CHAPTER I

POLAROGRAPHY

SECTION (A) : Introduction and Modern Developments

SECTION (B) : Instrumentation
Among the modern instrumental methods which have been rapidly developed to extreme versatility, Polarography enjoys a prominent place. This technique first discovered by Prof. J. Heyrovsky was later developed by Ilkovic who laid the foundation of theoretical ground work. As a tribute to the vast horizons that it has encompassed during its development its discoverer Prof. Heyrovsky was awarded the Nobel Prize in the year 1959.

The method of Polarography consists of unique type of electrolysis which involves the transfer of ions to and fro from the electrode followed by electrochemical reduction/oxidation with the condition that mass transfer process takes places only by diffusion to the total exclusion of convection and migration processes. In addition, the electrolysis is carried out on a dropping mercury electrode, D.M.E. (which has a very small surface area for a very short duration) so that there is practically no change in the concentration of the electro-reducible or-oxidisable species. Under these conditions, Polarography deals with three fundamental variables, the composition of the test solution, the potential applied to the dropping mercury electrode and the current flowing through the cell. A current-voltage curve called a 'polarogram' yields substantial information useful in electroanalytical Chemistry.

A SIMPLE POLAROGRAPHIC CIRCUIT:

Fig. 1.1 represents the simplified version of a manual polarograph. The solution under investigation is placed in
FIG 1.1 SIMPLE CIRCUIT DIAGRAM FOR POLAROGRAPHIC ANALYSIS.

FIG 1.2 A TYPICAL CURRENT-VOLTAGE CURVE.
cell C. The dropping mercury electrode B is dipped into it. The mercury pool at the bottom of the cell which is formed by the falling mercury drops or any other standard half cell (like a S.C.E.) is made the anode A. The anode is joined through the sliding contact S of the rheostat A to the positive terminal of the battery B while the cathode (D.M.E.) is connected to the negative pole of the battery through a galvanometer G. A variable shunt 'S' serves to read a wide range of current values.

The variation of applied voltage across the electrolytic cell is accomplished by the slide contact on the rheostat. The galvanometer readings so obtained oscillate between a maximum and a minimum. It is common practice to record the average current for reversible reactions and maximum current for irreversible reactions.

Polarography, in essence, consists in recording the current flowing through the electrolytic cell with gradual increase in applied potential. A current voltage curve (polarogram) is then constructed by plotting current along the vertical axis and applied potential along the horizontal axis. Such a curve has the potential to reveal many useful informations on the nature of species under investigation. As we follow a polarogram, we find that initially a very small current called the residual current flows through the cell. After the residual current is over, a sudden rise in current value is observed indicating that ions have begun to discharge at the D.M.E. Consequently there are lesser number of ions available for
discharge around the cathode. A concentration gradient thus sets in. The ions from the bulk of the solution start diffusing to the cathode. As we apply larger cathodic potential, a point is finally reached when all the ions reaching the D.M.E. are reduced. At this stage, the concentration of the depolariser around the electrode drops to practically zero. Since the transfer of the depolarizer has been made only through diffusion, any further increase does not cause any increase in current. The current at this stage is called the limiting current.

THE LIMITING CURRENT:

The limiting current consists of three portions as described in the following lines.

I. Residual Current -

When a potential is applied to the electrode, the depolarizer ions form an electrical double layer around it. Some potential is required to charge this double layer. The corresponding current called the 'condenser current' accounts for the major portion of residual current. A small contribution towards the residual current is also made by the reducible impurities present which when reduced allow the passage of a small current called the 'faradaic current'. Residual current is thus a sum of condenser current and the faradaic current.
II. The Migration Current

It is the general tendency of a charged depolarizer to be attracted towards the oppositely charged electrode causing what is known as the migration current. This is in addition to the contribution made by diffusion. We have already stipulated that the depolarizer should reach the electrode by diffusion alone. The migration current must, therefore, be eliminated. The magnitude the migration current depends upon the transport number of the depolarizer ion. All practical polarographic work is, therefore, carried out in solutions containing a large excess of a supporting electrolyte with ions with a high transport number and a substantially more cathodic decomposition potential than the depolarizer ions. In the presence of excess supporting electrolyte (at least 50 times), the transport number of depolarizer ions becomes practically nil resulting in almost complete elimination of the migration current. The addition of supporting electrolyte has another favourable effect. The cell current drops to a minimum value thus minimizing the IR drop. Consequently the potential across the cell is practically equal to the applied potential.

III. The Diffusion Current

We have already considered two components that make up limiting current. After the elimination of migration current as stated and subtraction of the residual current from the total limiting current, the remaining component which represents the flow of current solely due to diffusion of depolarizer, is
called the diffusion current.

Kemula\textsuperscript{2} and Ilkovic\textsuperscript{3-4} were pioneers in studying the various factors which govern purely diffusion current and deduced the following equations.

\[ i_d = 706 \ nCD^{1/2} m^{2/3} t^{1/6} \text{ for instantaneous current} \quad \cdots (1) \]

and

\[ i_d = 607 \ nCD^{1/2} m^{2/3} t^{1/6} \text{ for mean current} \quad \cdots (2) \]

where the symbols have the following significance

- \( i_d \) = diffusion current in microamperes
- \( n \) = number of electrons involved in the electrode reaction for each particle of the depolarizer
- \( C \) = concentration of the depolarizer in millimoles/litre
- \( m \) = rate of flow of mercury through the D.M.E. in mg/second
- \( t \) = drop time in seconds.

The constant 706 or 607 is a combination of natural constants. It is slightly temperature dependent and these values are true at 25° C.

The Ilkovic equation is important because it accounts quantitatively for many factors which influence the diffusion current. Thus with all other factors remaining constant, the diffusion current is directly proportional to the concentration of the electroactive material. This is of fundamental importance in quantitative analysis.
The original Ilkovic equation neglects the effect of curvature of mercury drop surface on diffusion current. Several workers have proposed modified equations for spherical diffusion to the D.E.L.E. rather than linear diffusion. Lingane and Loverbridge\(^5\) allowed this by multiplying the right hand side of the Ilkovic equation by \[ 1 + \left( AD^{1/2} t^{1/6} m^{2/3} \right) \] so that it becomes

\[ i_d = 607 nD^{1/2} Cm^{2/3} t^{1/6} \left[ 1 + \left( AD^{1/2} t^{1/6} / m^{2/3} \right) \right]. \tag{3} \]

\(A\) is a numerical constant whose value is 39. But Strehlow and Von Stackelberg\(^6\) gave \(A\) the value of 17 and so did Muller.\(^7\) Value intermediate between these two extremes have been provided by other workers.\(^8-9\)

Ilkovic equation has also been modified by Matsuda who proposed the following equation:

\[ i_d = 709 nG D^{1/2} m^{2/3} t^{1/6} \left[ \left\{ \left. \frac{1 + 35.5 D^{1/2} m^{-1/3} t^{1/6}}{266 D^{1/2} m^{-1/3} t^{1/6}} \right\}^2 \right. \right] \tag{4} \]

The most sophisticated treatment gives \(A\) a value of 34.7 and also provides another term:

\[ i_d = 607 nD^{1/2} Cm^{2/3} t^{1/6} \left[ 1 + 34.7 D^{1/2} t^{16} m^{-2/3} + 100 (D t^{1/3} / m^{2/3}) \right]. \tag{5} \]

This is known as Koutecky equation.

Several other attempts\(^12-14\) have been made and have ended up in equations similar to (5) differing only in the numerical value of \(A\).
FACTORs AFFECTING DIFFUSION CURRENT:

The various factors which can affect the diffusion current are summarised below:

1. **Concentration of the Depolarizer** -

   As the Ilkovic equation clearly indicates, the diffusion current is directly proportional to the concentration of the electroactive species provided there are no side reactions other than reduction/oxidation.

2. **Diffusion Co-efficient of the Depolarizer** -

   If the media is not changed, the size of the depolarizer and hence the rate of diffusion remains the same. Therefore, under similar conditions of media and temperature the diffusion co-efficient of the depolarizer does not vary causing no effect on diffusion current.

3. **Capillary Characteristics** -

   If the concentration, diffusion co-efficient and number of electrons involved do not vary, diffusion current is directly proportional to $m^{2/3} t^{1/6}$ at a given temperature. But since '$m$' is directly proportional to pressure and '$t$' is inversely proportional to pressure, it does not change sufficiently with change in height of mercury column i.e. the mercury pressure. It has been established that $m^{2/3} t^{1/6}$ is directly proportional to the corrected height of mercury column. The Ilkovic equation, therefore, provides the relation
\[ \frac{i_d}{a_{corr.}^{1/2}} = \text{constant} \quad \text{(6)} \]

It is the general practice to use this relationship to ascertain the diffusion controlled nature of a polarographic wave.

4. Temperature

The effect of temperature on diffusion current should be considered in the light of former's effect on viscosity, interfacial tension of mercury and diffusion co-efficient of the depolarizer. Effect due first three of these factors is so small that it can be conveniently ignored. Effect of temperature on diffusion coefficient is quite considerable (2-3 per cent/degree). This amounts to 1-1.5 per cent per degree rise in temperature for diffusion current. Making allowance for other factors, the temperature co-efficient of diffusion current should not exceed 2 per cent per degree provided the electrode reaction is entirely diffusion controlled.

5. Nature of the Media

In a complexing medium, it is found that \( i_d \) of a metal ion undergoes a decrease which is largely due to the increase in size of the diffusing species. Larger is the size of the depolarizer, smaller is the diffusion current.

Similarly increased viscosity of the medium has a retarding effect on the movement of electroactive species towards the D.M.E. The \( i_d \) must, therefore, decrease with
increased viscosity of the medium obeying the relation
\[ i_d = n^{-1/2} \]

**HALF WAVE POTENTIAL:**

The potential at which the current due to reduction/oxidation of the electroreducible species is half as large as the diffusion current is called the Half wave Potential \( (E_{1/2}) \). It reflects the ease of reduction/oxidation of a substance. This potential which has been derived from thermodynamic considerations by He-yrovsky and Ilkovic\(^{16}\) is practically independent of concentration of depolarizer in solution, the size of the mercury drops, the drop time and the galvanometer sensitivity and is characteristic of an ion in a given media at a specific temperature. A positive or a negative sign is generally prefixed on \( E_{1/2} \) according as whether the potential is more positive or more negative than the potential of a saturated calomel electrode (S.C.E.) which is almost always taken as the standard reference electrode.

**FACTORS AFFECTING HALF WAVE POTENTIAL:**

The following lines contain a brief account of the effect of various variables on half wave potential:

**Effect of temperature** differs for reversible and irreversible polarographic waves. For a reversible wave the temperature coefficient of \( E_{1/2} \) is always less than \( \pm 2 \) per cent per degree. For an irreversible wave, however, the temperature co-efficient of \( E_{1/2} \) may exceed several volts.
Half wave potential for a reversible wave is independent of depolarizer concentration.

The capillary characteristics \( m \) and \( t \) also do not affect the half wave potential. A negligibly small dependence on \( m^{1/3} t^{1/6} \) is observed when the diffusion coefficients for the oxidised and the reduced forms are different. This is too small and hence neglected. \( E_{1/2} \) shifts to a positive potential as \( t \) increases in the case of totally irreversible waves.

The media in which the depolarizer is oxidised/reduced play an important role. For example in a complexing medium, the \( E_{1/2} \) almost invariably shifts to a negative side.

Variation of half wave potentials in non-aqueous media has been investigated by Amis\(^{17}\) and Schaap\(^{18}\). Kirchmayer\(^{19}\) has concluded that \( E_{1/2} \) for the reduction of a metal ion depends on the structure of amalgam formed. Sellers and Vandenborgh\(^{20,21}\) have studied the effect of ionic strength on half-wave potential. Zahradnik and Parkanyi\(^{22}\) have published a review on the correlation between half-wave potential and the quantum mechanical characteristics of the depolarizer.

**POLAROGRAPHIC MAXIMA:**

It is sometimes observed that at the top of a polarogram an abnormal increase in current takes place followed, at sufficiently negative potential, by the limiting current value. This phenomenon is known as polarographic maxima. The maxima thus obtained may have the shape of an acute peak or a rounded hump.
These maxima can be classified into two types: the streaming and the non-streaming type. When the mercury drop falls down with a spinning motion, there is a vigorous motion of the ions around the electrode and hence larger number of ions reach the cathode resulting in a sudden rise in current value. This is called the maxima of the streaming type.

Non-streaming maxima, on the other hand, appears to originate from catalytic reasons. Both types of maxima can be eliminated by the addition of small quantities of surface active substances like gelatin, Triton X-100 etc. A large concentration of a maxima-suppressor is always to be avoided for obtaining good results. Large concentrations are liable to distort the wave and shift its position specially in the case of irreversible reductions. The maximum permissible limits of concentration are 0.005 per cent, 0.002 per cent and 0.004 per cent of gelatin, Triton-X-100 and methyl red respectively.

OTHER TYPES OF POLAROGRAPHIC CURRENTS

**Kinetic Current**

It has been observed that in some cases, a chemical reaction takes place before the electrode reaction proper can occur and the product of the preceding reaction is also reduced at the D.M.E. In such cases, the height of the wave is partly or wholly governed by the rate of the preceding reaction. The component of the total current which is due only to chemical reaction, as stated, is termed as Kinetic Current. Let us, for example, consider Y as the depolarizer which is converted
into electroactive $O$ which is then reduced to $R$ as seen

$$\frac{K_e}{K_D} O + ne \rightarrow R$$

Obviously, the magnitude of the kinetic current should be proportional to the concentration of the depolarizer $Y$. Paul Dehahay$^{25}$ has attempted an excellent derivation on kinetic currents.

**Adsorption Current**

Sometimes, the electroactive species or the product of the electrode reaction gets adsorbed on the surface of the E.M.F. resulting in a prewave near the residual current and a post wave near the limiting current$^{26}$ these maxima typed pre-waves and the postwaves are called the adsorption current. The adsorption current is proportional to the height of the mercury column and is independent of the concentration of the electroactive species.

**Catalytic Current**

When the electroactive species has been reduced/oxidised, sometimes the mere presence of a third substance regenerates the original substance from the electrode product. This regenerated species is again available for electrode reaction resulting in additional current called the catalytic current. In some cases the catalyst generates a different substance which is also reducible.
Catalytic waves have a non-linear dependence on the catalyst concentration. The catalytic waves have been used for the quantitative determination of exceedingly small amounts of original electroactive substances.

MODERN DEVELOPMENTS:

During the first twenty years after the invention of polarography, attention was mainly directed towards the interpretations of the current voltage curves such as the study of nature of a complex reducible reversibly or irreversibly. By the discovery of theoretical treatment of irreversible reductions, it has now become possible to understand the mechanism of electrode reactions.

The first attempt towards automation was made by Heyrovsky and Shikata who introduced automatic recording of polarograms on a photographic plate. This was later made the pen-recording type. It is a tribute to the development of new methods that the limit of sensitivity now stands extended to $10^{-9}$ M. In addition, greater resolution of successive waves is possible.

The following lines describe in brief the modern polarographic methods which owe their development to the classical method.
OSCILLOGRAPHIC POLAROGRAPHY:

It consists of two techniques discussed below:

(i) Oscillographic Polarography with Controlled Current

This method was first developed by Heyrovsky and Forejt. In this method, the current is controlled and potential variations with time are noted. A fifty c/sine wave A.C. voltage of about 100V is applied across the polarographic cell and a large variable resistance. The large resistance accounts for the most part of the voltage drop. A D.C. voltage is then superimposed over the A.C. voltage across the cell to determine the A.C. voltage sweep. A stationary potential time curve is obtained on the CRO screen if the frequency of the time sweep is synchronized with that of the A.C. voltage. The curve, so obtained, is a double polarogram in which the potential range is swept out both in forward and backward directions. Useful information regarding the electrode processes is available from the comparative study of these curves.

(ii) Oscillographic Polarography with Controlled Potential

Davis and Seaborn have made a major contribution towards the development of this technique. In this method, a controlled drop life of the order of seven seconds is adjusted since for a drop life of seven seconds, no significant change in the surface area of the drop takes place for the last two seconds. During the last two seconds, a rapid voltage sweep is
applied and the consequent changes in current are observed on the CRO screen. In this case, a stationary current voltage curve is obtained which appears to be a conventional D.C. polarogram with a maxima. This maxima is due to the rapid stripping of the depolarizer from the vicinity of the D.E.E. during the rapid voltage sweep (0.5 V/2s). The peak height \( i_p \) is a measure of the concentration of the depolarizer.

**ALTERNATING CURRENT POLAROGRAPHY:**

There are four types of A.C. polarography described below:

1) **Sinusoidal A.C. Polarography**

   Much of the credit for the development of this technique should go to Breyer and co-workers. A small sinusoidal low frequency alternating potential is superimposed on the applied D.C. potential in a polarographic circuit. The current flowing through then consists of two parts (1) D.C. part related to mean potential \( E \) of the electrode and (2) A.C. part which is a peak when the A.C. component of the cell current is plotted against the applied D.C. voltage. The peak height is a measure of the concentration of the depolarizer.

2) **Square Wave Polarography**

   This method owes its development to Barker and Jenkins. The effect of interference due to capacity current in the previous method has been overcome in this method. A square wave voltage of 225 c/s of less than 30 mV is applied slowly on
the changing D.C. voltage so that at the end of each half cycle there is a superior faradaic to non-faradaic current ratio. The resolution of peaks separated by as little as 45 mV is thus effected for components in mixtures with component ratio of the order of 1 : 30000 can be estimated with accuracy. Determinations as low as $10^{-3}$ A are possible. However, this technique does not provide good results for irreversible reductions. Another drawback makes itself felt due to the 'capillary response' at the detachment of each drop when a small amount of the electrolyte is sucked into the tip of the capillary which causes unstable response on the recorder.

(iii) **Pulse Polarography**

In this method Barker and co-workers\(^{53}\) have attempted to eliminate 'capillary response' encountered in square wave polarography. They have applied a voltage pulse at some specific instance in the drop-life time minimising the 'capillary response' even when the investigations are carried out at a high sensitivity.

(iv) **Radio Frequency Polarography**

The instability of the response produced by minor defects\(^{54}\) in the D.M.E. result in limited sensitivity for square wave polarography. In this method, a radio frequency attachment has been developed which virtually eliminates any response due to capillary defects. In this technique an amplitude modulated radio frequency current of 200 kc/s is
passed through the cell. The radio frequency current is fully
modulated by a square wave voltage taken from the circuits
of the polarographs. The polarograph measures the magnitude
of the low frequency a.c. caused by faradaic rectification at the interface of the electrode and the solution. This
technique is very useful in the estimation of concentrations
as low as $10^{-9} M$.

APPLICATIONS OF POLAROGRAPHY:

Industry and research have been making gainful use of
the various polarographic methods. Determinations of the order
of $10^{-9} M$ are now possible. Components of mixtures with high
component ratio can be precisely determined.

Polarography has come to stay as a useful tool in
metallurgical analysis. Thus traces of lead and cadmium in
copper, chrome in steel, alkali metals in aluminium, cadmium, zinc, lead and copper in zinc ores, manganese and
calcium in waters, molybdenum in ores have been accurately
determined by polarography.

Polarography has also been used in food industry for
the determination of lead in tinned food, aldehydes in
spirit, ascorbic acid in fruits and vegetable, iodine in
table salt.

In medicine, nitro compounds in exhalations and urine cystine and proteins in clinical analysis have been
advantageously determined.
All these determinations have taken advantage of the fact that the method of polarography is characterised by small sample requirement, speed, sensitivity and selectivity. There is sufficient evidence to indicate that polarography as a tool of analysis has ample scope in the advancement of scientific knowledge.
SECTION (B)

INSTRUMENTATION

A manual polarograph with scalamp galvanometer as current recorder with automatic arrangement of standardisation was used for recording current voltage variation. The polarographic unit was standardized with a W.G. Pye Vernier Potentiometer N 7568.

Dropping Mercury Electrode -

The basic and the principal part of the polarographic analysis is the unpolarizable, micro-electrode which here in use was a dropping mercury electrode throughout the investigation. The dropping mercury electrode consists of a glass capillary connected to a reservoir of mercury by means of a flexible tubing. The reservoir, the tubing and the capillary are filled with doubly distilled mercury. The mercury reservoir and capillary both were clamped on a suitable stand and could be lowered or raised as per the specific situations. A short platinum wire sealed at the end of a glass tube which is dipped in the reservoir serves to connect the D.M.E. with the polarograph.

Reference Electrode -

The reference electrode used in polarography must fulfill the condition that its potential remains unaltered during the recording of the polarographic data by applying varying potential. To a larger extent this is being fulfilled by a saturated
calomel electrode which was therefore used as a reference electrode throughout the investigations.

**Polarographic H-Cell** -

An H. cell comprises two compartments, one for filling the test solution and the other for saturated potassium chloride solution where S.C.E. is dipped. The compartment for test solution is also provided with a side tube which allows passage of Hydrogen through the test solution for expelling dissolved oxygen.

The two compartments are separated by means of a sintered glass disc in combination with KCl saturated agar-agar bridge.

**Thermostat** -

The temperature for investigation was maintained constant by means of electrically driven thermostant.

**pH Meter** -

A standard wide range glass electrode in conjunction with a saturated calomel electrode connected to a Tothniwal pH meter were used to make pH measurements.

**Experimental Procedure** -

The measurements of the drop time were usually carried out in 1M. potassium chloride with a short circuited system at a given mercury pressure. Using a stop-watch, the life of 10 drops
was measured and the average value of \( t \) computed. Such sets of measurements were repeated two or three times to determine the correct value for \( t \). For the evaluation of \( m \), mercury was collected for chosen and measured period of time. The mercury was dried and weighed and its consumption per second \((m)\) was computed in mgs.

The thermostated \( \text{II} \) cell was first filled with the test solution and the pure hydrogen bubbled through it for ten minutes. The capillary of the dropping electrode was now dipped in to the solution and the polarographic circuit completed by dipping the S.C.E. into the other compartment of the cell. The applied potential on the cell terminals was gradually increased and the corresponding current value read in the galvanometer.

All the current data recorded have been corrected for the residual current.
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