Study on Third Phase Behavior for the Nitric Acid-Tri-Butyl Phosphate System Using Conductivity Measuring Technique

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ABSTRACT

Conductivity measurements of the organic phase have been done for the extraction of nitric acid by tri-n-butyl phosphate (TBP) in order to understand the third phase formation mechanism. Experiments were conducted at different nitric acid (2-14M) and TBP (20 to 90 vol%) concentrations. Experimental results indicated that conductivity variation of the organic phase can be correlated to the moisture as well as the species present in the organic phases. A higher value of conductivity was observed for third phase than the other two organic phases which is observed to be formed at high nitric acid concentration > 10M. The higher conductivity of third phase is attributed to the movement of nitric acid in the micro-emulsion globules due to the extraction of both nitric acid and moisture near third phase formation limit. A thermodynamic model has also been developed for the calculation of speciation of TBP-HNO$_3$ complex.

Key words: Third Phase, Conductivity, Species of TBP-HNO$_3$, Purex.

1. INTRODUCTION

Spent nuclear fuel discharged from the nuclear reactor needs to be reprocessed to recover the plutonium formed in the reactor as well as un-burnt uranium from the fuel [1-7]. Solvent extraction plays a vital role for the separation and purification of U and Pu from the fission products [3-7]. Apart from the recovery of uranium and plutonium, the trans-plutonide elements such as Am, Cm, etc., also needs to be separated from the high active waste solution, to reduce the burden of radio toxicity and surveillance of the radioactive waste. Various classes of solvents have been reported for the recovery of U, Pu and trans-plutonides [3-4 & 8-11]. The solvents that have been reported are di 2-ethylhexyl phosphoric acid (HDEHPA), Octyl phenyl N,N-di isobutyl carbamyl methyl phosphinoxide (CMPO), tri-n-butyl phosphate (TBP), tri cyclohexyl phosphate, phosphonates, amines (TIOA, TOA, etc.), amides (DOHA, TEDGA, THEDGA) [3-4 and 8-11]. These extractant employed during extraction of actinides may lead to the formation of third phase [12-14] in which homogeneous organic phase splits into two phases when the solubility of plutonium nitrate-TBP complex (Pu(NO$_3$)$_4$.2TBP) exceeds certain limit is called limiting organic concentration (LOC) [13]. The organic phase which is having higher density is called third phase and organic phase with lower density is known as light organic phase. The

limiting concentration of Pu in the organic phase before splitting is known as the saturated phase. A complete understanding of the third phase phenomenon is important from a process safety perspective. If third phase is formed it may lead to serious process upsets, such as criticality and increased losses of actinides (plutonium) due to entrainment of aqueous phase to organic phase or vice versa.

In view of safety implication a method of detection of third phase is essential. Third phase formation mechanism has been explained by Osseo-Asare [15] by taking into phenomenon of the reverse micelles while forming the third phase. Extensive studies on the mechanism of third phase formation using different methods such as small angle X-ray or neutron scattering studies etc. have been reported in the literature [16-21], but the reported methodologies may not be suitable for the adaptation in plant to monitor the formation of third phase. It is also reported that spectrophotometry can be employed for third phase detection [18,19], but remotisation of this method is difficult, hence a simple method of detection is required. Chiarizia et al have reported that TBP-HNO$_3$ complexes have surfactant property [16-18] and when they are present in the non-polar medium such as normal paraffin hydrocarbon may enhance conductivity of the organic phase in presence of charge conducting channels such as moisture [22-24]. Hence
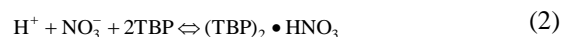
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conductivity measurement was thought to be a suitable technique for the detection of the third phase formation during extraction cycles of reprocessing of fast reactor fuels. Authors of the present work have reported that the third phases formed during extraction of U^{4+} from nitric acid medium by TBP is having higher conductivity as compared to light organic phase as well as saturated organic phase [25, 28]. The increased conductivity of the organic phase may be due to presence of nitric acid but not due to U^{4+}. The conductivity of the organic phase increase drastically at the third phase formation limit by extracting more and more acid into the organic phase [18], hence the knowledge of TBP-HNO$_3$ species in the organic phase is also essential for explaining the conductivity variation of the organic phase. Therefore, detailed studies on TBP-HNO$_3$ speciation studies were carried out during extraction of nitric acid by TBP in NPH. The results are reported in the present paper.

Extraction equilibria

The speciation of TBP-HNO$_3$ in the organic phase can be determined equilibrium extraction data of nitric acid as a function of nitric acid as well as TBP concentration in the organic phase. It is reported that the species TBP-HNO$_3$ formation does not depend on the moisture content [29]. The extraction equilibria for TBP-HNO$_3$ system can be written as

$$H^+ + NO_3^- + TBP \Leftrightarrow TBP \bullet HNO_3 \qquad (1)$$

$$H^+ + NO_3^- + 2TBP \Leftrightarrow (TBP)_2 \bullet HNO_3 \qquad (2)$$

$$H^+ + NO_3^- + TBP \bullet HNO_3 \Leftrightarrow TBP \bullet 2HNO_3 \qquad (3)$$

The equilibrium constants for Eqs (1) through (5) in terms of activities and activity coefficients are,

$$K_{H1} = \frac{a_{TBP \cdot HNO_3}}{a_{TBP} \cdot a_{HNO_3}} = \frac{[TBP \bullet HNO_3] \cdot \gamma_{TBP \cdot HNO_3}}{[H^+] \cdot [NO_3^-] \cdot \gamma_{12}^2 \cdot [TBP_f] \cdot \gamma_{TBP_f}} \qquad (4)$$

$$K_{H2} = \frac{a_{(TBP)_2 \cdot HNO_3}}{a_{TBP}^2 \cdot a_{HNO_3}} = \frac{[(TBP)_2 \bullet HNO_3] \cdot \gamma_{(TBP)_2 \cdot HNO_3}}{[H^+] \cdot [NO_3^-] \cdot \gamma_{12}^2 \cdot [TBP_f]^2 \cdot \gamma_{TBP_f}^2} \qquad (5)$$

where γ_{12} refers to a stoichiometric mean activity coefficient of nitric acid on molar scale, a's are the activity of the species involved and square brackets represent molar concentrations of species. Separating the organic phase activity coefficients from the right side of Eqs (4) through (6)

$$K_{H1}^* = K_{H1} \frac{\gamma_{TBP_f}}{\gamma_{TBP \cdot HNO_3}} = \frac{[TBP \bullet HNO_3]}{[H^+][NO_3^-] \cdot \gamma_{12}^2 [TBP_f]} \qquad (6)$$

$$K_{H2}^* = K_{H2} \frac{\gamma_{TBP_f}^2}{\gamma_{(TBP)_2 \cdot HNO_3}} = \frac{[(TBP)_2 \bullet HNO_3]}{[H^+][NO_3^-] \cdot \gamma_{12}^2 [TBP_f]^2} \qquad (7)$$

$$K_{H3}^* = K_{H1} K_{H3} \frac{\gamma_{TBP_f}}{\gamma_{TBP \cdot 2HNO_3}} = \frac{[TBP \bullet 2HNO_3]}{[H^+]^2 [NO_3^-]^2 \cdot \gamma_{12}^4 \cdot [TBP_f]} \qquad (8)$$

$$K_{H3} = \frac{a_{TBP \cdot 2HNO_3}}{a_{TBP \cdot HNO_3} \cdot a_{HNO_3}} = \frac{a_{TBP \cdot 2HNO_3}}{K_{H1} \cdot a_{TBP} \cdot a_{HNO_3}^2} = \frac{[TBP \bullet 2HNO_3] \cdot \gamma_{TBP \cdot 2HNO_3}}{K_{H1} \cdot [H^+]^2 [NO_3^-]^2 \gamma_{12}^4 \cdot [TBP_f] \cdot \gamma_{TBP_f}} \qquad (9)$$

In this study, the equation for the estimation of γ_{12} was determined by a least-square method using experimental data of Davis and Bruin which is expressed as,

$$\gamma_{12} = 1.001 - 1.1[HNO_3]^{1/2} + 1.69[HNO_3] - 1.25[HNO_3]^{1.5} + 4.41[HNO_3]^2$$
$$- 0.027[HNO_3]^3 + 9.32 \times 10^{-4}[HNO_3]^4 \qquad (10)$$

The free TBP concentration [TBP$_f$] in the organic phase is calculated by subtracting the amount of HNO$_3$ extracted into the organic phase. Then the equation for the free TBP can be written as,

$$[TBP_f] = [TBP_0] - [TBP \bullet HNO_3] - 2[(TBP)_2] \qquad (11)$$

or,

$$[TBP_f] = [TBP_0] - K_{H1}^*[H^+][NO_3^-] \cdot \gamma_{12}^2 \cdot [TBP_f] - \qquad (12)$$
$$- 0.5 K_{H3}^*[H^+]^2[NO_3^-]^2 \cdot \gamma_{12}^4 \cdot [TBP_f]$$

Solving Eq (12) which is quadratic in [TBP$_f$] value of free TBP can be obtained. The various species present in the organic phase by carrying out the non-linear regression analyses of the experimental data and various species present in the organic phase were calculated.

2. EXPERIMENTAL

Tri-n-butyl phosphate of required concentrations was prepared from the AR grade tri-n-butyl phosphate by dissolving it in heavy normal paraffin hydrocarbon. Nitric acid of the required acidity is prepared from the AR grade nitric acid and deionized water.

5 mL each of nitric acid and TBP of required concentrations were taken in an extraction vial and equilibrated for ten minutes in vortex shaker. The organic and aqueous phases were separated after centrifugation. Nitric acid concentration in the organic and aqueous phase was determined through potentiometric titration method by employing the autotitrator, and sodium carbonate solution as titrant. The conductivity of the organic phases was determined by conductivity probes details of which are described elsewhere [25].

Moisture content in the organic phase was determined Karl-Fisher method. Conductivity measurements of the organic samples were determined by using conductivity Sensor Probe and details were reported elsewhere [25].

3. RESULTS AND DISCUSSION

Figure 1 shows variation in the conductivity of the organic phase as a function of concentration of nitric acid aqueous phase and TBP. It is noticed that for a given TBP concentration the plot of conductivity *vs* nitric acid concentration in the organic phase can be classified into three portions and the transition depends upon the composition of different species of TBP-HNO$_3$ in the organic phase. The conductivity of organic phase increases steadily with increase in acidity up to (2-8M) (portion-1). The initial increase in conductivity may be attributed to increased concentration of nitric acid in organic phase leading to increased movement of charges due to percolation phenomenon. The conductivity of organic phase nearly remains same in the second portion of the plot (8 to10 M) which may be attributed to the percolation threshold due to formation of the reverse micelles in the organic phase. Beyond 10M feed nitric acid concentration (portion-3) conductivity of organic phase increases steeply.
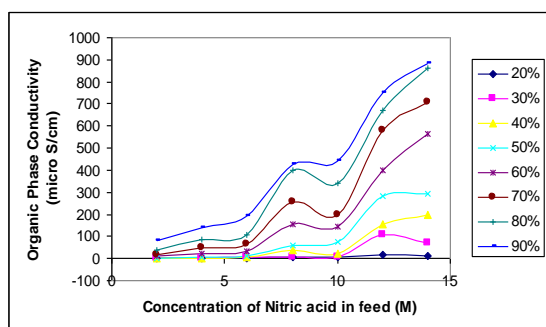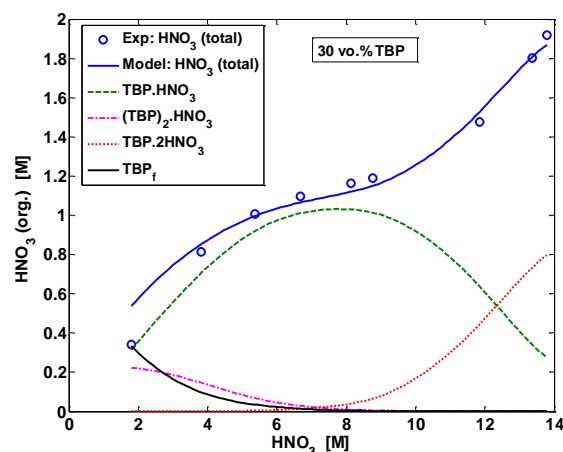

Figure 1: Variation of organic phase conductivity as a function of concentration of feed nitric acid and TBP.
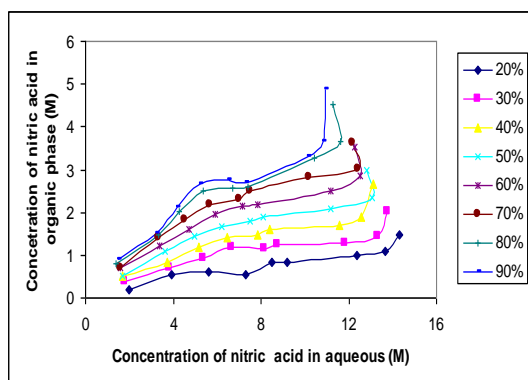
Figure 2: Concentration of nitric acid in the organic phase as a function of feed acidity and TBP concentration

In this region there is likely change in micro-structure of micro-emulsion globules [18]. This change in micro-structure may lead to formation of third phase.

Fuqiang Guo et al [23] and Mehta and Kawaljit [24] reported that the percolation of the charges to take place in the microemulsion globules, concentration of the moisture in the organic phase is essential. Apart from this, they stated that when micro-structure emulsion globules takes place it extracts more and more acid along with moisture. Hence, it is necessary to determine the concentration of moisture as well as speciation of TBP-HNO$_3$ present the organic phase in order to understand the third phase formation mechanism.
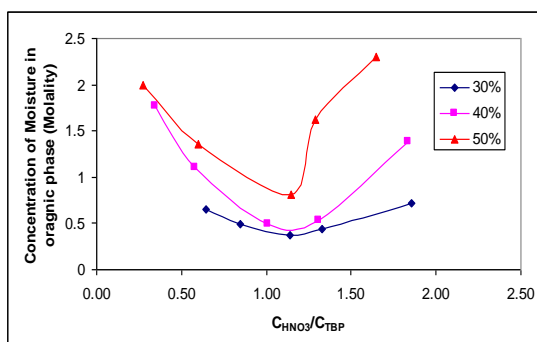

Figure 3: Various species of TBP-HNO$_3$ complex in the organic phase as a function aqueous phase nitric acid concentration for 30 % TBP.

Figure 3 shows the variation of organic phase acidity as a function of equilibrium acidity for a given TBP concentration. It is observed from this figure that concentration of the nitric acid increases with increase in the feed acidity as well TBP concentration. The concentrations of the nitric acid in the organic phase as a function of aqueous acidity were used for the calculation various species present
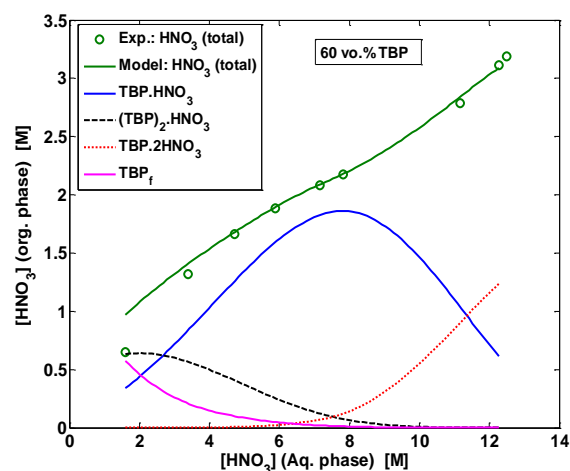
Figure 4: Various species of TBP-HNO$_3$ complex in the organic phase as a function aqueous phase nitric acid concentration for 60 % TBP.

Figure 5: Variation of the moisture in the organic phase as a function of in the organic phase and TBP concentration.

in the organic phase by solving Eqs (7-12). The various species of TBP-HNO$_3$ complex calculated from the analysis of experimental data are shown in Fig. 4 & 5 for 30 vol% TBP and 60 vol% respectively.

It observed from these figures that (TBP)$_2$. HNO$_3$ concentration decreases in the range of 2-8M nitric acid and beyond 8M acidity the concentration of this species in negligible. On the hand the concentration of TBP.HNO$_3$ complex increases with acidity and has maximum at about 8M acidity and then decreases drastically beyond 9M. Whereas concentration of TBP.2HNO$_3$ in the organic phase remains very small up to 8M acidity and then increases drastically beyond 9M acidity. This increased concentration of TBP.2HNO$_3$ indicates that micro-structure of micro-emulsion globule is changed drastically, hence more nitric acid get extracted beyond 10M aqueous acidity. Comparison of concentration of the (TBP.HNO$_3$)$_2$, TBP.HNO$_3$ and TBP.2HNO$_3$ in organic for 1.09M and 2.18M TBP concentration indicates that the concentration of all these species are higher in 2.18M TBP. In view of this increased concentration of these species in the organic phase it is expected that the probability of charges movement in the micro-emulsion globules should be higher when the TBP concentration is high.

As mentioned earlier that concentration of moisture in the organic phase also plays an important role in the understanding the conductivity of the organic phase. Hence variation of moisture concentration in the organic Fig. 5 as function of ratio of nitric acid concentration in the organic and its TBP concentration (C$_{HNO3}$/C$_{TBP}$) It is noticed from this figure that the moisture in the organic decreases with increase in C$_{HNO3}$/C$_{TBP}$ in the organic phase to certain limit and then increases with C$_{HNO3}$/C$_{TBP}$. This increased moisture content in the organic phase (when C$_{HNO3}$/C$_{TBP}$ > 1) indicates the change in the micro-structure of micro-emulsion globules

4. CONCLUSIONS

Nitric extraction studies by TBP indicated that the different species are present in the organic phase. Concentration of these species changes as a function of feed acidity as TBP concentration in the organic phase. Moisture in the organic phase decrease with increase in acid to certain value and then increases beyond a certain limit where the formation of the third phase takes place. Speciation of TBP-HNO$_3$ and moisture in the organic phase is employed for explaining the variation of conductivity of the organic phase.

5. REFERENCES

[1]. Nuclear chemical Engineering, Bendict. M., Pigford. T.M. and Levi. H.W, Second Edition McGraw Hill Book Co., New York (1981)

[2]. Engineering for Nuclear Fuel Reprocessing, Long. J.T, Gordon Breach publishers, New York (1981)

[3]. A.P. Paiva, P. Malik, (2004) Recent advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes, *Journal of Radioanalytical and Nuclear Chemistry*, **261**: 485-496.

[4]. R.V. Subba Rao, M. Venkataraman, R. Natarajan, Baldev Raj, Operating experience of Fast Reactor Spent Fuel Reprocessing facility, CORAL, Proceedings of Global 2009, Paris, France, September 6-11, 2009, Paper 9126

[5]. R. Natarajan, (1998) Challenges in Fast Reactor Fuel Reprocessing, *Indian Association of Nuclear Chemists and Allied Scientists Bulletin*, **14:** 27-32,

[6]. R. Natarajan, B. Raj, (2007) Fast reactor fuel reprocessing technology in India, *Journal of Nuclear Science and Technology*, **44:** 393-397.

[7]. M. Venkataraman, R. Natarajan and Baldev Raj, CORAL: A stepping stone for establishing the Indian Fast Reactor Fuel Reprocessing Technology, Proceedings of GLOBAL 2007, held at Boise, Idhao, 208-216

[8]. W.W. Schulz, E.P. Horwitz, (1986) Recent progress in the extraction chemistry of actinide ions, *Journal of the Less Common Metals,* **122**: 125-138.

[9]. W.E. Kedder, J.C. Sheppard, A.S. Wilson, (1960) The extraction of actinide elements from nitric acid solutions by tri-n-octylamine, *Journal of Inorganic and Nuclear Chemistry* **12**: 327-335

[10]. K.K. Gupta, V.K. Manchanda, M.S. Subramanian, R.K. Singh, (2000) Solvent extraction studies on U(VI), Pu(IV) and fission products using N,N-dihexyloctanamide, *Solvent Extraction and Ion Exchange,* **18**: 273-292.

[11]. P.R.Vasudeva Rao, Proceedings of DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science Technology, pp 5-14, (eds) P.N. Pathak, R.M. sawant, K.L. Ramkumar, V.K. Manchanda, Kalpakkam (2010)

[12]. P.R. Vasudeava Rao, T.G. Srinivasan A. Suresh., (2010) Third phase formation in the extraction of thorium nitrate by trialkyl phosphates, *IOP Conference Series: Materials Science and Engineering*, DOI 10.1088/1757-899X/9/1/012056.

[13]. P.R.V. Rao, T.G. Srinivasan, (2001) Third Phase Formation in Extraction Of Actinides, Proceedings of Nuclear and Radiochemistry symposium, 59-67, edit K. L. Ramakumar, R. M. Kadam, V.N. Vaidya and D.S.C. Purushotham, BARC, Mubmbai.

[14]. P.R. Vasudeva Rao, Z. Kolarik, (**1996)** A review ot third phase formation in extraction of actinides by neutral organophosphonus extractants *Solvent Extraction and Ion Exchange*, **14**: 955-993.

[15]. K Osseo-Asare, Nanoscience in Aqueous Processing, Procesdings of XXV, International Mineral Processing Congress (IMPC), Brisbane, Australia (2010)

[16]. R. Chiarizia, Ken L. Nash, Mark P. Jensen, P.Thiyagarajan, Ken C. Littrell, (2003) Application of the Baxter Model for Hard Spheres with Surface Adhesion to SANS Data for the U(VI)−HNO$_3$, TBP−n-Dodecane System *Langmur*, **19**: 9592-9599.

[17]. J Plaue, A. Gelis, Czerwinski, P. Thiyagarajan and R Chiarizia., (2006) Small-Angle Neutron Scattering Study of Plutonium Third Phase Formation in 30% TBP/HNO$_3$ /Alkane Diluent Systems*Solvent Extraction and Ion Exchange*, **24**: 283-298.

[18]. R. Chiarizia, M. P. Jensen, M. Borkowski, J.R. Ferraro, P. Thiyagarajan, K.C. Littrell, (2003) Third Phase Formation Revisited: The U(VI), HNO3-TBP, n-Dodecane System, *Solvent Extraction and Ion Exchange*, **21**: 423-433.

[19]. J. Plaue, S. Goeury, J. Petchsaiprasert, M. Draye, J. Foos, K. Czerwinski , Separation for the Nuclear Fuel Cycle in 21st Century, Chapter 8, 119-133, ACS Symposium series, American Chemical Society, Washington D C (2006)

[20]. Filip Strubbe, Alwin R.M. Verschueren, Luc J.M. Schlangen, Filip Beunis and Kristiaan Neyts (2006) Generation current of charged micelles in nonaqueous liquids: Measurements and simulations, *Journal of Colloid and Interface Science,* **300**: 396-403.

[21]. S. Nave, C. Mandin, L. Martinet, L. Berthon, F. Testard, C. Madicc, Th. Zem (2004) Supramolecular organisation of tri-n-butyl phosphate in organic diluent on approaching third phase transition, *Physical Chemistry Chemical Physics*, **6**: 799-808.

[22]. A. M. Khan, S. Saha, (2008) Determination of critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) and the effect of low concentration of pyrene on its Cmc using ORIGIN software, *Journal of the Chemical Society of Pakistan*, **30**: 186-191

[23]. Fuqiang Guo, Hongfei Li, Zhifeng Zhang, Shulan Meng, Deqian Li., (2006) Reversed micelle formation in a model liquid-liquid extraction system, *Journal of Colloid and Interface Science,* **332**: 396-403.

[24]. S.K. Mehta, Kawaljit, (2002) Phase diagram, physical properties of a waterless sodium bis(2-ethylhexylsulfosuccinate) ethylbenzene -ethyleneglycol microemulsion: An insight into percolation, *Physical Revew* E 65., 021502-09

[25]. S. Subbuthai, R. Ananthanarayanan, P. Sahoo, A. Nageswara Rao, R. V. Subba Rao (2012) Feasibility studies for the detection of third phase during reprocessing of fast rector fuels, *Journal of Radio analytical and Nuclear Chemistry*, **292**: 879-883.

[26]. S. Subbuthai, R.V. Subba Rao, P. Sahoo, A. Nageswara Rao, Mechanism of increased conductivity in the third phase using indigenous sensor P 133, Chemistry Research Scholars Meet 2011, July 14-15, IGCAR, Kalpakkam (2011)

[27]. S. Subbuthai, P. Sahoo, A. Nageswara Rao, R. V. Subba Rao, P23, Studies on the aggregation tendency of the TBP-HNO$_3$ in the low dielectric constant medium during development of a sensor for detection of third phase, *International Conference on Vistas in Chemistry* 2011 (ICVC-2011), 11-14 october' 2011 held at IGCAR, Kalpakkam

[28]. S. Subbuthai, P. Sahoo, A. Nageswara Rao, R.V. Subba Rao*,* Studies on understanding the mechanism of the enhanced conductivity of the third phase in PUREX process during reprocessing of fast reactor fuel, *Journal of Radio analytical and Nuclear Chemistry*, DOI 10.1007/s10967-012-2279-8

[29]. J.M. Schaekers, Atomic Energy Corporation of South Africa, Pretoria, South Africa, I-185-I190.

[30]. K. Alcock, S.S. Grimley, T.V. Healy, J. Kennedy, H.A.C. Mckay, (1956) The extraction of nitrates by tri-n-butyl phosphate (TBP). Part 1.-The system TBP + Diluent +

H$_2$O+HNO$_3$ *Transactions of the Faraday Society*, **52**: 39-47.

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