

Solvent Extraction Studies of Mixed Chelates of Europium

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Mixed chelates of europium with β -diketones and oxine have been studied by solvent extraction using carbon tetrachloride as the medium. Extraction of europium by mixtures of HBFA-HFTA, HBFA-HTFA as well as oxine-HBFA/HFTA/HTFA have been studied (where HBFA=benzoyltrifluoroacetone, HTFA=trifluoroacetylacetone and HFTA=furoyltrifluoroacetone). Mixed complexes are formed in all the cases and the nature of the extracted species and their equilibrium constants have been evaluated by graphical methods.

Mixed chelate formation in solution has been studied by various methods^{1,2}. Mixed chelates of metals like copper, zinc, indium and europium with ligands like HTTA and isopropyltropolone have been reported³. Mixed chelates of lutetium⁴ and uranium⁵ have been reported. In our laboratories, a systematic study of indium⁶, hafnium⁷ and uranium⁸ systems have been carried out. In continuation of this work, solvent extraction studies on the formation of mixed chelates of europium with two β -diketones or a mixture of a β -diketone and oxine are presented here. The studies using oxine have been made with a view to assessing the possibility of formation of adducts besides mixed chelates.

Materials and Methods

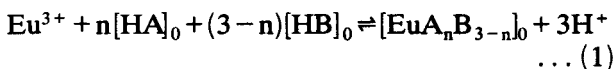
Europium, in the form of ¹⁵²+¹⁵⁴Eu, was obtained from Isotope Group, BARC. Benzoyltrifluoroacetone (HBFA), furoyltrifluoroacetone (HFTA) and trifluoroacetylacetone (HTFA) (all from K&K Labs, USA) and oxine (BDH, AR) were used as a solution in carbon tetrachloride (E. Merck, GR).

Extraction experiments were carried out by equilibrating for 6 hr at 30±2°C the aqueous phase (10 ml) containing europium (~10⁻⁵ M), sodium chloride to maintain the ionic strength at 0.5 and acetic acid + sodium hydroxide (~0.02 M) to adjust the pH with an equal volume of the organic phase containing the extractants. The two phases were separated and the pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter (M/s Beckman Instruments Inc, USA). Europium in the two phases was assayed by gamma counting using a thallium-activated sodium iodide crystal with a single channel analyser (M/s ECIL, Hyderabad). Background correc-

tions were applied in all the cases. The mass balance for europium was good.

Results and Discussion

The mixed chelate formation of europium with two ligands, HA and HB, can be described by Eq. (1)



and the equilibrium constant is given by Eq. (2)

$$K_{\text{BA}} = K_{(3-n),n} = \frac{[\text{EuA}_n\text{B}_{3-n}]_0 [\text{H}]^3 [\text{Eu}]^{-1} [\text{HA}]_0^{-n}}{[\text{HB}]_0^{-(3-n)}} \quad \dots (2)$$

where the charges have been omitted for convenience. The distribution ratio (D) is given by Eq. (3).

$$D = \frac{[\text{EuA}_3]_0 + [\text{EuA}_2\text{B}]_0 + [\text{EuAB}_2]_0 + [\text{EuB}_3]_0}{[\text{Eu}]} \quad \dots (3)$$

Substituting in terms of equilibrium constants and on rearranging, we get

$$F_0 = D[\text{H}]^3/[\text{HA}]_0^3 = K_{03} + K_{12}[\text{L}] + K_{21}[\text{L}]^2 + K_{30}[\text{L}]^3 \quad \dots (4)$$

where [L] represents $[\text{HB}]_0/[\text{HA}]_0$ and can be solved for various equilibrium constants by graphical methods.

Extraction of europium was studied using a mixture of β -diketones or a β -diketone and oxine. Various β -diketones were selected in order to study the influence of the terminal groups of the β -diketones on the stability of mixed chelates.

Europium-HBFA-HFTA system

Extraction of europium was studied in the presence of a mixture of HBFA (HA) and HFTA (HB). The distribution ratio (D) was measured as a function of pH at fixed [HBFA] and [HFTA]. Studies were also made at varying [HBFA] or [HFTA]

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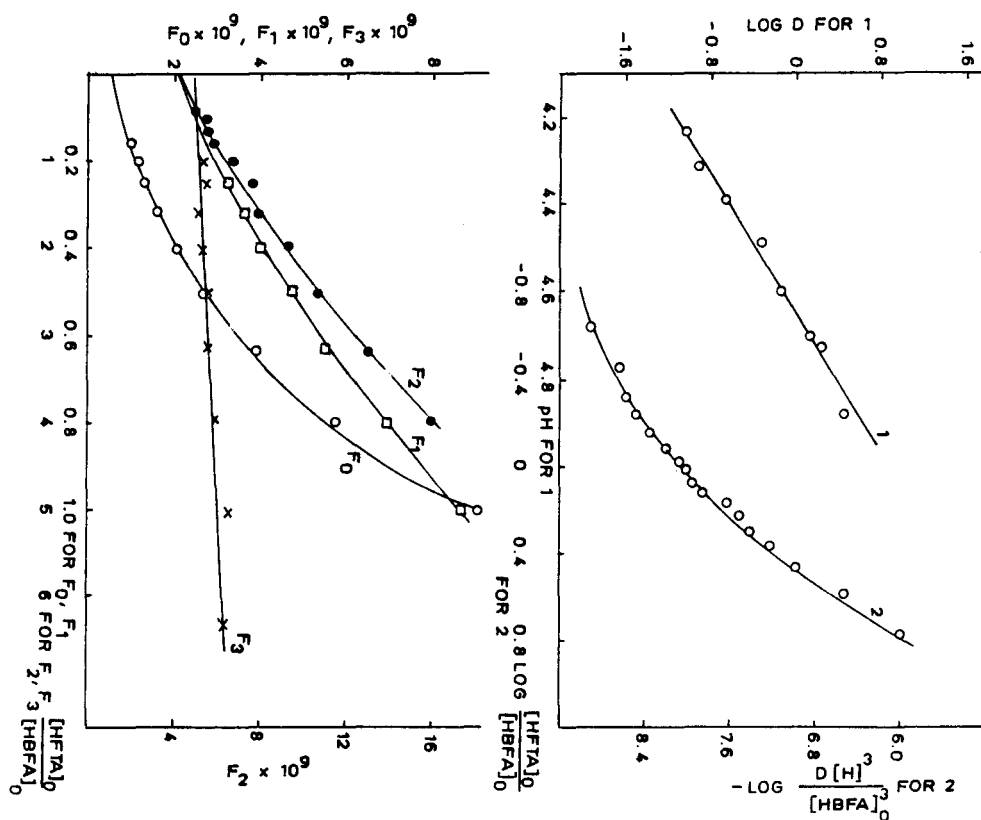


Fig. 1—Europium-HBFA-HTFA system (Plots 1 and 2 represent the plot of $\log D$ versus pH and $\log D \frac{[H]^3}{[HBFA]^3}$ versus $\frac{[HTFA]_0}{[HBFA]_0}$ respectively. Other plots represent the various F_i functions)

while maintaining the pH and concentration of the either β -diketone constant. The concentrations of the β -diketones were calculated taking into account the partition coefficients of the two β -diketones^{9,10}. Values of partition coefficients were obtained from literature as $\log P_{HA}=2.47$ for HBFA and 0.82 for HTFA. The dissociation constants (pK) for HBFA and HTFA are 6.01 and 6.18 respectively⁹.

The plot of function F_0 , calculated using Eq. (4) resulted in a curve (Fig. 1) indicating the formation of mixed chelates. The plot of F_0 versus $[L]$, when extrapolated to $[L] \rightarrow 0$, gives the value of K_{03} as the intercept. Another function F_1 can be written as

$$F_1 = \frac{F_0 - K_{03}}{[L]} = K_{12} + K_{21}[L] + K_{30}[L]^2 \quad \dots (5)$$

A plot of F_1 versus $[L]$ gives the value of K_{12} as the intercept when $[L] \rightarrow 0$. Other functions can be written in a similar manner and solved to obtain the various equilibrium constants. Typical plots are given in Fig. 1 and the equilibrium constants are presented in Table 1.

Table 1—Values of Equilibrium Constants

System (HA—HB)	K_{BA}	$-\log K_{BA}$
HBFA—HTFA	K_{03}	9.30
	K_{12}	8.70
	K_{21}	8.40
	K_{30}	8.60
HBFA—HTFA	K_{12}/K_1	7.66
	K_{21}/K_1	6.90
HTFA-oxine	K_{03}	7.92
	K_{12}	7.00
HBFA-oxine	K_{03}	8.36
	K_{12}	9.30
HTFA-oxine	K_{21}	8.32
	K_{12}/K_1	6.12

Europium-HBFA-HTFA system

Extraction of europium using a mixture of HBFA (HA) and HTFA (HB) was also studied in a similar manner. The concentration of HTFA in the organic phase was calculated taking into account the dissociation constant⁹ (K_a) and partition coefficient (P) using the relation (6)

$$[HTFA]_0 = \frac{P_{HTFA}[HTFA]_{tot}}{1 + P_{HTFA} + K_a[H]^{-1}} \quad \dots (6)$$

where $P_{\text{HTFA}} = 0.646$ and $pK_a = 6.09$. Extraction of europium was studied around pH 5.6 by varying the concentration of HBFA (0.001 to 0.01 M) at a fixed concentration of HTFA (0.0165 M) and also at varying concentrations of HTFA and a fixed concentration of HBFA (0.01 M). Extraction of europium occurred at a higher pH of 5 to 6 and hence the aqueous phase complexes of Eu-TFA were to be considered for the analysis of data. The formation of $(\text{Eu TFA})^{2+}$ can be described by the reaction (7)



with the equilibrium constant K_1 given by Eq. (8)

$$K_1 = [\text{Eu TFA}][\text{H}]/[\text{Eu}][\text{HTFA}]_0 \quad \dots (8)$$

Assuming Eu-TFA to be the predominant species in the aqueous phase, Eq. (5) can be rearranged to get

$$F_0 = \frac{D[\text{H}]^3[\text{HTFA}]_0}{[\text{HBFA}]_0^3[\text{H}]} = \frac{1}{K_1} \{K_{03} + K_{12}[\text{L}] + K_{21}[\text{L}]^2 + K_{30}[\text{L}]^3\} \quad \dots (9)$$

where $[\text{L}]$ represents $[\text{HTFA}]_0/[\text{HBFA}]_0$. Various functions were calculated from the data and were analysed to obtain the various constants by the graphical method. The values of K_{12}/K_1 and K_{21}/K_1 were calculated as 2.2×10^{-8} and 1.27×10^{-7} respectively, indicating the formation of mixed chelates. However, the higher pH of extraction and the presence of $(\text{Eu} - \text{TFA})^{2+}$ complex in the aqueous phase complicates further analysis of the data.

Europium-HBFA-oxine system

Mixed complex formation of europium using mixtures of HBFA (HA) and oxine (HB) was also studied in a similar manner. Studies were made at fixed concentrations of HBFA and oxine of 0.01 M each and varying pH in the range of 4.2 to 4.6. Studies were also made at a nearly constant pH of about 4.5 and varying concentrations of one ligand at a fixed concentration (0.01 M) of the other ligand. The concentration of oxine in the organic phase was calculated taking into account the influence of protonation and partition coefficient of oxine¹⁰, ($P_{\text{Hox}} = 10^{2.06}$) using Eq. (10),

$$[\text{Hox}]_0 = P_{\text{Hox}}[\text{Hox}]_{\text{tot}} / \left\{ 1 + P_{\text{Hox}} + \frac{[\text{H}]^2 + K_1 K_2}{K_1 [\text{H}]} \right\} \quad \dots (10)$$

where K_1 and K_2 represent the dissociation constants of oxine¹¹, being equal to 5.09 for pK_1 and 9.02 for pK_2 .

Extraction of europium in the presence of varying concentrations of HBFA and oxine was found to be higher than that due to the reagents alone. The data were analysed on the basis of formation of mixed chelates in order to obtain the values of equilibrium constants. The function F_0 or $D[\text{H}]^3[\text{HBFA}]_0^{-3}$, plotted as a function of $\log\{[\text{Hox}]_0/[\text{HBFA}]_0\}$ resulted in a smooth curve indicating the presence of mixed chelates. The various constants were calculated as described earlier (Table 1). The value of K_{30} could not be evaluated because of relatively small changes in the values of F_j functions at higher concentrations of oxine indicating the contribution of $\text{Eu}(\text{ox})_3$ to the extraction to be small compared to those of mixed chelates. Details of analysis and the plots are not presented for the sake of brevity.

Europium-HTFA-oxine system

Extraction of europium in the presence of HTFA was studied in a similar manner around pH 4.3 and the data were analysed in a similar manner. The values of K_{03} and K_{12} were calculated as 1.2×10^{-8} and 1.0×10^{-7} , respectively while those for the higher complexes could not be evaluated from the data.

Europium-HTFA-oxine system

Studies were also extended to the extraction of europium by a mixture of HTFA and oxine around pH 4.9. The concentrations of oxine and HTFA in the organic phase were calculated using Eqs. (6) and (10), respectively. The data were analysed considering the presence of $(\text{Eu} - \text{TFA})^{2+}$ in the aqueous phase as discussed in an earlier section. The plot of $\log F_0$ versus $\log [\text{L}]$ where $[\text{L}]$ represents $[\text{Hox}]_0/[\text{HTFA}]_0$ indicated the absence of extraction by HTFA alone under the present experimental conditions and the predominance of the first mixed chelate, $\text{Eu}(\text{TFA})_2\text{ox}$. The values of constants are summarised in Table 1.

The results obtained in the case of β -diketones can be attributed to the formation of mixed chelates. The values of stabilisation constants (K_s) were calculated for Eu-HBFA-HTFA system. The values of K_s given by Eq. (11)¹

$$K_s = K_{\text{obs}}/K_{\text{stat}} \quad \dots (11)$$

were found to be 0.78 for $\text{Eu}(\text{BFA})_2\text{FTA}$ and 0.91 for $\text{Eu}(\text{BFA})(\text{FTA})_2$, indicating that the complexes were stabilised as expected on the basis of statistical factors. However, in the case of Eu- β -diketone-oxine systems, the values of K_{03} obtained from the data on mixed chelates were somewhat higher than those obtained on binary systems.

This indicated the probable formation of adducts with oxine in addition to mixed chelates. Sekine and Dyrssen³ also found evidence for the formation of self-adducts or adducts with one of the ligand (isopropyltropolone, IPT) in their studies on the formation of mixed chelates of europium with HTTA and IPT. An increase in the values of K_{03} by a factor of 5 to 10 can probably be attributed to this effect.

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