

## MIXED-LIGAND CHELATE EXTRACTION OF NEODYMIUM(III) WITH THENOYLTRIFLUOROACETONE AND VARIOUS SULPHOXIDES

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**Summary**—Mixed-ligand chelate extraction of Nd(III) into benzene with mixtures of thenoyltrifluoroacetone (HTTA) and bis-2-ethylhexyl sulphoxide (B2EHSO) or di-*n*-octyl sulphoxide (DOSO) or diphenyl sulphoxide (DPhSO) or trioctylphosphine oxide (TOPO) from thiocyanate solutions has been studied. A very high synergistic enhancement of the order  $10^3$  has been observed in these systems. Thus this mixed-ligand chelate system may be useful in the extraction and separation of Nd(III) from other metal ions. The mechanism of extraction can be explained by a simple chemically based model presented in this paper.

Mixed-ligand chelate extraction systems involving an acidic chelating agent and a basic neutral ligand are powerful and highly improve the extraction efficiency of metal ions. Many studies have been carried out on the synergistic extraction of trivalent lanthanides using a mixture of thenoyltrifluoroacetone (HTTA) and a neutral unidentate ligand such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO) or bidentate ligands such as *n*-octyl(phenyl)-*N,N*-diisobutyl carbamoylmethyl phosphine oxide (CMPO).<sup>1-4</sup> Compared with these, the systematic study of the synergistic extraction systems involving sulphoxides as neutral ligand is sparse.<sup>5-6</sup> Further, no clear understanding of the intricate mechanism of the extraction of these systems has yet been reached. Thus a more detailed investigation of synergistic extraction of lanthanides with a fundamental chelating agent, HTTA and different sulphoxides as neutral ligand is desirable.

In the present paper the mixed-ligand chelate extraction of Nd(III) with HTTA in the presence of various sulphoxides as neutral donors has been studied. Due to the limitations of the traditionally used graphical methods for the analysis of synergistic solvent extraction data,<sup>1,7</sup> recourse was taken to theoretical analysis using a computer in the present study. The formation constants of the mixed-ligand chelate species of different neutral donors have been determined by non-linear regression analysis and compared with their donor properties.

### EXPERIMENTAL

The tracer solution of <sup>147</sup>Nd was purchased from the Board of radiation and Isotope Technology (BRIT), India. HTTA obtained from Aldrich Chemical Co., was dried in vacuum over P<sub>2</sub>O<sub>5</sub> for several hours.<sup>8</sup> The stock solution of HTTA in benzene was equilibrated prior to use with dilute perchloric acid for several hours to allow hydration of HTTA.<sup>9</sup> TOPO purchased from Fluka A.G. was purified by the method described elsewhere.<sup>10</sup> DOSO and DPhSO were synthesized in our laboratory according to the procedure already described.<sup>11</sup> B2EHSO was obtained from Fairfield Chemical Co., USA and purified by the method reported in the literature.<sup>12</sup> All the other chemicals used were of reagent grade.

The aqueous phase was 1.0M sodium thiocyanate solution except in experiments on the role of SCN<sup>-</sup> concentration. The pH was adjusted to 3.0 to ensure stability using perchloric acid. After equilibration with the solvent concerned, 2.0 ml of the aqueous phase containing <sup>147</sup>Nd isotope (25 μl) and 2.0 ml of the organic phase were equilibrated for 30 min in an air-thermostat at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium was attained within 5 min. After phase separation, 1 ml aliquots of both the phases were pipetted out for the estimation of the metal by counting the gamma activity using a NaI(Tl) well-type scintillation detector connected with a single-channel analyser (GRS 23B). The distribution coefficient, *D*, was taken as the ratio of

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the activity of the tracer in the organic phase to that present in the aqueous phase. All the computer programs are written in FORTRAN 77 and executed on a 32 bit mini-computer (HCL HORIZON).

### RESULTS AND DISCUSSION

The neodymium ion in the aqueous phase takes a variety of complex forms in the presence of thiocyanate ions, but under the present experimental conditions it is sufficient to consider only the first two complexes as defined by equation (1).<sup>13</sup>



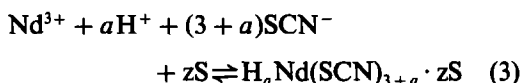
where  $i = 1$  and  $2$ .

Then the total Nd(III) in the aqueous phase ( $Nd_t$ ) is given by

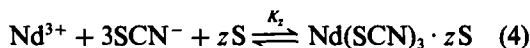
$$\begin{aligned} Nd_t &= \text{Nd}^{3+} + \text{Nd}(\text{SCN})_2^{+} + \text{Nd}(\text{SCN})_2^{+} \\ &= \text{Nd}^{3+} \{1 + \beta_1[\text{SCN}^-] + \beta_2[\text{SCN}^-]^2\} \quad (2) \end{aligned}$$

The stability constants  $\beta_1 = 6.47$  and  $\beta_2 = 1.30$  were obtained from the literature.<sup>13</sup>

The mechanism of extraction of Nd(III) from thiocyanate media by sulphoxides or TOPO may be represented as



where 'S' is the extractant. The effect of pH on the extraction of Nd(III) at constant thiocyanate (1.0M) and sulphoxide (1.0M B2EHSO) concentration has been studied. It was found that the  $D$  values are constant in the pH range from 2.5 to 4.5. Hence the value of 'a' in equation (3) is equal to zero and the extraction equilibrium can be written as



$$K_z = \frac{[\text{Nd}(\text{SCN})_3 \cdot z\text{S}]}{[\text{Nd}^{3+}][\text{SCN}^-]^3[\text{S}]^z} \quad (5)$$

Then the  $D$  of Nd(III) can be represented from equations (2) and (5) as

$$D = \frac{\Sigma K_z [\text{SCN}^-]^3 [\text{S}]^z}{\{1 + \beta_1[\text{SCN}^-] + \beta_2[\text{SCN}^-]^2\}} \quad (6)$$

The effect of thiocyanate concentration on the extraction of Nd(III) with 1.0 M B2EHSO in benzene has been studied and the results are shown in Fig. 1. The distribution coefficient

rapidly increases with increasing  $\text{SCN}^-$  concentration. The slope of the plot  $\log \{D(1 + \beta_1[\text{SCN}^-] + \beta_2[\text{SCN}^-]^2)\}$  against  $\log [\text{SCN}^-]$  is  $3 \pm 0.1$ , suggesting that the metal species extracted into the organic phase is associated with three thiocyanate ions.

The variation of Nd(III) with the concentration of B2EHSO, DOSO and TOPO has been studied using 1.0M thiocyanate (pH = 3) as the aqueous phase. From the slopes of the plots (Fig. 2)  $\log \{D(1 + \beta_1[\text{SCN}^-] + \beta_2[\text{SCN}^-]^2)\}$  vs  $\log [\text{extractant}]$ , it is clear that four molecules of B2EHSO, DOSO, DPhSO (slope =  $4 \pm 0.1$ ) and three molecules of TOPO (slope =  $3 \pm 0.1$ ) are associated with the extractable complex in the respective extractions. These distribution data (Figs 1 and 2) were further analysed for confirming the mechanisms, by non-linear regression analysis using equation (6), assuming  $\text{Nd}(\text{SCN})_3 \cdot z\text{S}$  where  $z = 3$  or  $4$ . The best fit between the experimental and calculated  $D$  values was obtained when the formation of the species,  $\text{Nd}(\text{SCN})_3 \cdot 4\text{B2EHSO}/4\text{DOSO}/4\text{DPhSO}/3\text{TOPO}$  were assumed. The equilibrium constants for the above species are given in Table 1.

The mechanism of the extraction of Nd(III) by HTTA in benzene from thiocyanate media is governed by the equilibrium:

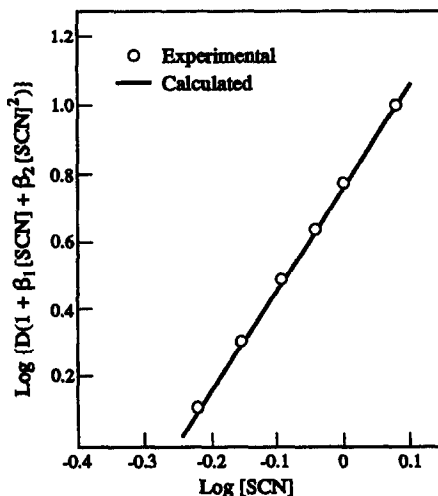
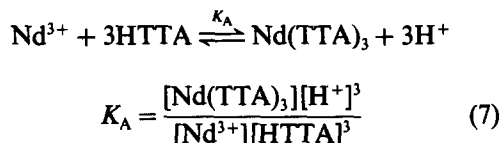


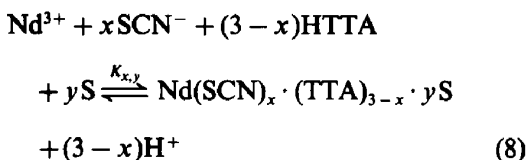
Fig. 1. Effect of thiocyanate concentration on the extraction of Nd(III) with 1.0M B2EHSO in benzene.  $Nd(III) = 1.0 \times 10^{-6}M$ .

Then the distribution coefficient,  $D_A$ , is given by

$$D_A = \frac{K_A [\text{HTTA}]^3}{\{1 + \beta_1 [\text{SCN}^-] + \beta_2 [\text{SCN}^-]^2 [\text{H}^+]^3\}}$$

For confirming the above mechanism, the variation of  $D_A$  of Nd(III) with the concentration of HTTA (0.1–0.3M) was studied using 1.0M thiocyanate solution (pH = 3) as the aqueous phase. The slope of the plot  $\log \{D_A(1 + \beta_1 [\text{SCN}^-] + \beta_2 [\text{SCN}^-]^2 [\text{H}^+]^3)\}$  against  $\log [\text{HTTA}]$  is  $3 \pm 0.1$ , indicating that the species extracted is  $\text{Nd}(\text{TTA})_3$ . The extraction constant of the above species was determined by non-linear regression analysis (Table 1).

When Nd(III) is extracted with a mixture of HTTA and sulphoxide or TOPO from thiocyanate solutions, the extraction equilibrium may be written as



where S = neutral oxo-donor and  $x = 0, 1, 2$  and  $y = 1, 2$ .

$$\begin{aligned} K_{x,y} &= \frac{[\text{Nd}(\text{SCN})_x (\text{TTA})_{3-x} \cdot y\text{S}] [\text{H}^+]^{3-x}}{[\text{Nd}^{3+}] [\text{HTTA}]^{3-x} [\text{SCN}^-]^x [\text{S}]^y} \\ D &= \frac{\sum_{x,y} K_{x,y} [\text{HTTA}]^{3-x} [\text{SCN}^-]^x [\text{S}]^y}{[\text{H}^+]^{3-x} \{1 + \beta_1 [\text{SCN}^-] + \beta_2 [\text{SCN}^-]^2\}} \end{aligned} \quad (9)$$

As is well known,<sup>1</sup> chelating agents are weak acids and the neutral donors (S) are bases, there is a possibility that the chelate and neutral donor may interact in the organic phase leading to the reduced concentration of free chelate (HTTA) and S. This side reaction may be written as



The constants  $K_{x,y}$  and  $K_1$  were obtained by the non-linear regression analysis by the following procedure.

- (1) Assume values for  $K_{x,y}$  and  $K_1$ .
- (2) The equilibrium concentrations of the species occurring in equation (9) were determined with the knowledge of initial concentrations of [HTTA] and [S] and the assumed value of  $K_1$  by solving a quadratic equation.
- (3) Values of  $D$  under the given conditions were calculated from equation (9) and compared with the experimental values.

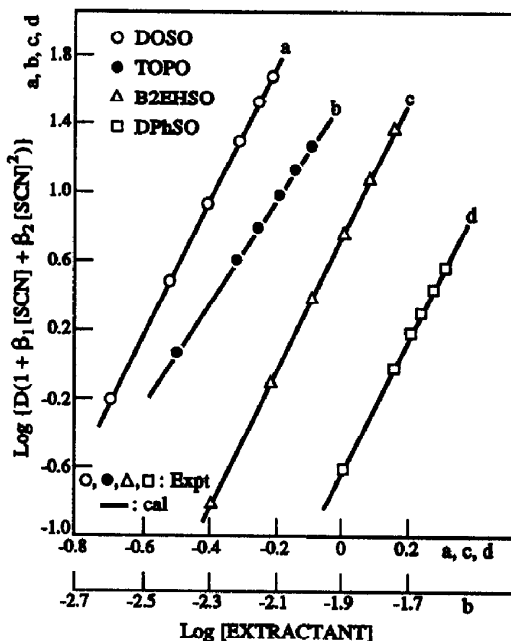


Fig. 2. Log-log plots for the variation of the extraction of Nd(III) with the concentration of B2EHSO, DOSO, DPhSO and TOPO. Aqueous phase: 1.0M thiocyanate of pH = 3, Nd(III) =  $10^{-6}M$ .

- (4) The values of the assumed equilibrium constants which lead to minimum root mean square fractional error,  $y$ , where

$$y = \sqrt{\frac{1}{N} \sum_{i=1}^N \left\{ \frac{D_{\text{cal},i} - D_{\text{expt},i}}{D_{\text{expt},i}} \right\}^2}$$

for all the experimental data were taken to be the equilibrium constants for the system under consideration.

The extraction of Nd(III) with a mixture of HTTA and neutral oxo-donor ( $S = \text{B2EHSO}$ , DOSO, DPhSO and TOPO) in benzene from an aqueous phase of 1.0M thiocyanate solutions (pH = 3) has been studied and the results are shown in Figs 3–6 ([HTTA] vs  $\log [D$  or  $\Sigma D]$ ) where  $D$  represents the distribution coefficient of Nd(III) with the mixture of extractants and  $\Sigma D = D_{\text{HTTA}} + D_5$ ). A very high synergistic

Table 1. Equilibrium constants for the extraction of Nd(III) with B2EHSO, DOSO, DPhSO, TOPO and HTTA from thiocyanate solutions

Extractant	Complex	Log equilibrium constant
B2EHSO	$\text{Nd}(\text{SCN})_3 \cdot 4\text{B2EHSO}$	$0.78 \pm 0.02$
DOSO	$\text{Nd}(\text{SCN})_3 \cdot 4\text{DOSO}$	$2.57 \pm 0.05$
DPhSO	$\text{Nd}(\text{SCN})_3 \cdot 4\text{DPhSO}$	$-0.61 \pm 0.01$
TOPO	$\text{Nd}(\text{SCN})_3 \cdot 3\text{TOPO}$	$7.29 \pm 0.15$
TTA	$\text{Nd}(\text{TTA})_3$	$-6.94 \pm 0.14$

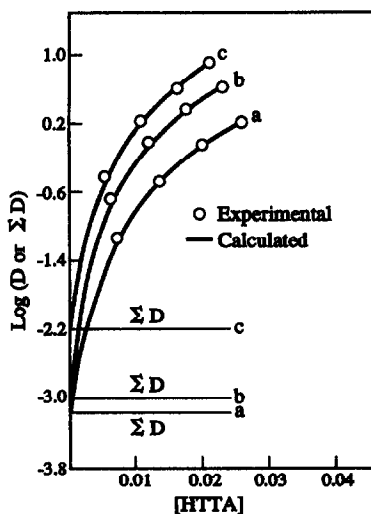


Fig. 3. Extraction of Nd(III) with mixtures of HTTA + B2EHSO in benzene. Aqueous phase: 1.0M thiocyanate of pH = 3, Nd(III) =  $1 \times 10^{-6}M$ ; (a) 0.1, (b) 0.2M and (c) 0.3M of B2EHSO.

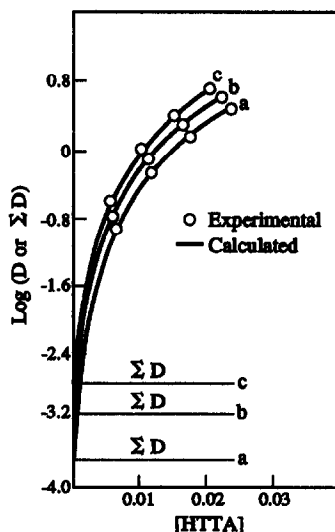


Fig. 5. Extraction of Nd(III) with mixtures of HTTA + DPhSO in benzene. Aqueous phase: 1.0M thiocyanate of pH = 3, Nd(III) =  $1 \times 10^{-6}M$ ; (a) 0.3M, (b) 0.4M and (c) 0.5M of DPhSO.

enhancement of the order  $10^3$  has been observed. These distribution data were analysed using equation (9). The best fit between the experimental and calculated distribution coefficients were obtained when the formation of mixed-ligand chelate species,  $Nd(SCN)_x \cdot (TTA)_{3-x} \cdot yS$  ( $x = 0, 1, 2$  and  $y = 1, 2$ ) were assumed. The extraction and interaction constants were determined by the procedure

mentioned earlier and are shown in Tables 2 and 3, respectively. It can be clearly seen from Table 3 that the interaction between HTTA and neutral oxo-donor follows the order: DPhSO < B2EHSO < DOSO < TOPO, which is in the order of basicity of the compounds. Further, the interaction constants of TOPO and

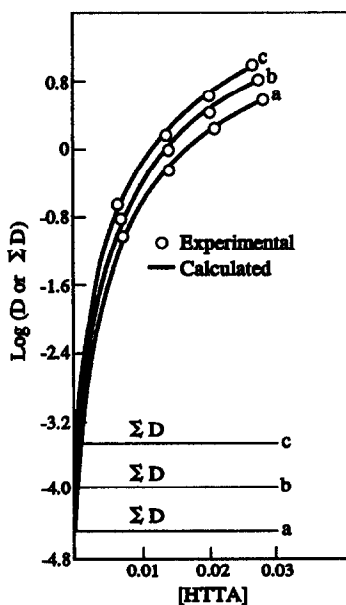


Fig. 4. Extraction of Nd(III) with mixtures of HTTA + DOSO in benzene. Aqueous phase: 1.0M thiocyanate of pH = 3, Nd(III) =  $1 \times 10^{-6}M$ ; (a) 0.03M, (b) 0.04M and (c) 0.05M of DOSO.

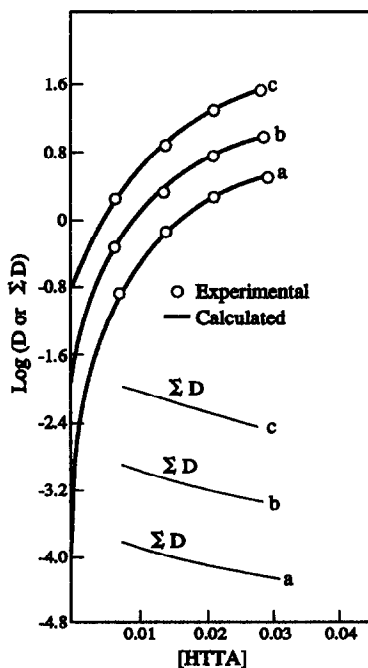


Fig. 6. Extraction of Nd(III) with mixtures of HTTA + TOPO in benzene. Aqueous phase: 1.0M thiocyanate of pH = 3, Nd(III) =  $1 \times 10^{-6}M$ ; (a) 0.0005M, (b) 0.001M and (c) 0.002M of TOPO.

Table 2. Log equilibrium constants for the extraction of Nd(III) with mixtures of HTTA + sulphoxide or TOPO(S)

Complex	B2EHSO	DOSO	DPhSO	TOPO
Nd(TTA) <sub>3</sub> · S	-2.60 ± 0.05	-3.44 ± 0.07	-2.65 ± 0.05	-0.37 ± 0.007
Nd(TTA) <sub>3</sub> · 2S	-1.89 ± 0.04	0.29 ± 0.006	-1.90 ± 0.04	3.91 ± 0.08
Nd(TTA) <sub>2</sub> · (SCN) · 2S	0.12 ± 0.002	0.44 ± 0.008	-0.90 ± 0.02	4.18 ± 0.08
Nd(TTA) · (SCN) <sub>2</sub> · 2S	—	1.41 ± 0.03	-0.08 ± 0.001	5.36 ± 0.01

DOSO, determined by the present theoretical method are in good agreement with the experimentally determined values reported elsewhere.<sup>14</sup>

The present study clearly shows that the complexes, Nd(SCN)(TTA)<sub>2</sub> · 2S, Nd(SCN)<sub>2</sub> · (TTA) · 2S seems to be involved in the extraction of Nd(III) from thiocyanate media with HTTA + neutral oxo-donor, in addition to Nd(TTA)<sub>3</sub> · S/2S which has been observed predominantly in the extraction of trivalent lanthanides from perchlorate media by several investigators.<sup>1</sup> This difference possibly arises due to the presence of SCN<sup>-</sup> ions in the aqueous phase which competes with HTTA during metal-chelate formation, resulting in the extraction of the above species. In the case of B2EHSO as neutral ligand, only Nd(SCN)(TTA)<sub>2</sub> · 2B2EHSO seems to be involved in the extraction of Nd(III) apart from the usual complexes, Nd(TTA)<sub>3</sub> · B2EHSO and Nd(TTA)<sub>3</sub> · 2B2EHSO.

It was believed that the infrared frequency of the phosphoryl group could serve as a measure of its basicity in organophosphorus compounds.<sup>15,16</sup> In sulphoxides, the S → O frequency in different compounds was observed to be nearly constant and thus could not be a guide to their properties. Shankar and Venkateswarlu<sup>17</sup>

developed a new method for assessing of phosphine oxides and some sulphoxides (diphenyl sulphoxide and dibutyl sulphoxide) based on the shift of the symmetric stretching frequency of OH of water on coordination with the donor. Based on this method, in the present study equal molarities of B2EHSO, DOSO, DPhSO and TOPO in carbontetrachloride were equilibrated with double distilled water. The IR spectra of the organic phase in the region 3000–4000 cm<sup>-1</sup> were recorded on a Perkin Elmer recording spectrophotometer (model 299B) using a LiCl prism and CaF<sub>2</sub> cell. Carbontetrachloride equilibrated with double distilled water was used as the blank. The observed IR shifts are shown in Table 4. The increase in values of Δν<sub>OH</sub> clearly indicate the increase in donor strengths of the solvating agents (DPhSO < B2EHSO < DOSO < TOPO). It can be seen from Table 1 that the extraction constants of different sulphoxides and TOPO are in good agreement with their donor properties (Δν<sub>OH</sub> value). The synergistic extraction constants and interaction constants of different neutral ligands (Tables 2 and 3) also increase with the donor strength of the reagent (Δν<sub>OH</sub>): DPhSO < B2EHSO < DOSO < TOPO.

In conclusion, a very high synergistic enhancement in the extraction of Nd(III) has been observed with a mixture of HTTA and neutral oxo-donor (sulphoxide or TOPO). The mechanism of extraction can be explained by a simple chemically based modal presented in this paper.

Table 3. Equilibrium constants (K<sub>i</sub>) of the adducts formed between synergistic extractants

Equilibrium	Log K <sub>i</sub>
HTTA + TOPO ⇌ HTTA · TOPO	1.37 ± 0.03
HTTA + DOSO ⇌ HTTA · DOSO	0.45 ± 0.009
HTTA + B2EHSO ⇌ HTTA · B2EHSO	0.06 ± 0.001
HTTA + DPhSO ⇌ HTTA · DPhSO	-0.02 ± 0.001

Table 4. Shift of the OH frequency of coordinated water bonded to different sulphoxides and TOPO

Extractant	Position of ν <sub>OH</sub> on extraction	Δν <sub>OH</sub> <sup>*</sup>
DPhSO	3480	160
B2EHSO	3440	200
DOSO	3430	210
TOPO	3370	270

\*OH frequency of uncoordinated water = 3640 cm<sup>-1</sup>.

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