PART-I

POLAROGRAPHY
CHAPTER 1

POLAROGRAPHY

1.1 INTRODUCTION AND BASIC PRINCIPLES

Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode. Voltammetric indicator electrodes may be made from quite a large number of materials, say for instance mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or in motion and the solutions in which these are used may be stationary or quiet.

Polarography was the first of the voltammetric techniques to gain prominence. Certainly the most popular constant potential method is d.c. polarography at a dropping mercury electrode (DME). The reason being that there are several advantages peculiar to the DME, these are described further.

The essential features of current potential curves obtained with DME are shown in Fig. 1.1. Curve b is the polarogram of a dilute solution of hydrochloric acid and the curve a being obtained under exactly the same conditions after addition of a small concentration of cadmium ion. Here, each oscillation represents the life cycle of one drop. It is the difference between the currents on the two curves which is of interest. No detectable change of current results at potentials less negative than about –0.5 V from the addition of cadmium ion. The reason being that these potentials are insufficiently negative to bring about the reduction of any appreciable fraction of the cadmium ion at the surface of the drop. At potentials more negative than this, however, a wave appears, i.e., the reduction of cadmium ion proceeds more and more rapidly as the potential becomes more negative until eventually, at potentials more negative than about –0.7 V is attained. It is so fast that cadmium ions are reduced as rapidly as they get diffused from the bulk of the solution up to the surface of the electrode. The rate of this diffusion depends on a number of factors. Out of these the concentration of cadmium ion in the bulk of the solution is of special importance. More concentrated the solution, the greater the rate at which cadmium ions reach, the electrode surface, and the greater the diffusion current that results from their reduction. The proportionality between the diffusion current and the concentration of the substance responsible for the wave is the basis for nearly all quantitative polarographic analysis. The ease of reduction or oxidation differs for different substances, and is reflected by the position of the wave with respect to the potential.
axis. This is termed by a parameter called the half wave potential \(- E^{1/2}\). This is defined as the potential at which the current due to the reduction or oxidation of the substance responsible for the wave, is half as large as on the plateau. The half wave potential of cadmium ion can be seen in Fig. 1.1 (a). Under a set of defined experimental condition, each ion has its own characteristic half wave potential which is the basis of qualitative polarographic analysis. In cases, the electrode reaction may be so rapid that equilibrium is closely approached at every potential in a time much shorter than the drop life. This indicates the wave to be reversible. Studying the effects of potential and solution composition on the currents along the rising part of the wave provides information on the thermodynamics of the half reaction.

![Polarogram](image-url)

(a) 1 F hydrochloric acid with 0.5 mM (b) 1 F hydrochloric acid alone

Cadmium ion

Fig. 1.1: Polarogram

In some cases the electrode reaction may involve a step having a large activation over potential than the variation of the current potential and solution composition are due to kinetic rather than thermodynamic effects. In such cases information on the mechanism of the rate determining step can be secured.

Polarographic analysis can be used directly for the determination of any substance solid, liquid or gaseous, organic compounds containing conjugated double or triple bonds including polynuclear aromatic ring systems, as well as compounds like oximes, imines, ketones, aldehydes nitro diazo compounds and halo substituted compounds.
One of the most important advantages of polarography and other voltammetric techniques is that two or even more substances can be determined by a single current potential curve.

Another important analytical technique closely related to polarography is that of amperometric titration.

Polarography is getting more widely used in fields such as biochemistry and pharmaceutical chemistry. Even it has been used to study such diverse topics like hydrolysis, solubility, complex formation, absorption, kinetics of chemical reactions and mechanism of electrode reactions.

1.2 POLAROGRAPHS AND THEIR APPLICATIONS

There are two kinds of polarographs: manual and recording. With a manual instrument, the potential applied to the cell is adjusted to some desired value and the current is measured. A single point on the polarogram is thus obtained. If the whole curve is wanted, the procedure must be repeated many times. This is tedious, specially when several waves or a complex polarogram is to be observed as such, the manual polarograph is not very convenient. For such observations a recording instrument is most suitable. The manual polarographs are not a disadvantage either. The diffusion-current measurements can be made more precisely and more quickly with manual than with recording polarograph.

In a recording polarograph, the potential applied to the cell is obtained from a motor-driven voltage divider. Two procedures have been most frequently employed for recording the current. In one, the current is passed through a galvanometer, and the deflections of the galvanometer are recorded photographically or a piece of photographic paper moving at a known rate past a slit. In the other, which is now by far the more common, the current is passed through a standard resistor in series with the cell, and the resulting iR drop is presented to a strip-chart recording potentiometer, which plots the iR drop against time. Correlating the rates of motion of the chart and the voltage divider makes it possible to interpret the curve as a plot of current against applied potential. Usually, a recording polarograph employs a rate of change of potential of about 0.2 volt per minute and furnishes a complete polarogram in about 10 minutes.

1.3 THE POLAROGRAPHIC CELLS AND THE EXPERIMENTAL SET UP

The cell is that portion of the apparatus that contains the solution which is being studied. It also includes a non-polarizable electrode to which the potential of the dropping electrode is referred.

The most important part of a cell is its reference electrode. Two kinds of reference electrodes, “internal” and “external” are in general use. An internal electrode is in direct contact with the solution being studied, while an external electrode is separated from it by a salt bridge or a porous membrane. Internal electrodes are chiefly valuable in routine analyses in which a limited constancy of potential is unimportant. They are also often used in work (when very high negative potentials) where contamination by alkali metal ions or other constituents of a salt bridge would be harmful; in cells containing
only one or two drops of solution are used. Here the difficulty arises by bringing an external electrode into contact with so small a volume of the sample. In continuous polarographic analysis, where the slow contamination of an external electrode would eventually render its potential as uncertain as that of an internal one.

Internal reference electrode is made by coiling about 15–20 cm of 14 gauge silver wire into a helix. It is often convenient to coil it around the dropping electrode. In a solution containing an ion $X^-$ that forms an insoluble silver salt, the potential of this electrode depends only on the activity of $X^-$ in the solution, provided of course, that the solution is saturated with Ag $X$. If its solubility is very small, enough Ag $X$ to satisfy this requirement will be formed by reaction with dissolved oxygen, an air saturated solution is placed in contact with the electrode before deaeration. If the solution is neutral and unbuffered, it may involve partial hydrolytic precipitation of heavy metal ions. The electrode should not be used unless a precipitate results when a drop of solution containing 0.01 M silver ion is added to 10 ml of the sample solution. Otherwise the concentration of dissolved silver ion, and hence the potential of the silver electrode, may change considerably during the recording of the polarogram. In addition the concentration of silver ion may become high enough to give rise to substantial current at the dropping electrode.

The silver electrode is not workable in solutions containing ammonia, cyanide, thiosulphates and high concentrations of halides as well as in solutions containing only nitrate, acetate perchlorate and other ions whose silver salts are appreciably soluble.

The coating of insoluble salts that terms on the electrode when it is used as the anode cell should be removed by treatment with ammonia, thiosulphate, or cyanide, followed by rinsing with distilled water.

1.4 THE HALF-WAVE POTENTIAL AND ITS SIGNIFICANCE

The most important constant in polarography is the half-wave potential. Chemical, thermodynamic and structural information may be obtained from the measurements of the half-wave potentials of reversible and irreversible waves under varying experimental conditions.
The manner in which the current is affected by electrode potential on the rising part of the wave is to be noted. On the plateau, electron transfer is so fast that the ions or molecules of the electroactive substances are reduced or oxidized as rapidly as they arrive or are formed at the electrode surface. As the potential moves from the plateau of the wave towards its foot, the rate of the electron-transfer process decreases and the reduction or oxidation becomes less and less complete.

It is convenient to divide electrode reactions into two extreme classes: (i) Reversible reactions, and (ii) irreversible reactions. (i) The reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variation of current with potential reflects the changing position of the equilibrium and is described by Nernst equation. The other extreme is that of totally irreversible reactions, which are so slow that they proceed only by a fraction of the way towards equilibrium during the life of each drop.

For these reactions it is the rate of the electron-transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential. The polarographic data serve to elucidate the kinetics of the rate determining step in totally irreversible processes.

1.4.1 Significance of Half-wave Potentials

It follows from the equation derived on current potential curves that the half-wave potentials given by the term, $\frac{RT}{nF} \ln \frac{\sqrt{D}}{V}$, equals the standard oxidation-reduction potential found with other indicator electrodes such as platinum electrodes. This property holds only for an oxidation-reduction system, whose oxidized and reduced terms are both present in the solution, e.g., $Fe^{2+}/Fe^{3+}$. This was confirmed by many previous workers.

If one of the two terms (may be the reduced one) reacts with the material of the electrode (metals with information of an amalgam), then the half-wave potential differs from the standard oxidation-reduction potential for the metal/ion system. It can be readily shown that the difference between the half-wave and the standard potential is given by the free energy of amalgamation.

1.4.2 Influence of Ionic Strength on Half-wave Potentials

Very accurate measurements point to the fact that the half-wave potentials of cations depend on the ionic strength. Get shifted to more negative potentials with increasing ionic strength. This is caused by the dependence of $E_{1/2}$ on the activity coefficients of both the oxidized form $f$ and the reduced form $f'$. This is when the activities are considered instead of concentration. The potential of an oxidation-reduction system is given by the formula:

$$E = E^0_{\text{Red}} - \frac{RT}{nF} \ln \frac{f_{\text{Red}}}{f_{\text{ox}}}$$ ...

where ( ) denote the activities.

On expressing the above equation in terms of concentrations the following equation results:
The half-wave potential is defined by the relationship

\[ \frac{\text{[Red]}_0}{\text{[ox]}_0} = \sqrt{\frac{D}{D'}} \]  

...(3)

On obtaining this condition, we obtain

\[ E_{\frac{1}{2}} = E^0 - \frac{RT}{nF} \ln \left( \frac{f'}{f} \right) - \frac{RT}{nF} \ln \sqrt{\frac{D}{D'}} \]  

...(4)

For the half-wave potential.

In this equation the last two terms depend on the ionic strength. If cations are deposited a very dilute amalgam is formed and \( f' \) is virtually one. The activity coefficient \( f \) of the cation in the supporting electrolyte is, however, less than one and since \( f \) decreases with increasing ionic strength, \( E_{\frac{1}{2}} \) is shifted to more negative potentials. Lingane studied it first [2].

Vlek [1] made more accurate thermodynamic calculations and recommended that \( E_{\frac{1}{2}} \) be extrapolated to \( \mu = 0 \):

\[ (E_{\frac{1}{2}})_{\mu = 0} = E^0 - \frac{RT}{nF} \ln \sqrt{\frac{D_0}{D'_0}} \]  

...(5)

\( [D_0] \) and \( D'_0 \) are the corresponding diffusion coefficient for \( \mu = 0 \).

The half-wave potentials calculated from the thermodynamic standard potentials for \( \mu = 0 \) agreed with the extrapolated half-wave potentials as was shown by Vlek [1] in cases of \( \text{Tl}^+ \), \( \text{Pb}^{2+} \) and alkali metals.

### 1.4.3 Factors which Affect the Half-wave Potentials

1. The temperature coefficient of the half-wave potential is mostly between -2 and +2 mv/degree. For a reversible wave it may be either positive or negative. For an irreversible wave it is usually positive and may exceed several millivolts per degree.

2. The half-wave potential is almost always independent of the concentration of the electroactive species (i.e., of the diffusion current) after proper correction is applied for the \( iR \) drop. However, the half-wave potential of a reversible wave does not vary with concentration if a solid product is formed, or more generally, whenever the number of the ions or molecules of the product of variable activity differ from the number of ions or molecules of reactant of variable activity in the equation for the half-reaction. Such variations can be described only by thermodynamic equations. The half-wave potential of an irreversible wave may also vary with concentration of the reaction mechanism involving some rate governing step that is not the first- or pseudo-first order. When it does vary, it most often becomes more negative as the concentration increases.
3. The half-wave potential of a reversible wave is nearly independent of the capillary characteristics, i.e., m and t. When the diffusion current obeys the Koutecky equation and when the diffusion coefficient of the oxidized and reduced species differ a small dependence of the half-wave potential on $t^{1/6}$ and $m^{1/3}$ can be predicted. Changes in m, t and the concentration of the electroactive species may, however, produce apparent variations of the half-wave potential unless both are corrected. The iR drop always produces an apparent shift of the half-wave potential toward more negative values for the cathodic waves and toward more positive values for anodic waves and the shift is proportional to the limiting current.

4. The half-wave potential of a totally irreversible wave, however, varies significantly with t, becoming more positive for a cathodic wave as t increases. The magnitude of the variation depends on $\alpha_n$ and may be used for its evaluation. Typically, if $\alpha_n = 0.5$, the half-wave potential becomes about 20 mV more positive if t is doubled.

5. Changes in the nature and concentration of supporting electrolyte may effect the half-wave potential in many ways. For reversible waves the effect is due to complex formation. Quite some information about the identities and dissociation constants of reversibly reduced metal complexes can be obtained from polarographic measurements. In the reversible reduction or oxidation of an organic compound it is the pH of the supporting electrolyte that is most important. For such processes it is possible to obtain information concerning the occurrence and equilibrium constants of acid-base reactions involving the oxidized and reduced forms of the couple.

6. When a complex metal ion is reversibly reduced to a metal soluble in mercury, its half-wave potential is always more negative than that for the reversible reduction of the corresponding simple or aquo-complex ion. The difference being related to the free energy of dissociation of the complex. When complex formation takes place the half-wave potential is usually more negative when a metal ion is reduced to a lower oxidation state and when the product remains dissolved in the solution phase. The opposite effect is only occasional and when it takes place it signifies that the reduced complex is more stable than the oxidized one. Hydrogen ion is nearly always consumed in the reversible reduction of an organic compound, and as such the half-wave potential for such a process always becomes more negative as the pH is increased. It may remain constant over a certain range of pH values because of the influence of prior or subsequent proton transfer reactions.

7. Complex formation may cause the half-wave potential in the irreversible reduction of a metal ion to become either more negative or more positive. This depends on the nature of the ligand used. Example could be of nickel ion. The half-wave potential is -1.01 V vs. SCE in 0.1 F sodium per chlorate but no wave in ethylene diamine tetra acetate solutions. Where as in media containing thiocyanate or high concentration of halide, the half-wave potentials of nickel (II) are considerably more positive than -1.0 V. The reason being that these
ligands facilitate electron transfer and decrease activation energy involved in the reduction. The half-wave potentials for the irreversible reduction of an organic compound may also get affected by a chemical reaction with the supporting electrolyte. The example could be of carbonyl compounds. The half-wave potentials are altered by addition of ammonia or hydroxylamine, which converts them into imines or oximes. In the absence of any reaction with the supporting electrolyte the double layer effects and the liquid-junction potential can also produce changes in the half-wave potentials.

8. When there a change made in the supporting electrolyte concentration, the half-wave potential may be affected in irreversible waves. Where upon the rate of electron-transfer steps on equilibrium position of some fast chemical reaction that precedes it, could be the reason and also the potential difference between the electrode and that surface and thus the rate of electron transfer. The direction and magnitudes of these double-layer effects depend on the potential at which the wave occurs, on the nature of ionic medium, on the charge on the species actually reduced and on the mechanism by which the reduction occurs. In some cases the half-wave potential become more negative on increasing the salt concentration while in others it becomes more positive. Large shifts have been observed. It is therefore desirable to keep the nature and concentration of the supporting electrolyte nearly constant specially while studying irreversible processes. In studying the behaviour of an organic compound, the results can be obtained consistent by using buffers of identical ionic strengths [3].

9. In reversible waves, the effects of salt concentration on the half-wave potentials are due to mass-action effects on complex equilibria, changes of activity coefficients of the species involved in the half reaction and variations of liquid-junction potential [4]. All these can be referred to the data (5) on the half-wave potential of cadmium ion in nitrate solutions at ionic strengths up to 12 M.

10. In non-aqueous solutions having low dielectric constants, electroactive ions will be largely converted with ion pairs or higher ionic aggregates. In this, it may be pointed out that one consequence of the Stern double-layer theory is that the dielectric constant decreases rapidly as the electrode surface is approached, becoming as small as 2 or 3 or the electrode-solution interface even in an aqueous solution. The transient formation of an ion-aggregate under these condition has no effect on the half-wave potential of a reversible wave, but because it may alter the charge borne by the electroactive species it may affect that of an irreversible one.

References