ABSTRACT

The present thesis deals with the behaviour of metal ions and their complexation with some organic ligands on a DME, as abstracted in the following six chapters.

CHAPTER ONE:

It deals with the introduction to polarography and its applications to the work cited in the thesis. The current-voltage behaviour of a depolarizer on a DME has been discussed from the view point of the process of electrode reaction i.e. reversible, irreversible and quasi-reversible processes. The kinetic parameters as obtained by Gellings' method for quasi-reversible reactions, and by Koutecky's method for irreversible reactions have also been dealt. The principle of separation of polarographic waves of various cations by differential complexation has also been discussed. A brief description of the methods for the study of binary and ternary complexes of 'd' and 'f' block elements have also been mentioned.

CHAPTER TWO:

It deals with the polarographic behaviour vis-a-vis kinetics of electrode reactions of trivalent...
Ce, Pr and Nd in varying concentrations of potassium chloride in presence of 0.314 gelatin in the pH range between 2.2 to 3.2. It is observed that:

(i) At lower concentration of potassium chloride (0.1 mol dm\(^{-3}\) to 0.5 mol dm\(^{-3}\)) an irreversible reduction wave is observed, which attains a quasireversible nature on subsequent increase of potassium chloride concentration, and finally in 1.0 mol dm\(^{-3}\) potassium chloride concentration, almost reversible three electron reduction wave is observed, with each of the three metal ions under study.

(ii) The polarographic study of Ce(III) is preferred at pH 2.75 ± 0.02, whereas Pr(III) and Nd(III) are studied at pH 2.4 ± 0.02, because at these corresponding pH values a meaningful limiting current is observed, which allows an accurate measurement of \(E_{1/2}\) and other polarographic data.

(iii) The \(E_{1/2}\) values for Ce(III), Pr(III) and Nd(III) are -1.85, -1.81 and -1.79 V vs SCE respectively, and are independent of the respective metal ion concentration. However, in the reported experimental conditions, the diffusion current is proportional to the metal ion concentration, thereby permitting their polarographic estimations.
Thus under the reported experimental conditions, potassium chloride can be recommended as a suitable supporting electrolyte for the electroreduction and polarographic estimations of Ce(III), Pr(III) and Nd(III) respectively.

CHAPTER THREE

It deals with the results of the polarographic studies on binary complexes of trivalent Ce, Pr and Nd with the derivatives of acetic and benzoic acids on a DME, using either Lingane's method or Deford and Hume's method.

The chelating tendency of the derivatives of acetic acid is noteworthy. It is interesting to note that glycine, IDA and NTA have a remarkable similarity due to the presence of amino as well as acetic acid groups. It is observed that glycine and IDA both independently form 1:1 and 1:2 complexes with Ce(III), while NTA forms 1:1 complex species with Ce(III). On the other hand Pr(III) and Nd(III) give 1:1 complex species with glycine, IDA and NTA respectively.

Benzoic acid and its substituted hydroxy derivatives have been extensively used for complex formation with various metal ions. In the present study benzoic acid, protocatechuic acid (3, 4 dihydroxy benzoic acid) and salicylic acid have been used as ligands.
It is observed that benzoic acid forms 1:1 complex with all the three metals, while protocatechuic acid forms 1:2 complex species with each of the three metals under study. On the other hand salicylic acid forms 1:1 and 1:2 complex species with Ce(III), while Pr(III) and Nd(III) both forms 1:2 complex with salicylic acid.

CHAPTER FOUR:

It deals with the polarographic study of binary and ternary complexes of Pb(II) with some organic ligands. The study of binary complexes was done separately, prior to the study of ternary complexes. Similar conditions were maintained in both simple and mixed systems.

Beford and Hume's method has been applied to deduce the stoichiometry and stability constants of the consecutive complexes. It has been observed that Pb(II) forms 1:1, 1:2 and 1:3 consecutive complex species with each of the citraconic acid (CA), itaconic acid (ICA) and urea respectively, whereas nicotinic acid (NA) forms 1:1 and 1:2 consecutive complex species with Pb(II).

To study ternary complexes polarographically among these ligands, following three mixed systems were reported.
(i) Pb(II)-itaconate-urea system

In this system, urea being a weaker ligand, its two fixed concentrations 0.1 and 0.025 mol dm$^{-3}$ were selected, whereas the concentration of itaconic acid was varied. Schaap and McMaster's treatment of the observed polarographic data revealed the formation of the following three mixed ligand complexes.

1. $[\text{Pb}(\text{I.A})(\text{UREA})] \quad 1:1:1 \quad \log \beta_{11} = 3.39$
2. $[\text{Pb}(\text{I.A})(\text{UREA})_2] \quad 1:1:2 \quad \log \beta_{12} = 5.20$
3. $[\text{Pb}(\text{I.A})_2(\text{UREA})]^{-} \quad 1:2:1 \quad \log \beta_{21} = 5.92$

Addition and substitution of the ligands has been discussed.

(ii) Pb(II)-itaconate-nicotinate system

In this system nicotinic acid being a weaker ligand, two fixed concentrations of it at 0.1 and 0.25 mol dm$^{-3}$ were selected, while the concentration of itaconic acid was varied. In subjecting the observed polarographic data to Schaap and McMaster's treatment, following three mixed complexes are obtained.

1. $[\text{Pb}(\text{I.A})(\text{NA})]^{-} \quad 1:1:1 \quad \log \beta_{11} = 3.00$
2. $[\text{Pb}(\text{I.A})(\text{NA})_2]^{-} \quad 1:1:2 \quad \log \beta_{12} = 5.35$
3. $[\text{Pb}(\text{I.A})_2(\text{NA})]^{-} \quad 1:2:1 \quad \log \beta_{21} = 5.52$
The addition and substitution of the ligands has also been discussed.

(iii) **Pb(II)-citraconate-nicotinate system**

Here also the concentration of nicotinic acid is fixed at 0.2 and 0.4 mol dm\(^{-3}\), separately and that of citraconic acid concentration is varied, in each case. The Schaap and McMaster's treatment of the observed polarographic data revealed the formation of following mixed complexes.

1. \([\text{Pb(CA)}(\text{NA})]^{1-}\) 1:1:1 \(\log \beta_{11} = 2.88\)
2. \([\text{Pb(CA)}(\text{NA})_{2}]^{2-}\) 1:1:2 \(\log \beta_{12} = 3.45\)
3. \([\text{Pb(CA)}_{2}(\text{NA})]^{3-}\) 1:2:1 \(\log \beta_{21} = 4.08\)

The addition and substitution of the ligands has also been discussed.

**CHAPTER FIVE**

It deals with the separation of polarographic waves of few cations, having \(E_{1/2}\) values so close together, that the waves are almost superimposed, but the problem has been tackled by utilizing their differential complexation with salicylic acid and iminodiacetic acid.

Polarographic waves of \(\text{Zn(II)} + \text{Ni(II)}\) and
Zn(II) + Co(II) in a mixture have been separated with IDA. The waves are $0.3 \pm 0.02$ V apart in the former case and $0.35 \pm 0.02$ V apart in the latter. The separation of Ni(II) + Co(II), in a mixture, is not reproducible with IDA. The polarographic waves of Zn(II) + Co(II) and Ni(II) + Co(II), in a mixture, have been separated with SA. The waves are $0.32 \pm 0.03$ V and $0.30 \pm 0.03$ V apart from each other, respectively. The separation of polarographic waves of Zn(II) + Ni(II) with SA is poor as the waves are only $0.1 \pm 0.01$ V apart. The polarographic waves of Zn(II) + Ni(II) and Co(II) in a mixture have been separated by SA. However, a poor separation is observed with IDA.

Similarly polarographic waves of a mixture containing Cu(II) + Cd(II) in ammonium thiocyanate was separated with either IDA or SA. Both the ligands are equally effective in bringing out the separation. The waves are $0.15 \pm 0.02$ V apart from each other. However, with IDA a poor separation is observed.

CHAPTER SIX

It deals with the amperometric estimations of trivalent La, Ce, Pr and Nd with tetrazine and naphthaline 4RS, separately, used as complexing agents, to form precipitate.
Tetrazine gives a well defined reduction wave in ammonium chloride and ammonium hydroxide buffer at pH 8.20 ± 0.1, with \( E_{1/2} = -0.68 \) V vs SCE. The plateau potential on the wave = -0.82 V vs Hg pool anode system, was applied for carrying out amperometric titrations. The proposed method has been also tested in presence of various diverse cations. The current volume titration curves obtained were well defined, indicating 1:1 stoichiometric ratio for metal ligand complexation in each case.

Naphthalene scarlet 4RS, a basic azo dye, also gives a well defined wave in ammonium chloride and ammonium hydroxide buffer at pH 8.1 ± 0.1, with \( E_{1/2} = -0.65 \) V vs SCE. An amperometric titration technique was used to estimate these metal ions, at a plateau potential on the wave = -0.85 V vs Hg pool. The current-volume titration curves obtained were well defined, indicating 1:1 stoichiometric ratio for metal reagent complexation in each case. The proposed method has been tested in the presence of several cations and anions. The precision and accuracy of the titration procedures adopted has been also discussed.