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Role of Acetohydroxamic Acid in Selective Extraction of Technetium and Uranium Employing *N,N*-Dihexyloctanamide as Extractant

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Straight chain *N,N*-dihexyloctanamide (DHOA) has been identified as a promising alternate extractant to tributyl phosphate (TBP) for the reprocessing of uranium based spent fuels. The present work compares extraction behavior of technetium using DHOA and TBP solutions in *n*-dodecane, under varying experimental conditions such as acidity (0.5–6 M HNO₃); extractant concentration (1.1 and 1.5 M), and uranium loading (50 g/L, relevant for Pu rich spent fuel feed solutions). The effect of acetohydroxamic acid concentration on U, Pu, Np, and Tc extraction behavior has also been investigated. Pu(IV)-AHA interaction and its influence on extraction using TBP and DHOA extractants has been studied spectrophotometrically. The experimental data suggest that 1.1 M DHOA is better than 1.1 M TBP with respect to co-extraction of Tc and U, and U decontamination with respect to Np/Pu.

Keywords acetohydroxamic acid; amide; reprocessing; technetium; uranium

INTRODUCTION

Reprocessing of spent nuclear fuel is vital for the long-term global nuclear power growth and is the major motivation to develop novel schemes for the separation of uranium, and plutonium from other elements with high decontamination factors (DFs). The PUREX process has undergone several modifications to address the issues of high burn up, fewer solvent extraction cycles, and reduced waste arisings (1). However, the experience gained over last five decades on the reprocessing of spent fuel has identified some major drawbacks of TBP such as

- lower distribution ratio (*D*) of Pu(IV) compared to U(VI), which can lead to Pu losses to raffinate,
- deleterious nature of degradation products (mono- and dibutyl phosphoric acids) leading to decreased decontamination of U and Pu from fission products, loss of U and Pu to organic phase during stripping and

- production of large amounts of secondary radioactive waste in the form of P₂O₅/inorganic phosphates during thermal/chemical treatment (2,3).

These shortcomings may pose a serious challenge, particularly during the reprocessing of short-cooled (MOX) thermal reactor as well as fast reactor fuels with larger Pu content and significantly higher burn up (4).

In this context, high molecular weight *N,N*-dialkyl amides have drawn the attention of radiochemists as potential extracting agents for actinides and have been proposed as alternatives to TBP for the reprocessing of irradiated fuels. Their main advantages over TBP are:

- the innocuous nature of the radiolytic degradation products viz. mainly carboxylic acids and amines which can be easily washed out by water, thereby simplifying the solvent treatment and
- the complete incinerability leading to smaller amounts of secondary waste (5,6).

Extensive studies carried out at Radiochemistry Division, BARC have shown that straight chain *N,N*-dihexyloctanamide (DHOA) is a promising alternate to TBP for reprocessing of Pu rich spent fuels (7). DHOA extracts Pu(IV) more efficiently than TBP, both at trace-level concentration as well as under uranium/plutonium loading conditions. Uranium extraction behavior of DHOA is, however, similar to that of TBP during the extraction cycle. Stripping behavior of U and Pu was better with DHOA than that with TBP. DHOA also offers better fission product and structural materials decontamination than that with TBP.

Under the Global Nuclear Energy Partnership (GNEP) program, efforts are being made by countries with a developed nuclear technological base to provide safe nuclear power to other countries and to minimize proliferation concerns worldwide (8). As a consequence, separation scientists have been presented with a challenge of developing proliferation resistant flow sheets for the reprocessing of spent fuels. As a part of the Advanced Fuel

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Cycle Initiative (AFCI), Argonne National Laboratory has developed the *UREX*⁺ process, which consists of five solvent extraction steps that separate dissolved spent fuel into seven fractions (9). The five solvent-extraction steps are:

- i. *UREX*: quantitative extraction of uranium and technetium;
- ii. *CCD-PEG*: recovery of Cs and Sr;
- iii. *NPEX*: recovery of plutonium and neptunium;
- iv. *TRUEX*: recovery of Am, Cm, and REE fission products; and
- v. *Cyanex 301*: separation of Am and Cm from REE.

The *UREX* process focuses on the co-extraction of uranium and technetium at 1 M HNO₃. Among the long-lived fission products, ⁹⁹Tc is an important beta emitting nuclide of concern ($t_{1/2} = 2.11 \times 10^5$ y, $E_{\beta\text{-max.}} = 295.5$ keV). It has high fission yield of about 6.13% for thermal neutron induced fission of ²³⁵U and therefore is an important radionuclide from the point of view of long-term nuclear waste management (10). Apart from the contamination of U and Pu products, technetium catalyzes the oxidation of hydrazine, which is used as a nitrite scavenger in the reductive separation of plutonium from uranium (10).

Upon dissolution of spent nuclear fuel in nitric acid, technetium passes into solution as pertechnetate ions. The solvent for the *UREX* process is the typical *PUREX* solvent, TBP dissolved in *n*-dodecane (30% v/v). In this process, a reductant/complexant is added to the scrub cycle to limit the extractability of plutonium and neptunium. The feed and the scrub are adjusted to 1 M HNO₃ to enhance the complexation of Pu and Np and increase the extractability of pertechnetate ion. The solvent, now loaded with uranium and technetium, is stripped of technetium in the Tc-Strip section using a high concentration of nitric acid. The Tc product stream is scrubbed of uranium in the Uranium Re-extraction section. The combined solvent is then scrubbed of excess nitric acid before entering the U-Strip section, where dilute nitric acid removes uranium from the solvent.

Hydroxamic acids are organic ligands of general formula (RCONHOH) which can act as strong chelating agents of metal ions by the formation of five-membered chelate rings (Fig. 1). As O,O donor ligands they have a strong affinity for "hard" metal ions such as Pu⁴⁺ (11). Simple hydroxamates such as formohydroxamic acid (FHA, R=H) and acetohydroxamic acid (AHA, R=CH₃) are hydrophilic ligands which are not extracted into the organic phase to any appreciable degree. Aqueous soluble FHA and AHA are very effective for the separation of uranium from neptunium and plutonium as they reduce neptunium and plutonium rapidly (12). Both FHA and AHA have been reported to form a red complex with Pu(IV) ions, which transform into the blue Pu(III) complex after standing for several hours. Hydroxamic acids undergo

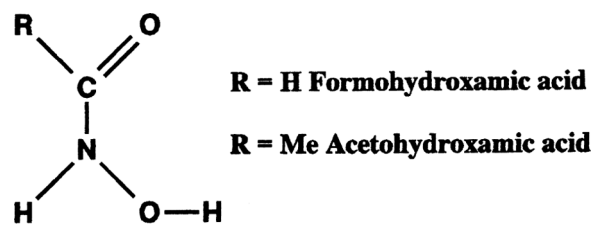
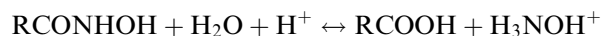


FIG. 1. Structure of hydroxamic acid.

hydrolysis to hydroxylamine and the pertinent carboxylic acid (12).



The hydroxamic acids are used at <3 M HNO₃, where the acid hydrolysis is suppressed (13). The hydroxamic acid instability in nitric acid does not affect operations of centrifugal contactors, where the processing time is expected to be short compared to the measured destruction half-life in nitric acid (14). The strength of interaction of hydroxamic acids with actinides is quantified by stability constant data (15,16).

In the present work, DHOA has been evaluated vis-a-vis TBP for U, Pu, Np, and Tc extraction under different experimental conditions such as

- a. acidity (0.5–6 M HNO₃);
- b. DHOA concentration (1.1 and 1.5 M),
- c. uranium loading (50 g/L, relevant for Pu rich spent fuel feed solutions), and
- d. AHA concentration (0.5 & 1.0 M).

The effect of time of equilibration on the distribution ratio values of Tc and Pu was also investigated. An attempt was made to spectrophotometrically investigate Pu(IV)-AHA interaction under various process conditions.

EXPERIMENTAL

Materials

DHOA synthesized at the Radiochemistry Division, BARC, was used in the present work (7). *n*-dodecane used in this study was of AR grade. TBP was washed with alkali prior to its use. ²³³U tracer ($\sim 10^{-4}$ M) was purified by anion exchange and was found by α spectrometry to be free from ²³²U and its daughter products. Pu (principally ²³⁹Pu) was purified by the solvent extraction procedure using HTTA (2-theonyltrifluoroacetone) as extractant and its radiochemical purity was ascertained by gamma spectrometry for the absence of ²⁴¹Am. Pu(IV) was extracted by 0.5 M HTTA in xylene at 1.0 M HNO₃ and stripped by 8.0 M HNO₃ and was used as stock for Pu(IV). ²³⁷Np was also purified using HTTA as extractant. ⁹⁹Tc and ²³⁷Np ($t_{1/2} = 2.14 \times 10^6$ y) were checked for their

purity by liquid scintillation counting and gamma spectrometry. It should be noted that no valency adjustment of Pu and Np was done. A stock solution of natural uranium (oxide form) was prepared by dissolving in nitric acid, and was used after suitable dilution.

Extraction Procedure

Pre-equilibrated solutions of DHOA and TBP (at desired concentrations) in *n*-dodecane with respective nitric acid solutions were used for solvent extraction experiments. Generally, 0.5 mL of the pre-equilibrated organic phases of TBP and DHOA were equilibrated for one hour with equal volume of the aqueous phases containing metal ions of interest at 298 K. The two phases were then centrifuged and assayed by taking suitable aliquots (25–50 μ L) from both the phases. ^{233}U , Pu, and Tc in the organic and aqueous phases were estimated by liquid scintillation counting using a dioxane based scintillator. The composition of the scintillator medium was: 0.7% (w/v) 2,5-diphenyloxazole (PPO), 0.03% (w/v) 1,4-di-[2-(5-phenyloxazolyl)]-benzene (POPOP), 1% (w/v) trioctyl phosphine oxide (TOPO), and 10% (w/v) naphthalene dissolved in one liter of dioxane. ^{237}Np counting (gamma energy: 86 keV) was done using an HPGe detector. The correction for counts in both the phases due to the decay products of natural uranium was done by performing experiments under identical conditions using natural uranium solutions under the desired conditions. The distribution ratio of the metal ions (D_M) was defined as the ratio of concentration of metal ion in the organic phase (expressed in terms of counts per unit volume per minute) to that in the aqueous phase. All the experiments were carried out in duplicate and the material balance was within error limits ($\pm 5\%$).

Spectrophotometric Studies

The characteristic absorption bands of Pu(III), Pu(IV), and Pu(VI) are observed at (560, 600), 476, and 831 nm, respectively. Spectrophotometric samples were prepared employing 2×10^{-3} M Pu(IV) under varying concentrations of AHA (2×10^{-4} –0.5 M) at 1–4 M HNO_3 . Finally, the extractability of Pu(IV) without/with 0.5 M AHA in 1.1 M TBP and 1.1 M DHOA solutions in *n*-dodecane was examined. Absorbance measurements were carried out at room temperature using suitable blanks. UV-vis spectrophotometer from JASCO, Japan (Model V 530) was used for recording the spectra and the absorbance measurements.

RESULTS AND DISCUSSION

Effect of Acidity

Extraction studies of Tc(VII) were carried out at varying acidities (0.5–6 M HNO_3) as pure tracer (^{99}Tc) as well as in the presence of 50 g/L U in the aqueous phase using 1.1 M

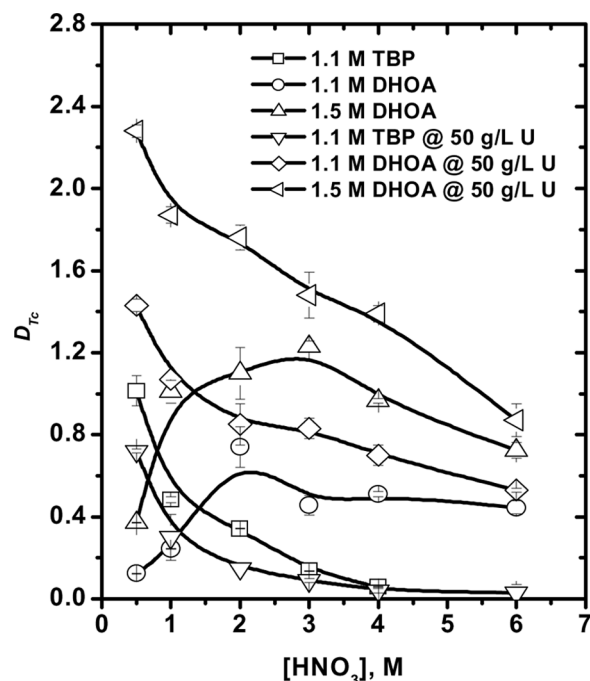


FIG. 2. Variation of D_{Tc} with aqueous phase acidity; T: 298 K.

TBP and 1.1 M/1.5 M DHOA solutions in *n*-dodecane (Fig. 2). A higher concentration of DHOA was chosen in view of the relatively lower extraction of uranium by 1.1 M DHOA as compared to that of 1.1 M TBP (17). When DHOA was used as extractant, the distribution ratio of Tc (D_{Tc}) initially increased with acidity from 0.5 M HNO_3 , passed through a maximum at ~ 2 –3 M HNO_3 , and decreased thereafter. The initial increase in D_{Tc} was explained in terms of the formation and extraction of pertechnic acid, HTcO_4 , as the extractable species with increased nitric acid concentration. On the other hand, the decrease in D_{Tc} values at higher acidity was attributed to the competition from the extracted nitric acid. Even though HTcO_4 formation will be favored at higher acidities, the extraction of nitric acid in the organic phase effectively reduces the free extractant concentration thereby suppressing the extraction of technetium. El-Kot and Pruett reported similar observation in the case of 1.1 M TBP as the extractant; however, the extraction maximum was observed at 0.5–0.6 M HNO_3 (18,19).

It was of interest to investigate the effect of uranium loading (50 g/L U) on technetium extraction. Remarkable enhancement in the extraction of technetium in the presence of uranium was reported at lower nitric acid concentrations (< 0.1 M). There was a minor decrease in D_{Tc} value from 0.48 (no U) to 0.3 (50 g/L U at 1 M HNO_3) in case of 1.1 M TBP (20). On the other hand, DHOA data indicate towards the salting out effect of uranium which facilitates the formation of HTcO_4 leading to its enhanced

extraction. It should be noted that uranium extraction is higher in the case of TBP as extractant as compared to that of DHOA (17). This suggests that the presence of a higher concentration of uranium in the case of the latter, which reduces the water activity and favors the formation of HTcO_4 and followed by its extraction in the organic phase. It appears that mixed uranium-technetium complexes are responsible for a higher extraction at $>2\text{ M HNO}_3$ as shown by the following equilibrium:

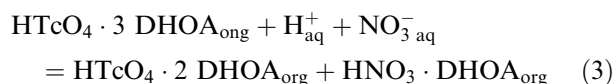
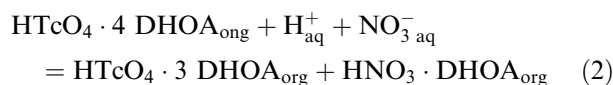
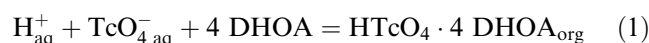


Where $\text{L}=\text{TBP}$ or DHOA . These studies suggest that DHOA appears better for Tc recovery as compared to TBP under *UREX* process conditions. Similar observations were made during the coextraction behavior of $\text{Tc}(\text{VII})$ and $\text{U}(\text{VI})$ by *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) from nitric acid solution (21).

Stoichiometry of the Extracted Species

To gain an insight into the nature of extracted species, technetium extraction studies were carried out as a function of DHOA concentration at different acidities (0.5, 1 and 4 M HNO_3). Figure 3 shows a gradual decrease in slope values with increased aqueous phase acidity (3.93 ± 0.04 (0.5 M HNO_3) to 2.48 ± 0.01 (4.0 M HNO_3)). This suggests increasing competition of nitric acid with

pertechnetic acid (HTcO_4) for extractant molecules. Similar observations have been reported during technetium extraction using TBP as the extractant (19). However, contrary to the TBP system where only three extractant molecules are present in the extracted species at 1 M HNO_3 , more than three DHOA molecules (slope: 3.58 ± 0.04) are associated with the extracted species. This makes the extracted species involving DHOA more organophilic as compared to that of TBP resulting in higher extraction of Tc . A step-wise reduction in the coordination of HTcO_4 with DHOA for increasing HNO_3 concentration of the aqueous phase can be expressed by the following equilibrium reactions:



It appears that at 0.5 M HNO_3 Eq. (1) dominates but at 4 M HNO_3 Eq. (2) and (3) are dominating. Generally amides extract nitric acid by forming 1:1 Amide- HNO_3 adduct as the predominant species (22). The free extractant concentration was calculated by subtracting the the organic phase nitric acid concentration. The latter was measured by titration of the organic phase in neutralized ethanol medium using standard NaOH solution.

Effect of Acetohydroxamic Acid

To ensure the selective extraction of U and Tc from spent fuel dissolver solution, extraction of Pu and Np need to be suppressed. In this context, an attempt was made to compare the extraction data of Tc , U , Pu , and Np for 1.1 M DHOA and 1.1 M TBP for the aqueous phases containing 50 g/L U and 0.5/1.0 M AHA solutions at 1 M HNO_3 . Table 1 lists the distribution data of U , Pu , Np , and Tc in the presence of 50 g/L U at 1 M HNO_3 containing 0.5 M and 1.0 M AHA . It may be noted that the distribution ratio values of uranium and technetium are invariant in the absence/presence of AHA in the aqueous phase. It is also evident that DHOA offers better Tc recovery as compared to that of TBP . Typically, $>50\%$ extraction of Tc can be achieved using 1.1 M DHOA maintaining organic-to-aqueous phase ratio as 1; while $\sim 23\%$ Tc can be extracted under identical conditions using 1.1 M TBP as the extractant. This data indicates that the number of stages required for quantitative extraction of Tc will be lower in the case of 1.1 M DHOA and 1.5 M

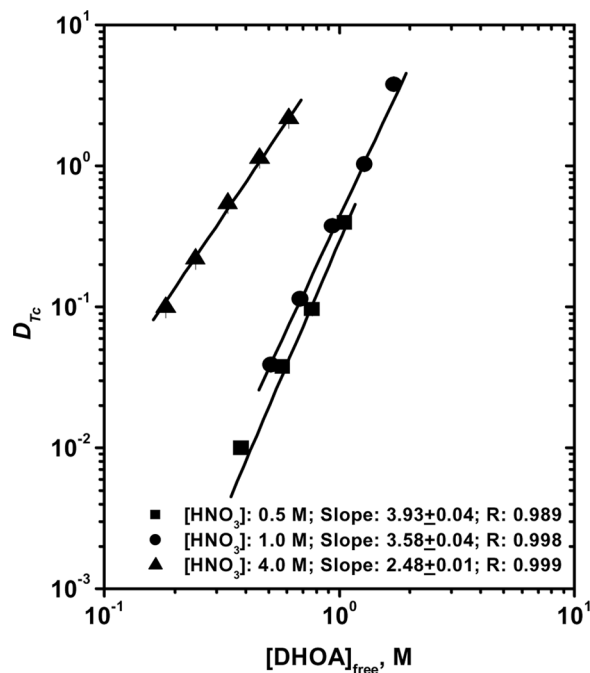


FIG. 3. Variation of D_{Tc} with DHOA concentration at different acidities; T: 298 K.

TABLE 1
Extraction data of different metal ions in the presence of 50 g/L U at 1 M HNO₃; Extractant(s): 1.1 M TBP & 1.1 M DHOA solutions in *n*-dodecane; T: 298 K

Element	$D_M @ 50 \text{ g/L U in } 1 \text{ M HNO}_3$					
	0.5 M AHA			1.0 M AHA		
	1.1 M TBP	1.1 M DHOA	1.5 M DHOA	1.1 M TBP	1.1 M DHOA	1.5 M DHOA
Tc	0.3	1.1	1.9	0.3	1.1	1.9
U	3.9	2.0	3.7	3.8	2.0	3.7
Pu	2.2×10^{-2}	$\sim 10^{-4}$	7.4×10^{-3}	8.8×10^{-3}	$\sim 10^{-4}$	4.7×10^{-3}
Np	1.9×10^{-2}	4×10^{-3}	6.0×10^{-3}	1.2×10^{-3}	1.0×10^{-3}	6.0×10^{-3}

DHOA as compared to that of 1.1 M TBP. In addition, DHOA offers better decontamination for Tc over Pu and Np than that of TBP.

Figure 4 compares the separation factor (SF) values of U over Pu/Np for 1.1 M TBP, 1.1 M DHOA and 1.5 M DHOA solutions as extractants in the presence of 50 g/L U at 1 M HNO₃. The data suggest that 1.1 M DHOA is better than 1.1 M TBP as extractant for the selective extraction of U over Pu/Np under the conditions of the experiment. The SF values for U over Pu (D_U/D_{Pu}) are significantly higher for 1.1 M DHOA ($\sim 20,000$) than those for 1.1 M TBP (180) and 1.5 M DHOA (500) using 0.5 M AHA in the aqueous phase. Use of 1.0 M AHA marginally improved the SF values U over Pu/Np for all the extractants.

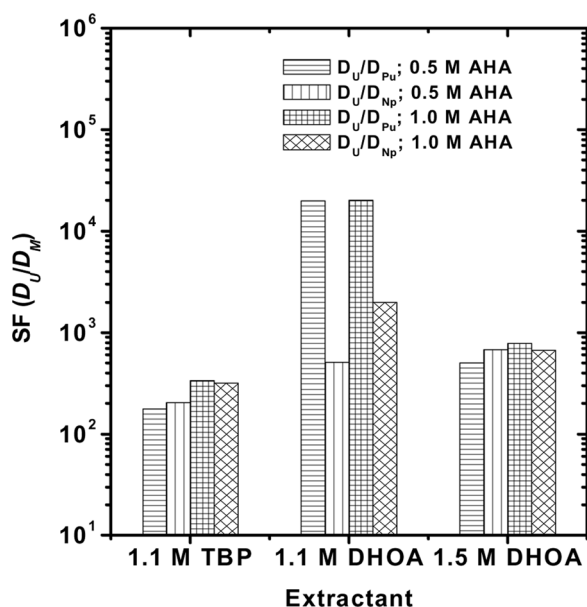


FIG. 4. Separation factors with DHOA and TBP; Aqueous phase: 50 g/L U @ 1 M HNO₃ containing AHA; Diluent: *n*-dodecane; T: 298 K; M: Pu or Np.

Stability of Acetohydroxamic Acid

Even though AHA is an organic ligand, it is proposed for use in the UREX⁺ process to reduce Np and Pu and the resultant hydrophilic complexes are separated from U by extraction with TBP. Few reports suggest that the pertechnetate ion can be reduced to Tc by AHA over long periods, which can alter its fate in the fuel cycle (23). It was of interest to investigate the effect of time of equilibration on D_{Tc} and D_{Pu} values from 1.0 M HNO₃ containing 0.5 M AHA (proposed scrub composition for UREX process) using 1.1 M TBP and 1.5 M DHOA as the extractants (Fig. 5). There was marginal variation in the extraction

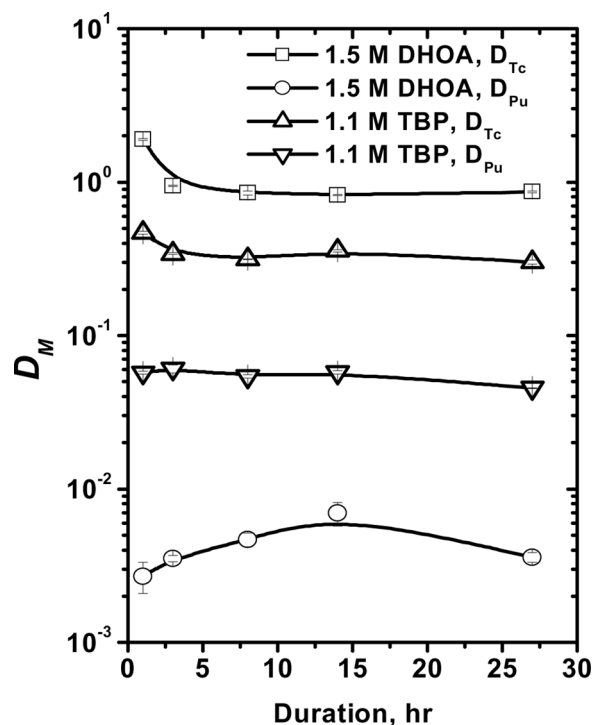


FIG. 5. Variation of D_M (M=Tc, Pu) with time of equilibration; Organic phase: 1.5 M DHOA & 1.1 M TBP/*n*-dodecane; Aqueous phase: 0.5 M AHA @ 1 M HNO₃; T: 298 K.

data of Tc and Pu under the conditions of the present work. It should be noted that though there is a minor decrease in D_{Tc} values for both TBP and DHOA between 1–3 hours, the kinetics is too slow to affect its extraction profile under the process conditions.

Spectrophotometric Investigation on Pu-AHA Interaction

The speciation of Pu(IV) in the presence of varying concentrations AHA (2×10^{-4} – 0.5 M) in 1 M HNO_3 undergoes significant changes. Earlier studies have demonstrated that three Pu-acetohydroxamate species are formed (24). Under conditions of low AHA concentrations (0.1 M AHA), mainly the mono-acetohydroxamate species of Pu are formed. However, under UREX process conditions (≥ 0.1 M AHA), the di-acetohydroxamate species of plutonium becomes predominant and also the concentration of Pu-tri-acetohydroxamate species grows up. It is evident from Fig. 6 that Pu(IV) absorption spectra is unaffected upto 2×10^{-3} M AHA concentration beyond which a significant enhancement in the absorbance values is observed due to Pu-AHA complexation. The color of the solution changed to dark brown/red Pu(IV)-hydroxamate complexes depending on AHA concentration.

The hydrolytic instability is a key feature of hydroxamic acids which should be taken into consideration during the development of a process flow sheet. Figures 7 and 8 show the effect of aqueous phase acidity and time on the absorption spectra of Pu-AHA complexes. AHA complexation decreases with increased acidity from 1 to 4 M HNO_3 .

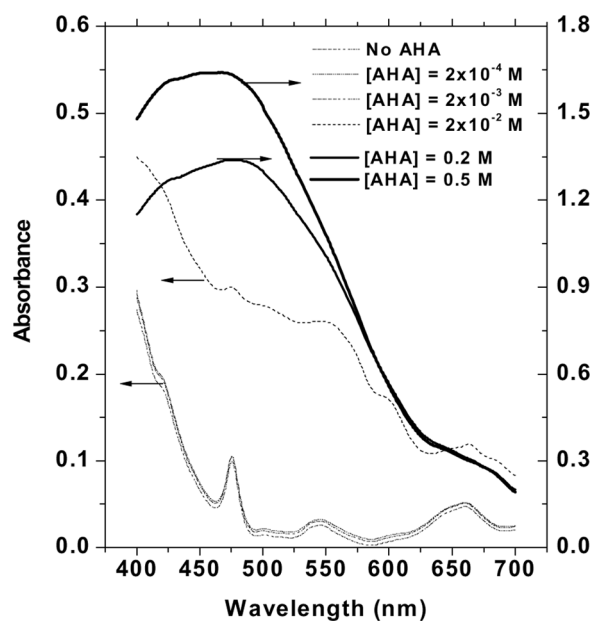


FIG. 6. Effect of AHA concentration on Pu(IV) absorption spectra; [Pu(IV)]: 2×10^{-3} M @ 1 M HNO_3 .

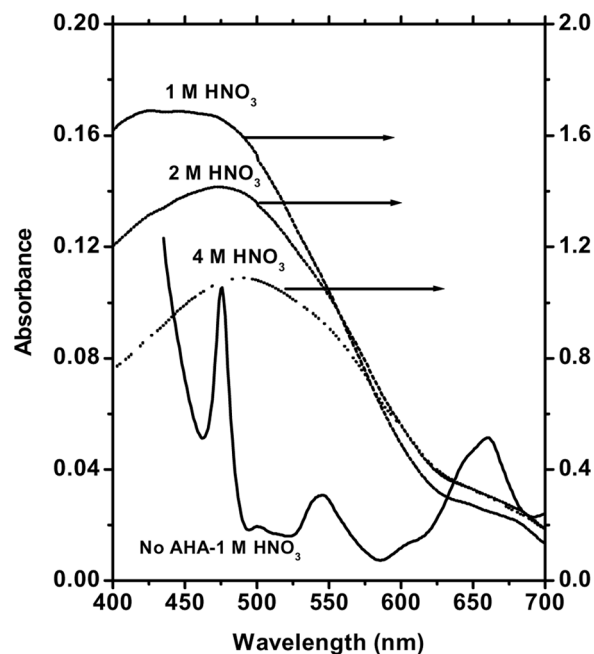


FIG. 7. Absorption spectra of Pu(IV)-AHA complex at different acidities; [Pu]: 2×10^{-3} M; [AHA]: 0.5 M.

Similarly, there is a decrease in the absorbance of Pu(IV)-AHA complex with time. It should be noted that only marginal decrease in the absorbance takes place with in 60 minutes duration which indicates towards an induction period for the hydrolysis and reduction of Pu(IV) to Pu(III). Figure 9 shows clear signatures of the formation

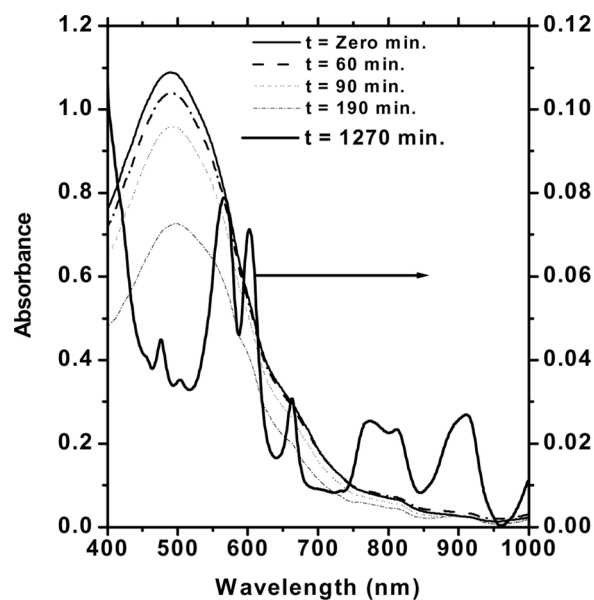


FIG. 8. Absorption spectra of Pu(IV)-AHA complex; Sample: 2×10^{-3} M Pu(IV) + 0.5 M AHA @ 4 M HNO_3 .

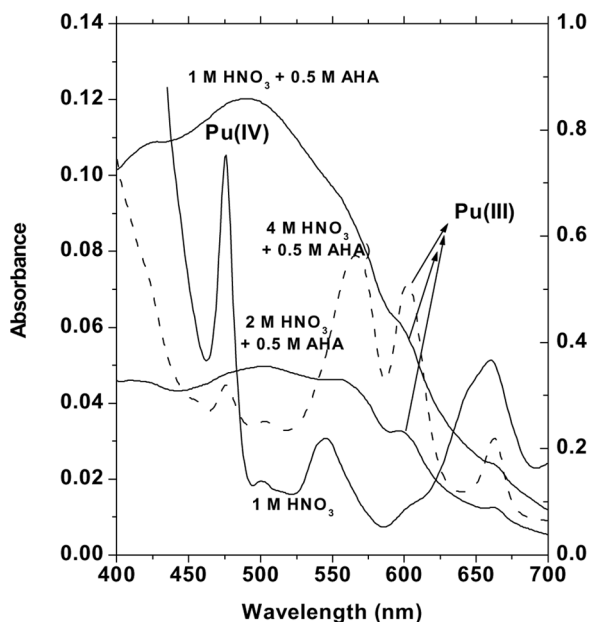


FIG. 9. Absorption spectra of Pu(IV)-AHA complex; [Pu]: 2×10^{-3} M; [AHA]: 0.5 M AHA @ 1–4 M HNO_3 ; Duration: 1270 minutes; Pu(IV) spectrum is given for comparison purpose.

of Pu(III) in the presence of 0.5 M AHA at 1, 2, and 4 M HNO_3 after 1270 minutes. Hydroxyl amine formed as a result of hydrolysis of AHA is responsible for the reduction of Pu(IV). Figure 10 shows a red shift in the characteristic wavelength of aqueous Pu(IV) absorption (476 nm) in the organic extracts, viz. 1.1 M TBP (489 nm) and 1.1 M

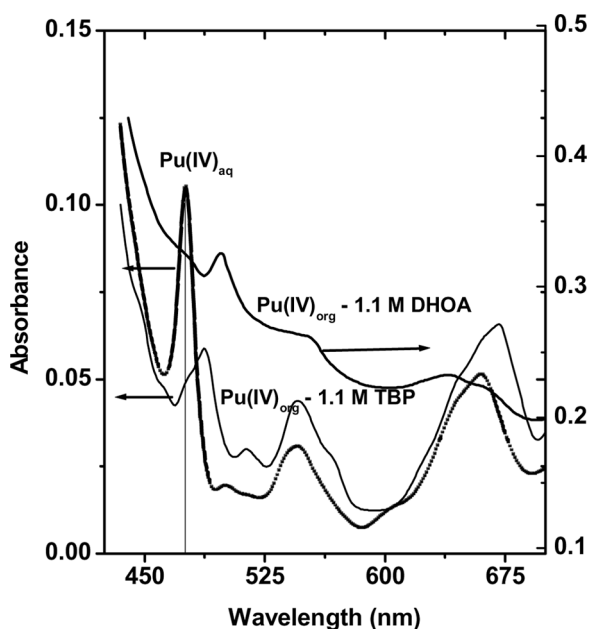


FIG. 10. Absorption spectra of Pu(IV) in organic extracts; $[\text{HNO}_3]$: 1 M; Diluent: *n*-dodecane.

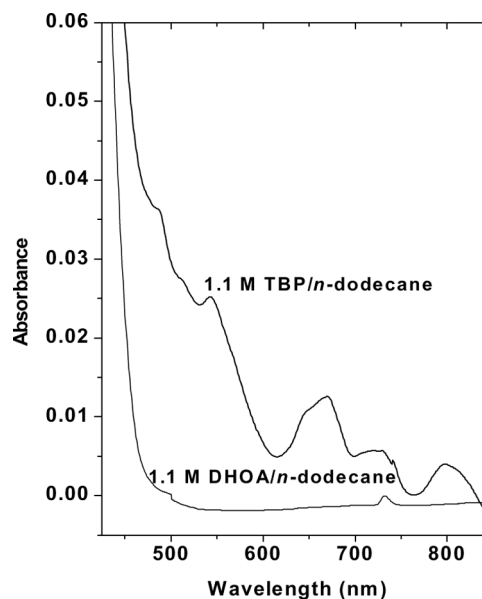


FIG. 11. Absorption spectra of extracted Pu(IV)-AHA complex; Aqueous phase: 2×10^{-3} M Pu(IV) + 0.5 M AHA @ 1 M HNO_3 .

DHOA (499 nm). This is in conformity with the relatively high affinity of DHOA for Pu over TBP (17). The absorption spectra of the organic phase/extract of Pu(IV)-AHA at 1 M HNO_3 were also recorded for 1.1 M TBP and 1.1 M DHOA solutions in dodecane. Figure 11 clearly demonstrates that Pu extraction observed in the case of TBP indicate the ternary complex extraction. This was also evident from visual observation of the TBP extract which became light brown in color after the extraction. By contrast, no extraction was observed in the case of DHOA as extractant. This explains why DHOA offers a better separation factor for U and Tc over Pu as compared to that of TBP under UREX process conditions.

CONCLUSIONS

DHOA was evaluated vis-a-vis TBP for selective extraction of U and Tc over Pu, Np. DHOA displays better extraction of Tc over TBP under the experimental conditions of the present work. 1.1 M DHOA offered better decontamination of U and Tc as compared to that of 1.1 M TBP. The proposed conditions for uranium and Tc extraction were: 1.1 M DHOA, 1 M HNO_3 and 0.5 M AHA as the as extractant, aqueous phase acidity, and the complexing/reducing agent, respectively. Tc extraction studies as a function of DHOA concentration showed a gradual decrease in the slope values with increased aqueous phase acidity (3.93 ± 0.04 (0.5 M HNO_3), 3.58 ± 0.04 (1.0 M HNO_3), and 2.48 ± 0.01 (4.0 M HNO_3)) suggesting the formation of higher solvates as compared to that of TBP as extractant. Extraction data of Tc, Pu, at 0.5 M

AHA in 1 M HNO₃, as a function of time revealed marginal effect on the AHA hydrolysis/degradation on the extraction profiles of Tc, Pu under process conditions. Spectrophotometric studies clearly demonstrated that Pu(IV) speciation was affected by the concentration of AHA, nitric acid, and time. AHA undergoes hydrolysis forming hydroxyl amine which was responsible for Pu reduction. AHA is quite stable and forms a deep brown colored complex with Pu(IV) ion at 1 M HNO₃. Unlike TBP, DHOA displayed negligible extraction of Pu-AHA-NO₃ complex which was responsible for a better separation factor of Tc over Pu.

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