



Liquid–liquid extraction of Pu(IV), U(VI) and Am(III) using malonamide in room temperature ionic liquid as diluent

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ABSTRACT

The extraction behavior of U(VI), Pu(IV) and Am(III) from nitric acid medium by a solution of N,N-dimethyl-N,N-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) in the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4mimNTf_2$), was studied. The distribution ratio of these actinides in DMDOHEMA/ $C_4mimNTf_2$ was measured as a function of various parameters such as the concentration of nitric acid, DMDOHEMA, NTf_2^- , alkyl chain length of ionic liquid. The extraction of actinides in the absence of DMDOHEMA was insignificant and the distribution ratio achieved in conjunction with $C_4mimNTf_2$, was remarkable. The separation factor of U(VI) and Pu(IV) achieved with the use of DMDOHEMA, ionic liquid was compared with Am(III) and other fission products. The stoichiometry of the metal-solvate was determined to be 1:2 for U(VI) and Pu(IV) and 1:3 for Am(III).

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1. Introduction

Room temperature ionic liquids (RTILs) are organic salts that melt at temperatures lower than 373 K [1]. Usually they are made up of a bulky, asymmetric organic cation and an inorganic or organic anion. RTILs are receiving increased attention for possible applications in the area of nuclear fuel reprocessing and waste management [2–7]. Essentially, they are being explored as possible substitute to molecular diluent in solvent extraction procedures and as an alternative to high temperature molten salt in non-aqueous reprocessing applications [2–7]. Several reviews have been published in literature detailing the scope of RTILs as the solvent medium for separations [4–7]. Excellent extraction of target metal is usually observed when traditional extractants are used in conjunction with RTIL diluents. Dai et al. [8] reported exceptional extraction of strontium(II) when ionic liquid was used as diluent. Visser et al. [9] studied the extraction of cesium and strontium from nitric acid medium by using various crown ethers in 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nmim][PF_6]$, $n=4, 6, 8$) ionic liquids.

The extraction of U(VI) from nitric acid medium in a solution of tri-n-butylphosphate (TBP) in C_4mimPF_6 or 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4mimNTf_2$) was reported by Giridhar et al. [10]. The results

indicated that uranium(VI) was extracted by the traditional solvation mechanism when the concentration of nitric acid was less than 4 M and by ion exchange mechanism thereafter. The mechanistic aspects of U(VI) extraction in TBP or glycolamide in ionic liquid was investigated in detail by Dietz and co-workers [11–13] and Shen et al. [14], respectively. The mode of uranyl ion partitioning in ionic liquid phase was shown to change from ion exchange to the traditional M-solvate complex with the increase of hydrophobicity of ionic liquid. The extraction behavior of Pu(IV) from nitric acid medium in a solution of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) or crown ether in ionic liquid was reported by Lohithakshan and Aggarwal [15,16]. Cation exchange was proposed for the extraction of Pu(IV) in ionic liquid phase.

Malonamides are promising candidates for the partitioning of minor actinides from high level liquid waste (HLLW) [17–22]. Due to the incinerability and formation of aqueous soluble radiolytic degradation products, amides have gained prominence over phosphorous based extractants. Among the diamides, N,N'-dimethyl-dibutyl-tetradecylmalonamide (DMDBTDMA) and N,N'-dimethyl-N,N'-di-octyl-2-(2-(hexyloxy)ethyl)malonamide (DMDOHEMA) are regarded as promising extractants for the separation of minor actinides [17–22]. The latter compound, DMDOHEMA has some advantages such as enhanced organophilicity and limited third-phase formation over DMDBTDMA. Recently, Shimojo et al. [23] studied the extraction of lanthanides in a diglycolamide derivative tetraoctyldiglycolamide (TODGA) present in $C_nmimNTf_2$. The authors reported exceptional extraction in ionic

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liquid media as compared to the isoctane system. Shen et al. [14] reported the extraction of U(VI) in tetrabutyl diglycolamide and tetramethyldiglycolamide present in ionic liquid medium. Efficient extraction of U(VI) at low acidities was reported in this case also. However, to the best of our knowledge the extraction behavior of actinides in the malonamide derivative, DMDOHEMA, has not been reported so far. Therefore, the aim of the present paper is to report the extraction behavior of U(VI), Pu(IV) and Am(III) in DMDOHEMA/ C_4 mimNTf₂ solution. The effect of various parameters such as the concentration of nitric acid, DMDOHEMA, NTf₂⁻, alkyl chain length of ionic liquid and temperature on the distribution ratio of actinides was studied and the results are reported in this paper.

2. Experimental

2.1. Materials

All the chemicals and reagents used in this study were of analytical grade. N,N-Dimethyl-N,N-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) was supplied by National Chemical Laboratory, Pune, India. 1-Methylimidazole and 1-chloroalkane were procured from Lancaster, UK. 1-Methylimidazole was distilled before use and other chemicals were used without any purification. Bis(trifluoromethanesulphonyl) imide lithium salt (LiNTf₂; NTf₂ = (NSO₂CF₃)₂) was procured from Fluka. The procedure for the synthesis of C_n mimNTf₂ is reported elsewhere [24]. ²³⁹Pu(NO₃)₄ and ²³³UO₂(NO₃)₂ in nitric acid solution (~0.5 M) were obtained from the Reprocessing Group, Indira Gandhi Centre for Atomic Research, India. ²⁴¹Am(III) was obtained from Oak Ridge National Laboratory (ORNL), USA as AmO₂. It was dissolved in nitric acid and used as tracer. The radioisotopes, ¹⁵²⁺¹⁵⁴Eu(III), ⁸⁵⁺⁸⁹Sr(II), ¹⁴⁴Ce(IV), ⁶⁰Co(II), ⁵⁴Mn(II) and ¹⁰⁶Ru(III) in dilute nitric acid were purchased from Board of Radiation and Isotope Technology, Mumbai.

2.2. Extraction procedure

All the extraction studies were carried out at 298 K. Various solutions of DMDOHEMA (0.1–0.5 M) in C_n mimNTf₂ ($n=4, 5, 6$) were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. The equilibration procedure involved mixing of equal volumes of aqueous and organic phases (1 ml each) in a 10 ml capacity test tube immersed in a constant temperature water bath. The tubes were rotated in upside down manner for about 1 h. The extraction of actinides as a function of nitric acid was studied by equilibrating the organic and aqueous phase consisting of desired concentration of nitric acid spiked with ²³³U(VI) tracer (or ²³⁹Pu(IV) or ²⁴¹Am(III) tracer = 20 mg/l). The concentration of nitric acid in the test solution was varied from 0.01 M to 8 M. After 1 h of equilibration, the radioactivity of ²³³U(VI) (²³⁹Pu(IV)) in both the phases was measured by liquid scintillation counting and the radioactivity of ²⁴¹Am(III) was measured by a well-type NaI(Tl) scintillation detector. The distribution ratios (D_M) of actinides were determined using Eq. (1). A similar experiment was performed with other ionic liquid diluents C_5 mimNTf₂ and C_6 mimNTf₂.

$$D_M = \frac{[M]_{IL}}{[M]_{aq}}, M = U(vi), Pu(iv) \text{ and } Am(iii) \quad (1)$$

2.3. Effect of NTf₂⁻ concentration

The effect of NTf₂⁻ concentration on the distribution ratio of actinides was studied by equilibrating the organic phase with aqueous phase containing desired concentration of nitric acid and

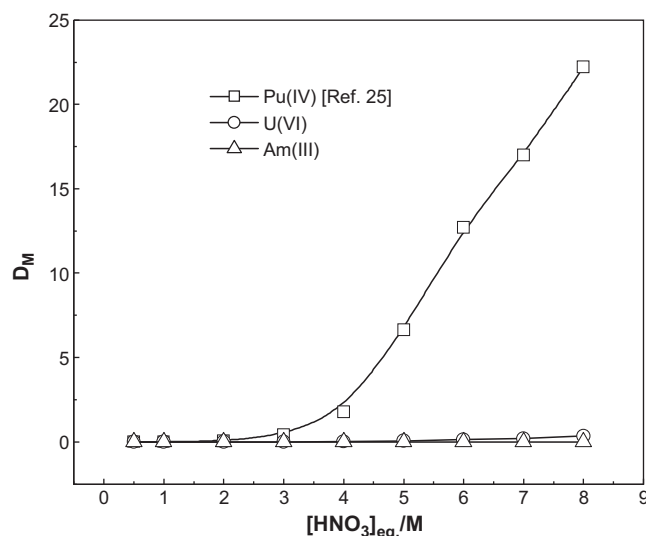


Fig. 1. Distribution ratio of Pu(IV), U(VI) and Am(III) in C_4 mimNTf₂. Aqueous phase: 0.5–8.0 M HNO₃. Equilibrium time = 1 h. $T = 298$ K.

NTf₂⁻ ions spiked with ²³³U(VI) (or ²³⁹Pu(IV) or ²⁴¹Am(III)) tracer. The concentration of additives NTf₂⁻ was varied by adding the required quantity of LiNTf₂ in aqueous phase. The distribution ratio of actinides was measured as described above.

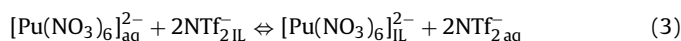
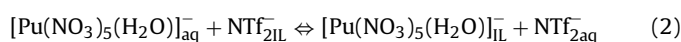
2.4. Effect of [DMDOHEMA]

The extraction of U(VI), Pu(IV) and Am(III) as a function of DMDOHEMA concentration in ionic liquid phase was studied by equilibrating the organic phase with aqueous phase containing desired concentration of nitric acid solution spiked with actinide tracers. The DMDOHEMA concentration in ionic liquid phase was varied from 0.1 M to 0.5 M.

3. Results and discussions

3.1. Extraction in C_n mimNTf₂

The extraction behavior of Pu(IV) in C_n mimNTf₂ ($n=4, 8$) is reported elsewhere [26] and the data are presented in Fig. 1. The extraction of Pu(IV) in C_4 mimNTf₂ is negligible ($D \leq 10^{-2}$) at nitric acid concentration lower than 2 M. A gradual increase in distribution ratio of Pu(IV) is observed above 3 M nitric acid. Previously, we investigated [25] the mechanism of plutonium(IV) extraction in C_n mimNTf₂ ($n=4, 8$) and reported that Eqs. (2) and (3) are responsible for the extraction of plutonium(IV) from nitric acid concentrations more than 2 M. The mechanism involved the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species present in aqueous phase with the NTf₂⁻ ion of ionic liquid phase (Eqs. (2) and (3)), as reported elsewhere [25]. In contrast to this observation, the distribution ratio of U(VI) and Am(III) in C_4 mimNTf₂ is negligible at all acidities. Since these metal ions do not form anionic species with nitrate ion as compared to Pu(IV), they are not extracted by anion exchange [26].



3.2. Extraction in DMDOHEMA/ C_n mimNTf₂

Fig. 2 shows the variation in the distribution ratio of Pu(IV) in 0.3 M DMDOHEMA/ C_4 mimNTf₂ as a function of nitric acid

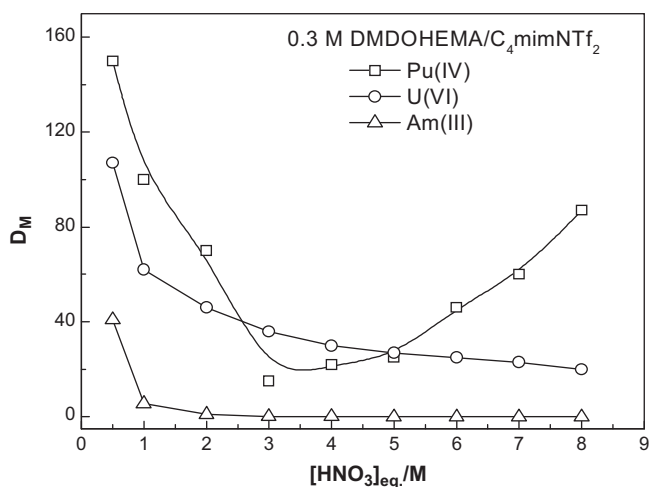


Fig. 2. Distribution ratio of Pu(IV), U(VI) and Am(III) in 0.3 M DMDOHEMA/C₄mimNTf₂. Aqueous phase: 0.5–8.0 M HNO₃. Equilibrium time = 1 h. *T* = 298 K.

concentration. It is observed that the distribution ratio of Pu(IV) initially decreases with increase in the concentration nitric acid. The distribution ratio reaches a minimum value at 3–4 M in nitric acid followed by increase in $D_{\text{Pu(IV)}}$ values. The trend observed in the presence of DMDOHEMA shows that there could be a couple of modes through which plutonium(IV) is extracted in DMDOHEMA/C₄mimNTf₂ phase (to be discussed below).

The extraction trend observed above 4 M nitric acid in 0.3 M DMDOHEMA/C₄mimNTf₂ (Fig. 2) compares well the trend observed above 4 M in C₄mimNTf₂ (Fig. 1). This indicates that plutonium(IV) could be extracted by the anion exchange of $[\text{Pu}(\text{NO}_3)_5(\text{H}_2\text{O})]^-$ or $[\text{Pu}(\text{NO}_3)_6]^{2-}$ species with NTf₂⁻ of ionic liquid phase in 0.3 M DMDOHEMA/C₄mimNTf₂ also (similar to Eqs. (2) or (3)). To confirm this, the variation in the distribution ratio of Pu(IV) in 0.3 M DMDOHEMA/C_nmimNTf₂ was studied as a function of $[\text{NTf}_2^-]_{\text{aq}}$ at 5 M nitric acid. The results are shown in Fig. 3. Since, the added LiNTf₂ was dissolved in the ionic liquid phase to some extent, the aqueous phase concentration of NTf₂⁻ ion at equilibrium was not known. In view of this, Fig. 3 shows the variation in the distribution ratio of Pu(IV) as a function of initial concentration of NTf₂⁻ ion

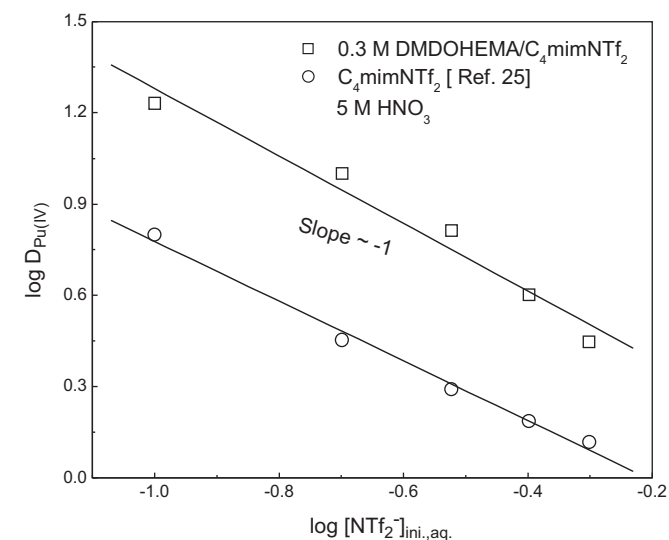


Fig. 3. Variation of distribution ratio Pu(IV) as a function of $[\text{NTf}_2^-]_{\text{ini}}$ in the aqueous phase. Organic Phase: C₄mimNTf₂ or 0.3 M DMDOHEMA/C₄mimNTf₂. Aqueous phase: 5 M HNO₃ + (0.1–0.5 M) LiNTf₂, Equilibrium time = 1 h, *T* = 298 K.

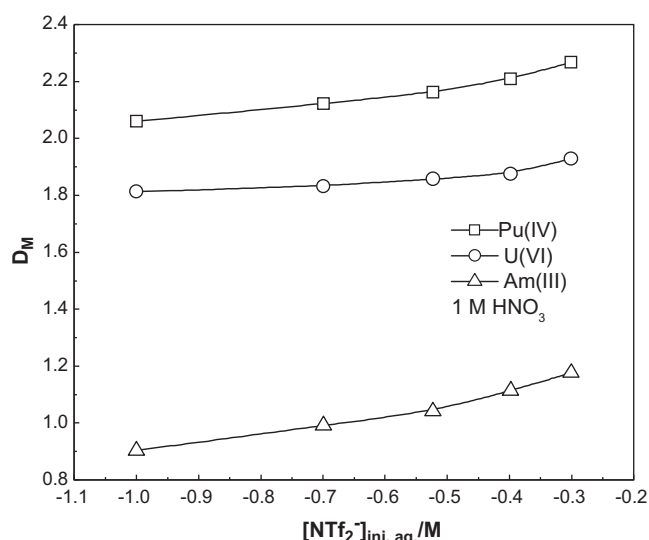


Fig. 4. Variation in the distribution ratio of Pu(IV), U(VI) and Am(III) as a function of initial NTf₂⁻ concentration in the aqueous phase. Organic phase: 0.3 M DMDOHEMA/C₄mimNTf₂. Aqueous phase: 1 M HNO₃ + (0.1–0.5 M) LiNTf₂, *T* = 298 K. Equilibrium time = 1 h, *T* = 298 K.

rather than equilibrium concentration. Eqs. (2) and (3) indicate that the extraction of plutonium(IV) should decrease with increase in the concentration of NTf₂⁻ ion in aqueous phase. It is observed from Fig. 3 that the distribution ratio of plutonium(IV) decreases with increase in the concentration of NTf₂⁻ ion in aqueous phase as expected (according to Eqs. (2) and (3)). The decreasing trend observed from such plot indicates the involvement of ion-exchange of anionic Pu(IV) species with NTf₂⁻ of organic phase. Moreover, the slope observed is comparable with the slope reported for the extraction of Pu(IV) in C₄mimNTf₂ [25] (Fig. 3). All these observations, confirm that the predominant mode of Pu(IV) extraction in 0.3 M DMDOHEMA/C₄mimNTf₂ above 4 M is through anion exchange [25]. Since U(VI) and Am(III) do not form such anionic species in significant quantities, the anion exchange is not observed at high acid concentrations [26]. Otherwise the $D_{\text{U(VI)}}$ and $D_{\text{Am(III)}}$ would have increased with increase of nitric acid concentration like Pu(IV) extraction. In addition, the extraction of Am(III) in 0.3 M DMDOHEMA/C₄mimNTf₂ above 2 M nitric acid is negligible.

Below 4 M nitric acid, the enhancement in distribution ratio of actinides in the presence of DMDOHEMA (Fig. 2) indicates the involvement of DMDOHEMA for extraction. In this range (0.5–4 M), the extraction of actinides could occur by ion exchange or by metal-solvate complex formation with DMDOHEMA/C₄mimNTf₂. The metal-solvate mechanism was reported for the extraction of U(VI) in TBP/C₄mimNTf₂ by Giridhar et al. [10] at nitric acid concentrations below 4 M nitric acid. However, the possibility of anion exchange is unlikely to occur in this region, since the abundance of anionic plutonium(IV) species (as well as U(VI) and Am(III) species) is negligible in the acid range 1–3 M [26,27]. It is well-known that plutonium(IV) is purified by anion exchange method only from 5 to 6 M nitric acid. These characteristics indicate that the abundance of U(VI), Pu(IV) and Am(III) anionic species, below 4 M, is insignificant and it is unlikely that these actinides are extracted by anion exchange from 0.5 to 4 M nitric acid. Nevertheless, the effect of $[\text{NTf}_2^-]_{\text{ini,aq.}}$ on the extraction of these actinides in 0.3 M DMDOHEMA/C₄mimNTf₂ from 1 M nitric acid medium was studied and the results are shown in Fig. 4. If the anion exchange is involved (Eqs. (2) and (3)) then the extraction of plutonium(IV) should decrease with increase in the concentration of NTf₂⁻ ion in aqueous phase. However, it is observed from Fig. 4 that the distribution ratio of U(VI), Pu(IV) and Am(III) increases with increase

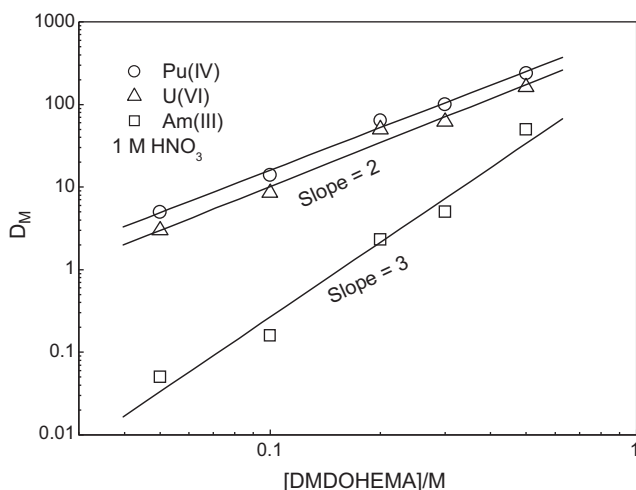


Fig. 5. Variation in the distribution ratio of Pu(IV), U(VI) and Am(III) as a function of DMDOHEMA concentration in ionic liquid phase. Organic phase: 0.05–0.5 M DMDOHEMA/ $C_4\text{mimNTf}_2$. Aqueous phase: 1 M HNO_3 , Equilibrium time = 1 h, $T = 298\text{ K}$. $O/A = 1$.

in the concentration of $[\text{NTf}_2^-]_{\text{ini,aq}}$. The results shown in Fig. 4 are inconsistent with the anion exchange observed in Fig. 3. Therefore, the study confirms that anion exchange is not responsible for extraction of actinides from nitric acid concentration less than 4 M.

3.3. Stoichiometry of extraction

Cation exchange is being reported as the primary mode of metal ion transfer in ionic liquid media [11–16,23]. The mechanism of U(VI) extraction in TBP dissolved in ionic liquid was investigated in detail by Dietz and Stepinski [11]. The authors reported that the mode of uranyl ion partitioning in TBP/ionic liquid changes from cation-exchange to the traditional metal-solvate complex extraction, with the increase of nitrate ion in aqueous phase and hydrophobicity of ionic liquid. In addition, the cation exchange is the predominate mode of metal ion transfer in systems such as Sr^{2+} in crown ether/ionic liquid [13], Pu(IV) in CMPO/ionic liquid [15], lanthanides in diglycolamide/ionic liquid [23], etc. In all those studies the authors reported the cation exchange of metal-solvate cation complex with $C_4\text{mim}^+$ ion of ionic liquid. Therefore the metal-solvate stoichiometry in the present case was also investigated by the slope analysis of extraction data. The variation of D_M ($M = \text{U(VI)}$, Pu(IV) and Am(III)) with $[\text{DMDOHEMA}]$ is shown in Fig. 5. Linear regression of the extraction data results in a slope of 2 for U(VI) and Pu(IV), indicating two molecules of DMDOHEMA are involved in the extraction, which is in good agreement with the value reported for molecular diluent [22]. In contrast to this observation as well as to those observed in molecular diluent (n-DD, slope 2) [19], a slope of 3 is obtained for the extraction of Am(III).

Fig. 6 shows the IR spectra of DMDOHEMA/ $C_4\text{mimNTf}_2$ before and after the extraction of U(VI) in ionic liquid phase. It is observed that the transmittance band occurring at 1640 cm^{-1} , due to $\text{C}=\text{O}$ stretching, is broadened and shifted to 1602 cm^{-1} upon uranium(VI) extraction from 0.1 M nitric acid medium in 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$. This indicates that the carbonyl moiety of DMDOHEMA is involved in coordination with U(VI) after extraction. The possibility of a cation exchange of the M -solvate complex with $C_4\text{mim}^+$ ion of the ionic liquid was investigated by measuring the absorbance of $C_4\text{mim}^+$ cation ($\sim 250\text{ nm}$) in nitric acid medium obtained after extraction. Fig. 7 shows the UV-visible absorption spectrum of $C_4\text{mimCl}$ in 0.5 M nitric acid. It is observed that the absorption maximum is observed at the λ_{max} of 250 nm. Fig. 7 also shows the absorption spectrum of aqueous phase obtained after the

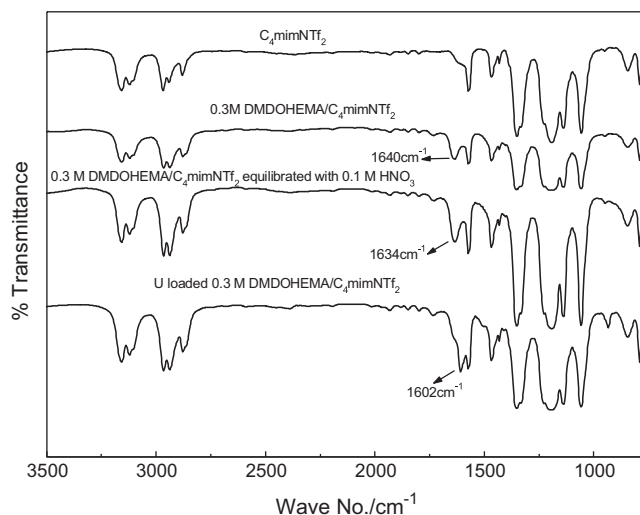


Fig. 6. FTIR spectra of ionic liquid solutions.

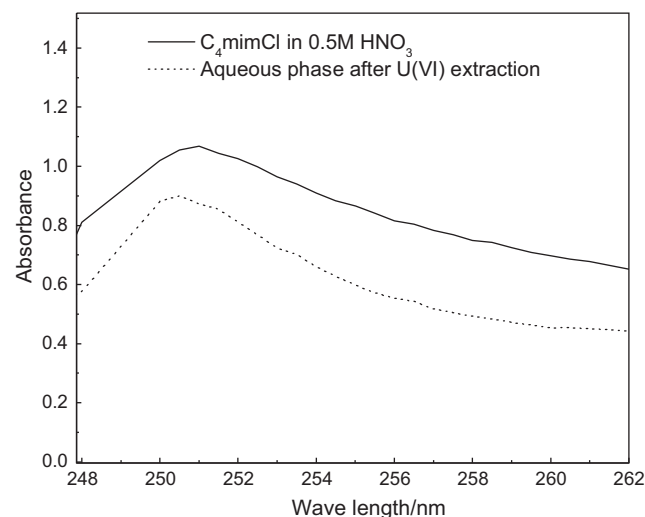


Fig. 7. Comparison in the absorption spectra of $C_4\text{mimCl}$ (10^{-2} M in 0.5 M nitric acid) and the aqueous phase obtained after U(VI) extraction. The aqueous phase used for extraction was U(VI) (10^{-3} M) in 0.5 M nitric acid and organic phase was 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$.

extraction of uranium(VI) from 0.5 M nitric acid medium. Comparable absorption spectrum observed in this case confirms that U(VI) is likely to be extracted by cation exchange mechanism below 4 M nitric acid medium. A similar mechanism could be responsible for the extraction of Pu(IV) and Am(III) also in ionic liquid medium below 4 M nitric acid. Based on these observations the following

Table 1

Separation factor of U(VI) and Pu(IV) achieved using ionic liquid medium at 3 M HNO_3 . Organic phase: 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$. Aq. Phase: 3 M HNO_3 spiked with different radioisotopes.

Metal ion	Separation factors of	
	U(VI) over M	Pu(IV) over M
$^{241}\text{Am(III)}$	228	107
$(^{152}+^{154})\text{Eu(III)}$	200	94
$(^{85}+^{89})\text{Sr(II)}$	1000	400
$^{144}\text{Ce(IV)}$	400	166
$^{60}\text{Co(II)}$	3600	1500
$^{54}\text{Mn(II)}$	2570	1070
$^{106}\text{Ru(III)}$	2500	1000

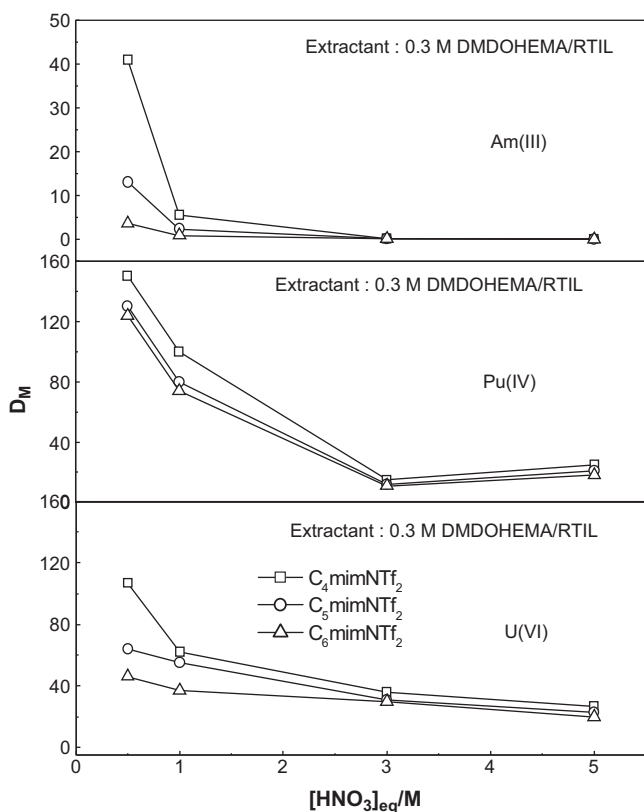
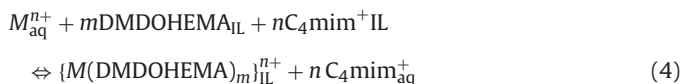


Fig. 8. Variation in the distribution ratio of U(VI), Pu(IV) and Am(III) as a function of alkyl chain length of $C_n\text{mimNTf}_2$. Organic phase: 0.3 M DMDOHEMA/ $C_n\text{mimNTf}_2$. Aqueous phase: 0.1–5.0 M HNO_3 , Equilibrium time = 1 h, $T = 298$ K.

equation can be proposed for the extraction of actinides from nitric acid medium below 4 M. However, more studies are needed to confirm the correct mechanism of extraction.



where M^{n+} is UO_2^{2+} , Pu^{4+} or Am^{3+} .

3.4. Nature of diluent

Fig. 8 shows the variation in the distribution ratio of actinides in 0.3 M DMDOHEMA/ $C_n\text{mimNTf}_2$ ($n = 4-6$). It is observed that the distribution ratio of actinides decreases with increase in chain length of alkyl group in $C_n\text{mimNTf}_2$. A similar behavior was also reported for the extraction of U(VI) and other metal ions in various systems [11,14]. This was attributed to the suppression in ion exchange mode of actinide transfer in ionic liquid phase, and

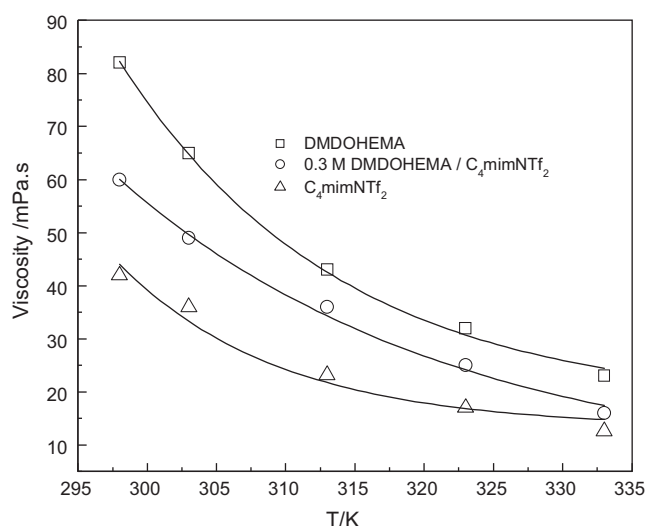


Fig. 9. Viscosity of DMDOHEMA, $C_4\text{mimNTf}_2$ and their solutions. $T = 298-333$ K.

switchover of extraction mechanism from ion exchange to the traditional solvation with the increase of hydrophobicity of ionic liquid (increasing chain length) [14].

3.5. Separation factor

Table 1 shows the separation factor (SF) of U(VI) and Pu(IV) achieved with the use of 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$ from other radionuclides. It is observed that a SF of >1000 is achieved for U(VI) from radionuclides such as ^{85}Sr , ^{60}Co , ^{54}Mn and ^{106}Ru . Similarly, a SF of >1000 for Pu(IV) is achieved from ^{60}Co , ^{54}Mn and ^{106}Ru . It is interesting to compare the distribution values obtained in the present study with those obtained in conventional molecular diluent n-DD. It was reported [20] that the distribution ratio of U(VI) in 1 M DMDOHEMA/n-DD increases from the value of ~ 3 at 0.1 M HNO_3 to ~ 200 at 4 M HNO_3 . Patil et al. [21] reported the distribution ratios of 34.1 and 15.5 for Pu(IV) and Am(III) extraction from 3 M HNO_3 using 1 M DMDOHEMA/n-DD. These studies [17,19–22] indicates that DMDOHEMA extracts Pu(IV), U(VI) as well as Am(III) when the diluent used was n-DD. In contrast to that study, the extraction of Am(III) is insignificant in the present case (≥ 3 M HNO_3) using ionic liquid diluent ($D_{\text{Am(III)}} < 10^{-2}$) as compared to U(VI) and Pu(IV) (see **Fig. 2**). This indicates that ionic liquid diluents offers enhanced stability to the U(VI) and Pu(IV) complex in organic phase. **Table 2** shows the comparison in the distribution ratio of actinides in various amide/ionic liquid systems. It is observed that DMDOHEMA in conjunction with the ionic liquid exhibits excellent extraction of actinides from nitric acid medium, over other amide/ionic liquid systems.

Table 2
Distribution ratios of Pu(IV), U(VI), Am(III) and Th(IV) in various amide/ionic liquid systems. Organic phase: extractants in ionic liquid diluent. Aqueous phase: 1 M HNO_3 spiked with the actinide tracers. Equilibrium time: 1 h, temperature = 298 K, O/A = 1.

Solvent systems	Distribution ratio of			
	U(VI)	Am(III)	Pu(IV)	Th(IV)
Present study (0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$)	62	41	100	–
0.01 M TBDA/ $C_4\text{mimPF}_6$	2.75 [14]	–	–	1.8 [3]
0.01 M MBDA/ $C_4\text{mimPF}_6$	2.25 [14]	–	–	7[3]
0.5 M DOBA/ $C_4\text{mimNTf}_2$	0.15 [28]	0.007	0.05 [28]	–
1 M DHOA/ $C_4\text{mimNTf}_2$	0.93	0.01	2	–

TBDA, tetrabutyl diglycolamide; MBDA, methylbutyl diglycolamide; DOBA, di-n-octylbutyramide; DHOA, dihexyloctanamide; $C_4\text{mimPF}_6$, 1-butyl-3-methylimidazolium hexafluorophosphate.

3.6. Viscosity measurement

Fig. 9 shows the effect of temperature on the viscosity (η , in mPa s) of 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$. It is observed that the viscosity of 0.3 M DMDOHEMA/ $C_4\text{mimNTf}_2$ decreases from 60 mPa s to 16 mPa s with increase of temperature from 298 K to 333 K; whereas the viscosity of $C_4\text{mimNTf}_2$ decreases from 42 to 12 mPa s in the same temperature range.

4. Conclusions

The extraction behavior of Pu(IV), U(VI) and Am(III) in DMDOHEMA/ionic liquid solution was studied. The extractant DMDOHEMA showed excellent selectivity for U(VI) and Pu(IV) in ionic liquid diluent, whereas in n-DD, Am(III) was also co-extracted. Above 4 M nitric acid, the primary mode of Pu(IV) transfer in ionic liquid phase was found to be anion exchange. However, below 4 M nitric acid the investigations indicate that the most plausible mechanism of actinides transfer in ionic liquid phase was cation exchange of metal–solvate complex with $C_4\text{mim}^+$ cation exchange of ionic liquid. The distribution ratio of actinides decreased with increase of alkyl chain length of $C_n\text{mimNTf}_2$ and SF of >1000 was obtained for actinides from many fission products. Our studies confirmed that the malonamide, DMDOHEMA, in conjunction with the ionic liquid showed excellent extraction of U(VI) and Pu(IV) from nitric acid medium, indicating DMDOHEMA/ionic liquid is a promising candidate for reprocessing applications.

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