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

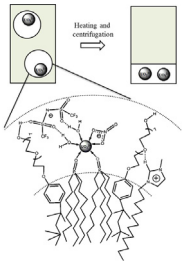
Song Gao, Taoxiang Sun, Qingde Chen, Xinghai Shen*

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

- $C_n$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



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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 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.

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 (X. Shen).

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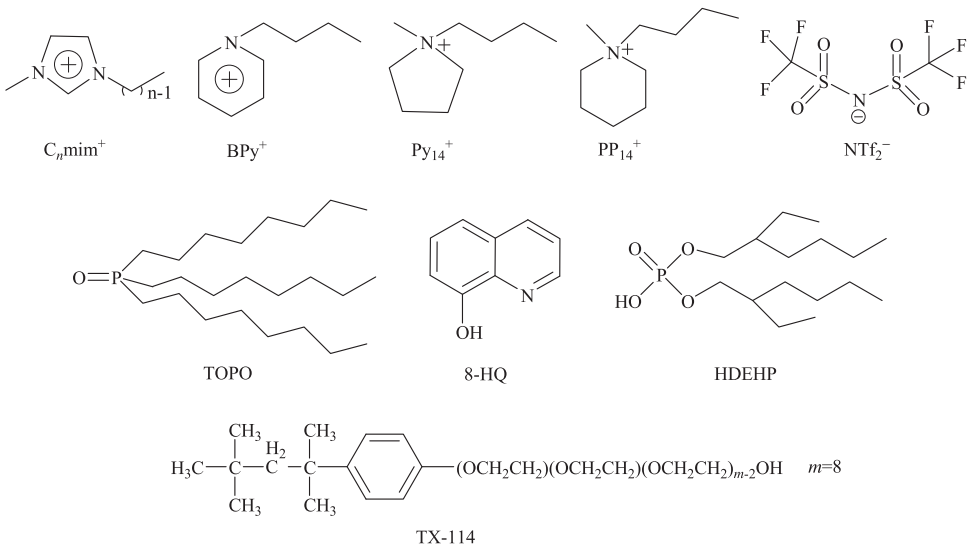

Scheme 1. The structures of the IL cations, the IL anion NTf_2^-, the surfactant TX-114, and the extractants used in this work.

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 ($C_n$mimBr) [29], 1-alkyl-3-methylimidazolium tetrafluoroborate ($C_n$mimBF_4) [30–32] and hydrophobic ILs, e.g., 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_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_4mimPF_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_4mimBr, C_4mimBF_4, C_4mimPF_6, $C_n$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_4mimBr, C_4mimBF_4, C_4mimPF_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%. $C_n$mimNTf_2 (n = 4, 6, 8, 10, 12) were synthesized via