CHAPTER V

SUMMARY AND CONCLUSIONS
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The present work deals with physico-chemical studies on some mixed-ligand complexes of lanthanides.

Chapter I of the thesis has been devoted to general introduction. Coordination characteristics of lanthanides have been discussed. It has been pointed out that the lanthanides are class 'a' acceptors. Unlike the 3d-elements they form predominantly ionic complexes. Their large ionic radii minimise covalent interactions and favour higher coordination numbers. They are highly electropositive and have little tendency to form complexes with \( \text{A} \) bonding ligands because the availability of the 4f-orbitals for bonding seems to be doubtful.

The earlier work on the complexes of lanthanides has been reviewed in chapter I. The literature survey on solid complexes and on complexes in solution has been dealt with separately. To the extent possible the description has been classified according to the nature of donor atoms. The aim and scope of the present work has also been spelt out in this chapter.
The lanthanides used in the present work are \( \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{and Sm}^{3+} \). EDTA has been used as a primary ligand; the secondary ligands being some hydroxy acids, thio acids, dicarboxylic acids, unsaturated acids, amino acids, phenols and phenolic acids and some analytical reagents.

A list of ligands along with some properties of lanthanides and other useful data are given in the appendix.

Chapter II incorporates a concise description of the methods used in the present work. Irving-Rossotti pH-titration technique as modified for the ternary complexes has been used for determining the stability constants. The general procedural details along with the relevant mathematical equations have been described.

Chapter III contains the experimental aspects of the work. The experimental data including the calculated values have been presented in the form of figures, and tables. A total of 33 figures have been incorporated which contain the pH-plots. Another set of the same number of figures gives the formation curves of the proton-ligand, 1:1 binary and 1:1:1 ternary complexes. The data presented in tables (which number 1 A–C to 32 A–C) include the values of B, \( \bar{E}_H \) and pL and
\[ n \] and \[ pL \] and the calculated values of the proton-ligand stability constants (\[ \log K^H_M \]), metal-ligand stability constants of the 1:1 binary complexes (\[ \log K^M_M \] and \[ \log K^M_M \]) and those of the 1:1:1 ternary complexes (\[ \log K^M_M \]). The standard deviation values (\[ \Delta \sigma \]) have also been shown in parenthesis as an indication of the precision of the calculated stability constant values.

The formation of mixed-complexes in these systems proceeds according to the equilibria \[ M + A \leftrightarrow MA; \]
\[ MA + L \leftrightarrow MAL, \] where \( M \) is lanthanide metal ion, \( A \) EDTA and \( L \) is secondary ligand. The secondary ligands have been divided into eight series for the sake of convenience.

Chapter IV deals with the results and discussion. It has been subdivided into three sections A, B and C. Section A contains some general remarks and series-wise discussions of the results obtained. The proton-ligand stability constants and the metal-ligand stability constants along with their \( \Delta \log K, \Delta G, \log K^M_M, \log K^{dM}(d)M, \) and \( \log K(s) \) values have been recorded in forty tables.

The nature of pH-plots has been discussed for various systems. The absence of hydroxo and poly-nuclear
species has also been pointed out in general. The observed trends in \( \log k^H \) values, the sequence of the \( \log K^M_{MA} \), \( \log K^M_{ML} \) and \( \log K^{MA}_{MAL} \) values, \( \Delta \log K \), \( \log K^{ML}_{(d)MA} \) and \( \log K^{(s)} \) have been explained. Wherever possible, a comparison has been made with the existing data on the lanthanides or even d-block elements.

The existence of hydroxo complexes has been taken into account in the case of amino acids and rubeanic acid; in these cases hydrolysis-corrected values of \( \log K^{MA}_{MAL} \) have been obtained.

The following conclusions have been drawn:

(i) Although the lanthanides are prone to hydrolysis, it has been observed in the present investigations that the formation of ternary complexes of the lanthanides takes place usually in a pH-range lower than that of the hydrolysis. The exceptional cases include the amino acids, where the hydroxo species cannot be ignored.

(ii) The stability constants of the binary and ternary complexes have been found to lie in the sequence \( \log K^M_{MA} \gg \log K^M_{ML} \gg \log K^{MA}_{MAL} \), irrespective of the nature of the secondary ligands studied. The \( \log K^{ML}_{(d)MA} \) values are consequently positive.
(iii) the log K values (log $K_{MA}^N$, log $K_{ML}^N$, log $K_{MAL}^M$, log $K_{MAL}^L$) with respect to metal ions have invariably been found to be in the order $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+}$.

(iv) the values of $\Delta \log K$ for all the ternary systems under study have been found to be negative due to electrostatic and steric repulsions during the formation of ternary complexes. The $\Delta \log K$ values appear to depend upon the charge on the secondary ligand, nature of donor atoms and steric factors.

(v) the general order of stability of the ternary complexes with respect to secondary ligands investigated in the present work is found to be:

0 - O donors (aromatic) > 0 - N dpmpra > 0 - 0 donors (aliphatic) > 0 - S donors.

(vi) the experimental values of log $K_{MAL}^M$ in the present work are always lower than the corresponding statistical values.

Section B of this chapter deals with some stability correlations. The validity of Born's relation has been tested. The fundamental properties of the lanthanides with which correlations have been sought
include the standard entropies, standard oxidation potentials, sum of the first three ionisation potentials and the total angular momentum. Mathematical expressions for some of these correlations have been developed. The correlations have been discussed on the basis of these expressions. Log - log correlations for the variations in log $K_{MAL}^M$ values with log $K_{MA}^M$ and log $K_{ML}^M$ have been studied and the slope values obtained from the least square plots have also been discussed.

The Born's relation is found to be valid, in general. The plots of stability constants vs the fundamental properties mentioned above, and the log - log plots have been shown in sixty different figures. The plots are roughly linear in nature for the group of lanthanides La$^{3+}$ to Sm$^{3+}$.

The l.f.s.e. values for the LN-EDTA chelates assuming them to be octahedral, have also been calculated. The largest value of l.f.s.e. for the (LN-EDTA)$^-$ chelates in the present work corresponds to 140 cm$^{-1}$, a value which is much less than the electron pairing energy (8000 cm$^{-1}$) for the lowest sub-level ($e_{2u}$) in the lanthanides. This suggests a 'high-spin' distribution of electrons in the (LN-EDTA)$^-$ chelates.
Section C of chapter IV has been devoted to the discussion of a probable model of the present lanthanide complexes.

The lanthanide complexes in this work are of higher coordination numbers, presumably eight or nine, in view of the hexadentate nature of the primary ligand EDTA and the bidentate or tridentate nature of the secondary ligands. The metal-ligand bond is predominantly ionic as indicated by the validity of Born's relation. They seem to be of 'high-spin' type on account of very low crystal field splitting. They are stabilised largely by the entropy effect. The stability correlations with the standard entropies of the lanthanides and the literature values of the entropy factors support this conclusion. The entropy stabilisation seems to be a consequence of the rupture of the inner hydration zone of the lanthanides.