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Separation of plutonium(IV) from uranium(VI) using phosphonate-based task-specific ionic liquid

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ABSTRACT

The extraction behavior of plutonium(IV) and uranium(VI) from nitric acid medium by a solution of diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethanesulfonyl)imide ($ImPNTf_2$) ionic liquid in the room temperature ionic liquid (RTIL), 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (alkyl = butyl, hexyl or octyl) was studied. The distribution ratio of Pu(IV) in $ImPNTf_2/amimNTf_2$ increased with increase in the concentration of nitric acid reached a maximum at 0.5 M in nitric acid followed by decrease. The $D_{Pu(IV)}$ values, then, reached a minimum at 4–5 M and thereafter increase. The distribution ratio of U(VI) was insignificant as compared to the distribution ratio of Pu(IV) that led to the unusual separation of plutonium (IV) from uranium(VI).

Keywords: Extraction; Room temperature ionic liquid; Plutonium; Uranium; Distribution ratio; Separation Factor

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1. Introduction

Room temperature ionic liquids (RTILs) are organic salts molten at temperatures lower than 373 K [1,2]. RTILs have several attractive physical and chemical properties suitable for nuclear fuel cycle applications [3–6]. RTILs are being explored as an alternative to traditional molecular diluent, *n*-dodecane (*n*-DD), in aqueous reprocessing [7–9]. Extraordinary and unusual extraction of metal ions have been reported in literature when customary extractants are used in conjunction with RTIL diluents [10–12].

In the recent past, task-specific ionic liquids are becoming popular in the area of solvent extraction [13–19]. The TSILs (or functionalized ionic liquids) are the new sub class of RTILs wherein the cation or anion moiety is grafted with a suitable functional group of interest. The presence of functional group in TSIL exhibits its unique and synergistic properties of both the ionic liquid and organic functionality. Visser et al. prepared several functionalized ionic liquids by attaching task specific functionalities such as urea, thiourea, thioether etc. to the imidazolium moiety and reported enhanced selectivity of heavy metal extraction [14,15]. Harjani et al. synthesized new class of TSILs containing aminodiacetic acid moieties and studied the separation of copper, nickel and cobalt [16]. Ouadi et al. prepared few TSILs bearing phosphoryl group in the pendant arm of alkyl quaternary ammonium ion [18]. The preliminary extraction data on those ionic liquids indicate that the distribution ratio of U(VI) varied significantly with the structure of TSIL. Recently Odinet et al. synthesized CMPO grafted functionalized ionic liquid for actinide separation [19].

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This paper deals with the results on the extraction behavior of Pu(IV) and U(VI) in solution of diethyl-2-(3-methyimidazolium)ethylphosphonate bis(trifluoromethanesulfonyl) imide (lImPNTf2) in 1-alkyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide (amimNTf2 (alkyl = butyl, hexyl, octyl)).

2. Experimental

2.1. Materials

All the chemicals and reagents used in this study were of analytical grade. 1-Methylimidazole, 1-chlorobutane, 1-chlorohexane were procured from Lancaster, UK. 2-Bromoethylethylphosphonate and bis(trifluoro methanesulfonyl)imide lithium salt (Li $(NSO_2CF_3)_2$; $NTf_2 = N(SO_2CF_3)_2$) were procured from Aldrich and Fluka, respectively. 1-Methylimidazole was distilled before use and other chemicals were used without any purification. Uranyl nitrate (^{233}U(VI)) and plutonium nitrate (^{239}Pu(IV)) solutions in dilute nitric acid (~0.5 M) were obtained from Bhabha Atomic Research Centre, India and dissolved in the required quantity of nitric acid.

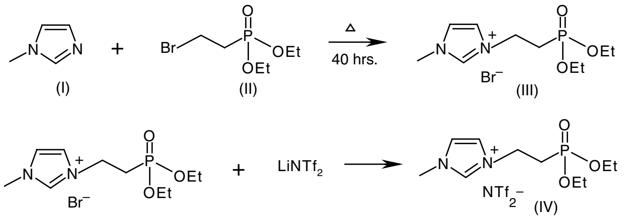
2.2. Effect of HNO_3 concentration

All the extraction studies were carried out at 298 K in duplicate with organic to aqueous phase ratio of unity. The solutions of $ImPNTf_2$ (0.4 M) in $amimNTf_2$ (a = butyl, hexyl, octyl) were prepared. The nitric acid solution of various concentrations ranging from 0.3 to 5 M was prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. Pu(IV) and U(VI) were purified by extraction in 0.05 M thenoyltrifluoroacetone/xylene and 5% tri-*n*-butylphosphate/*n*-dodecane, respectively, to remove the decay products. Extraction of plutonium (IV) (or U(VI)) as a function of nitric acid was studied by equilibrating 1 ml of organic phase with 1 ml of nitric acid solution containing ^{239}Pu(IV) tracer (20 mg/l) (or ^{233}U(VI) = 20 mg/l) using a constant temperature water bath maintained at 298 K. The concentration of nitric acid in the test solution was varied from 0.3 to 5 M. After two hours of equilibration, the radioactivity of ^{239}Pu(IV)(or ^{233}U(IV)) distributed between organic and aqueous phases were measured by liquid scintillation counting. The distribution ratio (D_{An}) of actinides, An (An = Pu(IV) and U(VI)) in organic phase was determined by using Eq. 1.

$$D_{\text{An}} = \frac{[\text{An}]_{\text{org}}}{[\text{An}]_{\text{aqs}}} \tag{1}$$

3. Results and discussions

The synthesis and characterisation of $amimNTf_2$ and $ImPNTf_2$ are described elsewhere [2,17]. The preparation scheme of ImPNTf2 is shown in the Scheme 1. Briefly, it involved refluxing a mixture of 1-methylimidazole (0.1 mol) with diethyl-(2-bromoethyl)phosphonate (0.15 mol) at 373 K for about 40 h. The resulting product (ImPBr) was washed few times with hexane followed by acetonitrile and dried in a rotary evaporator. Near quantitative yield was obtained. The TSIL, $ImPNTf_2$ was prepared by adding a pre-cooled aqueous solution of $LiNTf_2$ (1.3 mol) to the aqueous solution of ImPBr (1 mol) at 298 K. The entire mixture was stirred overnight and the bottom ionic liquid layer was separated, washed several times with water. The product was evaporated to remove moisture at 343 K using a rotary evaporator. Yield obtained was 70%. Viscosity of $ImPNTf_2$ was 42 cP at 303 K.



(I) 1-Methylimidazole, (II) Diethyl-(2-bromoethyl)phosphonate
(III) Diethyl-2-(3-methylimidazolium)ethylphosphonate bromide, ImPBr
(IV) Diethyl-2-(3-methylimidazolium)ethylphosphonate bis (trifluoromethanesulfonyl)imide, $ImPNTf_2$

Scheme 1. Synthesis of task specific ionic liquid, $ImPNTf_2$.

3.1. Extraction of Pu(IV) in RTILs

The extraction behaviour of Pu(IV) in the ionic liquid, 1-alkyl-3-methylimidazolium bis(trifluorometha nesullfonyl)imide ($amimNTf_2$) (where, alkyl = butyl, hexyl and octyl), was studied to understand the implication of using $amimNTf_2$ as diluent. The variation in the distribution ratio of Pu(IV) in $amimNTf_2$ as a function of concentration of nitric acid is shown in Fig. 1. It is observed that the distribution ratio is very low when the concentration of nitric acid is lower than 2 M. Gradual increase in distribution ratio is observed above 2 M and the $D_{\text{Pu(IV)}}$ values increases in the order $bmimNTf_2 < hmimNTf_2 < omimNTf_2$. The extraction of Pu(IV) above 2 M could be attributed to the anion exchange of $[Pu(NO_3)_{5+x}]^{-(1+x)}$ species from aqueous phase with NTf_2^- of $amimNTf_2$ as reported earlier [17]. Increasing the chain length of alkyl group attached to the imidazolium cation favours anion exchange.

3.2. Extraction of Pu(IV) in $ImPNTf_2$/$amimNTf_2$

The distribution ratio of Pu(IV) in a solution of $ImPNTf_2$ in $amimNTf_2$ is also shown in Fig. 1. It is

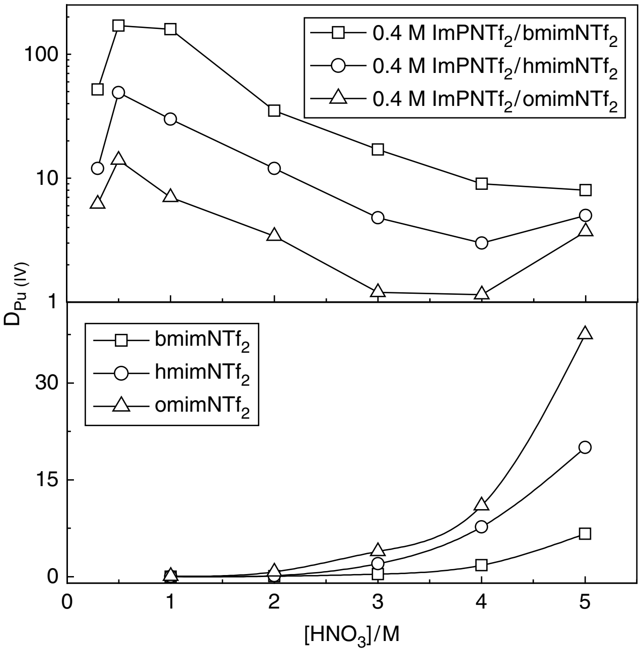


Fig. 1. Variation in the distribution ratio of Pu(IV) as a function of nitric acid. Organic phase: amimNTf$_2$ (a = butyl or hexyl or octyl) or 0.4 M ImPNTf$_2$/amimNTf$_2$. Aqueous phase: 0.3 - 5 M HNO$_3$, Equilibration time = 1 h, O : A = 1:1, T = 298 K.

observed that the $D_{Pu(IV)}$ increases with increase in the concentration of nitric acid (from 0.3 M), reaches a maximum value at 0.5 M followed by decrease in $D_{Pu(IV)}$ values. The decrease continued up to 4–5 M in nitric acid, followed by increase in $D_{Pu(IV)}$ values. Higher distribution ratios observed in the presence ImPNTf$_2$ as compared to amimNTf$_2$ at nitric acid concentrations below 3 M, could be attributed to the selective extraction of Pu(IV) by the task specific ionic liquid, ImPNTf$_2$. Moreover, the trend observed below 5 M, is similar to the trend reported for Pu(IV) by neutral extractants such as trialkyl phosphates and phosphonates [20,21]. The initial increase in $D_{Pu(IV)}$ with increase in nitric acid could be attributed to the increased formation of neutral plutonium species, [Pu(NO$_3$)$_4$], that are extractable by >P=O of ImPNTf$_2$. The distribution ratio reaches a maximum at the nitric acid concentration of 0.5 M. However, in neutral extractants the maximum was achieved only at 3–4 M [20,21]. Subsequently, the decrease in the distribution ratio of plutonium(VI) above 4 M, in case of neutral extractants, was attributed to the formation of inextractable anionic Pu(IV) complexes, $[Pu(NO_3)_{5+x}]^{-(1+x)}$ as well as to the protonation of the extractant. However, in ImPNTf$_2$/amimNTf$_2$ system, the correct reason for the decrease in distribution ratio observed above 0.5 M nitric acid is not clear, perhaps it could be due to protonation of ImPNTf$_2$. In addition, the abundance of anionic nitrate complexes would be negligible in this acid range (i.e., near 0.5 M). Therefore the most plausible reason for the decrease of distribution ratio of Pu(IV) above 0.5 M nitric acid could be the protonation of ImPNTf$_2$ ionic liquid. Nevertheless, these anionic species are formed in significant concentrations above 5 M. Under these conditions (>5 M), the anion exchange of $[Pu(NO_3)_{5+x}]^{-(1+x)}$, with NTf$_2^-$ of amimNTf$_2$ seems to predominate the extraction of plutonium and the $D_{Pu(IV)}$ values thus increases with increase in the concentration of nitric acid above 5 M.

It is also interesting to observe the dependence of Pu(IV) extraction on the nature of diluent. The distribution ratio of Pu(IV) in 0.4 M ImPNTf$_2$/amimNTf$_2$ increases in the order ImPNTf$_2$/bmimNTf$_2$ > ImPNTf$_2$/hmimNTf$_2$ > ImPNTf$_2$/omimNTf$_2$. This indicates that the use of amimNTf$_2$ diluent increases the extraction of Pu(IV) in the order bmimNTf$_2$ > hmimNTf$_2$ > omimNTf$_2$, which is the reverse order when ionic liquid alone (Section 3.1) is used for the extraction. The reason for this behavior is not clear. Moreover the presence of ImPNTf$_2$ in amimNTf$_2$ remarkably decreases the distribution ratio of Pu(IV) in the resultant solution at 5 M nitric acid. For instance, the distribution ratio of Pu(IV) in omimNTf$_2$ at 5 M nitric acid is 35, whereas $D_{Pu(IV)}$ value of 4 is obtained by the addition of 0.4 M ImPNTf$_2$ in omimNTf$_2$. The reason for such decrease in distribution ratio and the reversal of Pu(IV) extraction upon the addition of ImPNTf$_2$ in amimNTf$_2$ is not clear at present, and more studies are needed to understand this behavior.

3.3. Separation factor

The distribution ratio of U(VI) in 0.4 M ImPNTf$_2$/amimNTf$_2$ (a = butyl, hexyl and octyl) is shown in Table 1. It is observed that the distribution ratios of U(VI) are insignificant as compared to the $D_{Pu(IV)}$ values. It varies from 0.04 to 0.3 depending upon the concentration of nitric acid and the nature of diluent used. It is worthwhile to compare the data generated in the present study, with the distribution data reported for the extraction of U(VI) and Pu(IV) in phosphorous based neutral extractants such as TBP/*n*-DD [20] and DAAP/*n*-DD [21] (TBP = tri-*n*-butyl phosphate, DAAP = diamylamylphosphonate). Generally, the neutral extractants containing phosphoryl group (>P=O group), when used for extraction, exhibit a comparable distribution ratio for uranium (VI) and plutonium (IV) [20,21]. Table 1, shows the distribution ratios of U(VI) and Pu(IV) reported for tri-*n*-butyl phosphate [20] and diamylamylphosphonate [21] present in *n*-dodecane. It is observed that these distribution values are quite similar. This is due to the fact that these phosphates and phosphonates are neutral extractants and extract only the neutral species such as UO$_2$(NO$_3$)$_2$ for U(VI) and Pu(NO$_3$)$_4$ for Pu(IV) from nitric acid medium. Since the coordinating ability of these extractants with U(VI) and

Table 1
Distribution ratio of plutonium(IV) and uranium(VI) and their separation factors (SF = $D_{\mathrm{Pu(IV)}}/D_{\mathrm{U(VI)}}$). Organic phase: ImPNTf$_2$ in amimNTf$_2$, TBP/*n*-DD, DAAP/*n*-DD, O:A = 1:1, Eq. time = 1 h, *T* = 298 K

Solvent	Distribution ratio of						SF of Pu(IV) from U(VI) obtained in		
	U(VI) in			Pu(IV) in					
	1 M	3 M	5 M	1 M	3 M	5 M	1 M	3 M	5 M
0.4 M ImPNTf$_2$/bmimNTf$_2$	0.305	0.145	0.2	159	17	8	521	117.2	40
0.4 M ImPNTf$_2$/hmimNTf$_2$	0.15	0.09	0.16	30	4.2	5	200	46.6	31.2
0.4 M ImPNTf$_2$/omimNTf$_2$	0.080	0.044	0.135	7	1.2	3.7	12.5	27.3	27.4
1.1 M TBP/*n*-DD [17]	7.3	24.5	22	2.9	15	18	0.39	0.6	0.8
1.1 M DAAP/*n*-DD [18]	43	71.2	63	56	106	88	1.3	1.48	1.4

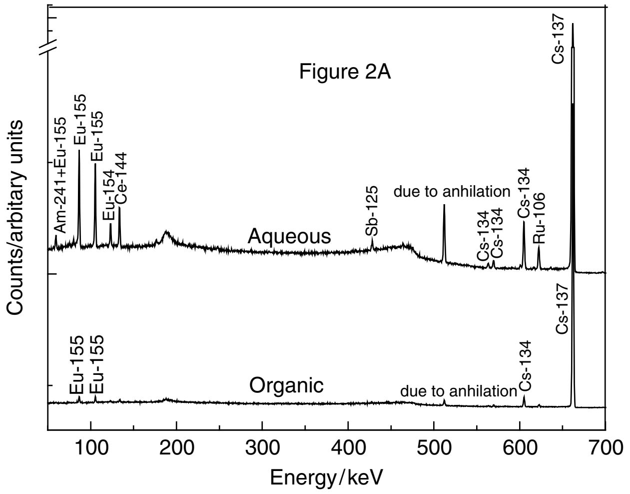
DAAP = diamylamylphosphonate.
TBP = tri-*n*-butyl phosphate.

Pu(IV) are not very different and, moreover, the diluent *n*-dodecane is inert, the distribution of uranium(VI) and plutonium(IV) realized for phosphates and phosphonate are fairly similar. This phenomenon leads to poor separation factor (quotient of $D_{\mathrm{Pu(IV)}}$ to $D_{\mathrm{U(VI)}}$) tending towards the value of unity, as shown in Table 1. However, the separation factors achieved using phosphonate based ionic liquid, ImPNTf$_2$, shown in Table 1, are amazing as they are nearly 10–500 times higher than the values obtained for traditional phosphoryl based neutral extractants. This could be attributed to the extraordinary and specific solvating ability of plutonium complexes in ionic liquid phase. This behavior can be suitability exploited for separating plutonium from uranium in PUREX process streams.

The task specific property of ImPNTf$_2$ was further confirmed by contacting the solution of 0.4 M ImPNTf$_2$/bmimNTf$_2$ with the aqueous solution containing 3 M nitric acid spiked with HLLW (155 Gwd/Te). Fig. 2 shows the gamma spectra of organic and aqueous phases obtained after the extraction. The energies range from 50 to 700 keV are plotted in Fig. 2a, and from 700 to 1,200 keV are plotted in Fig. 2b for clarity. It is observed that the extraction of fission products, such as cesium isotopes, europium isotopes, ^{144} Ce and ^{154} Eu by ImPNTf$_2$ is insignificant. From the gamma spectrum, the distribution ratio of ^{137}Cs, ^{155}Eu, ^{144}Ce were determined to be 0.19, 0.17 and 0.045 and the distribution ratio of other nuclides are much lower. This indicates the task specific property of ImPNTf$_2$.

4. Conclusions

The phosphonate functionalized ionic liquid, ImPNTf$_2$, was studied for the extraction of Pu(IV), U(VI)



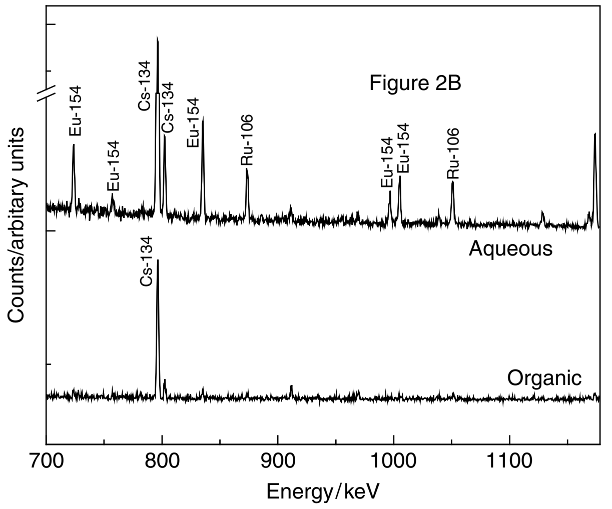


Fig. 2. Gamma spectrum of aqueous and organic phase Organic Phase: 0.4 M IMPNTf$_2$/bmimNTf$_2$. Aqueous phase: 4 M nitric acid spiked with HLLW (155 GWd/Te).

and fission products from nitric acid medium. The extraction behaviour of Pu(IV) in the ionic liquid, 1-alkyl-3-methylimidazolium bis(trifluoromethanesullfonyl) imide (amimNTf$_2$) increases in the order bmimNTf$_2$ < hmimNTf$_2$ < omimNTf$_2$. However, the distribution ratio of Pu(IV) in a solution of 0.4 M ImPNTf$_2$/amimNTf$_2$ increases in the order ImPNTf$_2$/bmimNTf$_2$ > ImPNTf$_2$/hmimNTf$_2$ > ImPNTf$_2$/omimNTf$_2$. The extraordinary separation factors of plutonium (IV) achieved with the use of ImPNTf$_2$ could be attributed to the task specific property of the extractant ionic liquid, that seems to facilitate the extraction and stabilization of the plutonium complex in ionic liquid phase and has the incredible ability to reject uranium (VI) fission products.

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