



## Solvent extraction of plutonium(IV) in monoamide – ammonium ionic liquid mixture



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### ABSTRACT

The extraction behavior of plutonium(IV) was studied in the room temperature ionic liquid, trioctylmethylammonium bis(trifluoromethanesulfonyl)imide ( $[N_{1888}][NTf_2]$ ) containing a monoamide, *N,N*-dihexyloctanamide (DHOA). The unusual extraction of Pu(IV) observed in this ionic liquid system was reported in this paper. The extraction behavior of plutonium(IV) was investigated as a function of various parameters, such as feed acid concentration, extractant and ionic liquid concentration, type of the extractants, equilibration time and temperature. Changing the extractant from DHOA to tri-*n*-butyl phosphate reduced the distribution ratio of Pu(IV). The extraction trend of Pu(IV) in neat  $[N_{1888}][NTf_2]$  was compared with those observed in other ionic liquids such as 1-alkyl-3-methylimidazolium bistriflimide ( $[C_n\text{mim}][NTf_2]$ ). Pu(IV) extraction in  $[N_{1888}][NTf_2]$  was found to follow a combination of anion exchange mechanism and neutral solvation pathway at feed acidities above 2 M  $HNO_3$ . The extraction of Pu(IV) in DHOA/ $[N_{1888}][NTf_2]$  was also compared with those observed in a molecular diluent system, DHOA/*n*-DD. All thermodynamic parameters governing the extraction of plutonium(IV) in  $[N_{1888}][NTf_2]$  was determined and discussed in detail. Stripping of Pu(IV) from the loaded ionic liquid phase was performed using dilute nitric acid.

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### 1. Introduction

Room temperature ionic liquid (RTIL) can be regarded as a sustainable alternative to the conventional molecular diluent, *n*-dodecane (*n*-DD), in solvent extraction process [1–4]. RTILs consist entirely of ions; they have negligible vapor pressure and non-volatile [5,6]. Replacement of volatile organic solvents by RTILs in solvent extraction could lead to inherently safer processes [7]. Several studies have been reported in literature on the use of ionic liquids as diluents and extractants in solvent extraction [8–28]. The ionic liquids used in those studies contained either bis(trifluoromethanesulfonyl)imide ( $[NTf_2]^-$ ) or hexafluorophosphate ( $PF_6^-$ ) anion [8–28]. Among these anions bis(trifluoromethanesulfonyl)imide is suitable for solvent extraction owing its resistance toward hydrolysis at high nitric acid concentrations. As far as the cation is concerned, most of the studies reported in literature are focused on imidazolium-based ionic liquids [8–27]. Such ionic liquids extract the metal ion essentially through cation exchange mechanism, wherein, the ionic liquid cation is lost into the aqueous phase during extraction. Although the loss of ionic liquid can

be minimized to some extent by varying the structure of ionic liquid, for example, by increasing the alkyl chain length of the cation or fluorination of the alkyl chain of anion, but, these modifications often resulted in a negative effect on the distribution ratios and extraction efficiency [28,29].

In contrast to imidazolium ionic liquids, trioctylmethylammonium chloride (Aliquat 336), trioctylmethylammonium nitrate, and trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) ionic liquids, do not exhibit any cation exchange with the metal ions from aqueous phase during extraction [30–35]. Some of these ionic liquids have already been studied as diluents in solvent extraction applications and the mechanistic aspects of extraction have been reported [32–34]. However, there is no report available in literature that emphasizes the application of trioctylmethylammonium bis(trifluoromethane-sulfonyl)imide ( $[N_{1888}][NTf_2]$ ) ionic liquid, for the extraction of Pu(IV).

In nuclear fuel reprocessing, *N,N*-dialkyl aliphatic amides have been extensively studied for the extraction of actinides from nitric acid medium [36,37]. From reprocessing and waste management point of view, amides offers very important advantages over the traditional organophosphorous compounds such as (i) amides form aqueous soluble degradation products, namely, carboxylic acids/amines upon radiolytic degradation (ii) amides are completely

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incinerable that would lead minimization of secondary waste. In view of this, Pathak et al. extensively studied the extraction behavior of actinides and other metal ions from a wide variety of nuclear wastes and recommended the employment of *N,N*-dihexyloctanamide (DHOA) [36,37] for reprocessing application.

In this paper, we report the advantages of using the ionic liquid, trioctylmethylammonium bis(trifluoromethanesulfonyl)imide ( $[N_{1888}][NTf_2]$ ), as diluent, for the extraction of plutonium(IV) in DHOA/ $[N_{1888}][NTf_2]$ . The extraction behavior of Pu(IV) in  $[N_{1888}][NTf_2]$  and DHOA/ $[N_{1888}][NTf_2]$  was investigated as a function of various extraction parameters. The extraction trend observed in  $[N_{1888}][NTf_2]$  was compared with those obtained in other class of ionic liquids and the molecular diluent, *n*-dodecane. The stripping of Pu(IV) from the loaded ionic liquid phase was also investigated.

## 2. Experimental

### 2.1. Materials and reagents

All the chemicals and reagents used in this study were of analytical grade and they were used as received without further purification. Nitric acid, acetone, Aliquat 336 (98%), tributyl phosphate (TBP) (98%) and  $LiNTf_2$  (99%) were purchased from Sigma–Aldrich.  $^{239}Pu(IV)$  in nitric acid solution ( $\sim 0.5$  M) was obtained from the Reprocessing Group, Indira Gandhi Centre for Atomic Research, India. Plutonium(IV) in the sample contained a mixture of isotopes such as 70%  $^{239}Pu$ , 24%  $^{240}Pu$ , 5%  $^{241}Pu$ , and 1%  $^{242}Pu$  [38]. The radiochemical purity of 99.9% for Pu(IV) was ascertained by TTA extraction. DHOA was kindly supplied by Heavy water board, India. Trioctylmethylammonium bis(trifluoromethanesulfonyl)imide ( $[N_{1888}][NTf_2]$ ) was synthesized according to the literature procedure [39]. The structure of the ionic liquid and DHOA are given in Fig. 1.

### 2.2. Instrumentation and analysis

The concentration of plutonium(IV) in aqueous and ionic liquid phases was determined by liquid scintillation counting. A refrigerated water bath (poly Science, Model-9100, USA) with a temperature controlling accuracy of  $\pm 0.01$  °C was used for the solvent extraction experiments. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction.

### 2.3. Equilibration procedure

All the extraction experiments were performed at 298 K unless otherwise mentioned. Various solutions of DHOA in  $[N_{1888}][NTf_2]$  were prepared. The concentration of DHOA was varied from

0.1 M to 1 M in the ionic liquid. The organic phase was pre-equilibrated with desired concentration of nitric acid in order to fix the equilibrium acidity. The equilibration procedure involved mixing of equal volumes of aqueous nitric acid and ionic liquid phases (1:1 volume ratio) spiked with  $^{239}Pu$  tracer (concentration:  $\sim 10^{-4}$  M). The extraction experiments were performed in a 10 mL capacity test tube immersed in a constant temperature water bath. The tubes were rotated in upside down manner. All the experiments were carried out in duplicate (some are in triplicate) and reported the extractions with the accuracy of  $\pm 5\%$ . After 1 h of equilibration, the two phases were separated by centrifugation and an aliquot (0.025 mL) was taken from both phases for Pu(IV) assay using liquid scintillation detector. The *distribution ratio* (*D*) was the ratio of the concentration of the metal ion in the ionic liquid phase to the concentration of the metal ion in the aqueous phase at equilibrium, was determined for Pu(IV) using Eq. (1).

$$D_{Pu(IV)} = \frac{[Pu]_{IL}}{[Pu]_{aq}} \quad (1)$$

The *extraction efficiency* (%*E*) was determined by using Eq. (2).

$$\%E = \frac{D}{D+1} \times 100 \quad (2)$$

Stripping efficiency was determined using Eq. (3).

$$\%S = \frac{[Pu(IV)]_{aq}}{[Pu(IV)]_{IL}} \times 100 \quad (3)$$

All the acid concentrations used for feed phase were standardized by acid–base titration. For thermodynamic studies, the extraction of Pu(IV) was carried out by changing the temperature of the water bath from 298 K to 333 K.

## 3. Results and discussions

### 3.1. Influence of feed acidity

The extraction of plutonium(IV) as a function of the nitric acid concentration was studied by equilibrating the ionic liquid phase with the aqueous phase (1:1 phase volume ratio) containing the plutonium(IV) nitrate (concentration:  $10^{-4}$  M). The aqueous phase acidity was varied from 0.5 M to 8.0 M. Since the nitrate ion present in nitric acid could quench the count rate during liquid scintillation counting; only small volume of aliquot (0.025 mL) was taken for counting to ensure that there was no quenching. Moreover, the results obtained from the triplicate compare well within  $\pm 5\%$ . The results are reported in Fig. 2. It can be seen that the distribution ratio of Pu(IV) increases with increase in the concentration of nitric acid. Pu(IV) is extracted appreciably in  $[N_{1888}][NTf_2]$

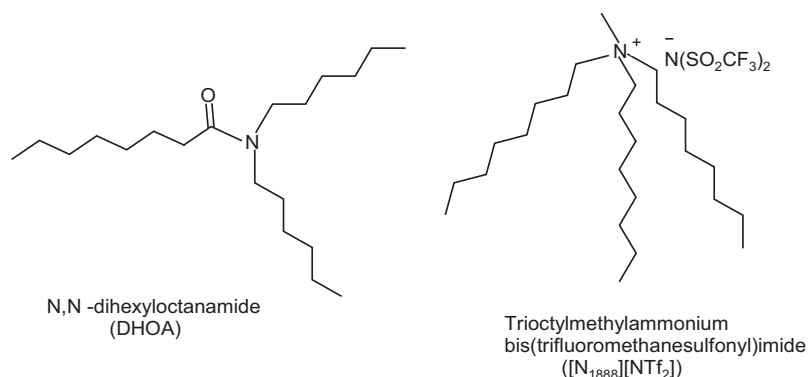


Fig. 1. Structure of the extractant and ionic liquid used in the study.

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