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SYNERGISTIC EXTRACTION OF EUROPIUM (III) BY COMPLEXATION WITH TPBD AND DOSO, TOPO, TPhPO FROM THIOCYANATE SOLUTION IN BENZENE

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ABSTRACT

Solvent extraction studies on Eu (III) from thiocyanate solutions are carried out using various extractants and their mixtures in benzene. The systems involving 4,4,4-trifluoro-1-phenyl-1,3-butadione (TPBD) as a synergist in the extraction of europium(III) using di-n-octyl sulphoxide (DOSO), Tri-n-octyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPhPO), 2-thenoyltetrafluoroacetone (TTA) and their mixtures has been investigated in benzene. At given extractant concentration (pH=3), the extraction of Eu (III) increases with thiocyanate concentration. The slope of the plot log D (where D is distribution coefficient defined as the ratio of concentration of metal in the organic phase to that present in the aqueous phase) against log [SCN⁻] is nearly 3 indicating the extraction of neutral species in to organic phase. Mixed species of the type Eu(TPBD)₃.S and Eu(TPBD)₃.2S were obtained with mixtures of TPBD and DOSO/TOPO/TPhPO (where S=DOSO/TOPO/TPhPO) may be responsible for the synergism, whereas species of the type Eu(TTA)₂.SCN.2S are obtained with mixtures of TTA and (DOSO/TOPO/TPhPO).

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INTRODUCTION

Rare earth element (REE) is a mine of new material and has very wide uses in industry. India has second largest abundant resources of rare earths and with its products and exports playing an important part in the world (Rose *et al.* 1960). REEs are important in nuclear energy programs, hence the separation and purification of rare earths is demanded. As well known, the separation between trivalent REEs is one of the most difficult tasks in separation chemistry due to their similar chemical properties. A large number of acidic and neutral organo-phosphorus and sulphur extractants have been widely employed industrially for the solvent extraction separation of REEs (Bautista *et al.* 1995). However, these reagents display various shortcomings, such as poor selectivity, third phase formation, etc. (Syouhei *et al.* 2006) In view of the ever increasing demand for high purity REEs as a group or from one another, there is a growing interest in the development of new and more selective solvent extraction reagents. Phosphorus and sulphoxide compounds have dominated the solvent extraction process as extracting agents. Thus, phosphorus and sulphoxide compounds find their place as promising extractants for number of metals including REEs (Kopyrsin, 1999; Kubota, 2003).

In the present work we investigated synergistic extraction of trivalent ¹⁵²⁺¹⁵⁴Eu from thiocyanate solutions. A well type NaI (TI) γ -ray scintillation counter used for the measurement of gamma activity of ¹⁵²⁺¹⁵⁴Eu. The systems involving 4,4,4-trifluoro-1-phenyl-1,3-butadione (TPBD) as a synergist in the extraction of europium using di-n-octyl sulphoxide (DOSO),

Tri-n-octyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPhPO), and their mixtures has been investigated in benzene (Kovalancik, 1992; Rehman, 2005). γ - ray spectrometry is non-destructive and stable for determination of low concentration of both natural uranium and thorium series K-40 and artificial isotopes like cesium-137 and other fission products (Peerani *et al.* 2002).

Experimental

Materials

Analytical grade reagents were used for the extraction studies as well as for the estimation of the metal, 4,4,4-trifluoro-1-phenyl-1,3-butadione (TPBD), 2-thenoyltetrafluoroacetone (TTA), Tri-n-octyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPhPO) obtained from Fluka A.G. (Switzerland) were used without any further purification. Di-n-octyl sulphoxide (DOSO) was synthesized as published in earlier literature (Krishna Reddy, 1978; Kobashi and Chappin, 1988). ¹⁵²⁺¹⁵⁴Eu was obtained from Board of Radiation and Isotope Technology [BRIT] India, and its radiochemical purity was ascertained by gamma ray spectrometry.

The Extraction Conditions

Solvent extraction studies were made on solutions of 0.1 -1.0 mol/dm³ sodium thiocyanate at 30°C. The initial pH of the aqueous phase was generally maintained at 3 by adding either hydrochloric or perchloric acid. The initial metal concentration was never exceeded 1X10⁻⁶ mol/dm³. Solutions of TPBD (0-0.5 mol/dm³), TTA (0-0.4 mol/dm³), TOPO (0-0.6 mol/dm³) TPhPO (0-0005 mol/dm³), DOSO (0-0.0065 mol/dm³) were used.

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Time of Equilibration

The rate of extraction of Eu[III] from thiocyanate solutions by TOPO, TPBD and TTA as extractants have been studied. The extraction equilibrium of Eu[III] from thiocyanate solutions is found to be attained within a contact period of 30 minutes in those systems. On the other hand, the equilibrium is attained within 5 minutes in all the systems with TPBD – DOSO, TPBD –TOPO, TPBD – TphPO, TTA –TTA – TOPO and TTA – TphPO mixtures. The equilibrations were effected by the wrist action shaking of the glass stoppered vials containing equal volumes of the two phases for 30 minutes. Suitable aliquot of both the phases were withdrawn for activity measurement. The experiments were conducted in duplicate and the extraction coefficient, D, is given by

$$D = \frac{C.F.M. \text{ With 1 or 2 ml of the organic phase}}{C.F.M. \text{ With 1 or 2 ml of the aqueous phase}} \dots\dots (1)$$

Methods of Estimation

Radiometric methods were employed for the estimation of Eu[III]. A small aliquot [$\sim 25 \lambda$] of the tracer $^{152+154} \text{Eu [III]}$ was introduced into the aqueous phase prior to the extraction studies. After equilibration suitable aliquot of each phase was pipetted out into counting vials. The activity was measured by a γ - ray spectrometer type GRS 20C with NaI [TI] crystal having well dimensions 16x40 mm deep. The total counts measured for both the phases were around 26000 per minute. More than 1000 counts were measured from the least active phase which was at least twice as activities as the background.

RESULTS AND DISCUSSION

The influence of thiocyanate concentration over the range [0-0.6 mol/dm³] on the extraction of Eu[III] from aqueous solutions at initial pH = 3 was studied with 0.02 mol/dm³ TOPO in benzene. The effect of thiocyanate concentration in the range 0-0.6 mol/dm³ at a given concentration of TOPO in benzene is given in Fig-1. The extraction of the metal increases rapidly with increase in thiocyanate concentration. The plot of log D vs. Log [SCN⁻] is linear [Fig.1] with a slope of ~ 3 . The dependence of extraction of Eu[III] from 0.1 mol/dm³ thiocyanate solutions and pH 3.0 with the concentration of TOPO [0-0.06 mol/dm³], and TPBD [0.5mol/dm³] in benzene is given in Fig-2. It is evident that the extraction of the metal is favored by higher extractant concentration (Reddy *et al.* 1999; Makrlik E 2010). The sigmoid dependence of D on the extractant concentration is observed. The log D-log extractant concentration plots are linear with slopes ~ 4 for TOPO and ~ 3 for TPBD/ TTA [Fig.2]. The synergistic enhancement is more pronounced at higher concentrations of the extractant.

Extraction of Eu(III) from 01 mol/dm³ thicyanate solutions by mixtures of TPBD-DOSO [0-0.3 mol/dm³ TPBD 0-0.0065 mol/dm³ DOSO in benzene), TPBD-TOPO [0-.0.4 mol/dm 0-0.00008 mol/dm are given in tables IV to XV. The log - log plots for extraction of Eu(III) from 0.1 mol/dm³ thiocyanate solutions by mixtures of TPBD-DOSO [0-0.3 mol/dm³ TPBD at constant 0-0.0065 mol/dm³ DOSO in benzene], TPBD-TOPO [0-.0.4 mol/dm³ at constant 0-0.00008 mol/dm³ TOPO in benzene), TPBD-TPhPO [0-0.3 mol/dm³ TPBD at constant 0.0005 mol/dm³ TPhPO in benzene], TTA-DOSO (0-0.1 mol/dm³ at constant TTA:0-0.08 mol/dm³ TOPO in benzene],

TTA-TPhPO [0-0.1 mol/dm³ TTA 0-0.1 mol/dm³; TPhPO:0-0.08 mol/dm³ in benzene]; TTA-TOPO [0-06 mol/dm³ TTA; 0-0.08 mol/dm³ TOPO in benzene], TTA - TPhPO [0-0.1 mol/dm³ TTA 0-0.01 mol/dm³ TPhPO in benzene] are given in figs. 3 and 4. Mixed species of the type Eu[TPBD]₃.S and Eu[TPBD]₃.2S [where S=DOSO/TOPO/TPhPO] may be responsible for the synergism. Whereas species of the type Eu[TTA]₂ SCN.2S are obtained with mixtures of TTA and DOSO/TOPO/TPhPO.

Table 1 Extraction of Europium (III) from Thiocyanate solutions by mixtures of TPBD and DOSO in benzene at pH=3

Concentration of NaSCN = 0.1mol/dm³

S.No.	TPBD mol/dm ³	DOSO 0.002 mol/dm ³	D _{1+D₂}	D _{SYN}
1	0.1	0.002	0.028	1.14
2	0.15	0.002	0.101	3.46
3	0.2	0.002	0.226	7.03
4	0.25	0.002	0.501	13.21
5	0.3	0.002	0.873	21.14
6	0.1	0.003	0.028	2.29
7	0.1	0.004	0.028	3.70
8	0.1	0.005	0.028	5.28
9	0.1	0.006	0.028	7.03

The slope of the plot, log D- log TPBD concentration at constant S concentration [Fig. 3] is ~ 3 indicating that the number of TPBD molecules participating in the complex formation are unaltered by the presence of the second extractant concentration. On the other hand the log D - log TTA concentration plot at fixed second extractant concentration [S] has a slope value ~ 2 showing that it involves both substitution and addition reactions [Fig. 5]. The log-log plots for the second extractant [s] at fixed TPBD/ TTA have slopes varying from 1 to 2 [Figs.4 & 6].

Table 2 Extraction of Europium (III) from Thiocyanate solutions by mixtures of TPBD and TOPO in benzene at pH 3 Concentration of NaSCN = 0.1mol/dm³

S.No.	TPBD mol/dm ³	TOPO mol/dm ³	D _{1+D₂}	D _{SYN}
1	0.1	0.00002	0.028	0.80
2	0.2	0.00002	0.226	5.01
3	0.3	0.00002	0.873	14.10
4	0.4	0.00002	1.930	30.20
5	0.1	0.00002	0.028	0.91
6	0.1	0.00004	0.028	2.51
7	0.1	0.00006	0.028	5.
8	0.1	0.00008	0.028	8.13

Table 3 Extraction Of Europium (Iii) From Thiocyanate Solutions By Mixtures Of Tpbpd And Tphpo In Benzene at Ph=3

Concentration of NaSCN = 0.1mol/dm³

S.No.	TPBD	TPhPO	D _{1+D₂}	D _{SYN}
1	0.10	0.0001	0.028	0.39
2	0.15	0.0001	0.101	1.08
3	0.20	0.0001	0.226	2.63
4	0.30	0.0001	0.501	8.71
5	0.1	0.0001	0.028	0.457
6	0.1	0.0002	0.028	1.250
7	0.1	0.0004	0.028	3.480
8	0.1	0.0005	0.028	4.660

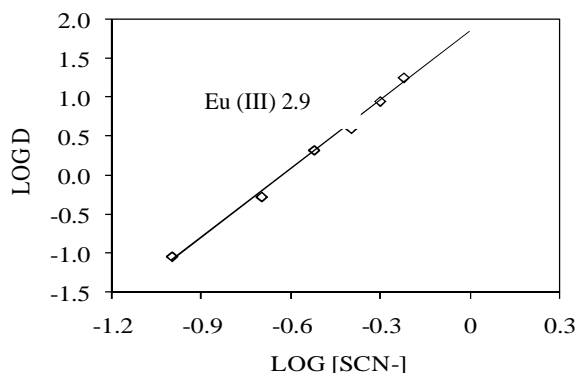


Fig.1 Effect of thiocyanate concentration on the extraction of Eu (III) by 0.02 mole/ dm³ TOPO in benzene

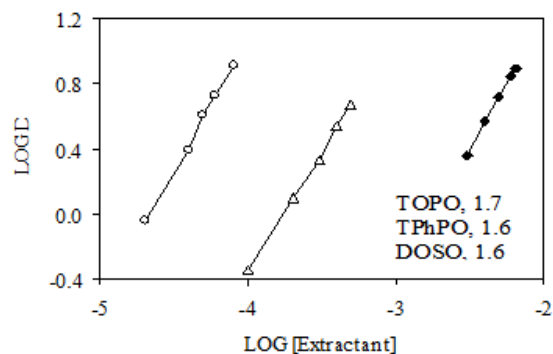


Fig.4 Variation of the extraction of Eu [III] from thiocyanate solutions by TOPO (○), TPhPO (Δ), and DOSO (◆) in presence 0.1 mol/dm³ TPBD in Benzene.

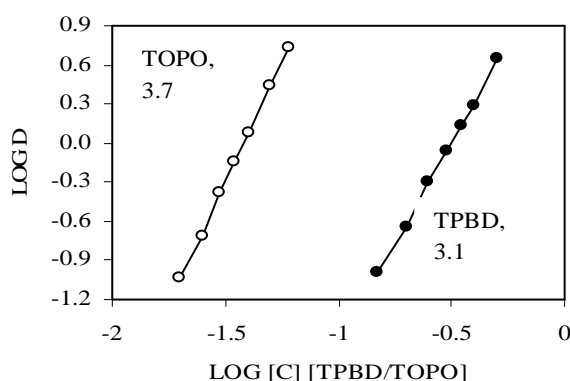


Fig.2 Variation of the extraction of Eu [III] from thiocyanate Solutions by 0.5 mol/dm³ TPBD (●) and 0.06 mol/dm³ TOPO (○) in Benzene.

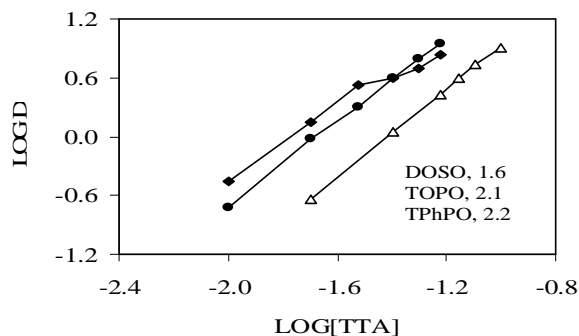


Fig.5 Variation of the extraction of Eu [III] from thiocyanate solutions by TTA in presence of 0.004 mol/dm³ TPhPO (Δ), 0.001 mol/dm³ TOPO (○), and 0.04 mol/dm³ DOSO (◆) in Benzene.

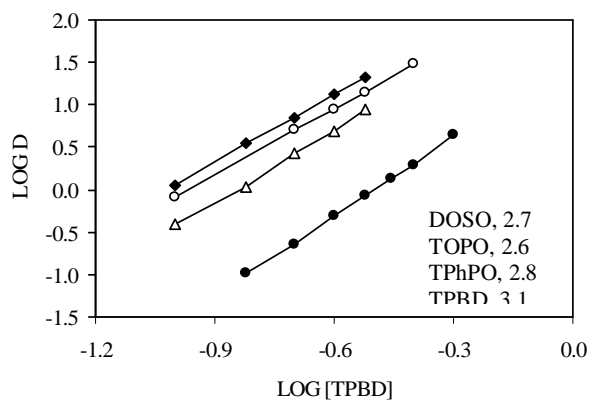


Fig.3 Variation of the extraction of Eu [III] from Thiocyanate solutions by TPBD in presence of 0.002 mol/dm³ DOSO (◆), 0.00002 mol/dm³ TOPO (○), 0.0001 mol/dm³ TPhPO (Δ) and pure TPBD (●) in Benzene.

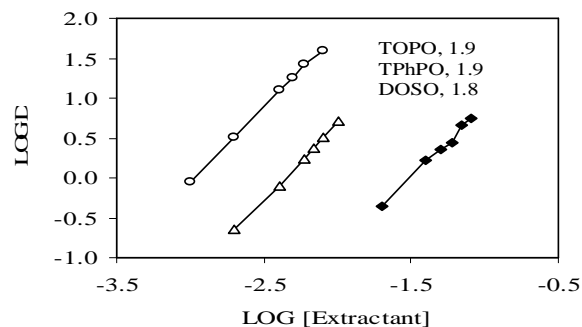
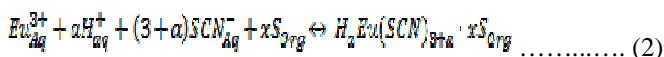


Fig.6 Variation of the extraction of Eu [III] from thiocyanate solutions by TOPO (○), TPhPO (Δ) and DOSO (◆) in presences TTA in Benzene.

The extraction mechanism of Eu(III) from thiocyanate medium by a solvating solvent such as DOSO/ TOPO/ TPhPO may be expressed by the following equation.



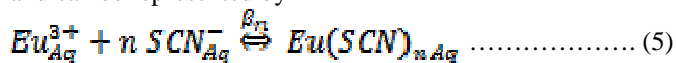
Where *S* is the extractant. The equilibrium constant *K_x* is represented by

$$K_x = \frac{[H_aEu(SCN)_{3+a} \cdot xS]_{Org}}{[Eu^{3+}]_{Aq} [H^+]_{Aq}^a [SCN^-]_{Aq}^{3+a} [S]_{Org}^x} \dots\dots\dots (3)$$

The total metal in the aqueous phase [*Eu_t*] is given by

$$Eu_t = Eu^{3+} (1 + \sum_1^n \beta_n [SCN^-]^n) \dots\dots\dots (4)$$

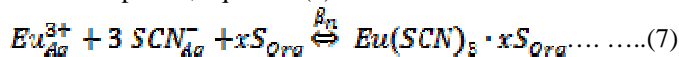
Where β_n stands for the concentration equilibrium constant and can be represented by



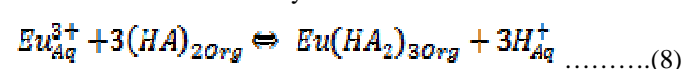
Substituting equation (5) in equation (1): introducing the modified form of equation (1) in equation (3) and assuming that $H_a M(SCN)_{3+a} \cdot XS$ is the only species getting extracted into the organic phase the expression obtained is

$$K_x^1 = \frac{D}{[H^+]_{Aq}^a [SCN^-]_{Aq}^{3+a} [S]_{Org}^x} \dots\dots\dots (6)$$

If H^+ ion is not participating in the formation of extractable metal complexes, equation (2) reduces to



The established extraction equilibrium in the perchlorate medium with respect to the chelating agent such as TTA/TPBD is described by



And the equilibrium constant K_p of this reaction is given by

$$K_p = D_A \cdot [H^+]_{Aq}^3 / [(HA)_2]_{Org}^3 \dots\dots\dots (9)$$

Where D_A is the distribution coefficient of the metal between TTA and the aqueous medium. Similarly, the equilibrium constant K_A with respect to the thiocyanate medium may be represented by the equation.

$$K_A = D_A \cdot F [H^+]_{Aq}^3 / [(HA)_2]_{Org}^3 \dots\dots\dots (10)$$

Where

$$F = (1 + \sum_1^n \beta_n [SCN^-]^n) \dots\dots\dots (11)$$

Assuming that $M(HA)_3$ is the only species getting extracted into the organic phase. It is evident from the third power dependence of D_A on the activity of $(HA)_2$ that no thiocyanate ion is associated with the extractable complex of the metal.

It has been provided already that pH has no direct influence on the extraction of Eu(III) from thiocyanate medium by sulphoxides and Tri-n-octyl phosphine oxide. Incorporating this observation, equation (7) takes the form

$$K_x^1 = \frac{D}{[SCN^-]_{Aq}^3 [S]_{Org}^x} \dots\dots\dots (12)$$

Taking logarithms on both sides of the equation (12) and rearranging we get

$$\log D = \log K_x^1 + 3 \log [SCN^-]_{Aq} + x \log [S]_{Org} \dots\dots\dots (13)$$

The nature of the extracted species may be elucidated from a study of the extraction behavior as a function of $[SCN^-]$ and $[S]$

The extraction of Eu(III) from thiocyanate solution at initial pH 3 by TOPO in benzene increases rapidly with increase in thiocyanate concentration under the experimental conditions equation (13) takes the form

$$\log D \propto 3 \log [SCN^-] \dots\dots\dots (14)$$

A plot of log D against log $[SCN^-]$ gives the number of thiocyanate ions that combine with the metal ion in forming species extractable into the organic phase. Thus, the slope analysis method yield anion solvation number 3 for Eu(III) fig.1. A third power relation between the metal and the thiocyanate ion shows clearly the extraction of neutral species into the organic phase. The increase in distribution ratio with increase in the thiocyanate concentration is due to the common ion effect.

When the extractant concentration in the organic phase is varied at constant aqueous phase concentration, equation [13] reduces to the form

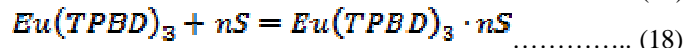
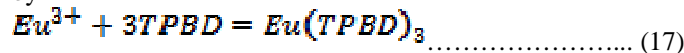
$$\log D \propto x \log [S] \dots\dots\dots (15)$$

The slope of the plot log D against log extractant concentration gives the solvation number, x (the number of extractant molecules attached to the metal in the organic phase). The extraction of Eu(III) increases with increase in the concentration of the extractant; and log D-log extractant concentration plots have slopes ~4 with respect to TOPO and ~3 with respect to TTA and TPBD [Fig.2]. It is understood that 4 molecules of TOPO and 3 molecules of TTA/TPBD are associated with each of the extracted metal species. The solvation number 4 with respect to dialkyl sulphoxides, TOPO and TBP are commonly observed in the extraction of trivalent lanthanides. Similar results have been reported with several neutral organophosphorus extractants. Thus the extractable complexes of Eu(III) from thiocyanate medium by TOPO, TTA and TPBD are $Eu(SCN)_3 \cdot 4TOPO$, $Eu(TTA)_3$ and $Eu(TPBD)_3$.

The mixture of two extractants say S^I and S^{II} extracts lanthanides more than the sum of the extractions due to individual components at the corresponding concentrations; and may be mathematically denoted as

$$D_{syn} = D_{S^I} + D_{S^{II}} + \Delta D \dots\dots\dots (16)$$

Where ΔD is the magnitude of the synergistic enhancement of extraction. The results clearly show that the formation of mixed ligand metal complexes are responsible for the enhancement and the extraction mechanism may be described by



If the activity coefficients of the species remain constant, the equilibrium constant K_{xy} is given by

$$K_{xy} = \frac{[Eu(TPBD)_3 \cdot nS]_{Org}}{[Eu^{3+}]_{Aq} [TPBD]_{Org}^3 [S]_{Org}^n} \dots\dots\dots (19)$$

$$= \frac{D_{syn}}{[TPBD]_{Org}^3 [S]_{Org}^n} \dots\dots\dots (20)$$

Taking logarithms and rearranging we get

$$\log D_{syn} = \log K_{xy} + 3 \log [TPBD] + n \log [S] \dots (21)$$

The $\log D_{syn}$ against $\log [TPBD]$ plot at constant S ($S=TOPO/TPhPO/DOSO$) concentration is a straight line with slope ~ 3 for $Eu(III)$ suggesting that 3 molecules of TPBD are associated with the synergistic species (Fig. 3). $\log D_{syn}$ against $\log [S]$ plot at constant TPBD concentration is also resulted in straight lines giving slopes between one and two but more nearer to one (Fig. 4) indicating that one or two molecules of S ($S=TOPO/TPhPO/DOSO$) are associated in the complex formation of mixed species.

It has been observed that $Eu(III)$ is extracted from thiocyanate medium, by TTA as $Eu(TTA)_3$ into benzene. On the other hand, the extraction of these metals from thiocyanate medium by $DOSO/ TOPO/ TPhPO$ (commonly denoted by S) is represented by $Eu(SCN)_3.4S$. It has been noticed that, [8,10], depending on the concentration of TTA used the slope of $\log D$ - $\log S$ concentration plots varied from 1 to 3 suggesting the existence of three forms of complexes respectively with solvation numbers one (when $[TTA] \gg [S]$), Two (when $[TTA] \approx [S]$), and three (when $[TTA] \ll [S]$) (Rama Krishna *et al.* 1978; Reddy *et al.* 1977). Likewise, the slopes of log-log plots vary again between one and three indicating that 1 to 3 molecules of TTA are associated in the extraction of the metal from thiocyanate medium into mixtures of TTA and S are depending on the composition of the mixture. Thus three complexes of the type $Eu(TTA)_3$; $Eu(TTA)_2(SCN)_2S$; $Eu(TTA)(SCN)_2.3S$ have been reported apart from the two complexes $Eu(TTA)_3$ and $Eu(SCN)_3.4S$. The log-log plots for $Eu(III)$ with TTA at constant S concentration from thiocyanate solutions (Fig.5) are straight lines with slopes ~ 2 . The corresponding log - log plots with S at constant TTA concentration also give straight lines with slopes ~ 2 . (Fig. 6) indicating the formation of a mixed species of the type $Eu(TTA)_2SCN.2S$.

CONCLUSION

The investigations made on the extraction of $Eu(III)$ with mixtures of a chelate (TPBD /TTA) and a solvating solvent (TOPO/TPhPO/DOSO) suggest the formation of both addition and substituted mixed ligand complexes. The thiocyanate forms zero charged species with $Eu(III)$ ($Eu(SCN)_3$) which is readily extracted by tri-n-octyl phosphine oxide and di-n-octyl sulphoxide. The present results show that tetra solvates such as $Eu(SCN)_3.4TOPO$ exist in the extraction of $Eu(III)$ by TOPO, TTA and TPBD form trisolvates of the type $Eu(TTA)_3$, $Eu(TPBD)_3$ with europium. The synergistic effect increases with increase in the concentration of the extractant. The association of anionic ligands with metal along with molecules of extractants employed is noticed in aqueous thiocyanate solutions when TPBD is employed as one of the extracting agents. The nature of different metal species transferred into the organic phase has been clearly established.

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