

ABSTRACT

Transition metals and lanthanides, which are characterised by partial fulfillment of electrons in (n-1) d and (n-2) f orbitals, respectively, have got a strong tendency to show variable valency, form complex compounds with a large number of ligands. Due to the presence of (n-1) d and 4f electrons and their transition to different energy levels they exhibit a number of physico chemical properties, such as magnetic, spectral, optical etc. These properties are used to increase the conductivity, magnetic susceptibility and optical properties of the concerned materials.

In the past, quite a good number of techniques have been employed by scientists for the study of metal : ligand complexation equilibria . Recently some electrochemical methods have attracted the attention of researchers for the said purpose. In the present work the author has aimed to show the most important application of polarography in co-ordination chemistry of transition metals and lanthanides which has been discussed in the thesis in five chapters.

Chapter number one of the thesis describes an introductory idea as regards to the metal complexes both binary and ternary. Various theories which have been put forward to explain the behaviour of metal complexes, have also been mentioned briefly with special reference to valence bond theory, crystal field theory and the molecular orbital theory.

A detailed introduction to the polarographic technique and its application for the determination of stoichiometric ratio and formation constants of binary and ternary complexes has also been mentioned. The chapter also discusses briefly amperometric titration techniques. Application of absorption studies for the determination of stoichiometric ratio and formation constants of the complexes under study has also been mentioned to supplement the results obtained by polarographic technique.

Chapter two of this thesis deals with the polarographic behaviour of metal ions viz., Zr (IV), Tb(III), Dy (III), Er(III) and Sm(III) and their complexes with 4(2-Pyridyl azo) Resorcinol, 1-(2-Pyridyl azo) Naphthol, 1,10 phenanthroline and methylene blue. Stoichiometry and formation constants of the chelates have been calculated using either Lingane's method or Defored and Hume's method.

On the basis of the observed polarographic data stoichiometry and formation constants of the complexes in the solution have been calculated to be as follows:

Complex species	Stoichiometry	Stability constants $\log \beta_1$
[Zr(PAR)] ⁴⁺	1:1	3.75
[Zr(PAN)] ⁴⁺	1:1	2.70
[Zr(MB)] ⁴⁺	1:1	2.4
[Tb(PAR)] ³⁺	1:1	4.83
[Tb(PAR)] ²⁺	1:1	3.38
[Dy(PAR)] ³⁺	1:1	4.65

★	[Dy(PAR)] ²⁺	1:1	4.12
	[Er(PAR)] ³⁺	1:1	3.99
	[Sm(PAR)] ³⁺	1:1	3.17
	[Tb(PAR)] ³⁺	1:1	4.27
	[Tb(PAR)] ²⁺	1:1	3.46
	[Dy(PAR)] ³⁺	1:1	4.33
	[Dy(PAR)] ²⁺	1:1	3.76
★	[Er(PAR)] ³⁺	1:1	2.77
	[Sm(PAR)] ³⁺	1:1	5.01
	[Tb(MB)] ³⁺	1:1	5.44
	[Tb(MB)] ²⁺	1:1	3.75
	[Dy(MB)] ³⁺	1:1	5.08
	[Dy(MB)] ²⁺	1:1	4.90
	[Er(MB)] ³⁺	1:1	5.01
	[Sm(MB)] ³⁺	1:1	2.17
	[Tb(1,10 Phen)] ³⁺	1:1	4.00
★	Dy(1,10 Phen)] ³⁺	1:1	5.24
	Er(1,10 Phen)] ³⁺	1:1	4.15
	Sm(1,10 Phen)] ³⁺	1:1	3.68

It may be specifically mentioned that the reduction of metal ions, Tb(III) and Dy(III) proceeds in two steps on the DME surface. On gradual increase in the ligand concentration half wave potential of the metal ion shifted to either positive or the negative direction and diffusion current gradually shortens for each of the reduction steps for the said metals. In solution two complex species, [M(L)]³⁺ and [M(L)]²⁺ exist, which are reduced at the DME surface producing two step

reduction waves, which enables the application of Lingan's method for the study of stoichiometry and formation constant of each species.

With 1, 10 phenanthroline Tb(III) and Dy(III) ions do not give (+2) step reduction wave and the half wave potential shifts towards negative direction, on gradual increase of the ligand concentration. This may be due to the greater complexing tendency of this reagent with metals.

It has been observed that 1:1 complex formation takes place in all the cases at lower pH values. However, precipitation takes place on increasing the pH of the test solution.

Chapter three of this thesis deals with the polarographic studies of ternary complexes of Tb(III), Dy(III), Er(III) and Sm(III) using PAR, PAN, NTA and 1, 10 phenanthroline. In all sixteen combinations of mixed systems have been studied polarographically, choosing one weaker ligand as primary and stronger as the secondary ligand. Studies were done at an ionic strength of 0.01 M potassium chloride and at pH 3.10 ± 0.1 . Stoichiometry and formation constants of binary complexes have been evaluated using Lingane's method of the observed polarographic data whereas Schaap and McMaster's method was used to study the stoichiometry and formation constants of ternary complexes.

It has been observed that 1:1:1 complexes formed in solution with stability constants values as under :

Complex system	log β_{11}
[Tb(PAN) (PAR)] ³⁺	7.51
[Dy(PAN) (PAR)] ³⁺	8.19
[Er(PAN) (PAR)] ³⁺	4.84
[Sm(PAN) (PAR)] ³⁺	8.44
[Tb(PAR) (NTA)] ³⁺	7.64
[Dy(PAR) (NTA)] ³⁺	8.50
[Er(PAR) (NTA)] ³⁺	7.89
[Sm(PAR) (NTA)] ³⁺	7.69
[Tb(PAR) (Phen)] ³⁺	7.82
[Dy(PAR) (Phen)] ³⁺	8.15
[Er(PAR) (Phen)] ³⁺	7.49
[Tb(NTA) (Phen)] ³⁺	9.04
[Dy(NTA) (Phen)] ³⁺	10.11
Er(NTA) (Phen)] ³⁺	9.93

The mixing constant $K_M = \beta_{11} / \sqrt{\beta_{01}\beta_{10}}$ and stabilisation constant $\log K_S = \log K_M - \log 2$ have been evaluated in each case on the basis of the numerical values obtained in each case. From the nature of values of $\log K_M$ and $\log K_S$ in each ternary system, it can be concluded that the formation of ternary complex is preferred over simple bis complexes in solution.

Chapter fourth deals with the amperometric estimations of some rare earths Tb(III), Dy(III), Er(III) and Sm(III) with above mentioned

ligands i.e., PAR, PAN, methylene blue and 1, 10 phenanthroline. Author's aim is to search out optimum conditions for amperometric titrations of aforesaid metal ions with the reagents under study. Favourable combinations of pH, ionic strength applied potential, experimental medium, buffer etc. have been described in case of each titration. Lowest detection limit values for the amperometric determination of titled metals with each reagent has been discussed. Titrations have also been performed in presence of various diverse ions, so as to find out their tolerance limit and hindrance which makes the estimation of metal ions easier in ores or compounds of natural origin.

The quantities of metal ions estimated using different reagents have been enlisted in their respective tables. At lower pH all the reagent forms 1:1 complex species with the above metal ions.

Among the analytical reagents used for the amperometric titrations, PAR has proved to be the most sensitive reagent for the amperometric determination of the titled metals estimating 0.1 mg of the metal/10 ml of the analyte successfully within a percentage error of less than 0.75% where as about 0.4 mg of metal/10 ml of analyte could be determined using others PAN, methylene blue, 1, 10 phenanthroline within an error of less than 0.75% in each case. The statistical data supported the utility of developed titrimetric procedures.

To supplement the results obtained by modern electroanalytical techniques traditional UV Spectrophotometric technique has been employed to the study of metal : ligand complexation equilibria in solution.

Chapter fifth of this thesis deals with the UV Spectrophotometric determination of complex formation equilibria of Tb(III), Dy(III), Er(III) and Sm(III) with PAR, PAN, methylene blue and 1, 10 phenanthroline. Job's method of continuous variation was applied to study the stoichiometry and formation constant of the complex species formed in solution. Results obtained by this technique are as follows :

[Tb(PAR)] ³⁺	1:1	3.47
[Dy(PAR)] ³⁺	1:1	4.50
[Er(PAR)] ³⁺	1:1	6.15
[Sm(PAR)] ³⁺	1:1	3.90
[Tb(PAN)] ³⁺	1:1	4.11
[Dy(PAN)] ³⁺	1:1	4.05
[Er(PAN)] ³⁺	1:1	3.84
[Sm(PAN)] ³⁺	1:1	5.68
[Tb(MB)] ³⁺	1:1	4.44
[Dy(MB)] ³⁺	1:1	4.14
[Er(MB)] ³⁺	1:1	3.91
[Sm(MB)] ³⁺	1:1	3.01
[Tb(Phen)] ³⁺	1:1	4.87
Dy(Phen)] ³⁺	1:1	5.28
Er(Phen)] ³⁺	1:1	4.57
Sm(Phen)] ³⁺	1:1	3.94

On the basis of the observed data and ongoing discussion in each chapter some meaningful conclusions have been drawn. Author's observations clearly show that polarographic method could be successfully used for the study of binary and ternary complexation equilibrium of the transition metals and rare earths. Moreover the amperometric methods could be developed for the trace analysis of the titled metals by titrating them with some ligands of modern analytical importance. The work has been successfully supplemented by UV spectral studies on the metal ligand complexation equilibrium.