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A novel phosphoramide task specific ionic liquid for the selective separation of plutonium (IV) from other actinides

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ABSTRACT

A novel phosphoramide task specific ionic liquid, diethyl-3-(-3-butylimidazolium)propylphosphoramide bis(trifluoromethanesulfonyl)imide ([BuImPA][NTf_2]), was synthesized and characterized by NMR and FTIR spectroscopy, for the first time. The extraction behavior of Pu(IV), U(VI) and Am(III) from nitric acid medium was studied by using [BuImPA][NTf_2] dissolved in the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][NTf_2]). The extraction was studied as a function of various parameters such as concentration of nitric acid, extractant concentration, temperature, alkyl chain length attached to imidazolium moiety etc. The distribution ratio of Pu(IV) in [BuImPA][NTf_2]/[C_4mim][NTf_2] increased with increase in the concentration of nitric acid, reached a maximum at 5 M nitric acid followed by a plateau. In contrast to this, the distribution ratio of U(VI) in [BuImPA][NTf_2] was quite less and showed a decreasing trend. The extraction of Am(III) was insignificant at all nitric acid concentrations. As a consequence, the separation factor of Pu(IV) over U(VI) and Am(III) achieved with the use of [BuImPA][NTf_2]/[C_4mim][NTf_2] varied from 10 to 10^3, respectively. The extraction stoichiometry of Pu(IV)-[BuImPA][NTf_2] was determined by the slope analysis of extraction data. The recovery of Pu(IV) from loaded organic was studied and the results are reported in this paper.

1. Introduction

Nuclear reactors employ natural or enriched uranium as the fuel [1]. The spent nuclear fuel discharged from the nuclear reactor contains fissile elements such as plutonium and depleted uranium, and several other elements formed by fission reaction, known as fission products. PUREX process has been adopted, worldwide, for the recovery of uranium and plutonium from the spent nuclear fuel [2,3]. It basically consists of a solvent extraction process using 1.1 M tri-*n*-butylphosphate (TBP) as extractant in *n*-dodecane (DD) as diluent. Several amides and phosphonates have been proposed as substitutes to TBP for the separation of uranium and plutonium [4–8]. However, all these reagents co-extract both uranium and fissile plutonium from nitric acid medium together with a minimal separation factor (<2). The aqueous phase rejected after the extraction of uranium and plutonium is known as high-level liquid waste [2,3]. It contains trivalent actinides such as Am(III) and Cm(III) and other fission products.

Room temperature ionic liquids (RTILs) have been proposed as possible substitutes to molecular diluent (*n*-DD) in solvent extraction applications. RTILs are organic salts molten at temperatures lower than 373 K [9]. Usually they are made up of a bulky asymmetric organic cation and an inorganic or organic anion. Excellent extraction of actinides is usually reported when molecular extractants such as TBP, amides are used in conjunction with RTIL diluents for extraction [10–14]. The cationic or anionic part of the room temperature ionic liquid tethered covalently with organic functionality is known as functionalized ionic liquid (FIL) or task specific ionic liquid (TSIL) [15]. These types of ionic liquids exhibit the properties of both ionic liquid and organic functionality. The use of functionalized ionic liquid could avoid the use of molecular extractants. Since the FILs are usually soluble in ionic liquid diluents, the solvent system is completely devoid of any molecular entities. Therefore, the use of functionalized ionic liquids in nuclear reprocessing applications could offers inherent advantages such as thermal stability and negligible vapour pressure.

Extensive studies have been carried out in the recent past for the separation of actinides from wide variety of feed solutions using FILs as medium [16–25]. For instance, we studied the separation of actinides and fission products using amide ([DOAIm][NTf_2]) and phosphonate ([ImP][NTf_2]) based functionalised ionic liquids [16,17]. These FILs showed remarkably high separation of Pu(IV) from U(VI) and Am(III). Similarly, some new task specific ionic liquids with diglycolamide (DGA) and phosphine oxide (CMPO)

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moiety anchored on imidazolium cation have been reported for the solvent extraction of actinides from nitric acid medium [18,19]. The authors reported the superior extractability of these FILs over conventional DGA and CMPO based extractants. In the very recent past, couple of TSILs bearing phosphate and phosphine oxide moiety have been reported in literature for the extraction of U(VI) and Nd(III) from nitric acid medium, respectively [20,21]. The authors reported efficient extraction of the target metal ions upon functionalization. However, the phosphoramide functionalized ionic liquids have not been studied in detail except one literature wherein the authors reported some preliminary extraction results of U(VI) in phosphoramide functionalized on ammonium based ionic liquid [22].

Therefore, the objective of the present paper is to report the synthesis of a new imidazolium based phosphoramide functionalized ionic liquid, [BuImPA][NTf_2], and the studies on the extraction of Pu(IV), U(VI) and Am(III) from nitric acid medium. The effect of various parameters on the extraction of these actinides was studied and the unique separation of Pu(IV) from other actinides U (VI) and Am(III) was established. The stripping of Pu(IV) from ionic liquid phase was carried out using oxalic acid. The extraction of actinides observed in the present TSIL was compared with those obtained in amide and phosphonate functionalized ionic liquids. The structure of the phosphoramide functionalized ionic liquid and [C_4mim][NTf_2] are shown in Fig. 1.

2. Experimental

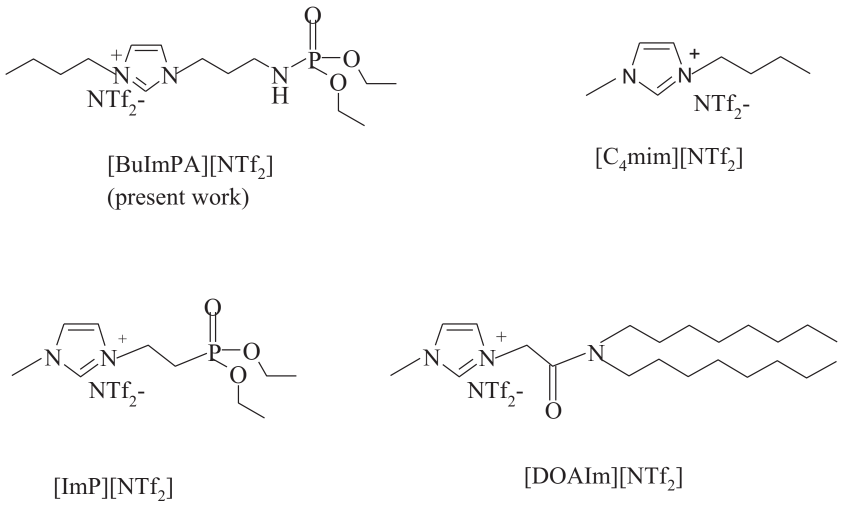
2.1. Materials

All the chemicals and reagents used in the study were of analytical grade. 1– (3-Aminopropyl)imidazole was procured from Aldrich. 1–Bromobutane and acetonitrile were procured from Merck. 1-Methylimidazole (Acros Organics) and triethylamine (Ranbaxy) were distilled before use and other chemicals were used without any purification. Lithium bis(trifluoromethanesulphonyl)imide was procured from Alfa Aesar. Diethylchlorophosphate was procured from Sigma-Aldrich. Dichloromethane was procured from Fischer Inorganics and Aromatics Limited, Chennai, India. The nitric acid was procured from Merck Specialities Private Limited, Mumbai, India and its solution of different concentrations was prepared by the diluting with distilled water. The solutions were standardized by acid-base titration. $^{239}Pu(NO_3)_4$ and $^{233}UO_2(NO_3)_2$ in nitric acid solution (~0.5 M) were obtained from the Reprocessing Group, Indira Gandhi Centre for Atomic Research, India. ^{241}Am(III) was obtained from Oak Ridge National Laboratory as AmO_2. It was dissolved in nitric acid and used as tracer. The procedure adopted for the preparation of [C_4mim][NTf_2] is described elsewhere [26].

2.2. Synthesis of diethyl-3-(-3-butylimidazolium) propylphosphoramide bis(trifluoromethanesulfonyl)imide ([BuImPA][NTf_2])

The reaction scheme for the synthesis of [BuImPA][NTf_2] is shown in Fig. 2. A solution of diethylchlorophosphate (28 g, 0.162 mol) in dichloromethane (50 mL) was added dropwise to a solution of 1-(3-aminopropyl)imidazole (20.3 g, 0.162 mol) and triethylamine (32.8 g, 0.324 mol) in dichloromethane (100 mL) at 5 °C. The reaction mixture was stirred over night at 5 °C, and the triethylamine hydrochloride formed was removed by filtration. The filtrate was dried in a rotary evaporation to obtain a yellowish viscous liquid, diethyl-3-imidazoliumpropylphosphoramide (I) with the yield of 60%. The product I was dissolved in acetonitrile and added to a solution of butyl bromide in acetonitrile (1:1.1 mol ratio) at 0 °C under vigorous stirring. The reaction mixture was stirred at room temperature for 72 h. Acetonitrile was then evaporated and product was dried in a rotary evaporator to obtain a brownish red liquid, diethyl-3-(3-imidazoliumpropyl)phosphoramide bromide (yield ~ 88%) (II). The product II was dissolved in deionised water and added slowly to the aqueous solution of bis(trifluoromethanesulfonyl)imide lithium salt (1:1.2) at room temperature. The mixture was stirred over night. The top aqueous layer was removed, and the bottom ionic liquid phase was washed with deionised water several times. The product was dried at 80 °C in a rotary evaporator yielding a thick viscous brownish oil (yield ~ 63%) of phosphoramide–functionalised ionic liquid (III). Similar procedure was adopted for the synthesis of methyl derivative ([MeImPA][NTf_2]) and propyl derivative ([PrImPA][NTf_2]) of the TSIL. The NMR spectra of the sample were recorded using a Bruker AVANCE III 400 MHz (AV 500) and FTIR spectra were recorded using Bomem FTIR spectrometer model – 103. The IR and NMR (^{1}H and ^{13}C) spectra of [BuImPA][NTf_2] and their precursors are given below. The NMR spectra of [MeImPA][NTf_2] and [PrImPA][NTf_2] derivatives are also given below.

Product I: δ_H (400 MHz; D_3CCOCD_3; Me_4Si): 1.82(m, 2H, $CH_2{-}\underline{CH_2}{-}CH_2{-}NH$), 3.38(m, 2H, ${-}\underline{CH_2}{-}NH{-}$), 2.5(m, 2H, $Im{-}\underline{CH_2}{-}CH_2{-}CH_2{-}NH{-}$), 3.88(q, 4H, ${-}O\underline{CH_2}CH_3$), 1.25(t, 6H, $2xC\underline{H_3}$ of



[BuImPA][NTf_2]
(present work)

[C_4mim][NTf_2]

[ImP][NTf_2]

[DOAIm][NTf_2]

Fig. 1. Structure of phosphoramide, phosphonate and amide based functionalised ionic liquids.