PART A

INTRODUCTION
CHAPTER I

POLAROGRAPHIC PRINCIPLES
A prime type of voltametry, which tells much about the degree of interaction between metal ions and complexing agents in solutions is polarography. The nature of the ligand species with complex forming ability can be elucidated by this technique. In polarography a linearly increasing voltage is applied between a dropping mercury electrode and a reference electrode placed in the solution and the resulting current is measured. This technique was introduced by Prof. J. Heyrovsky of Charles University, Prague.

A capillary attached to a mercury reservoir functions as a dropping mercury electrode. From the tip of the capillary, mercury drops fall down with a droptime ranging between 2-6 seconds. The standard calomel electrode is employed generally as the reference electrode. The electrical circuit and a typical polarogram are shown in the figure (cf. Fig. 1.1a, 1b).

The limiting current is generally directly proportional to the concentration of the electroactive species. This forms the basis for quantitative analysis in polarography. Ilkovic\(^1\) equation expresses the relationship between the limiting current \((i_d)\) and the concentration \((C)\) of the electroactive species (depolariser) in a diffusion controlled polarographic process.
Fig. 1.1 A - Schematic diagram of a simple manual polarograph. $E_{11}$: 2-4 V d.c source; $R_{11}$: voltage divider (rheostat or radio polarometer); $S_{11}$: SPST: On-Off switch, $S_{12}$: DPDT reversing switch for applying the positive or negative potentials to the dropping electrode; $S_{13}$: DPDT reversing switch for presenting positive or negative currents to the current measuring device; $V$: 0.3 V d-c voltmeter.

(Taken from "The Polarographic Principles" by L. Meites).
Fig. 1.1 B - Polarograms of (a) 1 M hydrochloric acid containing 0.5 mM cadmium ion and (b) 1 M hydrochloric acid alone.
(Taken from "The Polarographic Principles" by L. Meites).
In the above equation 'n' is the number of electrons involved in the process, 'm' is the mercury flow rate in mg/sec, 'D' is diffusion coefficient of the electroactive species in cm$^2$/sec, 't' is drop time in seconds and 'C' is the concentration of electroactive species in millimoles/litre.

Reversible and Irreversible Processes

The electrode reaction involving rapid exchange of electrons between the electrode and the depolariser in a polarographic process is said to be reversible. The following equation relating the electrode potential and the current was proposed for diffusion controlled polarographic reversible process by Heyrovsky and Ilkovic:

$$E_{dme} = E_{1/2} + \frac{RT}{nF} \ln \frac{i}{i_d-i}$$

In the above equation 'E_{dme}' is potential applied to the dropping mercury electrode, $E_{1/2}$ is the half-wave potential of the depolariser, 'n' is the number of electrons involved in the rate limiting process, 'F' is Faraday, and 'i' is the mean current at the applied potential, 'E', 'i_d' is the limiting current.

In an irreversible polarographic process, exchange of electrons between the electrode and the depolariser
Fig. 1.2 - Polarograms of (a) 0.4 mM lead (II) and (b) 0.5 mM nickel(II) in 0.1 F sodium chloride - 0.001 F hydrochloric acid containing 0.002% Triton-X-100.

(Taken from "The Polarographic Principles" by L. Meites).
takes place much more slowly and the equation for such processes is given as

\[ E = E_{1/2} + \frac{RT}{j_{\text{naF}}} \ln \frac{i}{i_d} - i \]  

(\( j \) = transfer coefficient for an irreversible diffusion controlled reduction). A similar equation is proposed for an irreversible oxidation process as

\[ E = E_{1/2} - \frac{RT}{j_{\text{naF}}} \ln \frac{i}{i_d} - i \]  

(\( j \) = transfer coefficient for the irreversible diffusion controlled oxidation). The shapes of the polarograms expected for reversible and irreversible processes respectively are shown in the Figs. 1.2a, 2b. The Ilkovic equation is equally applicable to the limiting currents of both reversible and irreversible processes. But the halfwave potentials of the electroactive species in the two types of processes will be very much different from each other. This separation in the half-wave potentials increases with the increase in the degree of irreversibility. The anodic and cathodic half-wave potentials are equal to each other generally in reversible processes while they are different in irreversible processes.

The following equation relates the current (\( i_c \)) in an irreversible process to the potential
\[ i_c = \frac{nFAC^0K \exp\left[-\alpha nF(E-E')/RT\right]}{\exp\left[\alpha nF(\bar{E} + 0.2412)/RT\right]} \]  

where \( F = \) Faraday; \( A = \) area of the electrode in \( \text{cm}^2 \); \( C = \) concentration of the species at the surface of the electrode in millimoles/litre; \( \alpha = \) transfer coefficient; \( K = \) rate constant; \( E = \) applied potential; \( E' = \) reference potential.

The reference potential is generally selected in two ways. In one case it is the formal potential of the depolariser in the solution under experimental conditions and in the second case it is -0.2412 Volts vs SCE. In practical polarography generally the second choice is preferred. Then the equation for the cathodic current is written as

\[ i_c = nFAC^0\kappa_{b,h} \exp\left[-\alpha nF(\bar{E} + 0.2412)/RT\right] \]  

The value of \( K_{b,h}^0 \) and \( \alpha \) are determined by the polarographic methods. The \( \alpha \) values lie in the range 0 to 1 and generally it is around 0.5. From the slope of the plot of \( E_{dme} \) vs log \( i/i_d - i \), 'n' the number of electrons involved in the rate limiting process is known. A slope of 0.059 obtained for a reversible process suggests that the process involves a single electron. The colorimetric determinations at the controlled potential corresponding to the diffusion current region of the polarogram indicates the total number of electrons \( (n) \) involved in
polarographic reduction process. If the number of electrons \( n_a \) obtained from \( E_{dme} \) vs \( \log i/i_d \) plot is less than the number \( n \) obtained, in the coulometric method, it is generally understood that the reaction is taking place in several steps and that the number of electrons involved in the rate determining step is \( n_a \).

The characteristics of reversibility are observed in the case of irreversible reactions which involve some reversible steps. Sometimes semi-log plot \( (E_{dme} \) vs \( i/i_d \) - i) slope indicates a reversible one electron reduction but the \( E_{1/2} \) of the anodic wave of the species will be different. The results of this nature suggest that the reversible electron transfer process is succeeded by a slower irreversible chemical processes. In the above mentioned process, the slope of the log plot suggests that, a reversible one electron reduction is the rate determining step. This is followed by the protonation step and the electron addition steps. The half-wave potential of the process is not at all influenced by the proton.

Ilkovic equation further points out that the limiting diffusion current depends on the value of \( m^{2/3} t^{1/6} \). The value of the latter in turn depends on the square root of the height of the mercury column \( \sqrt{H} \) where 'H' is height of mercury column. The dependence of limiting
current on $m^{2/3} \cdot t^{1/6}$, therefore is established graphically by plotting the limiting current ($i_d$) or the wave height ($h$) against ($\sqrt{H}$). The $i_d$ or $h$ vs $\sqrt{H}$ plot for diffusion controlled wave is therefore expected to be linear and shall pass through the origin.

**Reduction governed by the Kinetic Factors**

During the initial stages of the wave in an irreversible system, electron transfer takes place slowly than in the diffusion process. This suggests that there exists some degree of kinetic control on the current operating over this part of the wave. Kinetic currents are defined as those currents which are controlled by the rate of some chemical reactions occurring in the vicinity of the electrode process. The typical examples of kinetic currents are those observed in the polarographic reduction of pyruvic acid. Fig. 1.3, illustrates the polarographic waves obtained in the above cases.

**Influences of Adsorption on Reduction Process**

If the depolariser or the product of the electrode reaction is adsorbed on the surface of the mercury drop a change in the profile of the wave is found to be split into two, one of the waves is attributed to the adsorbed form of the species (Fig. I.4a, 4b). If the depolariser itself
Fig. 1.3 - The diagram showing a kinetic wave
Fig. 1.4 - The diagram showing (a) reduced form, (b) oxidised form.
is getting adsorbed, then the wave is observed at more negative potentials, in comparison to the normal wave. On the other hand if the product of the electrode, reaction is adsorbed, the adsorption wave is observed as a pre-wave. Many organic molecules exhibit adsorption waves.
REFERENCES