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# Third-phase formation in the extraction of thorium nitrate by *N*,*N*-dihexyloctanamide

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### ABSTRACT

*N,N*-dihexyloctanamide (DHOA) is an alternative candidate to tri-*n*-butylphosphate (TBP) for the reprocessing of spent nuclear fuels including those based on thorium. This paper reports the third-phase formation behavior of Th(IV) with varying phase modifiers, diluents, extractant/nitrate ion concentration and temperature using DHOA/*n*-dodecane as solvent. The Th(IV)-LOC (limiting organic concentration) values increased with increasing concentration of the alcohols (modifiers) and that of DHOA in the organic phase. No third phase was observed when diethyl benzene (DEB) and decahydronaphthalene (decalin) were used as diluents. There was a sharp increase in Th(IV)-LOC value from 39.6 g/L (1 M $HNO_3$) to 48.6 g/L (1 M $HNO_3$ + 1 M $NaNO_3$) beyond which a saturation behavior was observed for Th(IV)-DHOA/*n*-dodecane system. The Th(IV)–LOC values increased with temperature but decreased with the aqueous phase acidity.

*Keywords*: Thorium; Third-phase; Amide; TBP; Diluent; Phase modifier; Temperature

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## 1. Introduction

Advanced heavy water reactor (AHWR) is being developed in India with the specific aim of utilizing thorium for power generation. In this reactor, (Th, Pu)$O_2$ and (Th,$^{233}$U)$O_2$ with fissile material content in the range ~3–4% are proposed to be employed as the fuel materials [1]. The reprocessing of the irradiated AHWR fuel is quite challenging in view of the presence of Th, U and Pu along with fission products in the feed solution. Third-phase formation during the extraction of Th(IV) by TBP is one of the major limitations of thorium fuel cycle. The third-phase formation behavior is expressed in terms of limiting organic concentration (LOC) of the metal ion in the organic phase, above which third-phase formation occurs during extraction. Formation of third-phase during liquid–liquid extraction is observed when the solvate concentration in the organic phase exceeds its solubility limit in the diluent. Several interesting observations have been made on the third-phase formation behavior of metal ions in different extractant systems. There are several factors, which can affect the third-phase formation, viz. (a) organic phase composition, (b) aqueous phase composition, (c) ionic strength, and (d) temperature [2,3]. Generally, a small increase in the temperature is sufficient to enhance the LOC values significantly. The splitting of the organic phase into two phases (with different densities and viscosities) poses problems for hydrometallurgical operations, which are essential process requirements.

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During the reprocessing of spent nuclear fuel by solvent extraction, the occurrence of third-phase in the extraction should be avoided.

To realize a self-sufficient Th-$^{233}$U cycle, Atomic Energy of Canada Limited (AECL) initiated a programme for irradiation of Th-Pu fuel followed by the reprocessing of irradiated Th-Pu-$^{233}$U fuels. A primary process flowsheet was developed, which was essentially a modified version of the THOREX process using 1.1 M TBP in 10% diethylbenzene (DEB) and 60% ISOPAR (isoparaffinic kerosene) as the solvent [4]. A mixture of diluents was employed to overcome the third-phase formation problem due to co-extraction of thorium. The idea in this process was to co-extract U, Pu and Th leaving fission products and structural elements in the raffinate. Thereafter the three actinides were separated from each other using redox/complexing agents. However, there are a few other drawbacks associated with the use of TBP, which have caused concern to the separation scientists and technologists. 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, and (d) large volume of secondary (phosphate) waste. Therefore, there is a need to explore alternative extractants of TBP for nuclear fuel-reprocessing.

Extensive investigations have suggested that *N,N*-dialkyl aliphatic amides are promising alternatives to TBP in the reprocessing of spent nuclear fuel [5–7]. These extractants offer several advantages over organophosphorus compounds especially with respect to the (i) innocuous nature of their degradation products viz. carboxylic acids/amines, and (ii) possibility of incineration of the used solvent leading to reduced volume of secondary waste. Our group has been actively pursuing an R&D programme to identify *N,N*-dialkylamides as promising alternatives to TBP in the PUREX as well as in the THOREX process [7]. Branched chain *N,N*-di(2-ethylhexyl)isobutyramide (D2EHIBA) was found promising for the selective extraction of $^{233}$U over Th(IV), while the straight chain *N,N*-dihexyloctanamide (DHOA) appeared suitable for coextraction of $^{233}$U and Pu over Th(IV) [1,8]. Distribution studies on U, Pu and Th were carried out to compare 0.18 M TBP and 0.18 M DHOA solutions in *n*-dodecane as extractants for coextraction of $^{233}$U and Pu over Th(IV) for the reprocessing of spent fuel of proposed Th based advanced heavy water reactor (AHWR). Whereas TBP appeared more favourable for preferential extraction of U over Th, DHOA more favourable for preferential extraction of Pu over Th. Typically, the separation factor values for U/Pu over Th in the presence of 200g/L Th at 3.5 M $HNO_3$ for 0.18 M TBP and 0.18 M DHOA solutions were 60, 40 and 110, 130, respectively.

The present work evaluates the effects of different experimental parameters such as phase modifiers, nature of diluents, ligand concentration and nitrate ion concentration on the third-phase formation behavior of Th(IV) using 1.1 M DHOA in n-dodecane (diluent) as the extractant. An attempt has been made to compare the data with those of TBP and triamyl phosphate (TAP) reported in literature [9,10].

## 2. Experimental

DHOA used in the present work was synthesized at Radiochemistry Division, BARC, Mumbai, India, following reported procedure [7]. Stock solutions of Th(IV) of 300–350 g/L were prepared by dissolving nuclear grade $Th(NO_3)_4 \cdot 5H_2O$ in 0.5 M $HNO_3$. Suitable aliquots of the stock solution were evaporated and dissolved in the desired concentration of nitric acid. Other reagents used in this work were of AR grade. The extractant solutions were prepared by dissolving desired quantities of DHOA in different diluents. Equal volumes of the aqueous phase containing Th(IV) (300–350 g/L) and of the organic phase (1.1 M DHOA in *n*-dodecane) under desired conditions of acidity and temperature, were equilibrated with the organic phases to develop third-phase. The third-phase was redissolved by diluting the aqueous phase with respect to Th concentration by nitric acid solution of the same concentration. After equilibration, the two phases were allowed to settle for 1 h. The organic phases were assayed for the metal ion concentration to compute the LOC. Thorium estimation (in both phases) was carried out by complexometric titration at pH 1–2 with 0.01 M EDTA solution using xylenol orange as the indicator. The equilibrium nitric acid concentration of the aqueous phase was determined by alkalimetry using standard NaOH solution after complexing the metal ions with saturated solution of potassium oxalate. The concentration of amide containing thorium was calculated after its stripping with water, followed by equilibration with 8 M $HNO_3$. The amount of acid extracted in the organic phase was equal to amide concentration (1:1). The uncertainty associated with reported Th(IV)–LOC values (for 4 measurements) is within ±2%.

## 3. Results and discussion

### 3.1. Effect of organic phase composition

Fig. 1 shows the variation in Th(IV)–LOC values with increasing concentration of 1-octanol and 1-decanol, used as phase modifiers at 3.5 M $HNO_3$. It is evident that the Th(IV)–LOC value increases with increased concentration of the alcohols in the organic phase. At lower concentrations (up to 6%), 1-decanol gives higher LOC value than 1-octanol. The enhancement can be attributed to larger carbon number of the alcohols from 8 to 10. Similar observations were made during the extraction of Pu(IV) in the presence of alcohols with 30% TBP/*n*-dodecane [3].

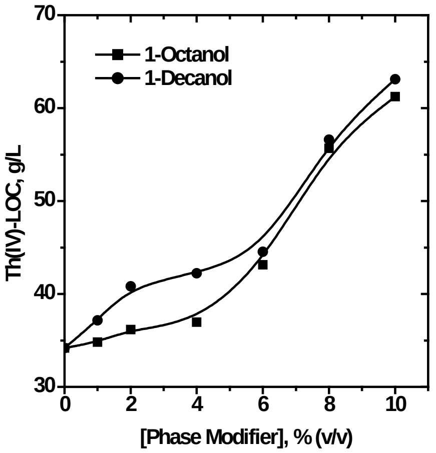

Fig. 1. Effect of phase modifier on Th(IV)–LOC. Extractant: 1.1 M DHOA/*n*-dodecane; [$HNO_3$]: 3.5 M; temperature: 298 K.

However, at higher concentrations (>6%), both the phase modifiers appear identical which was attributed to significant adsorption of alcohol molecules at the interface [11]. The alcohol molecules form densely packed adsorption layer suggesting significant competition with the DHOA molecules in the adsorption process.

To avoid the third-phase formation, a number of diluents (including aromatic) have been evaluated in the literature for the reprocessing of thorium based fuels [3, 4]. It was of interest to determine Th(IV)–LOC values for 1.1 M DHOA in different diluents. Fig. 2 compares the Th(IV)–LOC values for 1.1 M DHOA solution in different diluents such as *n*-dodecane, NPH (normal paraffinic hydrocarbon, $C_{11}$-$C_{13}$), Shell Sol T (synthetic isoparaffinic hydrocarbon), DEB (diethyl benzene, mixture of isomers), and decahydronaphthalene (decalin). Generally, the aromatic diluents display higher LOC values than the aliphatic diluents. However, the use of aromatic diluents in general is discouraged in view of their low flash points and instability in nitric acid medium.

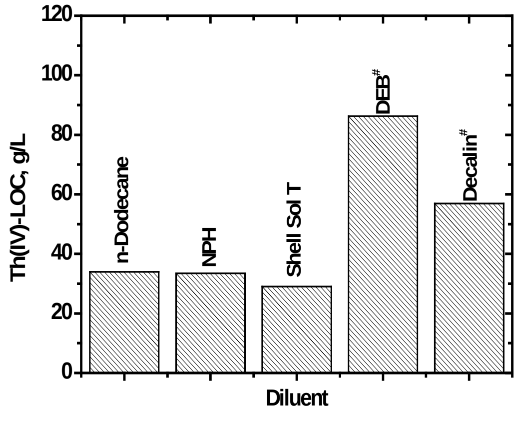

Fig. 2. LOC of Th(IV) with 1.1 M DHOA in various diluents. [$HNO_3$]: 3.5 M; $^{\#}$no third phase; temperature: 298 K. $^{\#}$Value denotes the maximum achievable loading.

The dielectric constants (ε) of the diluents used in the present work follow the order: *n*-dodecane (2.0) = NPH (~2.0) < Shell Sol T (2.0) < decalin (2.18) < DEB (2.7). The higher Th(IV)–LOC value for DEB and decalin can be attributed to their aromatic nature/higher dielectric constant values. In fact, no third-phase was observed in the case of DEB and decalin and the values refer to maximum achievable thorium loading. Generally, the aggregation of metal solvates is more pronounced in aliphatic diluents like *n*-dodecane than in aromatic diluents. The latter have better solvating power due to stabilization of single metal solvate by the more ordered high dielectric constant diluent molecules. It is reported that presence of branchings in the diluent increases the Th(IV)–LOC value significantly [12]. The present work shows minor variation in Th(IV)–LOC values (g/L) for *n*-dodecane (34), NPH (33), and Shell Sol T (29) probably indicating the presence of aliphatic impurities in Shell Sol T as the diluent.

For selective extraction of U(VI) and Pu(IV) over Th(IV), lower concentration of DHOA is proposed to be used. Therefore, it was desirable to determine Th(IV)–LOC values as a function of DHOA concentration. At 3.5 M $HNO_3$ and 298 K, the Th(IV)–LOC values (g/L) at 0.5, 1.0 and 1.5 M DHOA/*n*-dodecane were 7.4, 28.8, and 53.8, respectively. Similar observations have been reported for Th(IV)-TBP/TAP/*n*-dodecane systems [13,14]. Srinivasan et al. measured the LOC for thorium nitrate extraction from neutral medium as a function of the TBP and TAP concentrations (~0.35–1.8 M) in *n*-dodecane at 303 K. Whereas in the case of TBP/*n*-dodecane system, the Th(IV)-LOC (g/L) value increased from ~20 (0.35 M TBP) to ~90 (1.8 M); the corresponding values for TAP/*n*-dodecane system were 30 and 150, respectively [14].

### 3.2. *Effect of aqueous phase composition*

The aqueous phase composition also influences the third-phase formation behavior of the metal ions. A linear relationship was reported between the LOC values and the aqueous phase ionic strength (in the range 2–8 M $NO_3^-$/$ClO_4^-$) for Pu(IV)–TBP/*n*-dodecane system [3]. By contrast, there was a sharp increase in Th(IV)–LOC value from 39.6 g/L (1 M $HNO_3$) to 48.6 g/L (1 M $HNO_3$ + 1 M $NaNO_3$) beyond which a saturation behavior was observed for Th(IV)–DHOA/*n*-dodecane system (Table 1). The initial increase can be attributed to the dehydration of hydrated DHOA in the organic phase. Healy and McKay also reported progressive displacement of water from TBP phase during the extraction of metal ions like thorium and uranium [13]. However, further increase in $NaNO_3$ does not help in the solvation of $Th(NO_3)_4$ with DHOA molecules suggesting the incompatibility of the metal solvate in *n*-dodecane beyond this concentration.

Table 1
Effect of nitrate ion concentration on Th(IV)–LOC at 1 M $HNO_3$; extractant: 1.1 M DHOA/*n*-dodecane; temperature: 298 K

| $[NO_3^-]$, M | Th(IV)–LOC, g/L |
|---|---|
| 1 | 39.5 |
| 2 | 48.6 |
| 3 | 48.6 |
| 4 | 48.6 |
| 5 | 48.6 |
| 6 | 48.6 |

### 3.3 Effect of temperature

Fig. 3 shows the variation of Th(IV)–LOC values with temperature at 1, 3.5 and 6 M $HNO_3$. It is evident that LOC values increase with temperature but decrease with the aqueous phase acidity. This behavior can be attributed to the increased extraction of nitric acid, which reduces the free extractant concentration available for the extraction of thorium nitrate without formation of third-phase. Typically at 3.5 M $HNO_3$, Th(IV)–LOC (g/L) values for DHOA, TBP, and triamyl phosphate (TAP) are 34.0, 34.5, and ~70, respectively [9,15]. Thus TBP and DHOA display similar behavior with respect to third-phase formation during the extraction of thorium. Fig. 4 shows that with increasing temperature, the critical extractant DHOA:Th mole ratio falls, indicating an increased solubility of thorium nitrate–extractant solvates. This trend is observed irrespective of the presence of nitric acid in the organic phase [2,16]. The LOC value is influenced by solubility of the extracted species, and activity coefficients and the nitric acid concentration in the organic phase. This results in a change in the polarity of the solvent medium.

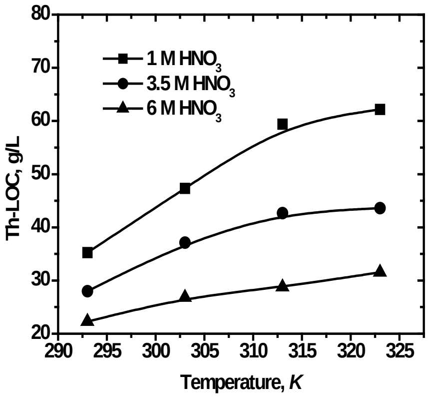

Fig. 3. Effect of temprature on Th(IV)–LOC at differenct acidities. Extractant: 1.1 M DHOA/*n*-dodecane.

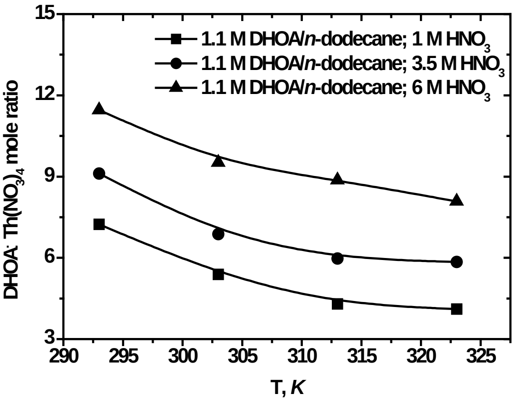

Fig. 4. Limiting DHOA:$Th(NO_3)_4$ mole ratios as a function of temperature.

Table 2
Composition of the third-phase; extractant: 1.1 M DHOA/*n*-dodecane; [$HNO_3$]: 3.5 M; temperature: 298 K

| Parameter | Organic phase | |
|---|---|---|
| | Diluent rich | Solvate rich |
| [Th], g/L | 4.7 | 106.7 |
| [DHOA], M | 0.12 | 2.2 |
| [$HNO_3$], M | 0.21 | 0.81 |

### 3.4 Analysis of organic phase under third-phase conditions

It was of interest to analyze the split organic phases to find the exact concentration of Th, DHOA and nitric acid after third-phase formation. Table 2 shows the data for thorium extraction at 3.5 M $HNO_3$ and 298 K. Generally, the feed acidity is maintained as ~3.5 M $HNO_3$ during reprocessing and therefore no such experiments were carried out to analyze the exact concentration of Th, DHOA and nitric acid at different acidities. It is evident that only a small fraction of Th, DHOA and $HNO_3$ is present in the upper diluent rich layer; while the heavier phase (the third-phase) is loaded with Th, $HNO_3$ and DHOA. The chemical analysis suggests the presence of $Th(NO_3)_4 \cdot (DHOA)_3$, and $HNO_3 \cdot$DHOA adducts in the heavier phase [7,17]. If the concentration (4.7 g/L, ~0.02 M) of Th in the diluents-rich phase is ignored, the [DHOA]:[$HNO_3$] ratio is approximately 1:2 which indicates the presence of DHOA·2$HNO_3$ complex (hemisolvate) in the diluent-rich phase. The trend shown in the present work is in conformity with those reported for Th(IV)-TBP-$HNO_3$ system [18]. Small-angle neutron scattering (SANS) measurements on Th(IV)-TBP-$HNO_3$ indicate the formation of aggregates, which are probably responsible for phase splitting. Borkowski et al. showed that the organic phase mainly contains trisolvated $Th(NO_3)_4 \cdot (TBP)_3$ along with small amount of $HNO_3$, presumably hydrogen-bonded to the trisolvate complex. Before phase splitting, SANS measurements on TBP solutions loaded with increasing amounts of either $HNO_3$ or of Th(IV) revealed the presence of large ellipsoidal aggregates with the major and minor axes having lengths up to about 230 and 24 Å, respectively. The size of the aggregates varied with the aqueous phase composition, i.e. $HNO_3$ only, $Th(NO_3)_4$ only, or both $HNO_3$ and $Th(NO_3)_4$. Interestingly, the size of the aggregates was largest when both $HNO_3$ and $Th(NO_3)_4$ were extracted by TBP in the organic phase. The third-phase formation is a result of the formation of larger size aggregates (micelles) in the organic phase.

## 4. Conclusions

The Th(IV)–LOC values increased with increased concentration of the alcohols (modifiers) in the organic phase. The third-phase formation behavior appears to be dependent on the dielectric constants of the diluents. No third-phase was observed in the case of DEB and decalin and the values refer to maximum achievable thorium loading. Th(IV)-LOC values increased with the concentration of DHOA in the organic phase. There was an increase in Th(IV)–LOC value from 39.6 g/L (1 M $HNO_3$) to 48.6 g/L (1 M $HNO_3$ + 1 M $NaNO_3$) for Th(IV)–DHOA/*n*-dodecane system. The Th(IV)-LOC values increased with temperature but a decrease was observed with increase in the aqueous phase acidity.

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