Highly selective extraction of uranium from nitric acid medium with phosphine oxide functionalized pillar[5]arenes in room temperature ionic liquid

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ABSTRACT

Three phosphine oxide functionalized pillar[5]arenes (POP5A) were evaluated for the extraction of uranyl ion from nitric acid feed solutions in room temperature ionic liquid (RTIL), 1-n-octyl-3-methylimidazolium hexafluorophosphate ($C_8mimNTf_2$). The host-guest interaction between POP5A and C_8mim^+ for the formation of [POP5A C_8mim]$^+$ complex was evidenced by 1D and 2D proton NMR spectroscopy and mass spectra technique before extraction, and also supported by theoretical calculation. High extraction efficiency and selective separation of UO_2^{2+} were achieved with the ligand bearing longer spacer exhibiting best solvent extraction performance. The distribution ratios of U(VI) in RTIL were significantly enhanced in the range of 0.1–1.8 M HNO_3 as compared with organic diluent. The extracted species were ascertained from the slope analysis method as well as Job plots method, and a supramolecular cation-exchange mechanism involving competitive host-guest interactions was found to dominate the extraction process. This extraction system was also examined for its ability towards extraction of lanthanides and Th^{4+}. The results revealed an excellent selectivity towards UO_2^{2+} over other metal ions. Stripping experiments showed almost a complete back extraction of UO_2^{2+} within four stages. With high selectivity towards UO_2^{2+} and efficient back extraction, this new POP5A-RTIL extraction system shows promise for future application of uranium recovery.

1. Introduction

Nuclear energy constitutes a major alternative nowadays to conventional energy sources like fossil energy because of its great potential in high energy density, near-zero carbon dioxide emissions and reliable base-load power [1,2]. The production of nuclear energy as implemented in most of the currently operating reactions relies on the use of fissile materials, which comprises mainly enriched uranium. Allowing for the increasing consumption of uranium resources worldwide (63,000 tU/yr for current usage) and the present measured storage (5.7 Mt) on the planet, it is imperative to recover uranium present in various sources, including coal ash, nuclear weapons stockpiles, depleted uranium tails and used fuel [3]. Particularly, uranium recovery from the spent nuclear fuel (SNF) in acidic feeds with a composition of uranium accounting for more than 95% [4] represents a demanding task for efficient utilization of the nuclear fuel. To this end, tremendous research efforts have been devoted to this respect. Liquid-liquid extraction of uranyl (UO_2^{2+}) is considered as one of the most applicable techniques [5–9] where extractants are crucial to the separation process. Along this line, organic extractants have long been attractive owing to their demonstrated behavior shown by P-based compounds such as TBP (tri-*n*-butyl phosphate) [10], TOPO (tri-*n*-octylphosphine oxide) [11], and D2EHPA (di-2-ethylhexylphosphoric acid) [12]. Generally, the attachment of these ligands to a macrocyclic platform such as calixarenes [13] preorganizes the chelating groups and results in an improvement of the extraction efficiency and selectivity [14]. Despite many reports on macrocycles used as preorganization platform for chelating groups, novel macrocyclic skeletons that can be used for this purpose are still scarce.

Pillararenes, a new class of pillar-shaped supramolecular macrocyclic hosts, were first synthesized by Ogoshi et al. [15] Different from their calixarene analogues, pillararenes are made up of hydroquinone units linked by methylene bridges at the *para*-positions, which leads to highly symmetrical pillar architecture. With easy modifiability on both sides of the pillar and its enclosed hydrophobic cavity, pillararenes have been used for molecular machines [16], hybrid absorbents [17], sensing [18,19], artificial transmembrane channels [20], controlled drug delivery [21], supramolecular polymers [22], liquid crystals [23], *etc.*

However, these macrocycles have never been used for extraction purpose until 2013 when we first reported on the use of phosphine oxides functionalized pillar[5]arenes (POP5A) for selective separation of some representative lanthanides and actinides [24]. In fact, pillar[5]arenes bearing varying functionalities have been shown to act as promising extractants for actinide/lanthanide ions [24–28]. Particularly, POP5A exhibited the efficient and selective extraction of UO_2^{2+} for simulated nuclear industry effluent. Further study revealed the importance of phenyl groups that are tethered to phosphorus on the pillararene platform for the enhanced efficacy and selectivity [25]. It should be noted that extraction studies on using this class of new macrocyclic extractants in our previous work are only limited to molecular diluents until our recent report [28].

Very lately, we have reported for the first time the extraction studies of pillararenes-based diglycolamide extractants (DGAP5As) in 1-n-octyl-3-methylimidazolium hexafluorophosphate (C_8mimNTf$_2$) [28]. In this extraction system, exceedingly high distribution ratios (D) towards Am(III) and Eu(III) were obtained and a unique mechanism involving competitive host-guest interactions was proposed. Thus, it is highly attractive to study the extraction behavior of other pillararenes-based extractants in diluents beyond traditional volatile organic compounds (VOC).

Room temperature ionic liquids (RTILs) are organic salts with melting points lower than 373 K [29]. Allowing for their secure and unique physicochemical properties such as low volatility and combustibility, wide liquidus range and thermal stability [30,31], RTILs are deemed as a class of solvent systems that are particularly suitable for use in advanced nuclear fuel separations systems [32–34]. Since the early reports of RTILs as diluents for extraction [35–37], a great number of studies have focused on RTIL-based extraction systems with the combination of organic extractants [38,39]. Interestingly, most extractants exhibit higher extraction efficiency and different extraction behavior in RTILs as compared with VOC [37,40], which is probably due to the ion-exchange mechanism in most RTILs systems [41,42]. Although an ion-exchange mechanism accompanied by loss of the IL to the aqueous phase constitutes a serious issue in potential applications of ionic liquids as green solvents [43], they can be designed by tailoring their molecular structures to suit the situations where this issue is not the major concern. For example, some particular processes dealing with dangerous high level radioactive wastes concern safety more than the release of IL to aqueous phase [31]. Therefore, RTILs are promising alternative diluents to VOC for nuclear fuel reprocessing. Despite the fact that many extractants have been studied for uranium extraction in RTIL-based systems, to our knowledge the application of pillararenes-based extractant for the extraction of uranium in RTILs has not been explored yet.

In the present paper, we report on uranyl separation using three POP5A ligands (**L-I**, **L-II**, and **L-III**) in RTIL (C_8mimNTf$_2$) (Fig. 1). The studies of host-guest interaction between POP5A and RTIL indicated the formation of $[C_8\text{mim·POP5A}]^+$, which may play an important role during extraction. The effects of contact time, aqueous acidity, extractant concentration and competing ions were discussed to elucidate the feasibility of such a POP5A-RTIL extraction system in separation of uranyl. High selectivity towards UO_2^{2+} over tested metal ions was achieved. To further investigate the extraction mechanism and extracted species, UV-visible spectroscopic studies were conducted and then a supramolecular cation-exchange mechanism involving competitive host-guest interaction was proposed. Moreover, stripping of extracted UO_2^{2+} from the organic phase was also performed to evaluate the possible reusability of the extraction system.

2. Experimental

2.1. Materials and apparatus

1-*n*-Octyl-3-methylimidazolium bis(trifluoromethane)-sulfonamide

(C_8mimNTf$_2$, ≥99%) and 1-n-octyl-3-methylimidazolium chloride (C_8mimCl, ≥99%) were procured from Cheng Jie Chemical Co. Ltd. Shanghai, and were used as received. UO_2^{2+}, Lu^{3+}, Th^{4+}, Eu^{3+}, Yb^{3+}, Gd^{3+}, Pr^{3+}, La^{3+}, Ce^{3+}, Sm^{3+}, Nd^{3+} and Er^{3+} were used as their nitrate salts (Aladdin Industrial Corporation, Shanghai, ≥99%). Guanidine carbonate (≥99%) and ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA, ≥99.5%) were purchased from Energy Chemical Co. Ltd., Shanghai. CDCl$_3$ were purchased from Cambridge Isotope Laboratories (CIL). Solvents used in the optical spectroscopic studies were HPLC grade. Suprapur nitric acid and ultrapure water were used for preparing nitric acid solutions. All other reagents were of AR grade.

Inductively coupled plasma optical emission spectroscopy (ICP–OES) was used to determine the concentrations of metal ions on PerkinElmer ICP optima 8000. The ^{1}H NMR spectra were recorded on a Bruker AVANCE AV II-400 MHz ([1]H: 400 MHz). High resolution mass (HR-MS) data were obtained by WATERS Q-TOF Premier. UV-spectra were measured by SHIMADZU UV-2450.

2.2. Synthesis of phosphine oxide-functionalized pillararene

The POP5A ligands were prepared as previously reported [24]. The structures were confirmed by ^{1}H NMR and HR-MS spectrometry. In view of the similarity in structures and properties between the three ligands, **L-I** was chosen as the representative compound for host-guest investigation and extraction mechanism study.

2.3. Liquid-liquid extraction

Solvent extraction studies were carried out by shaking a mixture of equal volumes (usually 1 mL) of organic phase with aqueous solution for 4 h (except specifically defined) in Pyrex tubes with 5 mL capacity in a vibrating mixer at 25 ± 1.0 °C. The organic phases were solutions of POP5A in C_8mimNTf$_2$ at different concentrations and the aqueous phase contained 10^{-4} M metal ions at a given acidity. After equilibration of the two phases, the tubes were centrifuged at 2000 rpm for 5 min. 0.5 mL aliquot of aqueous phase was removed into a volumetric flask using micro syringe and was then diluted to 10 mL for ICP-OES test (with a detection limit below 0.01 ppm). The distribution ratio (D) and extraction percentage (E) values could be calculated from the concentration of the aqueous phase before and after the equilibrium is reached according to the following equations:

$$D = \frac{C_i - C_f}{C_f} \tag{1}$$

$$\%E = \frac{C_i - C_f}{C_i} \tag{2}$$

where C_i and C_f are the initial and final concentration in the aqueous phases. All the experiments were carried out in duplicate (some are with triplicate) and all the results were obtained with uncertainty within ± 5%.

2.4. Stripping

Stripping studies were carried out using 0.05 M EDTA + 1.0 M guanidine carbonate as stripping agent. In a typical stripping experiment, the organic phase following an extraction process was mixed with 1 mL of aqueous solution containing stripping agent in a stoppered test tube and shaken for 4 h at room temperature (25 ± 1 °C) vigorously. After centrifugation and separation for 5 min, 0.5 mL aqueous of the extracted mixture was diluted to 10 mL and measured by ICP-OES. This procedure was repeated until the uranium loaded in organic phase was recovered completely. All the stripping experiments were conducted in duplicate with an error limit within 5%.