Synergism in the extraction of europium in the presence of alkylphosphates and sulphoxides

M SUDERSANAN and A K SUNDARAM*

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Abstract. Synergism in the extraction of europium(III) has been investigated using a mixture of naphthoyltrifluoroacetone and synergists like trioctylphosphine-oxide (TOPO), tributylphosphate (TBP), trihexylphosphate (THP), diphenyl-sulphoxide (DPSO) and benzylsulphoxide (BSO). Synergism decreases in the order: TOPO > TBP $\simeq$ THP > BSO > DPSO indicating a correlation between electron density at the donor atom and extent of synergism. The equilibrium constants for adduct formation have also been evaluated.

Keywords. Synergism; europium; extraction; alkyl phasphorus donors; sulphoxides: electron deusity; equilibrium constants.

1. Introduction

Synergism in the extraction of metals has been studied extensively using tributyl-phosphate as the donor. The use of sulphoxides however has been comparatively rare. A systematic study on the effect of various donors in promoting synergism in the extraction of europium has been made with a view to correlate the synergistic enhancement and the donor strength. The results are presented in this paper.

2. Experimental

Europium$^{152+154}$, obtained from the Isotope Group of this Centre was assayed using a thallium activated sodium iodide crystal in a γ-scintillation counter (M/s. Electronics Corporation of India, Hyderabad). Naphthoyltrifluoroacetone, HNTA (Eastman Organic Chemicals) was used as a solution in carbon tetra-chloride (M/s. B.D.H. AnalaR). Tri-n-octylphosphineoxide, TOPO (Koch-Light Lab.), tributylphosphate, TBP (B.D.H.), trihexylphosphate, THP (K and K Lab.), diphenylsulphoxide, DPSO (K and K Lab.) and benzylsulphoxide, BSO (K and K Lab.) were used as received.

---

* To whom all correspondence should be made.

P. (A)—7

Calculated amounts of europium ($\sim 10^{-5}$ M), sodium perchlorate to maintain the ionic strength constant at 1·0 and acetic acid to adjust the pH were made upto 10 ml. This was equilibrated at $25 \pm 1°$ C with an equal volume of carbon tetrachloride containing the extractants for about 4 hr which was sufficient for equilibration. The pH of the aqueous phase was measured after equilibration using a Beckman Expandomatic SS-2 pH meter. The distribution ratios were calculated from the data corrected for background activity. The precision of the measurements was about $\pm 2\%$.

## 3. Results and discussion

3.1. *Europium–HNTA system*

Extraction of europium by HNTA or synergism in the presence of various donors has not been reported earlier. Europium was extracted by HNTA in the pH region of 5·0 maintained by the addition of acetic acid. The distribution ratio was measured as a function of pH and concentration of HNTA. The partition coefficient of HNTA being very high (Schreck 1967), its transfer to the aqueous phase was neglected. The plots of log D vs pH and log $[HNTA]_0$ resulted in straight lines with slopes of about three. The extraction reaction can therefore be described in terms of extraction of Eu $(NTA)_3$ and the equilibrium constant K was calculated as $10^{-8·3}$. It was observed that extraction took place at a pH where hydrolysis could not be discounted. There was also loss of activity on the walls of the container indicating that the metal chelate was sparingly soluble and hydrolysis of the metal occurred simultaneously. However, addition of neutral donors eliminated this difficulty and adsorption on the walls was also negligible.

3.2. *Europium–HNTA–TOPO system*

Extraction of europium by a mixture of HNTA and TOPO was studied. Extraction by TOPO alone under the present experimental condition was negligible but was quite considerable by a mixture of HNTA and TOPO, with the pH of synergic extraction shifting to a lower value (figure 1). The distribution ratio for the synergistic species D was obtained by subtraction of the values for the individual extractants, if any, from the observed distribution ratio. The correction was, however, negligible in all the cases. The plots of log D vs pH and log $[TOPO]_0$ were linear with slopes of three and two respectively. A linear plot with a slope of three was obtained for the variation of log D with log $[HNTA]_0$. These plots are not presented here for the sake of brevity. The results indicated extraction of Eu $(NTA)_3 (TOPO)_2$, the extraction mechanism represented as

$$Eu^{3+} + 3 [HNTA]_0 + 2 [TOPO]_0 \xrightleftharpoons{K_{syn}} [Eu (NTA)_3 (TOPO)_2]_0 + 3H^+.$$

$$(1)$$
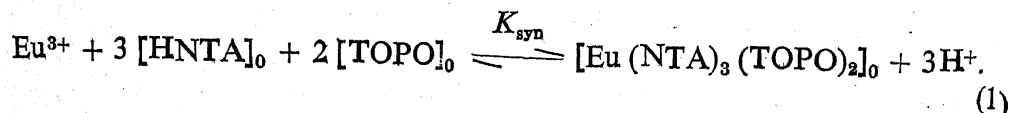
The equilibrium constant K_{syn} was calculated as $10^{4·5}$. The reaction in the organic phase for the co-ordination of TOPO with Eu(NTA)$_3$ can be written as
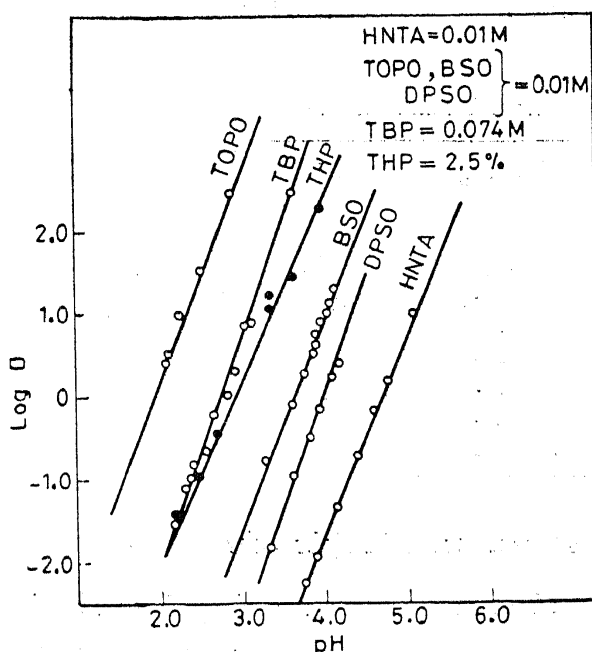
$$[Eu (NTA)_3]_0 + 2 [TOPO]_0 \xrightleftharpoons{K^*} [Eu (NTA)_3 (TOPO)_2]_0.$$

$$(2)$$
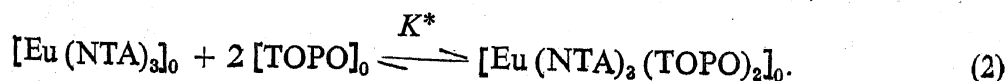
Figure 1.

The equilibrium constant K^* can be calculated from

$$K^* = K_{syn} K^{-1},$$ (3)

and is a measure of the stabilisation of the complex in the organic phase. The values of the equilibrium constants are summarised in table 1.

3.3. *Europium–HNTA–THP system*

Synergism in the extraction of europium was also studied in the presence of HNTA and THP. The variation of log D as a function of pH and concentrations of HNTA and THP indicated extraction of the adduct, $Eu(NTA)_3 (THP)_2$. The distribution ratio plotted for 0·01 M HNTA and 2·5% THP as a function of pH (figure 1) indicated an extraction power less than that for TOPO and TBP.

3.4. *Europium–HNTA–TBP system*

Extraction of europium by mixtures of HNTA and TBP was carried out to study the effect of donor strength due to the change of a substituent from hexyl to butyl group and the consequent effect on the electron density. The results indicated the extraction of an adduct containing three molecules of HNTA and two of TBP. The equilibrium constant was calculated as $10^{-0.1}$. The donor strength varies in the order TOPO > TBP ⩾ THP which agrees with the expected trend since the change from butyl to hexyl may only slightly reduce the electron density at the P = O group. On the other hand, the presence of phosphine oxide group considerably enhances the donor strength compared to phosphate group, so that the strength of adduct formation decreases in the order observed. A similar order has been observed in the case of other systems (More *et al* 1980; Ke and Li 1966; Bok *et al* 1974).

Table 1. Equilibrium constants for europium adducts

System	Equilibrium constant	
	$\log K_{syn}$	$\log K^{*}$
Eu–HNTA	$-8 \cdot 3$	..
Eu–HNTA–TOPO	$4 \cdot 5$	$12 \cdot 8$
Eu–HNTA–TBP	$-0 \cdot 10$	$8 \cdot 2$
Eu–HNTA–THP	$-0 \cdot 2$	$8 \cdot 1$
Eu–HNTA–BSO	$-1 \cdot 1$	$7 \cdot 2$
Eu–HNTA–DPSO	$-2 \cdot 0$	$6 \cdot 3$

3·5. *Synergism in the presence of sulphoxides*

Synergism was also studied in the presence of DPSO and BSO to investigate the effect of sulphoxides on synergism. Europium was not extracted by DPSO alone. The distribution ratio was measured as a function of pH and concentrations of HNTA and DPSO. The log–log plots of D vs $[H]$ and $[HNTA]_0$ were linear with slopes of three and that of D vs $[DPSO]_0$ had a slope of two indicating the coordination of three molecules of HNTA and two of DPSO. The equilibrium constant was calculated as $10^{-2 \cdot 0}$.

Studies were also made with benzylsulphoxide and the results indicated the formation of an adduct, $Eu(NTA)_3(BSO)_2$. The plot of $\log D$ vs pH (figure 1) indicated the lesser donor power of DPSO and BSO and the pH range of extraction. The extent of synergism in the case of sulphoxides was less than that with $P = O$ donors in conformity with the reduced donor power of $S = O$ group. The change in the substituent from an aromatic phenyl group to benzyl group slightly enhances the stability of adducts. Similar correlations have been observed in cerium and other systems (More *et al* 1980). The order of enhancement is less than that observed in the case of cerium. The smaller radii of cerium might probably account for the increased stabilisation of the adducts in the case of all the systems.

References

Bok L D C, Wessels G F S and Leipoldt J G 1974 *Z. Anorg. Allg. Chem.* **404** 76
Ke C H and Li N C 1966 *J. Inorg. Nucl. Chem.* **28** 2255
More A K, Sudersanan M and Sundaram A K 1980 *Indian J. Chem.* **19A** 926
Schreck H 1967 US Atomic Energy Comm. Report KFK 672
Schreck H 1968 *Chem. Abstr.* **69** 100053n.