PLAN OF WORK

The following plan has been drawn up for carrying out the research work contemplated for this thesis:

1. Theoretical basis of linear sweep voltammetry

Singh and Dutt (157-159) for reversible, quasi-reversible and irreversible electrode processes have developed the theory of linear sweep voltammetry, in hydrodynamic systems, in this laboratory. The boundary value problem has been solved by transforming convective diffusion equations to integral equation, which was solved numerically by taking one term of the series in the kernel of the integral equation. In the present investigation the constraint of retaining only one term in the kernel will be removed and increasing the number of terms in the series till the convergence is achieved, will solve the integral equation. The effect of the velocity of the solution flowing through the electrode, potential scan rate and initial concentration of the reactant, on the peak current will be studied. A simple procedure for determination of kinetic parameters i.e. standard rate constant and transfer coefficient will also be developed.

2. Coupled chemical reactions

The work on this aspect will include the study of electrode processes involving coupled homogeneous reactions in which charge transfer is preceded or followed by chemical reaction and the limiting current is controlled by kinetics of preceding or following chemical reactions as well

as by diffusion process. An equation which relates the limiting current to the rate constant and other experimentally measurable parameters like axial velocity of flow, potential scan rate will be derived. A simple procedure to determined the chemical reaction rate constant preceding or succeeding the electrode charge transfer will be developed. The electrode kinetics of the following coupled homogeneous reactions will be studied during the present investigations.

(a) EC processes:

(i) $O + ne^- \leftrightarrow R$

$$R \underset{k_b}{\overset{k_f}{\leftrightarrow}} Z$$

(ii) $O + ne^- \xrightarrow{k'} R$

$$R \underset{k_b}{\overset{k_f}{\leftrightarrow}} Z$$

(iii) $O + ne^- \xrightarrow{k'} R$

$$R + Z \xrightarrow{k_b} O$$

(iv) $O + ne^- \leftrightarrow R$

$$R \xrightarrow{k_b} Z$$

(b) CE processes:

(i) $Z \underset{k_b}{\overset{k_f}{\leftrightarrow}} R$

$$R \leftrightarrow O + n\,e^-$$

(ii) $Z \underset{k_b}{\overset{k_f}{\leftrightarrow}} R$

$$R \overset{k'}{\rightarrow} O + ne^-$$

(c) ECE processes:

(i) $$A + n_1e^- \leftrightarrow B$$

$$B \overset{k}{\rightarrow} C$$

$$C + n_2e^- \leftrightarrow D$$

(ii) $$A + n_1e^- \leftrightarrow B$$

$$B \overset{k}{\rightarrow} C$$

$$C + n_2e^- \overset{k'}{\rightarrow} D$$

(iii) $$A + n_1e^- \overset{k'}{\rightarrow} B$$

$$B \overset{k}{\rightarrow} C$$

$$C + n_2e^- \leftrightarrow D$$

(iv) $$A + n_1e^- \overset{k}{\rightarrow} B$$

$$B \overset{k}{\rightarrow} C$$

$$C + n_2e^- \overset{k}{\rightarrow} D$$

Current-potential curves for CE, EC and ECE processes will be derived theoretically and effect of various electrode parameters on the shape of these curves will be studied.

3. Experimental verification of theoretical equations

In order to verify theoretical expressions derived during the present investigations, experimental work for some of the above mentioned processes will be carried under linear sweep voltammetric conditions for the anodic oxidation of some aromatic (amino) and phenolic compounds.