

# Comparison of Extraction Behavior of Samarium in Tri-butyl Phosphate and Tri-*iso*-amyl Phosphate Extractants

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**Abstract:** This paper describes the comparison of extraction behaviour of samarium [Sm(III)] from nitric acid by two different extractants namely, tri-butyl phosphate (TBP) and tri-*iso*-amyl phosphate (TiAP) in diluent *n*-dodecane (nDD). The influence of the different factors affecting the extraction such as metal ions and extractants concentrations and temperature has been investigated. The experimental results indicated that Sm(III) has a higher extraction coefficient in TiAP than TBP. Further, the extraction yield was found to decrease with increase in metal ion concentration and temperature whereas it was found to increase with extractants concentration. The feasibility of samarium decontamination under process condition thereby enabling it to meet the final product specification with respect to neutron poison impurity.

**Keywords:** Solvent extraction, Distribution Ratio, Samarium, FBR spent nuclear reprocessing, TBP, TiAP.

## 1 Introduction

Xe<sup>135</sup> and Sm<sup>149</sup> have importance in terms of nuclear reactor operation and control because of very large neutron absorption cross sections. During fission as well as from the decay of fission products, fission yield of Xe<sup>135</sup> and Sm<sup>149</sup> are about 6.6% and 1.4% respectively. Sm<sup>149</sup> is an excellent absorber of neutrons and is therefore often used in nuclear reactor control rods, the capture of two neutrons by Sm<sup>149</sup> results in Sm<sup>151</sup>. The absorption cross sections of rare earth elements like gadolinium and samarium are much larger than boron. The absorption cross section for thermal neutrons is about 40,100 barns for Sm<sup>149</sup> and about 2,54,000 barns for Gd<sup>157</sup> isotopes [1].

The solution chemistry of transplutonium actinides and lanthanides which have the trivalent oxidation state are the most stable state and have similar chemical reactivity and solvent extractability. Lanthanides are non-radioactive and can be handled in relatively higher amounts/ concentrations without special safety precautions and possess excellent spectroscopic properties, have been used besides americium (Am-241) samarium as an analogue for Am(III). Lanthanide fission products, actinides are not extracted by TBP during PUREX solvent extraction process of irradiated

nuclear fuel but remain in the aqueous waste [2-3]. Since some of the rare earth, especially gadolinium, samarium and europium undesirable impurities have high neutron cross-section.

The separation of uranium and plutonium from the spent fuel of FBR (Fast Breeder Reactor), which contains a high content of plutonium with high specific activity with short cooling time is carried out by modified PUREX [4] process in COmpact Reprocessing of Advanced fuels in Lead shielded facility (CORAL). During this process, using TBP as the solvent and nitric acid as the salting agent, which generates high active raffinate waste contains radioactive actinides, short and long-lived fission products and corrosion products in 3-4M nitric acid is known as high-level liquid waste (HLLW). Prominent extractants that have employed are high molecular weight amines [5-9], carboxylic acids [10-11], Chelating exchangers such as TTA [12], solvating extractants like tri-*n*-butyl phosphate (TBP) [13-23] and organophosphorous acids [24-29]. Different investigators used several extractants have reported selective extractive separation of trivalent lanthanides from each other or waste streams [7,30-31]. The main limitations of TBP are (i) its relatively higher solubility in the aqueous phase, (ii) its vulnerability towards chemical and radiation degradation and (iii) third phase

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formation with tetravalent actinides [4]. Based on the limitation of TBP, TiAP has identified as the other extractant to TBP. Some recent studies carried out on the development for the processing of fast breeder reactor (FBR) reprocessing plants [32-33]. Before the deployment of TiAP in a reprocessing plant, it is essential to understand the extraction behaviour of some fission products as well. Hence, it is imperative that the distribution behaviour of samarium in PUREX solvent is studied. Thus, the present work aims to generate the equilibrium distribution data for samarium at conditions prevalent in FBR fuel reprocessing. Though extensive work has been carried out, the effect of various influencing parameters on the distribution of samarium between nitric acid and two different extractants like TBP and TiAP in n-DD phases at equilibrium both in presence/absence of uranium.

## 2 Experimental

### 2.1 Reagents

In all experimental Analytical grade reagents (99.9% pure) from Sigma Aldrich and Merck and de-ionised 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 used. Samarium used in the form of  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  which is 99.9% chemically pure from M/s Alfa Aesar. Samarium (III) stock solution 1 mg/mL prepared by dissolving 1.16 gm of salt in one liter of 1M nitric acid and standardised by titrimetry [34]. To make working solutions from this stock solution, with proper dilution for calibrating the spectrophotometric method using Arsenazo III as a chromogenic reagent for low concentration of samarium estimation [35]. The stock solution of uranyl nitrate was prepared and standardised by modified Davies and Gray method [36]. Free acidity estimated by potentiometry [37].

### 2.2 Instrumentation

Using Tapson's analytical single pan balance model 200 T having 0.001g accuracy for all weighing operations. A constant temperature water bath MIC-66A ( $\pm 0.10^\circ\text{C}$ ) (Modern Scientific Instrument Company, Mumbai) used for the temperature controlled studies. A double-walled glass container with provisions for mechanical mixing an outer jacket for temperature control used for the studying the temperature effect on samarium distribution. A vortex shaker from Heidolph Reax used for distribution experiments studies. To measure the absorbance of the solution using fiber optic aided spectrophotometer technique with 1 cm path length dip type probe made

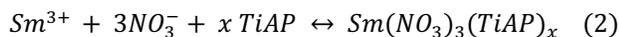
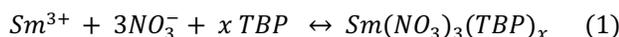
indigenously and pH adjustments were carried out using Chemlabs, digital pH-meter model Micro-07, Bangalore.

### 2.3 Extraction Procedures

Solvent extraction was carried out with the equal volume of solvent in diluents (pre-equilibrated with nitric acid), and aqueous phases in a centrifugal vial with sufficient free volume space for effective mixing using a vortex shaker of Heidolph Reax make at a speed of 1700 rpm for 30 minutes. The two phases were then allowed to disengage entirely, after which the acidity and samarium concentration was measured, with appropriate dilution if necessary. The free acidity of both phases was estimated using titration with standard sodium carbonate. Samarium estimation in both phases was made by spectrophotometry using Arsenazo III as the chromogenic reagent. All the measurements were carried out in duplicate, and their average used for the calculation of distribution coefficients. To determine the distribution coefficient of samarium ( $D_{Sm}$ ) by the ratio of the concentration of samarium in organic to aqueous phase at equilibrium. In all the experiments involved equilibrium mixing for about 30 minutes and then allowed to settle for about 5 minutes for phase separation. To maintain the aqueous to organic volume ratio was unity for all the experiments reported in this paper and experimental values were within the error band of  $\pm 5\%$ .

## 3 Results and Discussion

The extraction equilibrium behaviour of Sm(III) in the TBP- $\text{HNO}_3$  system is very similar to the trivalent lanthanides [22, 38] and have three TBP molecules coordinated to Sm(III) in the extracted species. The extractants TBP or TiAP, being a neutral ligand, extracts samarium 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 and 2) are represented as follows:

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

$$K = \frac{[\text{Sm}(\text{NO}_3)_3(\text{TiAP})_x]_{org}}{[\text{Sm}^{3+}]_{aq}[\text{NO}_3^-]_{aq}^3[\text{TiAP}]_{org}^x} \quad (4)$$

$$K' = \frac{D_{Sm}}{[\text{NO}_3^-]_{aq}^3[\text{TBP}]_{org}^x} \quad (5)$$

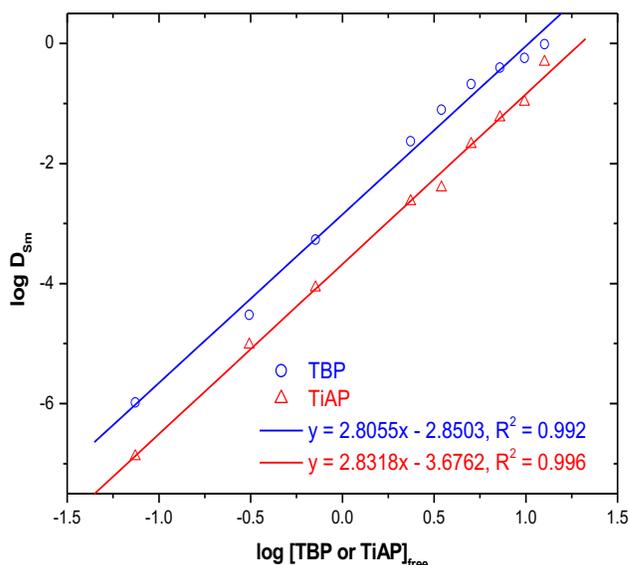
$$K' = \frac{D_{Sm}}{[\text{NO}_3^-]_{aq}^3[\text{TiAP}]_{org}^x} \quad (6)$$

Therefore, at constant nitrate concentration, variation of  $\log D_{Sm}$  with  $\log [TBP]_{org}$  for the extraction of Sm(III) can result in a slope of  $x$  according to the Eq. 7 and 8,

$$\log D_{Sm} = \log K' + x \log [TBP]_{org} \quad (7)$$

$$\log D_{Sm} = \log K' + x \log [TiAP]_{org} \quad (8)$$

Where  $K'$  is constant at constant nitrate concentration. The stoichiometry of the extracted species was performed by Classical slope analysis techniques of the data obtained from this work. At constant nitrate concentration, variation of  $\ln D_{Sm}$  with  $\ln [TBP]_{org}$  or  $\ln [TiAP]_{org}$  for the extraction of Sm(III) can result in a straight line with good a correlation coefficient of 0.992 for TBP and 0.996 for TiAP, the slope as the stoichiometric coefficient of TBP or TiAP and intercept as  $\ln K$  which is represented in Fig. 1 [22]. The data were fit using a straight line. The results indicate that the slope of the line was 2.805 and 2.832 which confirmed that almost three TBP or TiAP molecules co-ordinated to Sm(III) in the extracted species. The influences of the concentration of Sm (III), TBP,  $HNO_3$ , U(VI) and temperature on the distribution coefficient of samarium are measured. The obtained results are compared with an alternate solvent such as TiAP under similar conditions.

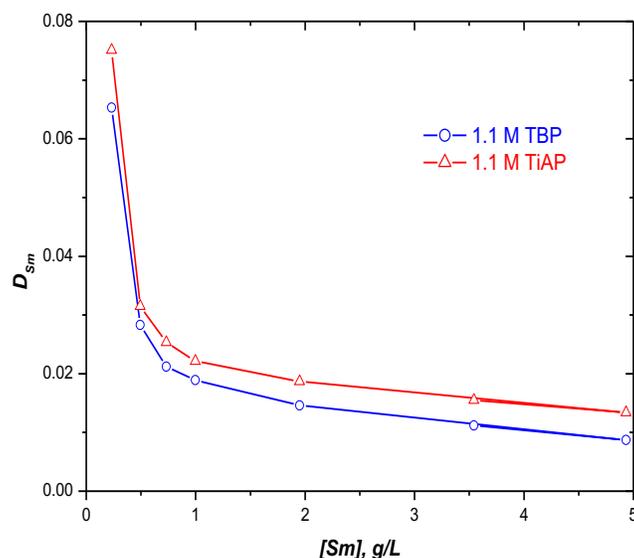


**Fig.1:** Validation of solvation number of TBP stoichiometry for Sm extraction. Conditions:  $[Sm] = 50 \text{ ppm}$ ,  $[HNO_3] = 3.8 \text{ M}$ , Solution volume =  $25 \text{ mL}$ ,  $T = 298 \text{ K}$ ,  $[TBP \text{ or } TiAP] = 0.366 - 3.66 \text{ M}$ .

### 3.1 Effect of Metal Ion Concentration

Extraction behaviour of different samarium concentrations ( $0.5\text{-}5 \text{ g/L}$ ) in the nitric acid solution of fixed the concentration of  $3.8\text{M}$  nitric acid into TBP and TiAP of

different concentrations in n-DD from  $0.73$  to  $2.2 \text{ M}$  were investigated. The results are presented in Fig. 2 which clearly indicates that the  $D_{Sm}$  decreases with increase in samarium concentration for a given TBP and TiAP concentration, and also it increases as a function of TBP and TiAP for given Sm concentrations at equilibrium (Fig.3). As the samarium concentration used in this study was very low, which is arrived based on criticality safety calculations for the fissile material concentrations prevailing in conventional fast reactor fuel reprocessing conditions, its loading is much less than the saturation limit of samarium loading. Hence, with the increase in Sm concentration  $D_{Sm}$  decreases. Fig.3 represents,  $D_{Sm}$  increases with increase in TBP and TiAP concentration due to the availability of free TBP/TiAP. TiAP is found to be more distribution ratio than TBP and same pattern. TiAP is suitable for the extraction of the Sm(III) than TBP.

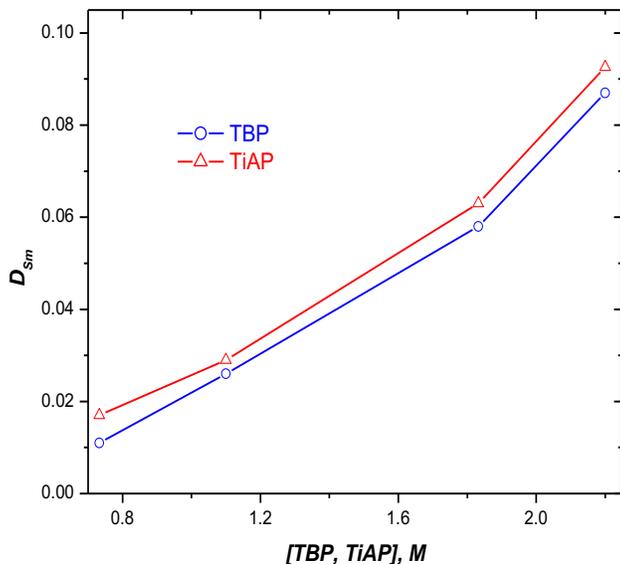


**Fig. 2:**  $D_{Sm}$  as a function of Samarium concentration. Conditions:  $[Sm] = 100\text{-}5000 \text{ ppm}$ ,  $[HNO_3] = 3.8 \text{ M}$ , solution volume =  $25\text{mL}$ ,  $[TBP] = 1.1 \text{ M}$ ,  $[TiAP] = 1.1 \text{ M}$ ,  $T = 298\text{K}$

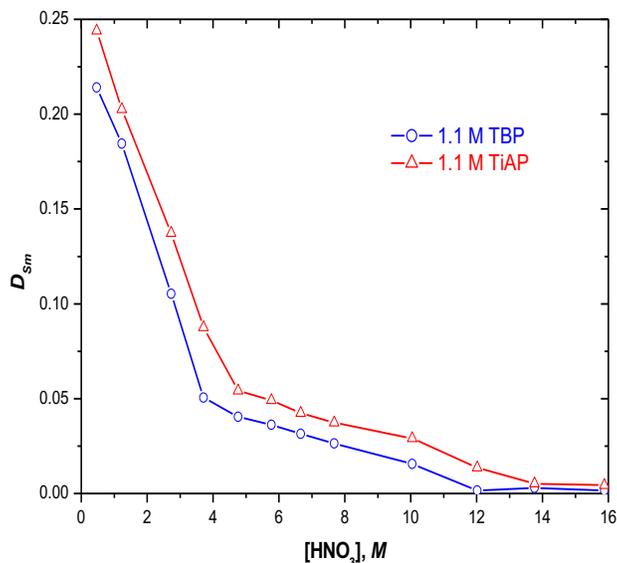
### 3.2 Effect of Nitric Acid Concentration

Extraction behaviour of samarium with both extractants ( $1.1 \text{ M TBP}$  and  $1.1 \text{ M TiAP}$ ) in n-DD from the different concentration of nitric acid from  $1$  to  $13.5 \text{ M}$  was investigated. Results indicate that the  $D_{Sm}$  decreases sharply up to  $4.5\text{M}$   $HNO_3$  and then marginally decreases from  $4$  to  $13.5 \text{ M}$  with the increase in nitric acid concentration as shown in Fig. 4. As the typical acidity employed in FBR fuel reprocessing is about  $4\text{-}6 \text{ M}$ , the results clearly indicates that the  $D_{Sm}$  value is lower in this acidity range. The extraction of Sm(III) with TBP and

marginally lower than that of TiAP which in turn result indicates that the possibility of achieving higher decontamination factors with TiAP than TBP solvents from HLLW of the PUREX process.



**Fig. 3:**  $D_{Sm}$  as a function of Samarium concentration. Conditions: [Sm] = 1400 ppm, [HNO<sub>3</sub>] = 3.8 M, solution volume = 25mL, [TBP or TiAP] = 0.7 -2.2 M, T = 298 K.

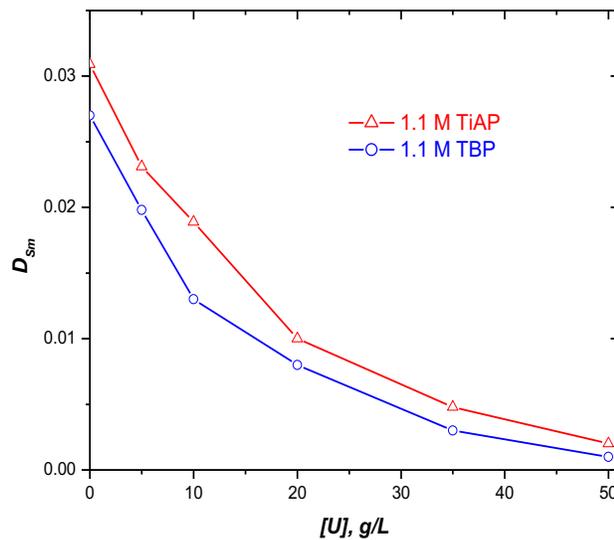


**Fig. 4:** Variation of  $D_{Sm}$  as a function of nitric acid concentration. Conditions: [Sm] = 1400 ppm, [HNO<sub>3</sub>] = 0.4 - 15.9 M, solution Volume = 25mL, [TBP] = 1.1 M, [TiAP] = 1.1 M, T = 298K.

### 3.3 Effect of Uranium Concentration

As uranium is the significant content in any nuclear reactor's spent fuel which is also the most extractable

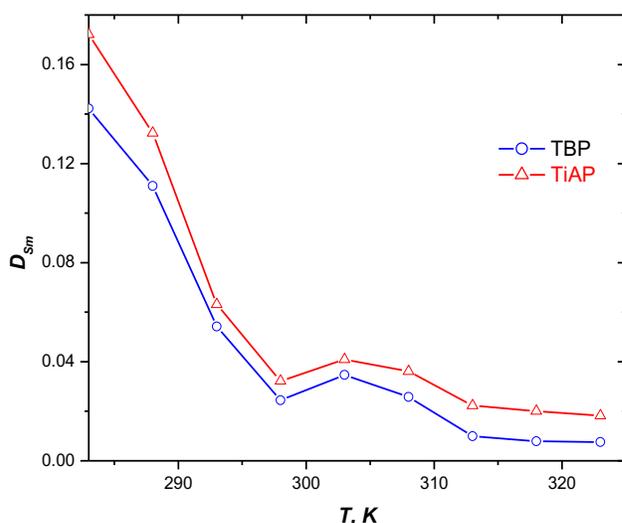
species by TBP, the distribution behavior of Sm(III) in TBP or TiAP in the presence of uranium as U(VI) was studied which would indicate the feasibility of Sm decontamination under typical PUREX process conditions. Thus experiments were carried out at a constant nitric acid concentration of 3.8 M, and 1.4 g/L of Sm(III) at various concentration of U(VI) up to 50 g/L loading in the organic phase (1.1 M TiAP or 1.1 M TBP) and  $D_{Sm}$  was determined in each case. The results as indicated (Fig.5) reveal that  $D_{Sm}$  decreases steadily with increasing U(VI) concentration from 0.5 to 50 g/L in the organic phase for both the solvents. The value of the  $D_{Sm(III)}$  is a decrease in the free extractant (TBP or TiAP) concentration in the organic phase with uranium loading. It is important to note that the extraction of Sm(III) with TiAP is marginally higher as compared to TBP which in turn indicate that TiAP as the extractant can yield slightly better decontamination factors than 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 thorium concentration from 0-175 g/L. This effect shows that Sm(III) is not extracted in the extraction of uranium and plutonium in the PUREX process and concluded that Sm decontamination during FBR fuel reprocessing is highly feasible.



**Fig. 5:** Effect of uranium on the extractability of samarium. Conditions: [Sm] = 1400 ppm, [HNO<sub>3</sub>] = 3.8 M, solution volume = 25mL, [TBP or TiAP] = 1.1 M, [U] = 0 - 50 g/L, T = 298K.

### 3.4 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 up to various temperatures depending on the process conditions. Hence the effect of temperature on the distribution behaviour of samarium in 1.1 M of TBP/n-DD and TiAP/n-DD system was studied by changing temperature between 283-326K and fixed nitric acid concentration of 3.89M. Though the actual temperatures during the process conditions may not reduce below 298K, lower temperatures were chosen for the sake of completeness. It can be seen from Fig.6 that  $D_{Sm}$  decreases with increase in temperature. It may be associated with the decrease in the release of water molecules upon the dehydration of  $Sm^{3+}$  ions during extraction. This is a 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, Sm(III) decontamination would not pose any serious problem.



**Fig. 6:** Effect of temperature on the extractability of samarium. Conditions: [Sm] = 1400 ppm, [HNO<sub>3</sub>] = 3.8 M, solution volume = 25mL, [TBP or TiAP] = 1.1 M, T = 283-326K

### 3.5 Thermodynamics Parameters

The influence of temperature on the extraction of Sm(III) from 3 M nitric acid medium using 1.1 M TBP and TiAP has been studied at the fixed concentration of samarium, in the temperature range of 283-326K. The Van't Hoff equation [39] can be used to calculate the enthalpy change

associated with the extraction of Sm(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.7. 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 1 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 energy required factors are the dehydration of M(III), transfer and dissolution of neutral species to the organic phase, deprotonation of TBP or TiAP if M(III)-nitrate complexes with (TBP-HNO<sub>3</sub> and TiAP-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 and TiAP, which are releases energy.

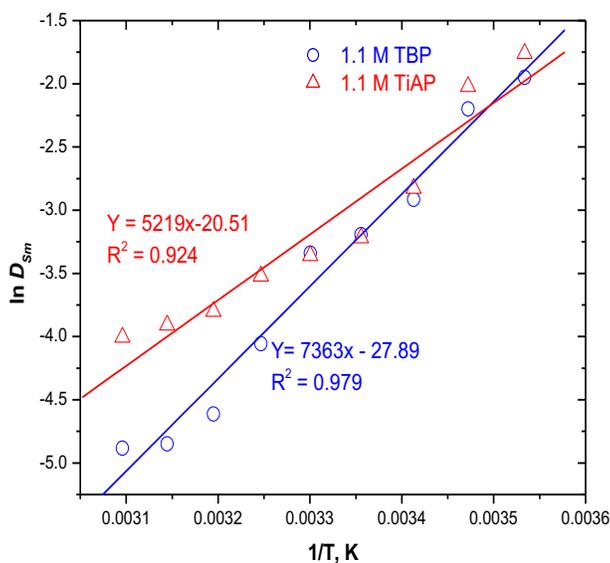
**Table 1:** Enthalpy change accompanied by the extraction of Sm(III) in 1.1M TBP and TiAP/n-DD.

Extractants, 1.1 M	$\Delta H_{tot}$ , kJ/mol	Slope	R <sup>2</sup>
TBP	-43.3 ± 6.2	7363	0.979
TiAP	-61.4 ± 2.9	5219	0.924

The obtained results show that the extraction of samarium is an exothermic process with a negative entropy change. Fewer water molecules need to be released. Hence the energy spent for this process is lower, and 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.

## 4 Conclusions

The extraction behaviour of samarium was investigated using TiAP, and the results were compared with TBP. The influence of parameters like nitric acid, metal ions, TBP and TiAP concentration, uranium loading and temperature also studies on the measurement of distribution ratio of Sm(III). The results indicate that the decontamination factors that can be achieved from uranium and plutonium against Sm(III) with TiAP are more or less similar to TBP. Also, the decrease in samarium distribution at higher temperature indicates better samarium decontamination when processing short cooled FBR spent fuel. Thus, to sum



**Fig. 7:** Van't Hoff's plot to determine the enthalpy of extraction. Conditions:  $[Sm] = 1400 \text{ ppm}$ ,  $[HNO_3] = 3.8 \text{ M}$ , solution volume =  $25 \text{ mL}$ ,  $[TBP \text{ or } TiAP] = 1.1 \text{ M}$ ,  $T = 283\text{-}323 \text{ K}$

up, it can be concluded that samarium can be employed as soluble neutron poison in FBR fuel reprocessing by the aqueous route to ensure nuclear criticality safety. The typical PUREX process chemistry offers greater flexibility in decontaminating samarium from reaching the final product thereby enabling it to meet the fresh fuel specification with respect to neutron poison impurity content.

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