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

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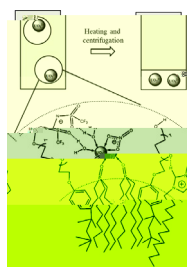
HIGHLIGHTS

- C 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$_4$mimNTf$_2$ 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



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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 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.

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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].

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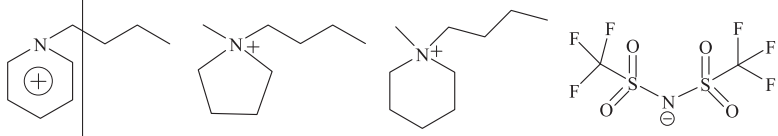
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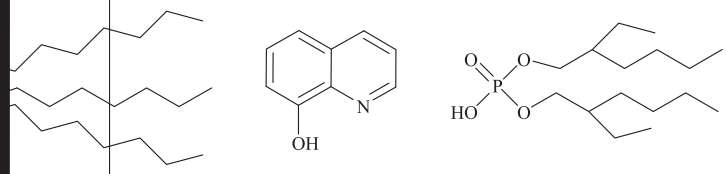
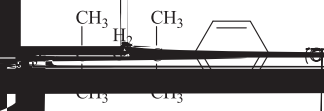
PP14+
NTf2−


TOPO
8-HQ
HDEHP



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), $UO_2(NO_3)_2{\cdot}6H_2O$ (Chemapol) and $La(NO_3)_3{\cdot}6H_2O$ (Beijing Chemical Plant) were of analytical grade and used without further purification.

2.2. I strume ts a d methods

In a typical CPE process, 10 mL of the aqueous solution containing TX-114 (10 mmol dm^{-3}), an IL (1 mmol dm^{-3}), $NaNO_3$ (0.1 mol dm^{-3}), an extractant (0.5 mmol dm^{-3}), and $UO_2(NO_3)_2$ (0.05 mmol dm^{-3}) were shaken for 2 h followed by standing for 2 h at 70 °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 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:

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

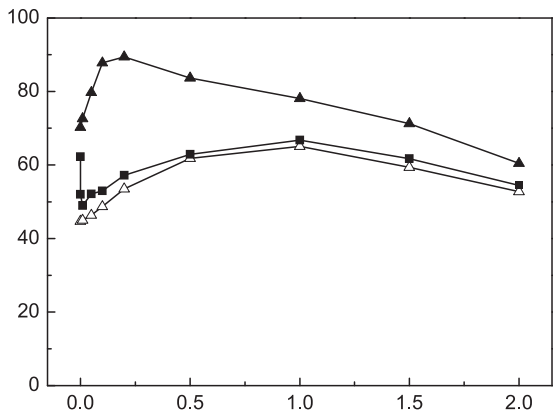
where C_i is the initial concentration of metal ion in the micellar solution, C_f is the final concentration of metal ion in aqueous phase after CPE, V_i is the volume of the micellar solution and V_f is the volume of aqueous phase after CPE.

The zeta potential experiments were performed on a Nano ZS90 instrument (Malvern, UK). ^{19}F NMR spectra were recorded on an AV400 MHz NMR spectrometer (Bruker, Germany) and the concentration of NTf_2^- in the surfactant-rich phase was obtained by the area ratio of ^{19}F NMR signal of NTf_2^- to the $-CF_3$ peak of benzotrifluoride ($C_6H_5CF_3$). In detail, the surfactant-rich phase was diluted with ethanol to 1 mL. Then approximate 300 μL samples were added to an NMR tube within a stem coaxial capillary tube containing $C_6H_5CF_3$ dissolved in *d*-acetone as external reference. Area integral of each peak near −81.10 ppm, which referred to the assigned value 1.00 of −63.90 ppm, was proportional to the NTf_2^- concentration.

3. Results and discussion

3.1. Effect of ILs o CPE

Four imidazolium based ILs with different anions, i.e., C_4mimBr, C_4mimBF_4, C_4mimPF_6, C_4mimNTf_2 were tested for CPE of UO_2^{2+} with a neutral extractant TOPO in TX-114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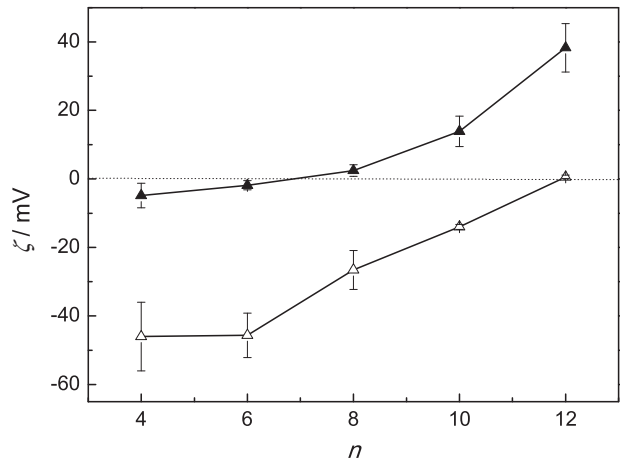


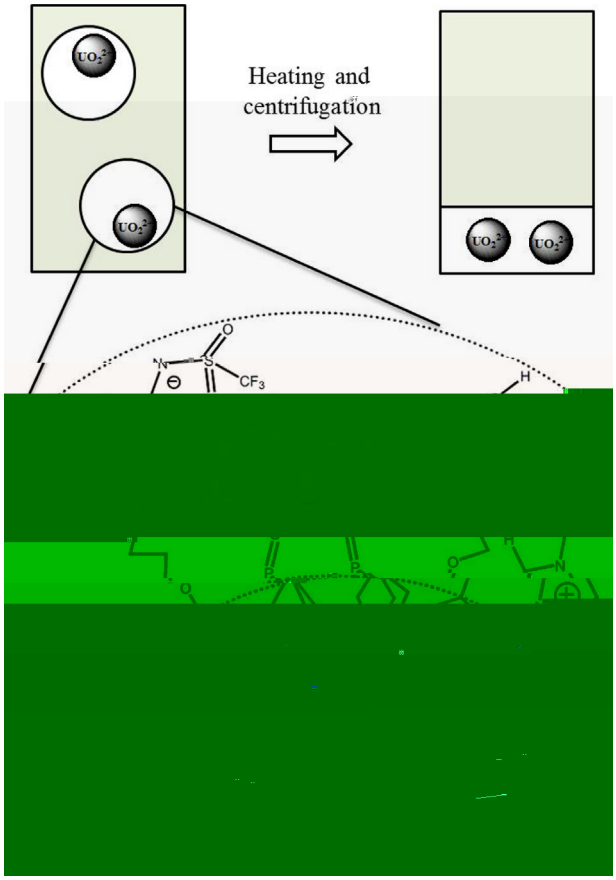
Fig. 5. Variations of ζ value of 10 mmol dm^{-3} of TX-114 micellar solution containing 0.2 mmol dm^{-3} of TOPO and 1 mmol dm^{-3} of IL (C mimBr (▲) and C mimNTf$_2$ (△)) as the alkyl chain of the imidazolium cation is lengthened.

of UO_2^{2+}. However, in the TOPO-C_4mimNTf$_2$ system, the existence of La^{3+} does not show an obvious effect on the extraction of UO_2^{2+}. Besides, the extraction efficiency of La^{3+} varies slightly when C_4mimNTf$_2$ is added. Therefore, the addition of C_4mimNTf$_2$ increases the separation factor of UO_2^{2+} and La^{3+}.

3.4. Zeta pote tial determi ati o a d ^{19}F NMR measureme t

The zeta potential (ζ) was measured for the aggregates formed by TX-114 and TOPO in the absence and presence of 1 mmol dm^{-3} of different ILs at 283 K (Fig. 5). Meanwhile, the content of NTf$_2^-$ in the surfactant-rich phase after extraction was detected by ^{19}F NMR (Fig. 6). The ζ value of the TX-114 micellar solution (10 mmol dm^{-3}) containing TOPO (0.2 mmol dm^{-3}) is -3 ± 2 mV. Upon the addition of 1 mmol dm^{-3} of C_4mimBr, C_4mimBF$_4$ and C_4mimPF$_6$, the ζ values are -5 ± 4, -3 ± 1 and -8 ± 1 mV, respectively. On the contrary, the addition of the hydrophobic IL C_4mimNTf$_2$ causes a significant decrease of ζ to a negative value of -46 ± 10 mV. Meanwhile, according to the results of ^{19}F NMR, nearly half of NTf$_2^-$ anions are concentrated into the surfactant-rich phase in C_4mimNTf$_2$ system. These results suggest that the anion NTf$_2^-$ penetrates into the TX-114 micelles for its hydrophobicity.

The value of ζ increases when the alkyl chain lengthens in both C mimBr and C mimNTf$_2$ systems (Fig. 5). Notably, the CP value



Scheme 2. A possible mechanism in CPE of UO_2^{2+} by TOPO using the hydrophobic IL $C_{12}mimNTf_2$ as additives.

in the literature [48]. Significant heat released was observed during the titration of UO_2^{2+} to NTf_2^-. The results show that NTf_2^- does not form inner sphere coordination compound with 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 UO_2^{2+}, NTf_2^- does not directly coordinate with UO_2^{2+}, that is, H_2O coordinates with U(VI) and NTf_2^- interacts with hydrated U(VI) via interacting with the H_2O molecules by hydrogen bonding. NTf_2^- interacts with U(VI) forming an "outer sphere" complex. Besides, at low acidity, the increase of the extraction efficiency in TOPO-$C_4mimNTf_2$ system (Fig. 3a) when increasing the concentration of HNO_3 suggests that there is an interaction between NO_3^- and the U(VI)-TOPO complex. Rao et al. has demonstrated that NO_3^- can coordinate with U(VI) forming an "inner sphere" complex in aqueous solution with a formation constant of $0.24 \pm 0.02\ dm^3\ mol^{-1}$ at 298 K [48,52]. Therefore, 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 NTf_2^- and NO_3^- interact with U(VI)-TOPO complex in the CPE system, that is, they both act as counterions in the CPE of UO_2^{2+}. Because NTf_2^- located in the micelles, UO_2^{2+} needs less NO_3^- to form neutral complex to enter the micelles. Therefore, the efficiency reaches the summit at lower HNO_3 concentration in the presence of $C_4mimNTf_2$, as compared to that in the absence of $C_4mimNTf_2$. Besides, the addition of $C_4mimNTf_2$ does not enhance the extraction of UO_2^{2+} by 8-HQ (Fig. 3b) or HDEHP (Fig. 3c), for the complex of HDEHP or 8-HQ with UO_2^{2+} is neutral and no counterion effect of 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, NTf_2^- locates in the corona of TX-114 micelles. With the increase in the alkyl chain, alkylimidazolium cations gradually penetrate into the micelles (e.g. $C_{12}mimNTf_2$). We propose herein a possible mechanism in CPE of UO_2^{2+} by TOPO upon the addition of the hydrophobic IL C mimNTf$_2$ (Scheme 2). More importantly, though NTf_2^- could coordinate with Ln^{3+} [53], the increase of separation factor of UO_2^{2+} from La^{3+} on the addition of $C_4mimNTf_2$ shows that $C_4mimNTf_2$ based system has higher selectivity of UO_2^{2+}. This is mainly attributed to the steric factor. When a UO_2^{2+} ion contacts with a micelle, TOPO, NTf_2^- and NO_3^- will adjust their relative positions to form an appropriate recognition sites for UO_2^{2+} in the micelles. On the contrary, La^{3+} coordinates with three or four TOPO molecules and three counterions [41], forming a larger complex than uranyl complex $UO_2(TOPO)_2L_2$ (L is counterion). Due to the steric effect, La^{3+} ions are hardly extracted into the micelles. Therefore, the above soft template of supramolecular recognition facilitates the extraction and concentration of UO_2^{2+} in the CPE method in presence of IL.

4. Conclusion

The addition of 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 $C_4mimNTf_2$ increases the separation factor of UO_2^{2+} and La^{3+}. On the contrary, $C_4mimNTf_2$ shows little influence on acidic extractant systems. Due to its hydrophobicity, 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 UO_2^{2+} in CPE method combining with IL, which is effective at both nearly neutral and acidic conditions.

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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.

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