

# Extraction Behavior of Europium Relevant to PUREX Process

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Received: 21 Oct. 2020, Revised: 29 Nov. 2020, Accepted: 23 Dec. 2020.

Published online: 1 Jan. 2021.

**Abstract:** The extraction behaviour of europium (Eu (III)) from nitric acid by the PUREX solvent, tri-butyl phosphate (TBP) in diluent *n*-dodecane (n-DD), has been brought out in this article. The feasibility of decontaminating the product streams in the PUREX process from Eu is established and is compared with other neutron poisons like Gd and Sm. The influence of the factors affecting the extraction such as nitric acid concentration, TBP concentration, metal ion concentration, temperature and the presence of uranium, on Eu (III) extraction has been investigated. The experimental results indicate that Eu(III) has a slightly higher extraction coefficient in TBP than Sm (III) and less than Gd(III). The temperature was found to be inversely proportional to the distribution coefficient of Eu ( $D_{Eu}$ ) with an enthalpy change of  $\Delta H = -56.08 \pm 2.1$  kJ/mol. High separation factors between U(VI) and Eu (III) has ensured the feasibility of Eudecontamination under typical FBR spent fuel reprocessing conditions.

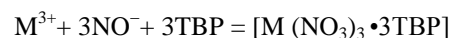
**Keywords:** Solvent Extraction, Distribution Ratio, Europium, FBR spent nuclear fuel reprocessing, TBP.

## 1 Introduction

Reprocessing of spent nuclear fuel aims at efficient and quantitative recovery of uranium and plutonium for their recycle for power production. Presently, modified PUREX (Plutonium Uranium Reduction Extraction) process is deployed for the reprocessing of spent mixed carbide (MC) fuel discharged from FBTR at the COmpact Reprocessing of Advanced fuels in Lead shielded (CORAL) facility in Kalpakkam, India [1]. In this process, the quantitative recovery of uranium and plutonium from the host of fission products is being achieved with a cumulative decontamination factor in the range of  $10^6$ - $10^8$  consistently. Europium is one of the troublesome fission products in terms of its chemistry in the PUREX process. TBP extracts some of the fission products, even under the most favourable conditions. Some of the long-lived and stable isotopes of Eu have very high neutron cross-sections. They can cause serious neutron poisoning problems in the reactor [2] if they are allowed to build up or incompletely removed in reprocessing. Eu isotopes such as  $^{152}\text{Eu}$ ,  $^{154}\text{Eu}$  and  $^{155}\text{Eu}$  are produced primarily as the fission products and have half-lives long enough ranging from 5 to 13 years to warrant potential concern. When a fissile nuclide such as an atom of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  fissions, it generally splits

asymmetrically into two large fragments, which can include the three Eu isotopes and two or three neutrons. The fission yield of  $^{155}\text{Eu}$  is about 0.03 % while the yield of the other two isotopes is much lower. During reprocessing, if Eu is not sufficiently removed from the product streams, the intense beta and gamma radiations from the Eu isotopes would reduce the overall decontamination factor of reprocessed fuel.

During the dissolution of the spent nuclear fuel in the PUREX process, the fission product Eu gets dissolved easily and exists as Eu(III) in nitric acid medium. TBP can extract trivalent lanthanides, but it is possible to fractionate these elements using solvent extraction. Trivalent lanthanides are extracted as a tri-solvated complex, as shown below:



In the past, different investigators used several extractants like high molecular weight amines [3-5], amides [6], carboxylic acids [7], chelating exchangers such as TTA [8], solvating extractants like tri-*n*-butyl phosphate (TBP) [9-17] and organophosphorus acids [18-21] and have reported selective separation of trivalent lanthanides from each other or from the waste streams [22-23]. Hesford *et al.* [24] revealed the evidence to indicate a definite number of TBP molecules attached to each metal nitrate molecule in the TBP phase. It was found to be two for the metal nitrates of

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the general formulae  $M(\text{NO}_3)_4$  and  $\text{MO}_2(\text{NO}_3)_2$ , and three for  $M(\text{NO}_3)_3$ . As TBP concentration increases from 1% to 5%, the D value also increases with slope lying between 2.7 and 3.1. At higher TBP concentrations, non-ideality may completely obscure the situation and a slope widely different from the limiting slope of 3 may be obtained. At lower acidities, Peppard *et al.* [12] found that there was a reversal in the trend of extractability after gadolinium and cautiously propose the molecular composition of species extracted as  $[\text{M}(\text{TBP})_\alpha(\text{H}_2\text{O})_{x-\alpha}](\text{NO}_3)_3$  in which x is probably 6 while  $\alpha$  varies with acidity and atomic number. Sengupta *et al.* [25] carried out photoluminescence based investigation to understand the complexation of Eu (III) with different ligands (TBP: tri-n-butyl phosphate, DHOA: di-n-hexyl octanamide, Cyanex 923: tri-n-alkyl phosphine oxide and Cyanex 272: Bis(2, 4, 4 trimethyl) pentylphosphinic acid) used for preferential separation of lanthanides and actinides in various stages of the nuclear fuel cycle. In the case of TBP and DHOA complexes, three ligand molecules are coordinated in monodentate fashion and three nitrate ion in a bidentate manner to Eu(III) to satisfy its nine coordination sites. In the case of Cyanex 923 and Cyanex 272 complexes, three ligand molecules, three nitrate ions and three water molecules are coordinated to  $\text{Eu}^{3+}$  in monodentate fashion. TBP and DHOA were found to form an inner-sphere complex with Eu(III) while the presence of three water molecules was seen in the primary coordination sphere for Eu complexes of Cyanex 923 and Cyanex 272. Rout *et al.* [26], studied the extraction behaviour of Eu (III) from nitric acid medium by a solution of n-octyl (phenyl) -N,N-diisobutylcarbamoyl methylphosphineoxide (CMPO) and TBP in room temperature ionic liquid (RTIL: 1-butyl-3-methylimidazolium-bis (trifluoromethanesulfonyl) imide (bmimNTf2)). By definition, RTILs are organic salts having a melting point lower than 373 K and suitable for nuclear fuel cycle application. Extraction of Eu(III) in 1.2M TBP/bmimNTf2 was insignificant, and it was of the order of  $\sim 10^{-2}$ . However, a remarkable enhancement in the distribution ratio is observed in the presence of CMPO. Ping Zhang *et al.* [27] reported that the distribution ratio of Eu(III) with HDBP and TBP, respectively on the  $[\text{HNO}_3]_{\text{eq}}$  and found that TBP did not efficiently extract Eu(III) although the distribution ratio increases with the increase of  $[\text{HNO}_3]_{\text{eq}}$ . Compared with that of TBP, HDBP presents a strong extraction capability to Eu(III), especially at low  $[\text{HNO}_3]_{\text{eq}}$  and the dependence of  $D_{\text{Eu}}$  on  $[\text{HNO}_3]_{\text{eq}}$  gives the opposite trend to that of TBP. Siekierski *et al.* [28] showed that both the activity coefficient of the complex in the organic phase and the activity of TBP is related to the solubility parameter of the diluent used. The diluents used could be divided into three groups: (1) aliphatic hydrocarbons, (2) aromatic and (3) substituted aliphatic or substituted aromatic hydrocarbons,  $\text{CHCl}_3$  and  $\text{CHBr}_3$ . The highest activity of TBP is observed in aliphatic hydrocarbons, and it decreases in this group with the length of the chain. The lowest activity is observed in  $\text{CHCl}_3$  and

$\text{CHBr}_3$ , both of which can form hydrogen bonds with TBP molecules. The event is intermediate in aromatic and substituted aromatic or substituted aliphatic hydrocarbons. Shevchenko *et al.* [29] connected the extractability by TBP with the dielectric constant of diluent. Later in their second paper, they also pointed out the parallels between the extraction and the polarizability of the diluent. On the other hand, Pushlenkov *et al.* [30] did not observe any correlation between the extraction by TBP and dielectric constant, dipole moment, or refractive index of the diluents. Taube *et al.* [31] pointed out that the extraction depends on the electrostatic interaction between the complex and permanent or induced dipoles in the diluent molecules. From all the above observations in the literature, it could be inferred that the understanding of the distribution behaviour of Eu under typical PUREX process is still not complete. Hence, this must be investigated systematically. The present work aims to generate the equilibrium distribution data for Eu at conditions prevalent in typical FBR fuel reprocessing. We have carried out systematic work to understand the effect of various influencing parameters on the distribution of Eu between nitric acid and TBP in n-DD phases at equilibrium both in presence and absence of uranium, which is the subject of the present article. The data generated through this work would serve as an input in fine tuning the process flow sheet for FBR spent fuel reprocessing to decontaminate Eu to the required level.

## 2 Experimental

### 2.1 Preparation of Stock Solutions

The typical concentration of total Eu estimated in 100Gwd/T burnt PFBR MOX fuel is around 340 mg/kg of the spent fuel [32]. The fission yield data in the literature also provides similar numbers for the yield of Eu in thermal and fast fissions [33]. The typical composition of fission products solutions in 4M nitric acid based on FBTR mark-1 fuel, 150 Gwd/t one year cooled is listed in table.1. Hence in all our experiments, we have chosen 300 mg/L as the typical concentration of Eu(III) in the feed solution for determining its distribution in 30% TBP under various conditions. The stock solution of Eu(III) was prepared by dissolving the appropriate amount of Eu(III) nitrate hexahydrate salt which is 99.9% chemically pure from M/s Alfa Aesar in distilled water to obtain 500 mg/L of Eu(III). This stock solution was then standardised by spectrophotometry. It was used for all the experiments with proper dilution using nitric acid and water to get a feed of 300 mg/L of Eu(III) in required nitric acid concentration [34]. The stock solution of uranyl nitrate was prepared and standardised by the modified Davies and Gray method [35]. The stock solution of nitric acid of various concentrations was prepared by diluting AR grade nitric acid, which is around 15.5M with Millipore water of appropriate quantity. These stock solutions were then standardised by titrimetric using sodium carbonate solution as the primary standard [36]. Sodium carbonate primary standard solution

was prepared by accurately dissolving an appropriate amount of the salt in Millipore water.

**Table 1:** Typical composition of fission products and corrosion products in 4M nitric acid based on FBTR mark-1 fuel, 150 Gwd/t one year cooled

Chemical form of the Elements used	Quantity (g/L)	Chemical form of the Elements used	Quantity (g/L)
Ca(NO <sub>3</sub> ) <sub>2</sub>	2.608	Ba(NO <sub>3</sub> ) <sub>2</sub>	0.922
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.61	Zr(NO <sub>3</sub> ) <sub>2</sub> ·x·H <sub>2</sub> O	2.479
(NH <sub>4</sub> )Mo <sub>7</sub> O <sub>24</sub> ·7H <sub>2</sub> O	2.052	Pd(NO <sub>3</sub> ) <sub>3</sub>	2.317
Sm(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.111	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	2.383
Sb <sub>2</sub> O <sub>3</sub>	0.041	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	1.300
*(Nd(NO <sub>3</sub> ) <sub>3</sub> )	0.265	AgNO <sub>3</sub>	0.153
Ru(NO <sub>3</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	3.085	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.862
Nd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	3.868	Rh(NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	1.104
Eu(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.151	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.126
Gd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.092	Sr(NO <sub>3</sub> ) <sub>2</sub>	0.352
Cs(NO <sub>3</sub> )	2.061	Cd(NO <sub>3</sub> ) <sub>2</sub>	0.097
Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.363	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.085
Pr(NO <sub>3</sub> ) <sub>3</sub>	0.951	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.862
		Rb <sub>2</sub> CO <sub>3</sub>	0.181
*Nd in excess add to represent trans-uranic elements like Am, Cm, Np (Nd(NO <sub>3</sub> ) <sub>3</sub> )			

The stock solution of TBP in n-DD was prepared from pure solutions of TBP and n-DD, which were already characterised by Gas Chromatography [37]. 30% TBP stock solution was prepared by mixing 30% by volume of pure TBP and the rest of pure n-DD. The required quantity of this solution was prepared freshly before each experiment. DBP containing the stock solution of TBP was prepared by adding the required amount of DBP into 30% TBP on weight basis before each experiment.

In all experimental Analytical grade, reagents (99.9% pure) from Sigma Aldrich and Merck and distilled water were used. Nitric acid used for the experiments was 68% of M/s Fischer make. TBP of purity 99.9% was from M/s Fluka and n-dodecane with the purity of 99.9% from M/s Aldrich is used.

Before each solvent extraction experiment, the solvent (30% TBP) was pre-equilibrated with a nitric acid solution of appropriate concentration to maintain the nitric acid balance during solvent extraction.

## 2.2 Instrumentation

Metrohm make E526 autotitrator was used for the analysis of nitric acid in the feed and samples. pH adjustments were carried out using Chemlabs, digital pH-meter model Micro-07, Bangalore. A vortex shaker from Heidolph Reax was used for distribution experiments studies. Thermo Scientific

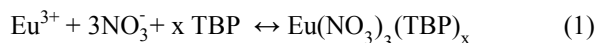
Evolution 201 spectrometer was employed for measuring the absorbance of the Eu(III)-Arsenazo(III) complex at 655nm ( $\lambda_{max}$ ) to estimate the amount of Eu(III) in the samples [34]. Constant temperature water was used for the temperature-controlled studies (Model: RE-107; Make: Lauda Dr. R. Wober GmbH & Co KG, Germany). A constant area stirred Lewis Cell unit made of hard borosilicate glass was employed for studying the temperature effect on Eu distribution. Using Tapson's analytical single pan balance model 200 T with an accuracy of 0.001g, all weighing operations were performed.

## 2.3 Experimental Procedures

Solvent extraction was carried out with the equi volume of solvent (30 vol% TBP in n-DD pre-equilibrated with nitric acid of required concentration) and aqueous phases in a centrifugal vial with sufficient free space for effective mixing using the Heidolph make multireaxvortex shaker at 1700 rpm for 30 minutes. The two phases were then allowed to disengage entirely, and the acidity and Eu concentration was measured. The free acidity was estimated using titration with standard sodium carbonate. Eu estimation was made by spectrophotometry. Eu(III) was analysed only in the aqueous phase, and the difference in concentration between the feed and equilibrated aqueous phase was assumed to be the concentration of Eu(III) in the organic phase. The calculated values are verified by analysing few of the organic samples by digesting them with hot concentrated phosphoric acid and dissolved in a minimum amount of dilute nitric acid for the assay of [Eu(III)]. The obtained results were used for the calculation of distribution coefficients of Eu ( $D_{Eu}$ ), which is the ratio of the concentration of Eu in organic to aqueous phase at equilibrium. *Electrode*

## 3 Results and Discussion

The extraction equilibrium behaviour of Eu(III) in the TBP-HNO<sub>3</sub> system is very similar to the trivalent lanthanides [12,38] and have three TBP molecules coordinated to Eu(III) in the extracted species. The extractant TBP, being a neutral ligand, extracts Eu from nitric acid medium and the following set of the equation represents the overall chemical reaction:



The apparent equilibrium constant (K), which is defined as the product of the equilibrium constant and the activity coefficients raised to the appropriate power of stoichiometric coefficients as per Eq.(1) is represented as follows:

$$K = \frac{[\text{Eu}(\text{NO}_3)_3(\text{TBP})_x]_{\text{org}}}{[\text{Eu}^{3+}]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}}^3[\text{TBP}]_{\text{org}}^x} \quad (2)$$

$$K = \frac{D_{\text{Eu}}}{[\text{NO}_3^-]_{\text{aq}}^3[\text{TBP}]_{\text{org}}^x} \quad (3)$$

Therefore, at constant nitrate concentration, the variation of

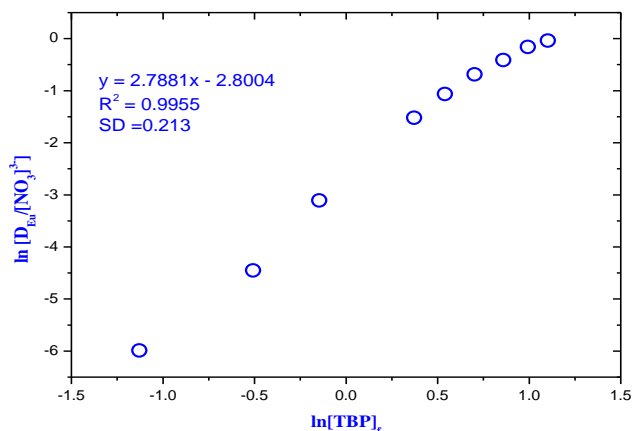
$\log D_{Eu}$  with  $\log [TBP]_{org}$  for the extraction of Eu(III) can result in a slope of  $x$  according to the Eq. 2 and 3,

$$\log D_{Eu} = \log K + x \log [TBP]_{org} \quad (4)$$

The stoichiometry of the extracted species was determined by the classical slope analysis technique [12, 38]. The results indicate that the slope of the line was 2.788 (Fig.1), which confirms that almost three TBP molecules are coordinated to Eu(III) in the extracted species. The influence of the concentration of Eu (III), TBP, DBP,  $HNO_3$ , U(VI) and temperature on the distribution coefficient of Eu were studied.

### 3.1 Effect of Metal Ion Concentration

The maximum Eu concentrations encountered during the reprocessing of typical FBR spent fuel is about 0.5g/L [35]. But during our experiment, there was not a measurable change in the  $D_{Eu}$  value in this concentration range of Eu. Hence a Eu concentration range of 0.5 to 5g/L was used in the present study. The  $D_{Eu}$  was evaluated as the function of both Eu and TBP concentrations at 3.7 M equilibrium concentration of nitric acid. The effect of [Eu] on  $D_{Eu}$  is presented in Fig. 2, which indicates that the  $D_{Eu}$  decreases with increase in Eu concentration in 1.1 M TBP concentration. Fig.3 graphically depicts the influence of TBP concentrations (0.7-2.2M in n-DD) on  $D_{Eu}$ . Results in fig.3 shows that  $D_{Eu}$  is directly proportional to TBP concentration which is due to the increase in the availability of free TBP.

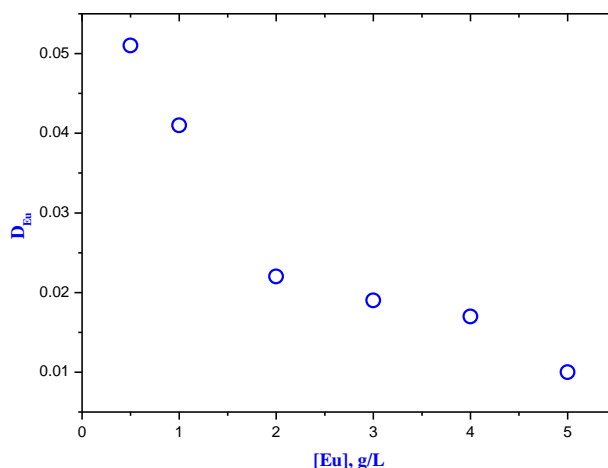


**Fig.1:** Plot to find the solvation No of TBP molecules during Eu extraction

Conditions: [Eu] = 0.05 g/L,  $[HNO_3]$  = 3.7 M, [TBP] = 0.366-3.66M, T = 298K.

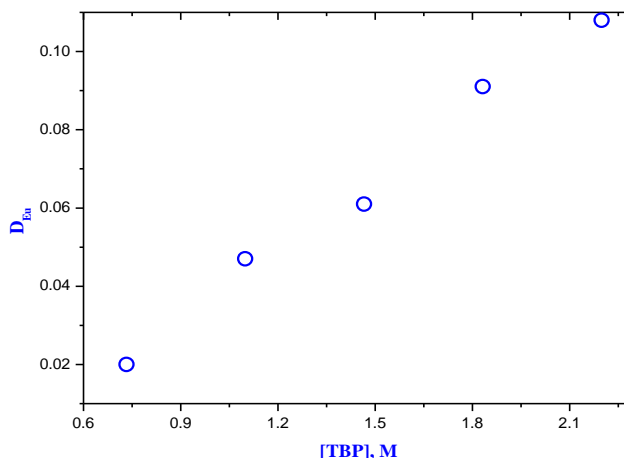
### 3.2 Effect of Nitric Acid Concentration

Extraction behaviour of Eu by 1.1 M TBP in n-DD from nitric acid of different concentrations ranging from 1 to 13.5M was investigated. Results, as shown in Fig. 4,



**Fig. 2:** Effect of the Eu concentration on  $D_{Eu}$   
Conditions: [Eu] = 0.5-5 g/L,  $[HNO_3]$  = 3.7M, [TBP] = 1.1 M, T = 298K.

Reveal that with an increase in nitric acid concentration, the  $D_{Eu}$  increases up to 3M, then marginally the same from 3 to 7M and again increases with increase in nitric acid. It indicates a probable change in the mechanism of extraction or the structure of the Eu-TBP complex as a function of acid concentration. The typical acidity employed in FBR fuel reprocessing is about 4-6M. As the value of  $D_{Eu}$  is pretty low in this acidity range, it confirms the possibility of achieving higher decontamination factor for Eu in the PUREX process.

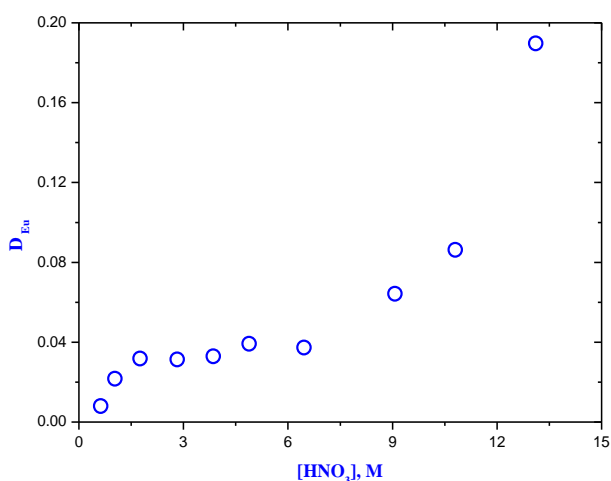


**Fig.3:** Effect of the TBP concentration on  $D_{Eu}$   
Conditions: [Eu] = 1 g/L,  $[HNO_3]$  = 3.8 M, [TBP] = 0.7-2.2 M, T = 298 K.

### 3.3 Effect of Uranium Concentration

As uranium is the significant content in the spent nuclear fuel, the distribution behaviour of Eu(III) in TBP in the presence of U(VI) was studied which would indicate the feasibility of Eu decontamination under typical PUREX





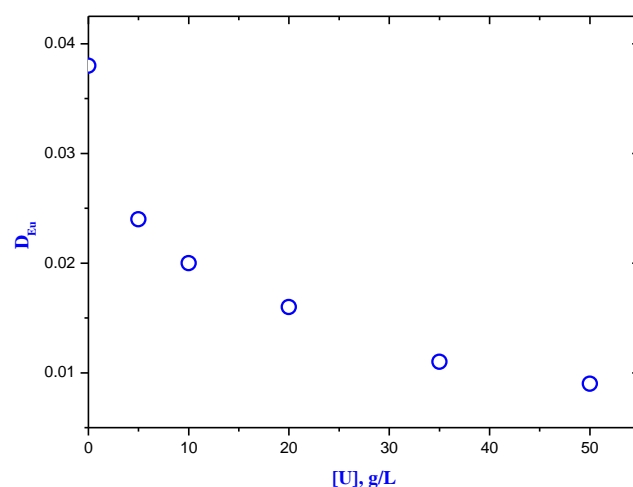
**Fig. 4:** Effect of the nitric acid concentration on  $D_{Eu}$ . Conditions:  $[Eu] = 1 \text{ g/L}$ ,  $[HNO_3] = 0.4 - 15.9 \text{ M}$ ,  $[TBP] = 1.1 \text{ M}$ ,  $T = 298\text{K}$ .

process conditions. Thus experiments were carried out at a constant nitric acid concentration of 3.8M, and 1.4g/L of Eu(III) at various concentration of U(VI) up to 50 g/L loading in the organic phase (1.1 M TBP) and  $D_{Eu}$  was determined in each case. The results, as indicated (Fig.5), reveal that  $D_{Eu}$  decreases steadily with increasing U(VI) concentration from 0.5 to 50 g/L in the organic phase for the solvents due to the decrease in the free extractant (TBP) concentration in the organic phase with uranium loading. It is important to note that the extraction of Eu(III) with TBP, which in turn indicate that, can yield slightly better decontamination factors that of TBP. It shows a good agreement with the results found in the literature [13] and reported that the distribution ratios of RE at 30 % TBP decrease with increasing uranium concentration from 0-175 g/L. This effect shows that Eu (III) is not extracted in the extraction of uranium and plutonium in the PUREX process and concluded that Eu decontamination during FBR fuel reprocessing is highly feasible.

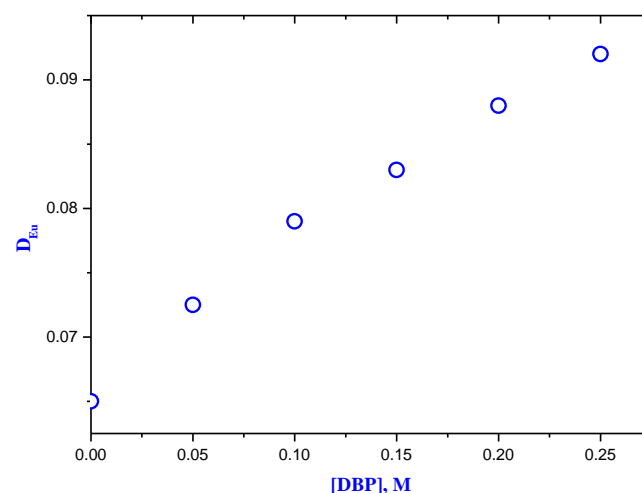
### 3.4 Effect of Dibutyl Phosphate

DBP is the degradation product of TBP which is bound to form more in FBR spent fuel reprocessing due to the higher concentrations of nitric acid and alpha emitting actinides. As DBP increases, it tends to hold all the extracted metal ions and certain fission products in the organic phase, ultimately leading to loss of fissile materials in the organic waste and thereby reduced recovery. Also, when the fissile materials are recovered from the organic waste by some suitable means, the retained FPs in the organics tends to reduce the decontamination factor for these recovered fissile materials. Hence from FBR spent fuel reprocessing point of view, it is very important to study the effect of the presence of DBP on  $D_{Eu}$ . The concentration of DBP generally encountered during the reprocessing of spent nuclear fuel is in the range of about 0-250 mg/L. But during our experiment, we couldn't find a measurable change in

the  $D_{Eu}$  value unless it is changed in percentage levels. Hence a concentration range of 1-5% of DBP was used in the present work. The  $D_{Eu}$  evaluated as a function of the concentration of DBP in 30% TBP at 4 M equilibrium concentration of nitric acid is plotted in figure 6.



**Fig. 5:** Effect of the U concentration on  $D_{Eu}$ . Conditions:  $[Eu] = 1 \text{ g/L}$ ,  $[HNO_3] = 3.8 \text{ M}$ ,  $[TBP] = 1.1 \text{ M}$ ,  $[U] = 0 - 50 \text{ g/L}$ ,  $T = 298\text{K}$ .



**Fig. 6:** Effect of the DBP concentration on  $D_{Eu}$ . Conditions:  $[Eu] = 1\text{g/L}$ ,  $[HNO_3] = 3.8 \text{ M}$ ,  $[TBP] = 1.1 \text{ M}$ ,  $[DBP] = 0-0.25\text{M}$ ,  $T = 298\text{K}$ .

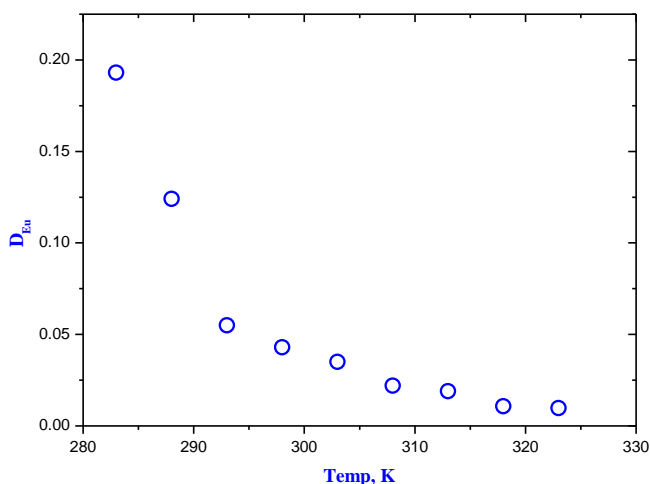
From the results in figure 5, it could be observed that the  $D_{Eu}$  increases almost linearly with DBP concentration in the organic phase. This behaviour of Eu(III) could most probably be due to the presence of acidic -OH group in DBP which stabilizes the complex with Eu(III) resulting in the better extraction of the metal ion. The results also mean that if the spent organic is not washed periodically, leading to the accumulation of DBP, the decontamination factor achievable from Eu would be proportionately lesser. Though this is applicable to all the extractable fission products, the consequence of Eu contamination would be severe as some of its isotopes have very high neutron

absorption coefficient [8]. It would significantly affect the purity of the product from the viewpoint of neutron poison impurity.

During the reprocessing of spent nuclear fuel, the spent organic is periodically washed with an alkali to remove the accumulated TBP degradation products. Hence in practice, DBP is not allowed to be accumulated beyond about 250 mg/L in any case. Thus from the above results which shows an appreciable retention of Eu (III) in the organic only on accumulation of DBP in percentage levels in the organic solvent, it can be concluded that during the actual reprocessing of the spent nuclear fuel, as Eu (III) exhibits poor retention with DBP below 500 mg/L, it is very much feasible to decontaminate the FBR spent nuclear fuel from Eu(III).

### 3.5 Effect of Temperature

When short cooled FBR spent fuel is reprocessed, due to the higher decay heat of the fuel, the process solutions may get heated depending on the process conditions. Hence the effect of temperature on the distribution behaviour of Eu in 1.1 M of TBP/n-DD system was studied by changing temperature between 283-326K at a fixed nitric acid concentration of 3.89M. Though the actual temperatures during the process conditions may not reduce below 298K, and lower temperatures were chosen for the sake of completeness. It can be seen from Fig.7 that  $D_{Eu}$  decreases with increase in temperature.



**Fig. 7:** Effect of the DBP concentration on  $D_{Eu}$   
Conditions: [Eu] = 1g/L, [HNO<sub>3</sub>] = 3.8 M, [TBP] = 1.1 M, T = 283-323K.

It may be associated with the decrease in the release of water molecules upon the dehydration of Eu<sup>3+</sup> ions during extraction. This is in good agreement with the results found in the literature [14]. Thus, it can be inferred that when processing very short-cooled fuel, where the process streams would be relatively warmer due to higher decay

heat of short-lived fission products, Eu(III) decontamination would not pose any serious problem.

### 3.6 Thermodynamic Parameters

The influence of temperature on the extraction of Eu(III) from 3 M nitric acid medium using 1.1 M TBP has been studied at the fixed concentration of Eu, in the temperature range of 283-323K. The Van't Hoff equation [39] can be used to calculate the enthalpy change associated with the extraction of Eu(III), which is written as in Eq. (9).

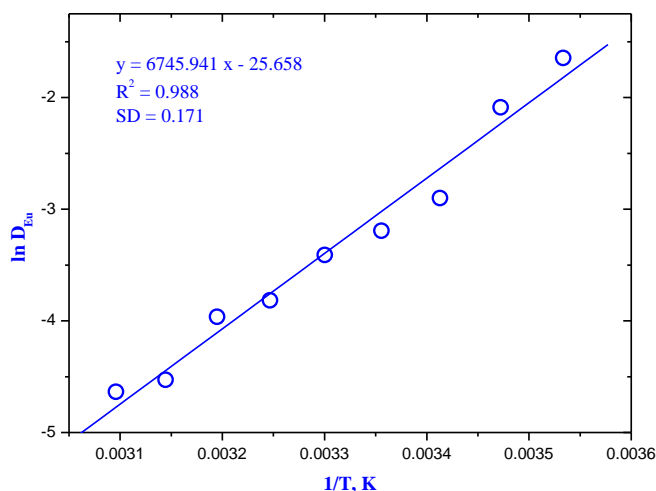
$$\frac{\partial \ln D}{\partial \left(\frac{1}{T}\right)} = \frac{-\Delta H}{R} \quad (9)$$

Where,  $\Delta H$  is the enthalpy change,  $\Delta G$  is the free energy change,  $R$  is the ideal gas constant (8.314 J/mol. K), and  $T$  is the absolute temperature (K). The plot of  $\ln D$  against  $(1/T)$  for the extraction of the metal ions is shown in Fig.8. The enthalpy of extraction can be calculated from the slope of straight lines obtained by the linear regression of extraction data. It can be seen from Table 2 that the extraction is exothermic. Several factors that control the overall enthalpy change ( $\Delta H_{tot}$ ) in solvent extraction procedures have been reported by Burger [40]. It is visualised to consist of the enthalpy change associated with factors based on the energy required and energy released. The necessary energy factors are the dehydration of M(III), transfer and dissolution of neutral species to the organic phase, deprotonation of TBP if M(III)-nitrate complexes with (TBP-HNO<sub>3</sub>) complex and rearrangement of the solvent and extracted complex. The formation of a metal-nitrate neutral species and complexation of the neutral species with free TBP, which are releases energy.

Table. 2: Enthalpy change accompanied by the extraction of Eu(III) in 1.1M TBP/n-DD.

Extractants, 1.1 M	$\Delta H_{tot}$ , kJ/mol	Slope	R <sup>2</sup>
TBP	-56.08 ± 2.1	6745	0.988

The obtained results show that the extraction of Eu is an exothermic process with a negative entropy change. Fewer water molecules need to be released. Hence the energy spent on this process is lower. Accordingly, the net enthalpy change (i.e. the difference of the energy corresponding to the formation of the extractable species and the energy spent in releasing the water molecules) is negative.



**Fig.8:** Van't Hoff's plot to determine the enthalpy of extraction

Conditions:  $[Eu] = 1 \text{ g/L}$ ,  $[HNO_3] = 3.8 \text{ M}$ ,  $[TBP] = 1.1 \text{ M}$ ,  $T = 283\text{-}323 \text{ K}$

## 4 Conclusions

The extraction behaviour of Eu was investigated using TBP, and the results were reported. The influence of parameters like nitric acid, metal ions, DBP, TBP concentration, uranium loading and temperature also studies on the measurement of distribution ratio of Eu(III). The results indicate that the decontamination factors that can be achieved for uranium and plutonium from Eu(III) with TBP. Also, the decrease in Eu distribution at higher temperature indicates better Eu decontamination when processing short cooled FBR spent fuel. The typical PUREX process chemistry offers greater flexibility in decontaminating Eu, thereby avoiding it from reaching the final product. This would facilitate the feasibility to meet the fresh fuel specification from the total metallic impurity content point of view.

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