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Evaluation of *N,N*-dihexyloctanamide as an alternative extractant for spent fuel reprocessing: batch and mixer settler studies

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ABSTRACT

Solvent extraction studies carried out at BARC, India on the evaluation of *N,N*-dialkyl amides as alternative extractants to tri-*n*-butyl phosphate (TBP) for reprocessing of spent fuel have suggested that straight chain *N,N*-dihexyloctanamide (DHOA) is promising alternative to TBP for the reprocessing of irradiated uranium based fuels. This paper presents the batch as well as mixer settler studies for uranium and plutonium extraction/stripping to evaluate DHOA vis-a-vis TBP for the reprocessing of Pu rich fuels. These studies showed that uranium extraction using DHOA as extractant was comparable to that of TBP; however, it displayed better stripping behavior than TBP. Plutonium extraction behavior was better in the case of DHOA as compared to that of TBP. However, Pu stripping data indicated towards the need of reducing agent in the stripping cycle for both the extractants.

Keywords: Reprocessing; Uranium; Plutonium; Dialkyl amide; TBP

1. Introduction

Five decades experiences on spent fuel reprocessing have identified certain problems with the use of tri-*n*-butyl phosphate (TBP) as extractant. Prominent amongst them are: (a) high aqueous solubility, (b) poor radiation stability and interference of degradation products during stripping of Pu/U, (c) poor decontamination factor (DF) values of Pu/U with respect to fission products, (d) low limiting organic concentration (LOC) of Pu(IV), and (e) generation of a large volume of secondary (phosphate) waste. In addition, the extraction and stripping behavior of U/Pu, and hydrodynamic properties such as viscosity, density, and phase disengagement time, are adversely affected as a consequence of the radiolytic degradation of TBP [1–5]. These limitations are of particular concern during the reprocessing of short-cooled thermal reactor fuels as well as fast reactor fuels. In this context, completely incinerable *N,N* dialkyl amides have been evaluated extensively as alternative extractants to TBP [6–9].

Studies carried out at Radiochemistry Division, BARC, India on the development of new extractants for reprocessing of spent fuel suggested that straight chain *N,N*-dihexyloctanamide (DHOA) is promising alternative of TBP in the reprocessing/coprocessing (co-extraction and co-stripping) of U and Pu of irradiated uranium based fuels [10–12]. DHOA displays better extraction behavior of plutonium and stripping behavior of uranium under simulated feed conditions. It offers opportunity to enrich the plutonium fraction with respect to uranium contamination in the product stream.

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DHOA appears distinctly better than TBP with respect to fission products (FPs) and structural materials (SMs) decontamination of U/Pu.

The radiolytic stability of DHOA was investigated to evaluate its performance under varying experimental conditions vis-a-vis TBP by gamma/alpha radiolysis [13,14]. TBP showed significant retention of Pu, U, and fission products in the irradiated TBP as compared to that of DHOA even after successive contacts with the stripping solutions. However, there was an increase in the density and viscosity for the irradiated solvents (TBP/DHOA). Detailed measurements of interfacial tension (IFT), viscosity, and phase separation time (PST) under uranium loading conditions suggested that DHOA can be used for spent-fuel reprocessing with a suitable adjustment of hydrodynamic parameters [15].

This paper deals with the evaluation of DHOA vis-a-vis TBP as extractants in batch as well as mixer settlers studies under the conditions relevant for reprocessing of Pu rich spent fuels.

2. Experimental

2.1. Synthesis and characterization of DHOA

DHOA was synthesized in our laboratory as per the method described elsewhere [10]. The product was purified by vacuum distillation. The overall yield was 80–90%. The vacuum distilled product was characterized by elemental analysis, I.R and P.M.R. spectra. The purity of the reagent was ascertained by the determination of amide content by non-aqueous potentiometric titration. The results showed that the product was >99% pure. The analytical data of DHOA are given in Table 1.

Table 1
Analytical data of DHOA

Parameter(s)	Details
Molecular formula	$C_{20}H_{41}NO$
Carbon (%)	76.6 (77.1)*
Hydrogen (%)	12.9 (13.3)*
Nitrogen (%)	4.72 (4.49)*
Amides (%)#	99.3
Viscosity (cP)	13.30
Basicity (K_H)	0.188
Density (gm/c.c)	0.81
Refractive index	1.45
Boiling point (°C)	183–185 (0.2 mm)
$\nu_{C=O}$ (cm^{-1})	1645

*Expected value.
#Determined potentiometrically.

2.2. Materials

TBP (Heavy Water Board, India) and *n*-dodecane (Transware Chemia Handelsgesellschaft, Hamburg, Germany) were used without further purification. 2-thenoyltrifluoroacetone (HTTA) and hydroxyl amine (NH_2OH) were of AR grade.

2.3. Radionuclides

^{233}U tracer (~10^{-4} M) was purified by anion exchange to eliminate the daughter products of ^{232}U and was found by alpha spectrometry to be free from ^{228}Th and its daughter products [16]. Pu (principally ^{239}Pu, ~10^{-4} M) was purified by solvent extraction procedure using HTTA as extractant and its radiochemical purity was ascertained by gamma spectrometry for the absence of ^{241}Am [17]. Pu(IV) was extracted by 0.5 M HTTA in xylene at 1.0 M HNO_3 and stripped by 8.0 M HNO_3 and was used as stock for Pu(IV). Further, the valency of Pu in the aqueous phase was adjusted and maintained in the tetravalent state by adding $NaNO_2$ as oxidant.

2.4. Extraction studies

Desired volumes of the pre-equilibrated organic phases (1.1 M TBP/DHOA) and the aqueous phases containing metal ions were kept for equilibration in the water bath for 30 min at 25°C. The two phases were then centrifuged and assayed by taking suitable aliquots (25–50 µl) from both the phases. ^{233}U and Pu in the organic and aqueous phases were estimated by liquid scintillation counting using 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-phenyloxazoyl)]-benzene (POPOP), 1% (w/v) trioctyl phosphine oxide (TOPO), and 10% (w/v) naphthalene dissolved in one litre of dioxane. 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 ions (uranium/plutonium) in the organic phase (expressed in terms of counts per unit volume per min) to that in the aqueous phase. For radiometric assay, usually concentration and aliquot sizes were adjusted suitably to give a count rate of 10000 to 50000 counts/min. However, in the cases where count rates were lower, a long period counting was performed to keep the relative standard deviation values within ±5%. These experiments were carried out in at least in duplicate and the material balance was within error limits (±5%).

2.5. Mixer settler studies

Counter-current mixer settler extraction/stripping studies were carried out using two different types of mixer settler units made of acrylic and perspex, respectively. An eight-stage mixer and settler unit with bed volumes of 30 ml (mixer), and 130 ml (settler) and a total hold up volume of ~1300 ml was indigenously fabricated using acrylic material. On the other hand, twelve-stage mixer-settler unit (made up of perspex polymer) was procured from Sonal France (Batteries No. 36, Brevete S.G.D.G.). The unit had a total hold up volume of ~500 ml with a mixer volume of ~10 ml and settler volume of ~30 ml.

Mixer settler runs were carried out by employing turbine-type agitators made up of stainless steel. Peristaltic pumps (PP 20) procured from M/s Miclins, Chennai, India, were used for adjusting the flow rate of aqueous/organic solutions while flexible polypropylene tubings were used for the transportation of the solutions. Only uranium extraction run was carried out using eight-stage mixer settler unit while other runs were performed employing twelve-stage unit.

Uranium concentration was measured by Davies Gray titration, and by spectrophotometry using 2-(5-bromo-2-pyridylazo-5-diethylaminophenol (Br-PADAP) as chromophores, respectively. Liquid scintillation counting was carried out for Pu samples. Acidity was measured by alkalimetry in the presence of saturated potassium oxalate solution.

3. Results and discussion

Currently, the proposed feed composition for the reprocessing of a typical Pu rich (relevant to fast reactor) spent fuel is 50 g/l U + 20 g/l Pu at ~4 M HNO_3. This feed is proposed to be prepared by external addition of uranium, which should be sufficient for electrolytic reduction of Pu to Pu(III) during partitioning cycle. During reprocessing, the proposed organic-to-aqueous phase ratio (O/A) in the extraction cycle is ~2.5, thereby diluting the uranium and plutonium concentrations in organic phase to 20 g/l and 7 g/l, respectively. In this context, it was of interest to evaluate the feasibility of reprocessing with a diluted feed solution having 20 g/l U + 7 g/l Pu at ~4 M HNO_3 employing TBP and DHOA as extractants. Therefore, U and Pu distribution (extraction/stripping) studies were carried out to evaluate TBP and DHOA in the presence of U (tracer, 20 & 50 g/l) by batch as well as mixer settler studies.

3.1. Batch distribution studies

Extraction studies were carried out to evaluate 1.1 M DHOA and 1.1 M TBP as extractants for the reprocessing of U and Pu under varying concentrations of nitric acid (0.5–6 M HNO_3) and of uranium (tracer, 20 & 50 g/l). Figs. 1–4 suggest that DHOA appears to be a better choice for reprocessing of U and Pu. The plutonium fraction can be enriched with respect to uranium in the product stream using DHOA as extractant [11]. The batch distribution data generated during these studies were used for the calculation of number of theoretical stages required for quantitative extraction of U and Pu from 4 M HNO_3 solutions in a continuous co-current/counter-current solvent extraction processes [18]. The general assumptions made during these calculations are:

(a) the two phases are completely immiscible,
(b) the volume of aqueous and organic phase is unchanged during the course of extraction.

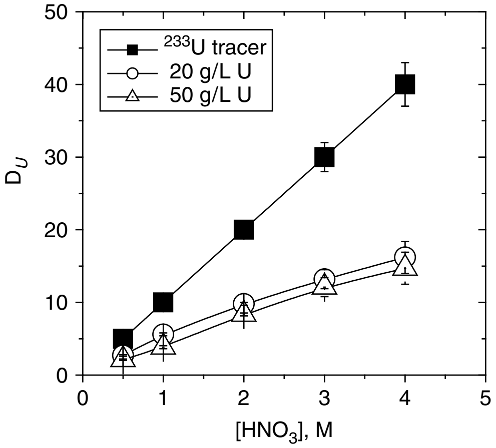

Fig. 1. Variation of D_U with aqueous phase U and HNO_3 concentration in the absence of Pu; Extractant: 1.1 M TBP/*n*-dodecane; T: 298 K; O/A: 1.

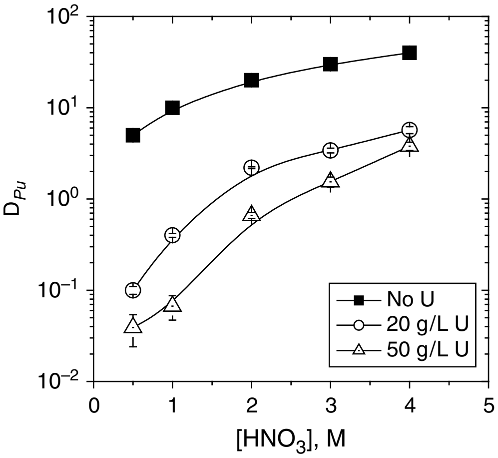

Fig. 2. Variation of D_{Pu} with aqueous phase U and HNO_3 concentration; [Pu]:~2 mg/l; Extractant: 1.1 M TBP/*n*-dodecane; T: 298 K; O/A: 1.

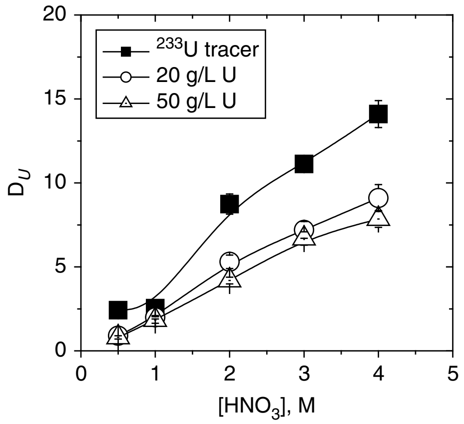

Fig. 3. Variation of D_U with aqueous phase U and HNO_3 concentration in the absene of Pu; Extractant: 1.1 M DHOA/*n*-dodecane; T: 298 K; O/A: 1.

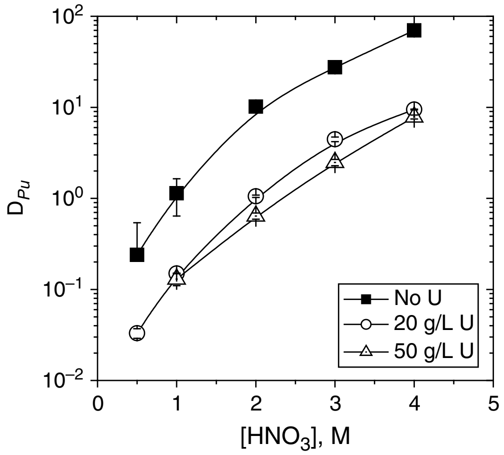

Fig. 4. Variation of D_{Pu} with aqueous phase U and HNO_3 concentration; [Pu]:~2 mg/l; Extractant: 1.1 M DHOA/*n*-dodecane; T: 298 K; O/A: 1.

Table 2 compares the behavior of 1.1 M TBP and 1.1 M DHOA solutions with respect to quantitative U and Pu extraction from 4 M HNO_3 solutions maintaining organic-to-aqueous phase ratio (O/A) as 1. It is evident that the two extractants do not show significant difference during the extraction of the metal ions. It is, however, interesting to note that plutonium extraction is better in DHOA.

3.2. Mixer settler studies

3.2.1. Extraction cycle for U

The uranium extraction studies were performed employing 1.1 M DHOA and 1.1 M TBP solutions in *n*-dodecane. The feed compositions were: 19.4 g/l U at 4.2 M HNO_3 (1.1 M TBP) and 25.4 g/l U (1.1 M DHOA) at 4.0 M HNO_3, respectively. The flow rates of the organic and aqueous phases were maintained as ~5 ml/min. Overall the O/A was maintained as 1.1. Analysis of the EXIT samples (organic and aqueous) suggested that equilibrium condition was reached after passing both the phases equivalent to one bed volume (~1300 ml). During the runs using 1.1 M TBP/*n*-dodecane as the extractant, the organic phase uranium concentration increased gradually from Stage 1 (5×10^{-3} g/l) to Stage 8 (17 g/l) (Figs. 5 and 6). Similar increase was observed in nitric acid concentration in the organic phase [stage 1 (0.6 M) to stage 8 (0.8 M)]. The loaded organic phase composition was 17.0 g/l U + 0.9 M HNO_3 and that of raffinate was 8.5×10^{-4} g/l U + 3.11 M HNO_3. Similar run employing 1.1 M DHOA/*n*-dodecane as the extractant showed that organic phase uranium concentration increased from Stage 1(3×10^{-3}g/l) to Stage 8 (24.5 g/l). Nitric acid concentrations in loaded 1.1 M TBP and DHOA phases were 0.8 M and 0.9 M, respectively. The loaded organic phase composition was 24.5 g/l U + ~1.0 M HNO_3 and that of raffinate was 2.0×10^{-4} g/l U + 2.8 M HNO_3. These studies suggested that uranium loss to raffinate and the acid uptake by the organic phase were comparable in both the extractants.

Table 2
Calculation of number of stages for quantitative extraction (99.9%) of uranium and plutonium; [U]: 20 g/l; [Pu]: ~2 mg/l; [HNO_3]: 4 M; O/A: 1; T: 298 K

Extractant	Metal ion	D_M	No. of stages for 99.9% in different modes	
			Co-current	Counter-current
1.1 M TBP	U(VI)	16	3	3
	Pu(IV)	5.7	4	4
1.1 M DHOA	U(VI)	9.7	3	3
	Pu(IV)	9.5	3	3

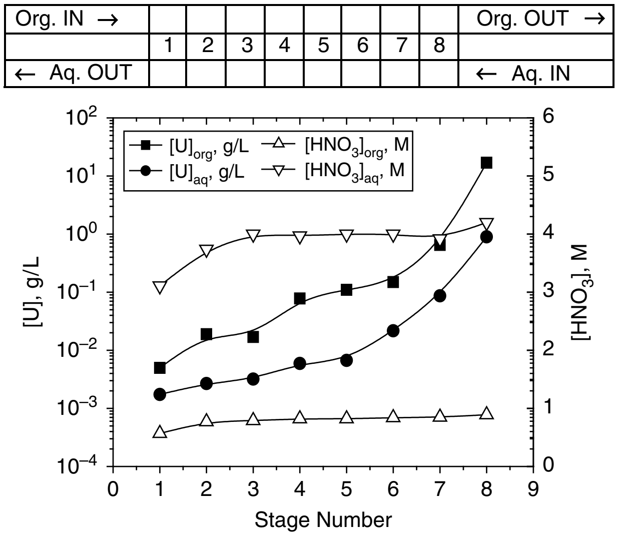

Fig. 5. Stage analysis data for uranium extraction; Feed: 19.4 g/l at 4.2 M HNO_3; Extractant: 1.1 M TBP/*n*-dodecane; O/A: 1.14.

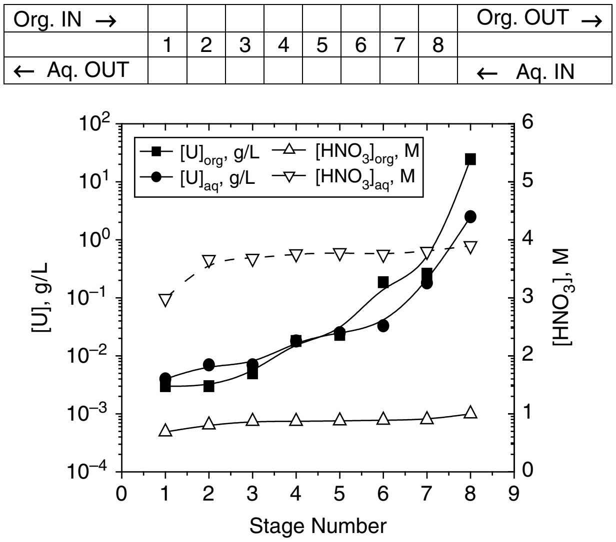

Fig. 6. Stage analysis data for uranium extraction; Feed: 25.4 g/l U at 4.0 M HNO_3; Extractant: 1.1 M DHOA/*n*- dodecane; O/A: 1.08.

3.2.2. Extraction cycle for Pu

Figs. 7 and 8 show the stage wise extraction profiles of Pu(IV) (~10^{-4} M) at 4 M HNO_3 using 1.1 M TBP and 1.1 M DHOA as extractants. Flow rates of the organic and aqueous phases were maintained as 9 and 10 ml/min, respectively (O/A: 0.9). The equilibrium condition was achieved within 90 min in the case of DHOA; while ~120 minutes were required for TBP system. Stage analysis data showed that whereas 4 stages were sufficient for quantitative Pu extraction using 1.1 M DHOA as extractant; >6 stages were required for 1.1 M TBP.

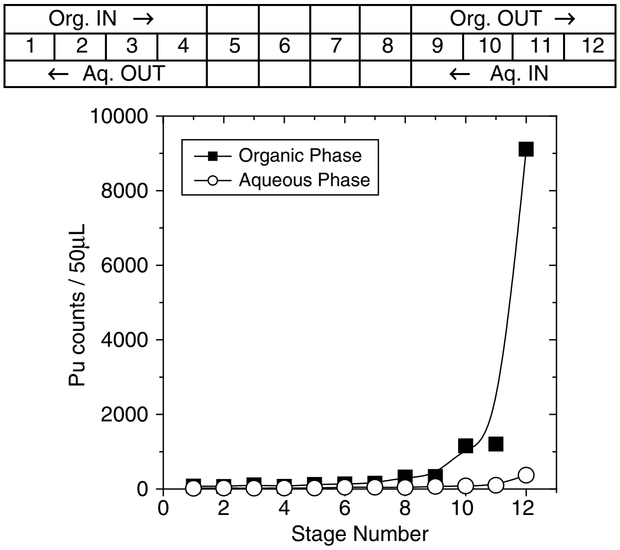

Fig. 7. Stage wise concentration profile of Pu(IV) during extraction cycle; Extractant: 1.1 M TBP/*n*-dodecane; Feed: 2 mg/l Pu at 4 M HNO_3; O/A: 0.9.

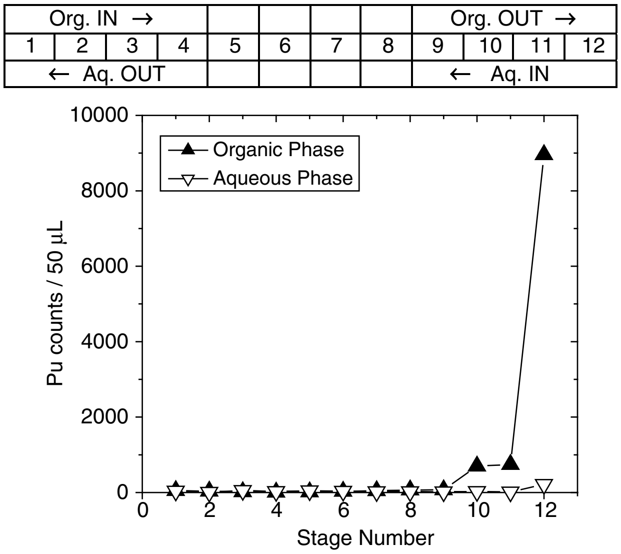

Fig. 8. Stage wise concentration profile of Pu(IV) during extraction cycle; Extractant: 1.1 M DHOA/*n*-dodecane; Feed: 2 mg/l Pu at \$ M HNO_3; O/A: 0.9.

3.2.3. Stripping studies

The loaded organic phases from U and Pu extraction cycles were used as feed solutions for stripping studies employing 12 stage mixer settler unit. The experimental details are listed in Table 3. Uranium and plutonium stripping studies were carried out using 0.01 M HNO_3 and 0.1 M HNO_3 solutions, respectively. The organic and aqueous phase flow rates were maintained as ~10 ml/min. These studies clearly demonstrate DHOA is better with respect to U and Pu stripping behavior. Whereas quantitative stripping of uranium could be achieved employing DHOA as extractant; only 33% Pu stripping was possible without reducing agent. By contrast, ~88% (U) and 28% (Pu) stripping can be was achieved employing TBP as extractant. Even though, Pu stripping behavior was relatively better in the case of DHOA, the data indicated towards the need of reducing agent for Pu stripping. It should be noted that batch stripping studies (in co-current mode using fresh 0.5 M HNO_3 as strippant) reported earlier showed that only six stripping stages were sufficient for quantitative stripping of Pu from loaded DHOA phase. On the other hand, >10 stages were required for Pu stripping from loaded TBP phase and it became further difficult with the aging of the organic phase. By contrast, no such Pu retention was observed for aged DHOA solution [12]. The decreased stripping % in the current study was attributed to the acid build up in the aqueous phase during the counter-current mixer settler run. ~1 M HNO_3 was present in the loaded organic phases during extraction cycles for both the extractants

Therefore, the stripping behavior of plutonium from loaded organic phases was compared under identical

Table 3
Comparison of performance of TBP and DHOA during 12 stage mixer settler runs for uranium and plutonium stripping from separately loaded (either with U or Pu) 1.1 M TBP and 1.1 M DHOA solutions in *n*-dodecane

Parameters	1.1 M TBP		1.1 M DHOA	
	U	Pu	U	Pu
Loaded organic phase	17.0 g/l, 0.9 M HNO_3	10500 cpm /50 λ, 0.7 M HNO_3	24.5 g/l, 0.9 M HNO_3	8000 cpm /50 λ, 0.7 M HNO_3
Strippants	0.01 M HNO_3	0.1 M HNO_3	0.01 M HNO_3	0.1 M HNO_3
O/A (stripping)	1	0.9	0.9	0.9
$[M]_{org,}$ stripped	2.1 g/l U	7600 cpm /50 λ	0.1 g/l U	5400 cpm /50 λ
$[M]_{aq,}$ stripped	15.2 g/l	2900 cpm /50 λ	22.2 g/l	2600 cpm /50 λ
$[H^+]_{aq}$, Stripped	0.6 M	0.7 M	0.3 M	0.6 M
Stripping %	87.6	~28	99.6	~33

experimental conditions employing 0.5 M NH_2OH + 0.5 M HNO_3 as stripping solution maintaining organic-to-aqueous phase ratio (O/A) as 1. Whereas two contacts with the stripping solution were sufficient for quantitative removal of plutonium (>99.9%) from DHOA solutions; 3–4 contacts were required in the case of TBP. Interestingly, aged Pu loaded TBP phases showed very poor stripping of Pu essentially due to the formation of the troublesome degradation products viz. dibutyl phosphate (DBP) along with the higher homologues of TBP, which are strong metal complexants [14].

4. Conclusions

Batch extraction data of uranium and plutonium were used to make an estimate the number of extraction stages required during the mixer settler operations. This exercise suggested that under the conditions relevant to the reprocessing of Pu rich spent fuels (emanating from fast reactors), the two extractants do not show significant difference in the extraction of uranium. However, plutonium extraction appears to be better in DHOA as compared to that of TBP. DHOA displayed better stripping behavior of U and Pu than TBP. However, Pu stripping data indicated towards the need of reducing agent in the stripping cycle for both the extractants. Quantitative Pu stripping could be achieved employing 0.5 M NH_2OH in 0.5 M HNO_3 in the case DHOA in single contact. By contrast, 3–4 contacts were required for complete removal of plutonium from loaded TBP phase.

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