ABSTRACT

Although a large number of instrumental procedures have been put forward by scientists for physico-chemical and analytical work, the polarographic technique has rapidly gained prominence among other physico-chemical methods of analysis. This technique can furnish detectable results upto a very low concentration of the substances under study. With the discovery of newer derived techniques from polarography, analysis of substances has been possible upto a concentration as low as parts per billion parts of the sample. With an intention to use polarographic and derived techniques to the study of metal complexes (both binary and ternary) and trace determination of some rare earths and transition metals, the present work has been discussed in the thesis in five chapters. The chapterwise details are as follows:

The first chapter of the thesis deals with the introductory idea as regards to the metal complexes, both binary and ternary. Various theories which have been put forward to explain the behavior of metal complexes, have also been mentioned briefly with special reference to valency bond theory, crystal field theory and molecular orbital theory.
detailed introduction to the potentiographic technique and its application for the determination of stoichiometric ratio and formation constants of binary and ternary complexes has been mentioned. A possible use of amperometric and biampereometric titration techniques for the trace determination of some metal ions has been discussed. Theoretical knowledge of the principles underlying the above electroanalytical techniques has also been mentioned in the chapter. The chapter also discusses briefly the application of absorption studies for the determination of stoichiometric ratio and formation constants of the complexes under study.

Chapter two in this thesis describes the potentiographic behavior of binary complexes of Tb$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ with iminodiacetic acid (IDA), Nitrilo triacetic acid (NTA), thymol blue, tetracobaltic acid (TBA) and diethylene triamine pentaacetic acid (DTPA). Stoichiometry and formation constants of the chelates have been calculated using either ligand method and/or Deford-Dumore's method.

The chelating tendency of the derivatives of acetic acid is noteworthy. It has been observed that IDA forms 1:1 and 1:2 complexes with the three rare earths under study, whereas NTA, TBA and DTPA form 1:1 chelates with each metal under study. The stability sequence in the complexes was found to be DTPA > TBA > NTA > IDA.
A study of metal complexes has assumed immense importance due to their large scale applications in day to day analytical works. The last four decades of the development of polarographic methods for the study of coordination compounds established the prominence of these methods. The chapter three of this thesis deals with the polarographic studies of binary and ternary complexes of In(II), Cd(II) and In(III) using γ-Nicotoline, Nicotinic acid and citraconic acid as ligands. The reduction of metal ions and their complexes was found to be reversible and diffusion controlled involving two electrons in case of In(II) and Cd(II) but three in case of In(III).

In all nine combinations of mixed systems have been studied polarographically, choosing one weaker ligand as primary and the stronger as secondary ligand. The studies were done at an ionic strength of 0.1 (adjusted with potassium chloride) and pH 6.6 ± 0.02, 6.5 ± 0.02 and 4.5 ± 0.02 for In(II), Cd(II) and In(III) complex systems respectively.

The study of binary complexes involved in the present investigation was done separately prior to the study of ternary complexes. Identical conditions of pH and temperature were maintained in both simple and mixed systems. Stoichiometry and formation constants of binary complexes have been evaluated using Deford and Hume's treatment of the observed polarographic data whereas Novak and Comarast's method was used to study the stoichiometry and formation constants of ternary complexes.
It has been observed that more than one complex species are formed with each ligand under study.

The stoichiometry and formation constants of the ternary complexes formed in solution are listed below:

\[ \text{Zn}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{2}}^{\text{2-}} \rightarrow \log \beta_{11} = 3.70 \]
\[ \text{Zn}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{2}}^{\text{2-}} \rightarrow \log \beta_{12} = 3.65 \]
\[ \text{Zn}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{11} = 5.00 \]
\[ \text{Zn}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{12} = 3.95 \]
\[ \text{Zn}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.00 \]
\[ \text{Zn}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.06 \]
\[ \text{Zn}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.86 \]
\[ \text{Cd}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{11} = 4.17 \]
\[ \text{Cd}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{12} = 4.75 \]
\[ \text{Cd}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 4.50 \]
\[ \text{Cd}^{2+} (\text{Nico})_{\text{2}}^{\text{2-}} (\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.45 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{11} = 3.00 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{12} = 4.50 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.55 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 4.66 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 4.70 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 6.22 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 6.06 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 5.11 \]
\[ \text{HM}^{2+} (\text{Nico})(\text{Y}^{3-})(\text{Nico})_{\text{1}}^{\text{1+}} \rightarrow \log \beta_{21} = 6.29 \]
The tendency of ligands to add to a complex and to substitute another ligand are shown in schemes. The mixing constant \( k_2 = \beta_1 \frac{\sqrt{c_2 \times I_2}}{c_2} \) and stabilisation constant \( \log K_e = \log K_M - \log 2 \) have been evaluated in each case. On the basis of numerical values obtained in each case, the existence and stability of complex species have been discussed. From the nature of values of \( \log K_e \) and \( \log \beta_1 \) in each ternary system, it can be concluded that the formation of ternary complexes is preferred over simple bis complexes in solution.

Chapter fourth deals with the amperometric estimations of some rare earths (Tb(III), Dy(III) and Er(III)) and Al(III). Alizarin red-S, 4-(2-mercaptobenzylazo) resorcinol, ethyl thymol blue and cupferron have been used as amperometric reagents. All these four reagents give well defined polarographic waves under suitable experimental conditions. 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. It was observed that in amperometric titrations, Alizarin Res-6, Cupferron and 4-(2-Pyridylazo) Resorcinol form 1:2 chelates with rare earths and transition metals under study whereas methyl thymol blue forms 1:1 chelates with the above metal ions. The ratios observed by the author have been supplemented by absorption studies.

Among the analytical reagents used for the amperometric titrations, 4- has proved to be the most sensitive for the amperometric determination of the titular metals estimating 0.1 mg of the metal / 10 ml. of the analyte successfully within a percentage error of less than 0.75% whereas about 0.1 mg of metal / 10 ml. of analyte could be determined using others, i.e. Alizarin Red-6, Cupferron and MT3 as amperometric reagents within an error of less than 0.7% in each case. The statistical t-test supported the utility of developed titrimetric procedures.

Chapter fifth of the thesis deals with the biampirical titrations of Rb⁺, Cs⁺, Sr³⁺ and Ca³⁺ with Alizarin Red-6 (AR) 4-(2-Pyridylazo) Resorcinol (LAR) 1-(2-Pyridylazo) Ruthenol-2 (RUL) Alenol-orange (AO) and Methyl thymol blue (MT3). These titrations have been performed at a very small potential i.e. 100 mV. Quantities of the metals ions measured biampiermetrically have been depicted in their respective tables. Statistical data have been calculated and reported in the text.