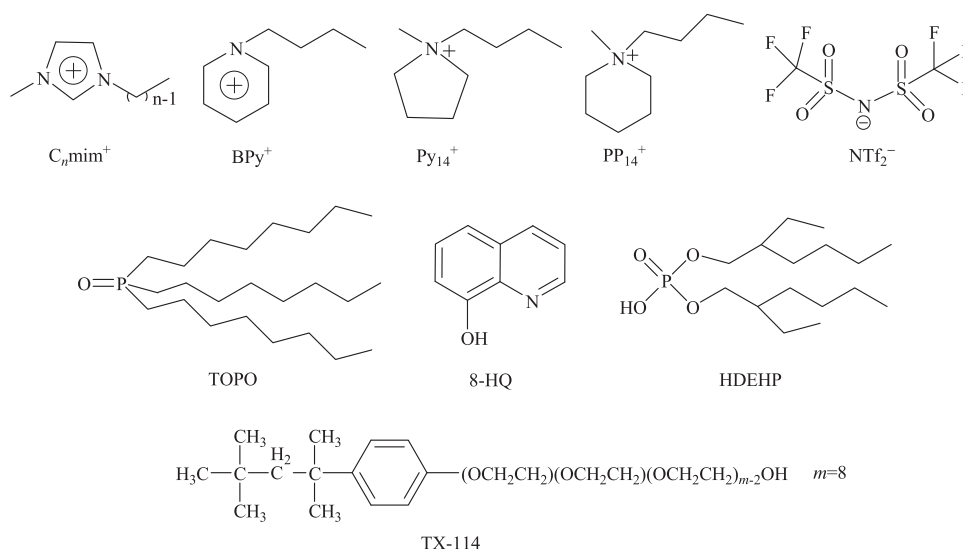
© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Cloud point extraction (CPE), a micelle-mediated process, has become one of the most preferred preconcentration and separation methods improving the sensitivity in trace metal ions determination and acting as an alternative to liquid–liquid extraction, owing

to several advantages including high efficiency and concentration factor, low cost, safety, environmentally friendly nature and versatility offered by this particular technique [1–4]. The methodology used is based on the fact that the micellar solution of non-ionic surfactants becomes turbid and separates into a concentrated phase containing most of the surfactant and a dilute aqueous phase, when heated beyond a temperature called cloud point (CP). The hydrophobic metallic chelates can remain preferentially in the micellar phase, thus being extracted into the surfactant-rich phase at a temperature above CP [2,4].

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



**Scheme 1.** The structures of the IL cations, the IL anion  $NTf_2^-$ , the surfactant TX-114, and the extractants used in this work.

CPE has been used to design efficient extraction procedures for the separation, preconcentration or purification of a variety of metal ions, such as transition metal ions (e.g., Pb(II), Cu(II)) [5–7] and rare earth metal ions (e.g., Gd(III), Eu(III)) [8,9]. Furthermore, it can be incorporated into several analytical techniques such as Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [2]. Uranium is a significant element acting as nuclear fuel for electricity production in power plants, which is also known to cause acute toxicological effects for human [10]. Hence, for both economy and environmental safety, it needs monitoring and recovering from the aqueous solution derived from both fabrication and reprocessing of spent nuclear fuel, which is usually controlled at a high acidic [11]. CPE has been used in the preconcentration of U(VI) for analysis and recovery [10,12–15]. The hydrophobic chelating agents, such as dibenzoylmethane (DBM) [10], 8-hydroxyquinoline (8-HQ) [13] and 1-(2-pyridylazo)-2-naphthol (PAN) [14] have been introduced into the CPE procedure of U(VI). The extraction efficiency of  $UO_2^{2+}$  by CPE using acidic extractants is usually very high at nearly neutral conditions but limited at high acidity [13]. The neutral extractant tributyl phosphate (TBP), which has high extraction efficiency at acidic condition in liquid–liquid extraction system, was also applied in the CPE of  $UO_2^{2+}$ . But the maximum efficiency was only 60% at pH 4 and decreased to 10% at pH 2 [15]. Thus, an important improvement of the CPE method is to make it efficiently apply at both nearly neutral and acidic conditions.

It has been demonstrated that CPE can be improved by many methods, e.g., changing the micellization of surfactant, increasing the solubility of micelles and optimizing the extractants. The first two methods are related to the physicochemical properties of a non-ionic surfactant solution, which can be adjusted by adding modifiers, e.g., ionic surfactants [16–22]. For example, a CPE procedure based on a mixed surfactant medium consisting of the anionic surfactant sodium dodecyl sulfate (SDS) and the non-ionic Triton X-114 (TX-114) has been designed to extract Cr(III) [16]. The above system combines both the hydrophobic and electrostatic interactions within the same extraction system.

Ionic liquids (ILs), which are composed of organic cations and organic/inorganic anions, have received increasing attention in many research fields because of their unique properties such as low melting points, negligible vapor pressure, non-flammability, and environmental benign [23–28]. Recently, both hydrophilic ILs, e.g., 1-alkyl-3-methylimidazolium bromide ( $C_n\text{mimBr}$ ) [29],

1-alkyl-3-methylimidazolium tetrafluoroborate ( $C_n\text{mimBF}_4$ ) [30–32] and hydrophobic ILs, e.g., 1-butyl-3-methylimidazolium hexafluorophosphate ( $C_4\text{mimPF}_6$ ) [33,34], were utilized in the modification of the physicochemical properties of the aqueous solutions of surfactants [29–37]. Also, the interaction mechanisms between ILs and micelles have been investigated. It was found that the properties of micellar solution such as critical micellization concentration (CMC), aggregation number, aggregate size, and dipolarity of micellar pseudo-phase can be altered by the addition of ILs. Although the modifications of these properties are significant, their practical applications are very few. Besides, ILs have received increasing attention in liquid–liquid extraction of metal ions because of their unique properties and they can provide an ionic environment for metal complexes, which improves the extraction efficiency [23–28]. A possible strategy is to introduce ILs in CPE to improve the extraction of metal ions. As far as we know, the IL  $C_4\text{mimPF}_6$  was reported to synergistically enhance the CPE of Ni(II) using diethyldithiocarbamate (DDTC) as extractant [38]. However, the system is only effective at pH above 6, and the mechanism is not clear [38].

In this work, we try to study the influence of ILs with different anions and cations, e.g.,  $C_4\text{mimBr}$ ,  $C_4\text{mimBF}_4$ ,  $C_4\text{mimPF}_6$ ,  $C_n\text{mimNTf}_2$  ( $NTf_2^-$  is bis[(trifluoromethyl)sulfonyl]imide,  $n = 4, 6, 8, 10, 12$ ) on CPE of  $UO_2^{2+}$ . Different kinds of extractants are used, including tri-octylphosphine oxide (TOPO), 8-HQ and bis(2-ethylhexyl) phosphoric acid (HDEHP). The structures of the IL cations, the IL anion  $NTf_2^-$ , the surfactant TX-114, and the extractants used in this work are shown in Scheme 1. More importantly, we try to give an understanding of the mechanism of CPE in the conjunction with IL to separate metal ions.

## 2. Experimental

### 2.1. Materials

TX-114 (>98%) was obtained from Alfa Aesar and used as received.  $C_4\text{mimBr}$ ,  $C_4\text{mimBF}_4$ ,  $C_4\text{mimPF}_6$ ,  $LiNTf_2$ ,  $BuPyNTf_2$  ( $BuPy^+$  is 1-butylpyridinium),  $Py_{1,4}NTf_2$  ( $Py_{1,4}^+$  is N-butyl-N-methylpyrrolidinium) and  $PP_{1,4}NTf_2$  ( $PP_{1,4}^+$  is N-butyl-N-methylpiperidinium) were purchased from Lanzhou Institute of Chemical Physics, China, and their purities were all over 99%.  $C_n\text{mimNTf}_2$  ( $n = 4, 6, 8, 10, 12$ ) were synthesized via

metathetical reaction and purified according to the method in the literature [39]. HDEHP (CP, Sinopharm) was purified by copper salt crystallization [40]. TOPO (Acros), 8-HQ (Sinopharm), SDS (Beijing Chemical Plant), sodium dodecyl sulfonate (SDSN, Sinopharm), Cetyltrimethylammonium bromide (CTAB, Sinopharm),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Chemapol) and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Beijing Chemical Plant) were of analytical grade and used without further purification.

## 2.2. Instruments and methods

In a typical CPE process, 10 mL of the aqueous solution containing TX-114 ( $10 \text{ mmol dm}^{-3}$ ), an IL ( $1 \text{ mmol dm}^{-3}$ ),  $\text{NaNO}_3$  ( $0.1 \text{ mol dm}^{-3}$ ), an extractant ( $0.5 \text{ mmol dm}^{-3}$ ), and  $\text{UO}_2(\text{NO}_3)_2$  ( $0.05 \text{ mmol dm}^{-3}$ ) were shaken for 2 h followed by standing for 2 h at  $70^\circ\text{C}$ . These experimental conditions were chosen to minimize the volume of surfactant-rich phase and to obtain a suitable efficiency range to discuss (see ESI). Separation of the two phases was achieved by centrifugation for 5 min at 4000 rpm. The aqueous phase was removed and the content of  $\text{UO}_2^{2+}$  was analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Leeman, USA). The extraction efficiency  $E$  was calculated by the following equations:

$$E = \frac{C_i V_i - C_f V_f}{C_i V_i} \times 100\%$$

where  $C_i$  is the initial concentration of metal ion in the micellar solution,  $C_f$  is the final concentration of metal ion in aqueous phase after CPE,  $V_i$  is the volume of the micellar solution and  $V_f$  is the volume of aqueous phase after CPE.

The zeta potential experiments were performed on a Nano ZS90 instrument (Malvern, UK).  $^{19}\text{F}$  NMR spectra were recorded on an AV400 MHz NMR spectrometer (Bruker, Germany) and the concentration of  $\text{NTf}_2^-$  in the surfactant-rich phase was obtained by the area ratio of  $^{19}\text{F}$  NMR signal of  $\text{NTf}_2^-$  to the  $-\text{CF}_3$  peak of benzotrifluoride ( $\text{C}_6\text{H}_5\text{CF}_3$ ). In detail, the surfactant-rich phase was diluted with ethanol to 1 mL. Then approximate  $300 \mu\text{L}$  samples were added to an NMR tube within a stem coaxial capillary tube containing  $\text{C}_6\text{H}_5\text{CF}_3$  dissolved in *d*-acetone as external reference. Area integral of each peak near  $-81.10 \text{ ppm}$ , which referred to the assigned value 1.00 of  $-63.90 \text{ ppm}$ , was proportional to the  $\text{NTf}_2^-$  concentration.

## 3. Results and discussion

### 3.1. Effect of ILs on CPE

Four imidazolium based ILs with different anions, i.e.,  $\text{C}_4\text{mimBr}$ ,  $\text{C}_4\text{mimBF}_4$ ,  $\text{C}_4\text{mimPF}_6$ ,  $\text{C}_4\text{mimNTf}_2$  were tested for CPE of  $\text{UO}_2^{2+}$  with a neutral extractant TOPO in TX-114 micellar solution and the results are shown in Fig. 1. The extraction efficiency is only about 45% in the absence of ILs.  $\text{C}_4\text{mimBr}$  and  $\text{C}_4\text{mimPF}_6$  show little effect on  $\text{UO}_2^{2+}$  extraction and  $\text{C}_4\text{mimBF}_4$  decreases the extraction efficiency. On the contrary, the extraction efficiency shows an obvious increase to nearly 75% as the hydrophobic IL  $\text{C}_4\text{mimNTf}_2$  is added. Other  $\text{NTf}_2^-$  based ILs with different cations, i.e.,  $\text{BuPy}^+$ ,  $\text{Py}_{1,4}^+$  and  $\text{PP}_{1,4}^+$ , provide similar effect on CPE. Meanwhile, the addition of  $\text{LiNTf}_2$  also improves the efficiency to 63%. All above results imply that  $\text{NTf}_2^-$  plays an important role in the extraction. However, in the absence of the extractant TOPO, the addition of  $\text{C}_4\text{mimNTf}_2$  shows no effect on the extraction (Fig. S3). For comparison, three common ionic surfactants, i.e., SDS, SDSN and CTAB, were also used as additives at the same molar concentrations as the ionic liquids. The additions of SDS and SDSN improve the extraction efficiencies to 64% and 49%, respectively, lower than that in  $\text{C}_n\text{mimNTf}_2$  system.

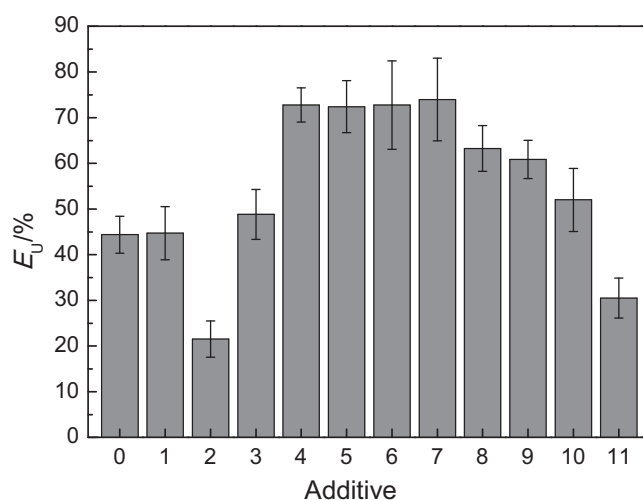


Fig. 1. The CPE efficiency of  $\text{UO}_2^{2+}$  by TOPO in the absence (0) and presence of  $1 \text{ mmol dm}^{-3}$  of  $\text{C}_4\text{mimBr}$  (1),  $\text{C}_4\text{mimBF}_4$  (2),  $\text{C}_4\text{mimPF}_6$  (3),  $\text{C}_4\text{mimNTf}_2$  (4),  $\text{BuPyNTf}_2$  (5),  $\text{Py}_{1,4}\text{NTf}_2$  (6),  $\text{PP}_{1,4}\text{NTf}_2$  (7),  $\text{LiNTf}_2$  (8), SDS (9), SDSN (10), CTAB (11).

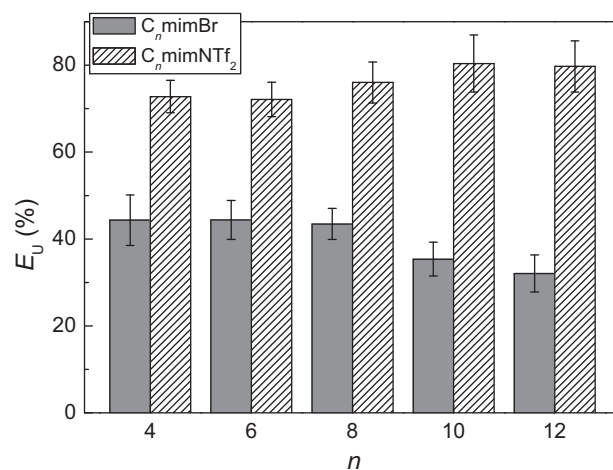


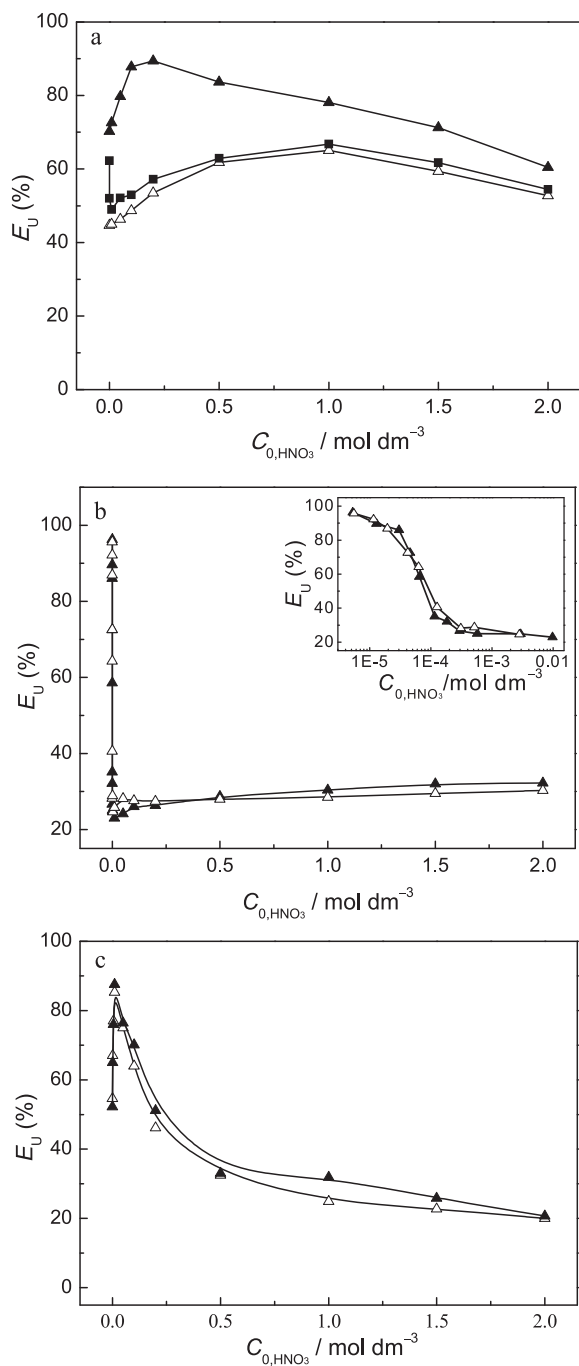
Fig. 2. The CPE efficiency of  $\text{UO}_2^{2+}$  by TOPO in the presence of  $\text{C}_n\text{mimBr}$  ( $1 \text{ mmol dm}^{-3}$ ) and  $\text{C}_n\text{mimNTf}_2$  ( $1 \text{ mmol dm}^{-3}$ ) with the variation of the alkyl length of imidazolium cation.

However, the addition of CTAB reduces the extraction efficiency to 34%.

Fig. 2 shows the effect of the alkyl length of the imidazolium cation on the extraction efficiency. In TOPO- $\text{C}_n\text{mimNTf}_2$  systems, while the extraction efficiency is enhanced greatly by the presence of ILs, it changes to a small extent within the scope from 70% to 80% as the alkyl moiety lengthens from  $\text{C}_4$  to  $\text{C}_{12}$ . Especially,  $\text{C}_{10}\text{mimNTf}_2$  and  $\text{C}_{12}\text{mimNTf}_2$  increase the extraction efficiency a little more obviously. In contrast, on the addition of  $\text{C}_n\text{mimBr}$  the extraction efficiency changes slightly when the alkyl moiety changes from  $\text{C}_4$  to  $\text{C}_8$ , but decreases when the alkyl chain lengthens to  $\text{C}_{10}$  and  $\text{C}_{12}$ . Once again, one can see that  $\text{NTf}_2^-$  plays an important role in the improvement of CPE of  $\text{UO}_2^{2+}$  by TOPO in TX-114 micellar solution.

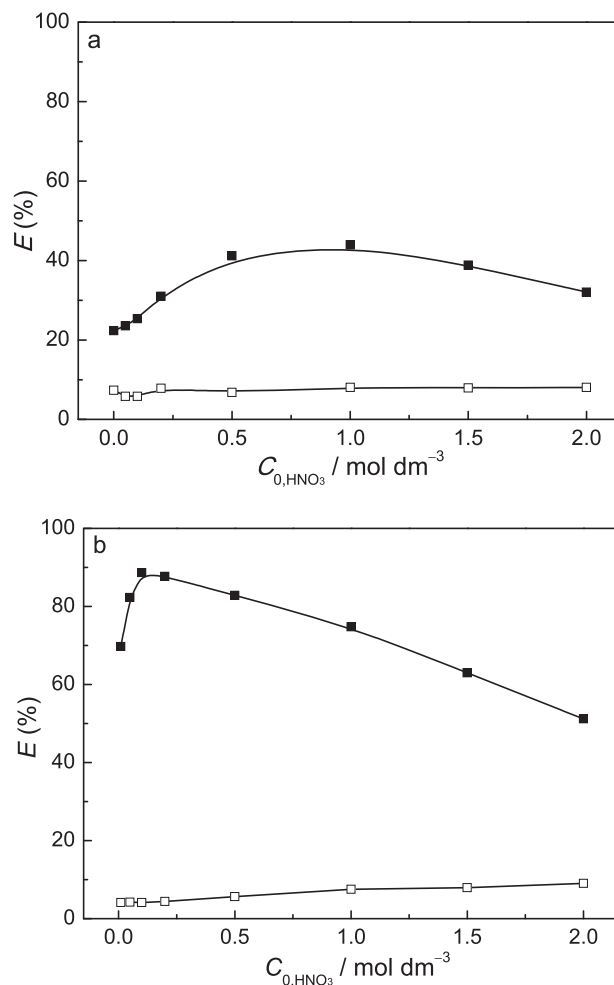
### 3.2. Effect of acidity on CPE

The effect of ILs on CPE of  $\text{UO}_2^{2+}$  by TOPO was also examined in different concentrations of nitric acid (see Fig. 3a). In the absence of ILs, TOPO displays relatively low extraction efficiency in nearly neutral condition, and the extraction efficiency increases when the acidity becomes high, due to the increase of the concentration of



**Fig. 3.** Effect of the acidity on the CPE efficiency of  $\text{UO}_2^{2+}$  by different extractants (TOPO (a), 8-HQ (b), HDEHP (c)) in the absence ( $\Delta$ ) and presence of  $1 \text{ mmol dm}^{-3}$  of  $\text{C}_4\text{mimNTf}_2$  ( $\blacktriangle$ ) or  $1 \text{ mmol dm}^{-3}$  of SDS ( $\blacksquare$ ). The inset is the magnifying plot from  $3 \times 10^{-6}$  to  $0.015 \text{ mol dm}^{-3}$  of 8-HQ.

the counterion  $\text{NO}_3^-$ . The extraction efficiency begins to decrease at the  $1 \text{ mol dm}^{-3}$  of acid concentration, owing to the competition between  $\text{UO}_2^{2+}$  and  $\text{H}^+$  to coordinate with TOPO. As  $\text{C}_4\text{mimNTf}_2$  is added into TOPO system, the extraction efficiency keeps high at both low and high acidities, with a trend similar to that in the absence of IL, except a lower  $\text{HNO}_3$  concentration corresponding to the maximum of  $E_U$ . When no extra  $\text{HNO}_3$  is added, the extraction efficiency is improved on the addition of SDS. However, as extra  $\text{HNO}_3$  is added, the added SDS shows little influence on the efficiency. This may be attributed to the protonation of the anion of SDS.



**Fig. 4.** The extraction efficiency of  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$  depending on  $C_{0,\text{HNO}_3}$  in the separation of  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$  by TOPO in the absence (a) and presence (b) of  $1 \text{ mmol dm}^{-3}$  of  $\text{C}_4\text{mimNTf}_2$ .  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$  coexist in aqueous phase and their initial concentrations are both  $0.05 \text{ mol dm}^{-3}$ .

On the contrary, the extraction efficiency in the CPE of  $\text{UO}_2^{2+}$  using 8-HQ and HDEHP decreases dramatically on the addition of acid and cannot be improved by the addition of  $1 \text{ mmol dm}^{-3}$  of  $\text{C}_4\text{mimNTf}_2$  (Fig. 3b and c). The extraction efficiency of 8-HQ is  $\sim 90\%$  when no extra acid exists, and decreases rapidly as only  $0.001 \text{ mol dm}^{-3}$  of  $\text{HNO}_3$  added, due to the fact that the neutral species  $[\text{UO}_2-(8\text{-HQ})_2]$  is very sensitive to the acidity and dissociates in acidic condition [13]. One can see that the CPE of  $\text{UO}_2^{2+}$  using 8-HQ is only effective at pH over 4 (Fig. 3b, inset), in spite of the IL  $\text{C}_4\text{mimNTf}_2$  added. In HDEHP system, though the efficiency increases at low acidity ( $C_{0,\text{HNO}_3} < 0.05 \text{ mol dm}^{-3}$ ), it decreases rapidly with the increase of acidity, no matter whether  $\text{C}_4\text{mimNTf}_2$  exists.

### 3.3. Separation of $\text{UO}_2^{2+}/\text{La}^{3+}$

In TRPO (trialkylphosphine oxide with alkyl chain from  $\text{C}_6$  to  $\text{C}_8$ ) process [41], TRPO has excellent extraction selectivity to tri-, tetra- and hexa-valent actinides and could extract tri-valent lanthanides when the concentration of  $\text{HNO}_3$  lowers than  $2 \text{ mol dm}^{-3}$ . To investigate the selectivity of TOPO in CPE, the separation of  $\text{UO}_2^{2+}$  and  $\text{Ln}^{3+}$  was studied ( $\text{La}^{3+}$  was selected as representative of  $\text{Ln}^{3+}$ ).

Fig. 4 shows the extraction efficiency of  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$  depending on  $C_{0,\text{HNO}_3}$  in the separation of  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$ . In single TOPO system, the presence of  $\text{La}^{3+}$  decreases the extraction efficiency

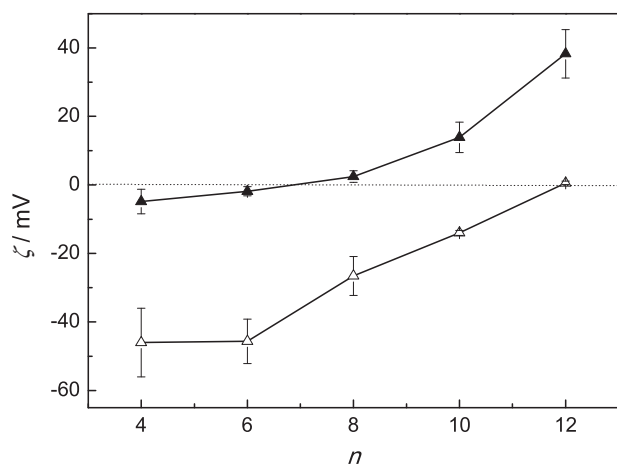


Fig. 5. Variations of  $\zeta$  value of 10 mmol dm<sup>-3</sup> of TX-114 micellar solution containing 0.2 mmol dm<sup>-3</sup> of TOPO and 1 mmol dm<sup>-3</sup> of IL (C<sub>n</sub>mimBr (▲) and C<sub>n</sub>mimNTf<sub>2</sub> (△)) as the alkyl chain of the imidazolium cation is lengthened.

of UO<sub>2</sub><sup>2+</sup>. However, in the TOPO-C<sub>4</sub>mimNTf<sub>2</sub> system, the existence of La<sup>3+</sup> does not show an obvious effect on the extraction of UO<sub>2</sub><sup>2+</sup>. Besides, the extraction efficiency of La<sup>3+</sup> varies slightly when C<sub>4</sub>mimNTf<sub>2</sub> is added. Therefore, the addition of C<sub>4</sub>mimNTf<sub>2</sub> increases the separation factor of UO<sub>2</sub><sup>2+</sup> and La<sup>3+</sup>.

#### 3.4. Zeta potential determination and <sup>19</sup>F NMR measurement

The zeta potential ( $\zeta$ ) was measured for the aggregates formed by TX-114 and TOPO in the absence and presence of 1 mmol dm<sup>-3</sup> of different ILs at 283 K (Fig. 5). Meanwhile, the content of NTf<sub>2</sub><sup>-</sup> in the surfactant-rich phase after extraction was detected by <sup>19</sup>F NMR (Fig. 6). The  $\zeta$  value of the TX-114 micellar solution (10 mmol dm<sup>-3</sup>) containing TOPO (0.2 mmol dm<sup>-3</sup>) is  $-3 \pm 2$  mV. Upon the addition of 1 mmol dm<sup>-3</sup> of C<sub>4</sub>mimBr, C<sub>4</sub>mimBF<sub>4</sub> and C<sub>4</sub>mimPF<sub>6</sub>, the  $\zeta$  values are  $-5 \pm 4$ ,  $-3 \pm 1$  and  $-8 \pm 1$  mV, respectively. On the contrary, the addition of the hydrophobic IL C<sub>4</sub>mimNTf<sub>2</sub> causes a significant decrease of  $\zeta$  to a negative value of  $-46 \pm 10$  mV. Meanwhile, according to the results of <sup>19</sup>F NMR, nearly half of NTf<sub>2</sub><sup>-</sup> anions are concentrated into the surfactant-rich phase in C<sub>4</sub>mimNTf<sub>2</sub> system. These results suggest that the anion NTf<sub>2</sub><sup>-</sup> penetrates into the TX-114 micelles for its hydrophobicity.

The value of  $\zeta$  increases when the alkyl chain lengthens in both C<sub>n</sub>mimBr and C<sub>n</sub>mimNTf<sub>2</sub> systems (Fig. 5). Notably, the CP value

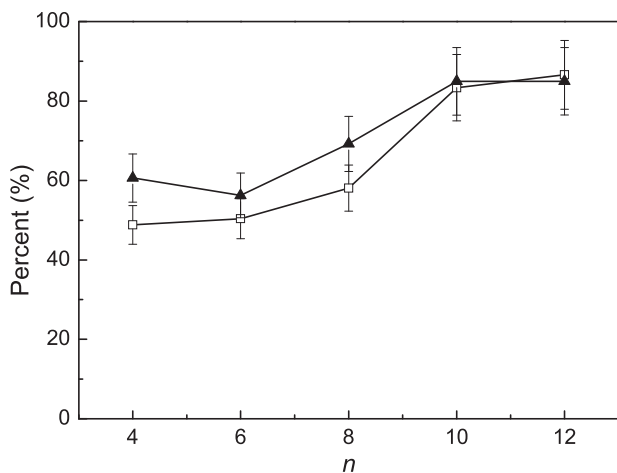


Fig. 6. Variations of the contents of NTf<sub>2</sub><sup>-</sup> in surfactant-rich phase with the alkyl length of imidazolium cation after CPE procedures in the presence (▲) and absence (□) of UO<sub>2</sub><sup>2+</sup>.

of the system containing 10 mmol dm<sup>-3</sup> of TX-114, 0.2 mmol dm<sup>-3</sup> of TOPO and 1 mmol dm<sup>-3</sup> C<sub>12</sub>mimNTf<sub>2</sub> is below 273.2 K, so the  $\zeta$  value of the C<sub>12</sub>mimNTf<sub>2</sub> system was measured at 278 K containing 10 mmol dm<sup>-3</sup> of TX-114 and 0.5 mmol dm<sup>-3</sup> instead of 1 mmol dm<sup>-3</sup> of C<sub>12</sub>mimNTf<sub>2</sub>, which is clear at the measured temperature. This increase is attributed to the fact that, with the increase in the alkyl chain, imidazolium cations gradually penetrate into the micelles [35,37]. The penetration of cations attracts more NTf<sub>2</sub><sup>-</sup> to enter to micelles. Therefore, as alkyl length of imidazolium cation increases, the concentration of content of NTf<sub>2</sub><sup>-</sup> in the surfactant-rich phase also increases (Fig. 6).

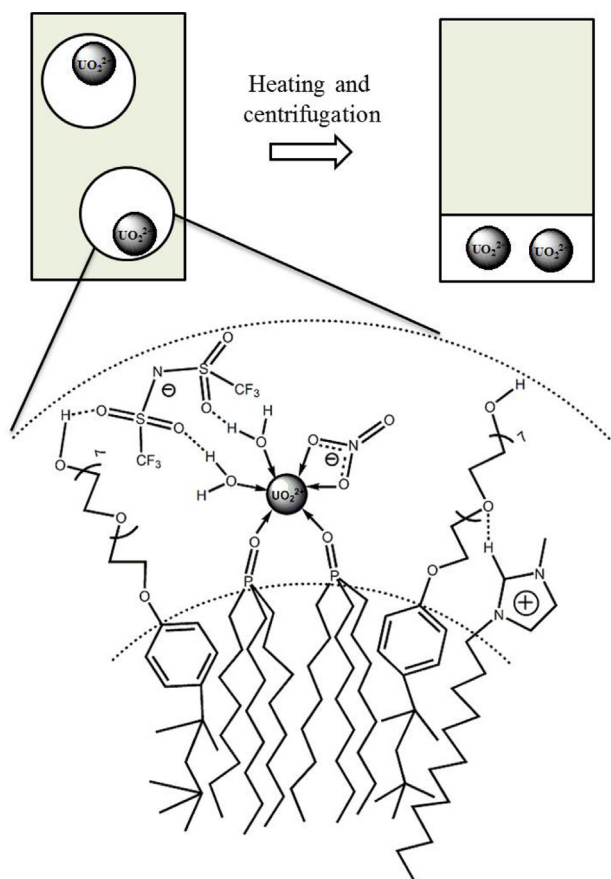
This phenomenon is similar to that in the interaction between ILs and  $\beta$ -cyclodextrin ( $\beta$ -CD) [42,43]. Our group reported previously that both the imidazolium cations with long alkyl chains and hydrophobic anions, e.g., NTf<sub>2</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>, can form inclusion complexes with  $\beta$ -CD [42,43]. The strength of interaction of cations and anions with  $\beta$ -CD follows the order C<sub>12</sub>mim<sup>+</sup> > NTf<sub>2</sub><sup>-</sup> ~ C<sub>10</sub>mim<sup>+</sup> > C<sub>8</sub>mim<sup>+</sup> > C<sub>6</sub>mim<sup>+</sup> ~ PF<sub>6</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > C<sub>4</sub>mim<sup>+</sup> [42,43], consistent with their hydrophobicity order.

#### 3.5. Discussion on the extraction mechanism

In single TOPO based CPE system, the positive coordination compound U(VI)-TOPO needs to interact with anions, e.g., NO<sub>3</sub><sup>-</sup>, to form neutral complex and dissolve in the TX-114 micelles. On the addition of hydrophobic ILs C<sub>n</sub>mimNTf<sub>2</sub>, the hydrophobic anion NTf<sub>2</sub><sup>-</sup> penetrates into the micelles, facilitating U(VI)-TOPO form neutral complex and dissolve in the TX-114 micelles. Thus, the extraction efficiency is increased upon the addition of NTf<sub>2</sub><sup>-</sup> based ILs. Due to the hydrophobicity of alkyl chain of IL, part of cations will penetrate into micelles, attracting more NTf<sub>2</sub><sup>-</sup> to penetrate into micelles, resulting in higher efficiency by C<sub>n</sub>mimNTf<sub>2</sub> than that by LiNTf<sub>2</sub>. As the alkyl length of imidazolium cation increases, the content of NTf<sub>2</sub><sup>-</sup> also increases, improving the efficiency. For hydrophilic ILs, e.g., C<sub>n</sub>mimBr and C<sub>4</sub>mimBF<sub>4</sub>, the anions prefer to stay in the aqueous phase, leading to no enhancement for extraction. With the increase in the alkyl length of C<sub>n</sub>mimBr, the extraction efficiency decreases, due to the electrostatic repulsion. This is similar to the situation of CTAB. Notably, BF<sub>4</sub><sup>-</sup> can coordinate with UO<sub>2</sub><sup>2+</sup> to form a water soluble compound [44], thus decreasing remarkably the CPE efficiency as mentioned above. Though PF<sub>6</sub><sup>-</sup> shows hydrophobic property, its effect on micelles is little according to the zeta potential measurements. As a result, the amount of PF<sub>6</sub><sup>-</sup> partitioning into the micelles should be much lower than that of NTf<sub>2</sub><sup>-</sup>, causing slight influence on extraction efficiency. SDS and SDSN can also penetrate into TX-114 micelles, making micelles negatively charged, thus, increasing the efficiency by electrostatic attraction. The fact that the efficiencies of SDS and SDSN systems are lower than that of NTf<sub>2</sub><sup>-</sup> based system, can be attributed to the different interaction mechanism with UO<sub>2</sub><sup>2+</sup>.

In the CPE of UO<sub>2</sub><sup>2+</sup> in this work, the improvement of extraction efficiency upon the addition of C<sub>n</sub>mimNTf<sub>2</sub> reflects that there must be an interaction between NTf<sub>2</sub><sup>-</sup> and the U(VI)-TOPO complex. It was found that NTf<sub>2</sub><sup>-</sup> does not complex UO<sub>2</sub><sup>2+</sup> in the absence of other ligands in aqueous solution [44]. Meanwhile, Rogers et al. have demonstrated that in the extraction of UO<sub>2</sub><sup>2+</sup> by octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in C<sub>8</sub>mimNTf<sub>2</sub>, NTf<sub>2</sub><sup>-</sup> is not present in the inner coordination sphere of UO<sub>2</sub><sup>2+</sup>, while the deficient complex UO<sub>2</sub>(NO<sub>3</sub>)(CMPO)<sup>+</sup> is coordinated by H<sub>2</sub>O directly [45]. Furthermore, single crystal of [(UO<sub>2</sub>)<sub>2</sub>(bet)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>][NTf<sub>2</sub>]<sub>4</sub> (bet is betainium) also shows that [(UO<sub>2</sub>)<sub>2</sub>(bet)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>4+</sup> is surrounded by four noncoordinating NTf<sub>2</sub><sup>-</sup> anions [46]. Our research group recently detected the interaction between NTf<sub>2</sub><sup>-</sup> and UO<sub>2</sub><sup>2+</sup> using isothermal calorimetric titration method [47], according to the method reported





**Scheme 2.** A possible mechanism in CPE of  $\text{UO}_2^{2+}$  by TOPO using the hydrophobic IL  $\text{C}_{12}\text{mimNTf}_2$  as additives.

in the literature [48]. Significant heat released was observed during the titration of  $\text{UO}_2^{2+}$  to  $\text{NTf}_2^-$ . The results show that  $\text{NTf}_2^-$  does not form inner sphere coordination compound with  $\text{UO}_2^{2+}$ . Instead, it interacts with hydrated U(VI) by hydrogen bonding [47]. Besides, it is well known that weak donor ligands, such as crown ethers or alcohols, could form out sphere coordination compounds with uranyl ions by hydrogen bonding [49–51]. Therefore, it is reasonable to infer that in CPE of  $\text{UO}_2^{2+}$ ,  $\text{NTf}_2^-$  does not directly coordinate with  $\text{UO}_2^{2+}$ , that is,  $\text{H}_2\text{O}$  coordinates with U(VI) and  $\text{NTf}_2^-$  interacts with hydrated U(VI) via interacting with the  $\text{H}_2\text{O}$  molecules by hydrogen bonding.  $\text{NTf}_2^-$  interacts with U(VI) forming an “outer sphere” complex. Besides, at low acidity, the increase of the extraction efficiency in TOPO- $\text{C}_4\text{mimNTf}_2$  system (Fig. 3a) when increasing the concentration of  $\text{HNO}_3$  suggests that there is an interaction between  $\text{NO}_3^-$  and the U(VI)-TOPO complex. Rao et al. has demonstrated that  $\text{NO}_3^-$  can coordinate with U(VI) forming an “inner sphere” complex in aqueous solution with a formation constant of  $0.24 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1}$  at 298 K [48,52]. Therefore,  $\text{NO}_3^-$  coordinates with the deficient U(VI)-TOPO complex in the CPE system. Based on our results in this work, it can be inferred that both the anions  $\text{NTf}_2^-$  and  $\text{NO}_3^-$  interact with U(VI)-TOPO complex in the CPE system, that is, they both act as counterions in the CPE of  $\text{UO}_2^{2+}$ . Because  $\text{NTf}_2^-$  located in the micelles,  $\text{UO}_2^{2+}$  needs less  $\text{NO}_3^-$  to form neutral complex to enter the micelles. Therefore, the efficiency reaches the summit at lower  $\text{HNO}_3$  concentration in the presence of  $\text{C}_4\text{mimNTf}_2$ , as compared to that in the absence of  $\text{C}_4\text{mimNTf}_2$ . Besides, the addition of  $\text{C}_4\text{mimNTf}_2$  does not enhance the extraction of  $\text{UO}_2^{2+}$  by 8-HQ (Fig. 3b) or HDEHP (Fig. 3c), for the complex of HDEHP or 8-HQ with  $\text{UO}_2^{2+}$  is neutral and no counterion effect of  $\text{NTf}_2^-$  occurs.

According to the research of the interactions between hydrophobic anions of ionic liquids and TX-114 micelles in aqueous solutions undergoing in our lab,  $\text{NTf}_2^-$  locates in the corona of TX-114 micelles. With the increase in the alkyl chain, alkyimidazolium cations gradually penetrate into the micelles (e.g.  $\text{C}_{12}\text{mimNTf}_2$ ). We propose herein a possible mechanism in CPE of  $\text{UO}_2^{2+}$  by TOPO upon the addition of the hydrophobic IL  $\text{C}_n\text{mimNTf}_2$  (Scheme 2). More importantly, though  $\text{NTf}_2^-$  could coordinate with  $\text{Ln}^{3+}$  [53], the increase of separation factor of  $\text{UO}_2^{2+}$  from  $\text{La}^{3+}$  on the addition of  $\text{C}_4\text{mimNTf}_2$  shows that  $\text{C}_4\text{mimNTf}_2$  based system has higher selectivity of  $\text{UO}_2^{2+}$ . This is mainly attributed to the steric factor. When a  $\text{UO}_2^{2+}$  ion contacts with a micelle, TOPO,  $\text{NTf}_2^-$  and  $\text{NO}_3^-$  will adjust their relative positions to form an appropriate recognition sites for  $\text{UO}_2^{2+}$  in the micelles. On the contrary,  $\text{La}^{3+}$  coordinates with three or four TOPO molecules and three counterions [41], forming a larger complex than uranyl complex  $\text{UO}_2(\text{TOPO})_2\text{L}_2$  (L is counterion). Due to the steric effect,  $\text{La}^{3+}$  ions are hardly extracted into the micelles. Therefore, the above soft template of supramolecular recognition facilitates the extraction and concentration of  $\text{UO}_2^{2+}$  in the CPE method in presence of IL.

#### 4. Conclusion

The addition of  $\text{NTf}_2^-$  based ILs have a significant effect on the improvement of the CPE using neutral extractants. The extraction efficiency keeps high when the system changes from nearly neutral to greatly acidic. Besides, the addition of  $\text{C}_4\text{mimNTf}_2$  increases the separation factor of  $\text{UO}_2^{2+}$  and  $\text{La}^{3+}$ . On the contrary,  $\text{C}_4\text{mimNTf}_2$  shows little influence on acidic extractant systems. Due to its hydrophobicity,  $\text{NTf}_2^-$  penetrates into the micelles, acting as a counterion in the CPE system, thus improving the extraction efficiency. A supramolecular recognition system has been constructed to selectively extract  $\text{UO}_2^{2+}$  in CPE method combining with IL, which is effective at both nearly neutral and acidic conditions.

#### Acknowledgments

The authors are grateful to Mr. Jingxin Yang (Beijing NMR Center) for his help in NMR measurements. This work was supported by National Natural Science Foundation of China (Grant No. 20871009 and B010901) and the Fundamental Research Funds for the Central Universities.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.10.014>.

#### References

- [1] M.F. Silva, E.S. Cerutti, L.D. Martinez, Coupling cloud point extraction to instrumental detection systems for metal analysis, *Microchim. Acta* 155 (2006) 349–364.
- [2] C.B. Ojeda, F.S. Rojas, Separation and preconcentration by a cloud point extraction procedure for determination of metals: an overview, *Anal. Bioanal. Chem.* 394 (2009) 759–782.
- [3] C.D. Stalikas, Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis, *Trac-Trends Anal. Chem.* 21 (2002) 343–355.
- [4] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, Micelle-mediated separation and cloud-point extraction, *Trac-Trends Anal. Chem.* 24 (2005) 426–436.
- [5] L.L. Zhao, S.X. Zhong, K.M. Fang, Z.S. Qian, J.R. Chen, Determination of cadmium(II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry, *J. Hazard. Mater.* 239 (2012) 206–212.
- [6] F. Shah, T.G. Kazi, H.I. Afridi, Naemullah, M.B. Arain, J.A. Baig, Cloud point extraction for determination of lead in blood samples of children, using different ligands prior to analysis by flame atomic absorption spectrometry: a multivariate study, *J. Hazard. Mater.* 192 (2011) 1132–1139.

- [7] S. Candir, I. Narin, M. Soylak, Ligandless cloud point extraction of Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), and Cd(II) ions in environmental samples with Tween 80 and flame atomic absorption spectrometric determination, *Talanta* 77 (2008) 289–293.
- [8] Y.C. Wei, Y.L. Li, X.J. Quan, W.P. Liao, Cloud point extraction and separation of copper and lanthanoids using Triton X-100 with water-soluble p-sulfonatocalix[4]arene as a chelating agent, *Microchim. Acta* 169 (2010) 297–301.
- [9] Y.J. Li, B. Hu, Cloud point extraction with/without chelating agent on-line coupled with inductively coupled plasma optical emission spectrometry for the determination of trace rare earth elements in biological samples, *J. Hazard. Mater.* 174 (2010) 534–540.
- [10] S. Shariati, Y. Yamini, M.K. Zanjani, Simultaneous preconcentration and determination of U(VI), Th(IV), Zr(IV) and Hf(IV) ions in aqueous samples using micelle-mediated extraction coupled to inductively coupled plasma-optical emission spectrometry, *J. Hazard. Mater.* 156 (2008) 583–590.
- [11] S.K. Das, C.S. Kedari, S.C. Tripathi, Spectrophotometric determination of trace amount of uranium(VI) in different aqueous and organic streams of nuclear fuel processing using 2-(5-bromo-2-pyridylazo-5-diethylaminophenol), *J. Radioanal. Nucl. Chem.* 285 (2010) 675–681.
- [12] H.S. Ferreira, M.D. Bezerra, S.L.C. Ferreira, A pre-concentration procedure using cloud point extraction for the determination of uranium in natural water, *Microchim. Acta* 154 (2006) 163–167.
- [13] A. Favre-Reguillon, D. Murat, G. Cote, J. Foos, M. Draye, Temperature-induced surfactant-mediated pre-concentration of uranium assisted by complexation, *J. Chem. Technol. Biotechnol.* 81 (2006) 1872–1876.
- [14] M.E.F. Laespada, J.L.P. Pavan, B.M. Cordero, Micelle-mediated methodology for the preconcentration of uranium prior to its determination by flow-injection, *Analyst* 118 (1993) 209–212.
- [15] E. Constantinou, I. Pashalidis, Uranium determination in water samples by liquid scintillation counting after cloud point extraction, *J. Radioanal. Nucl. Chem.* 286 (2010) 461–465.
- [16] E.K. Paleologos, A.G. Vlessidis, M.I. Karayannis, N.P. Evmiridis, On-line sorption preconcentration of metals based on mixed micelle cloud point extraction prior to their determination with micellar chemiluminescence – application to the determination of chromium at  $ng\ l^{-1}$  levels, *Anal. Chim. Acta* 477 (2003) 223–231.
- [17] D.L. Giokas, J. Antelo, E.K. Paleologos, F. Arce, M.I. Karayannis, Copper fractionation with dissolved organic matter in natural waters and wastewater – a mixed micelle mediated methodology (cloud point extraction) employing flame atomic absorption spectrometry, *J. Environ. Monit.* 4 (2002) 505–510.
- [18] D.L. Giokas, E.K. Paleologos, P.G. Veltsistas, M.I. Karayannis, Micelle mediated extraction of magnesium from water samples with trizma-chloranilate and determination by flame atomic absorption spectrometry, *Talanta* 56 (2002) 415–424.
- [19] N.N. Meeravali, S.J. Kumar, Determination of Cd, Pb, Cu, Ni and Mn in effluents and natural waters by a novel salt induced mixed-micelle cloud point extraction using ETAAS, *Anal. Methods* 4 (2012) 2435–2440.
- [20] M.B. Gholivand, A. Babakhanian, E. Rafiee, Determination of Sn(II) and Sn(IV) after mixed micelle-mediated cloud point extraction using alpha-polyoxometalate as a complexing agent by flame atomic absorption spectrometry, *Talanta* 76 (2008) 503–508.
- [21] T. Madrakian, A. Afkhami, A. Mousavi, Spectrophotometric determination of trace amounts of uranium(VI) in water samples after mixed micelle-mediated extraction, *Talanta* 71 (2007) 610–614.
- [22] N. Pourreza, M. Zareian, Determination of Orange II in food samples after cloud point extraction using mixed micelles, *J. Hazard. Mater.* 165 (2009) 1124–1127.
- [23] J.P. Hallett, T. Welton, Room-temperature ionic liquids: solvents for synthesis and catalysis, *2, Chem. Rev.* 111 (2011) 3508–3576.
- [24] 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.
- [25] 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.
- [26] 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.* (2010) 3897–3902.
- [27] C. Xu, X.H. Shen, Q.D. Chen, H.C. Gao, Investigation on the extraction of strontium ions from aqueous phase using crown ether-ionic liquid systems, *Sci. China Ser. B: Chem.* 52 (2009) 1858–1864.
- [28] L.Y. Yuan, C. Xu, J. Peng, L. Xu, M.L. Zhai, J.Q. Li, G.S. Wei, X.H. Shen, Identification of the radiolytic product of hydrophobic ionic liquid  $C_4mim\ NTf_2$  during removal of  $Sr^{2+}$  from aqueous solution, *Dalton Trans.* (2009) 7873–7875.
- [29] K. Behera, H. Om, S. Pandey, Modifying properties of aqueous cetyltrimethylammonium bromide with external additives: ionic liquid 1-hexyl-3-methylimidazolium bromide versus cosurfactant n-hexyltrimethylammonium bromide, *J. Phys. Chem. B* 113 (2009) 786–793.
- [30] K. Behera, S. Pandey, Ionic liquid induced changes in the properties of aqueous zwitterionic surfactant solution, *Langmuir* 24 (2008) 6462–6469.
- [31] R. Pramanik, S. Sarkar, C. Ghatak, V.G. Rao, S. Mandal, N. Sarkar, Effects of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid on Triton X-100 aqueous micelles: solvent and rotational relaxation studies, *J. Phys. Chem. B* 115 (2011) 6957–6963.
- [32] K. Behera, S. Pandey, Concentration-dependent dual behavior of hydrophilic ionic liquid in changing properties of aqueous sodium dodecyl sulfate, *J. Phys. Chem. B* 111 (2007) 13307–13315.
- [33] K. Behera, P. Dahiya, S. Pandey, Effect of added ionic liquid on aqueous Triton X-100 micelles, *J. Colloid Interface Sci.* 307 (2007) 235–245.
- [34] R. Rai, G.A. Baker, K. Behera, P. Mohanty, N.D. Kurur, S. Pandey, Ionic liquid-induced unprecedented size enhancement of aggregates within aqueous sodium dodecylbenzene sulfonate, *Langmuir* 26 (2010) 17821–17826.
- [35] S. Zhang, Y. Gao, B. Dong, L. Zheng, Interaction between the added long-chain ionic liquid 1-dodecyl-3-methylimidazolium tetrafluoroborate and Triton X-100 in aqueous solutions, *Colloids Surf. A: Physicochem. Eng. Asp.* 372 (2010) 182–189.
- [36] V.G. Rao, C. Ghatak, S. Ghosh, R. Pramanik, S. Sarkar, S. Mandal, N. Sarkar, Ionic liquid-induced changes in properties of aqueous cetyltrimethylammonium bromide: a comparative study of two protic ionic liquids with different anions, *J. Phys. Chem. B* 115 (2011) 3828–3837.
- [37] K. Behera, M.D. Pandey, M. Porel, S. Pandey, Unique role of hydrophilic ionic liquid in modifying properties of aqueous Triton X-100, *J. Chem. Phys.* 127 (2007) 184501.
- [38] C.J. Zeng, X.L. Xu, N. Zhou, Y. Lin, Synergistic enhancement effect of room temperature ionic liquids for cloud point extraction combined with UV–vis spectrophotometric determination nickel in environmental samples, *Spectrochim. Acta Pt. A-Molec. Biomolec. Spectr.* 94 (2012) 48–52.
- [39] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, highly conductive ambient-temperature molten salts, *Inorg. Chem.* 35 (1996) 1168–1178.
- [40] J.A. Partridge, R.C. Jensen, Purification of di-(2-ethylhexyl)phosphoric acid by precipitation of copper(II) di-(2-ethylhexyl)phosphate, *J. Inorg. Nucl. Chem.* 31 (1969) 2587–2589.
- [41] J. Chen, J.C. Wang, Overview of 30 years research on TRPO process for actinides partitioning from high level liquid waste, *Prog. Chem.* 23 (2011) 1366–1371.
- [42] Y.F. He, Q.D. Chen, C. Xu, J.J. Zhang, X.H. Shen, Interaction between ionic liquids and beta-cyclodextrin: a discussion of association pattern, *J. Phys. Chem. B* 113 (2009) 231–238.
- [43] J.J. Zhang, X.H. Shen, Multiple equilibria interaction pattern between the ionic liquids  $C_6mimPF_6$  and beta-cyclodextrin in aqueous solutions, *J. Phys. Chem. B* 115 (2011) 11852–11861.
- [44] C. Gaillard, A. El Azzi, I. Billard, H. Bolvin, C. Hennig, Uranyl complexation in fluorinated acids (HF,  $HF_4$ ,  $HPF_6$ ,  $HTf_2N$ ): a combined experimental and theoretical study, *Inorg. Chem.* 44 (2005) 852–861.
- [45] A.E. Visser, M.P. Jensen, I. Laszak, K.L. Nash, G.R. Choppin, R.D. Rogers, Uranyl coordination environment in hydrophobic ionic liquids: an in situ investigation, *Inorg. Chem.* 42 (2003) 2197–2199.
- [46] P. Nockemann, R. Van Deun, B. Thijs, D. Huys, E. Vanecht, K. Van Hecke, L. Van Meervelt, K. Binnemans, Uranyl complexes of carboxyl-functionalized ionic liquids, *Inorg. Chem.* 49 (2010) 3351–3360.
- [47] T.X. Sun, Application of ionic liquids in the extraction of Sr, Cs, U and Tc. Thesis for Doctor Degree, Peking University, 2013.
- [48] L.F. Rao, Thermodynamics of actinide complexation in solution at elevated temperatures: application of variable-temperature titration calorimetry, *Chem. Soc. Rev.* 36 (2007) 881–892.
- [49] P.G. Eller, R.A. Penneman, Synthesis and structure of 1:1 uranyl-nitrate tetrahydrate-18-crown-6 compound,  $UO_2(NO_3)_2 \cdot (H_2O)_2 \cdot 2H_2O \cdot (18-crown-6)$  – non-coordination of uranyl by crown ether, *Inorg. Chem.* 15 (1976) 2439–2442.
- [50] R.D. Rogers, A.H. Bond, W.G. Hipple, A.N. Rollins, R.F. Henry, Synthesis and structural elucidation of novel uranyl crown-ether compounds isolated from nitric, hydrochloric, sulfuric, and acetic-acids, *Inorg. Chem.* 30 (1991) 2671–2679.
- [51] D. Das, S. Kannan, D.K. Maity, M.G.B. Drew, Steric effects on uranyl complexation: synthetic, structural, and theoretical studies of carbamoyl pyrazole compounds of the uranyl(VI) ion, *Inorg. Chem.* 51 (2012) 4869–4876.
- [52] L.F. Rao, G.X. Tian, Thermodynamic study of the complexation of uranium(VI) with nitrate at variable temperatures, *J. Chem. Thermodyn.* 40 (2008) 1001–1006.
- [53] K. Binnemans, Lanthanides and actinides in ionic liquids, *Chem. Rev.* 107 (2007) 2592–2614.