

POLAROGRAPHY

The polarographic method of analysis has been developed by Jarsolov Heyrovsky, a Czech chemist in 1922, who received a Noble prize in chemistry in 1952. Since then this method has gain immense importance in analytical chemistry for determination of metal ions and other electroactive organic compounds.



Jarsolov Heyrovsky

The term polarography is applied to current -voltage curves when dropping mercury electrode is used as an indicator electrode. This method comes under the category called as **Voltammetry**.

Polarography is essentially an electrolysis on a microscale for the solution of substances in a concentration range of 10^{-6} to 10^{-2} M. the method is based on study of current- voltage relationship by using polarographic instrument.

The steadily increasing microvoltage is applied to a solution in polarographic cell having a saturated calomel electrode or a large mercury pool at the bottom of the cell which acts as anode and dropping mercury electrode as a cathode, current –voltage graph is obtained.

The nature of the graph measures amount of material and identify the nature of material present in solution.

Thus, qualitative and quantitative estimation can be done by using this method.

THE POLAROGRAPHIC APPARATUS

There are two main units of polarographic apparatus a plorographic cell and electrical instrument. Polarographic cells are of numerous types and different forms which are commercially available.

Simplest one consist of beaker type of glass cell with a lid. A large pool of mercury at the bottom of cell acts as anode terminal.

The lid has glass bend tubes for passing nitrogen gas and tip of dropping mercury electrode.

The dropping mercury electrode (DME) consists of a dropping funnel for mercury reservoir. It is connected to capillary tube of fine bore.

The effective glass capillary tube has a length of about 5-10 cm and a bore diameter of about 0.05 mm. the outer diameter of capillary tube may be 6-8 mm. the tip of capillary is cut fine and horizontal. The overall adjustment of DME is such that with the pressure of about 50 cm of mercury produces a drop weighing 6-10 mg in a full time of 3-6 seconds.

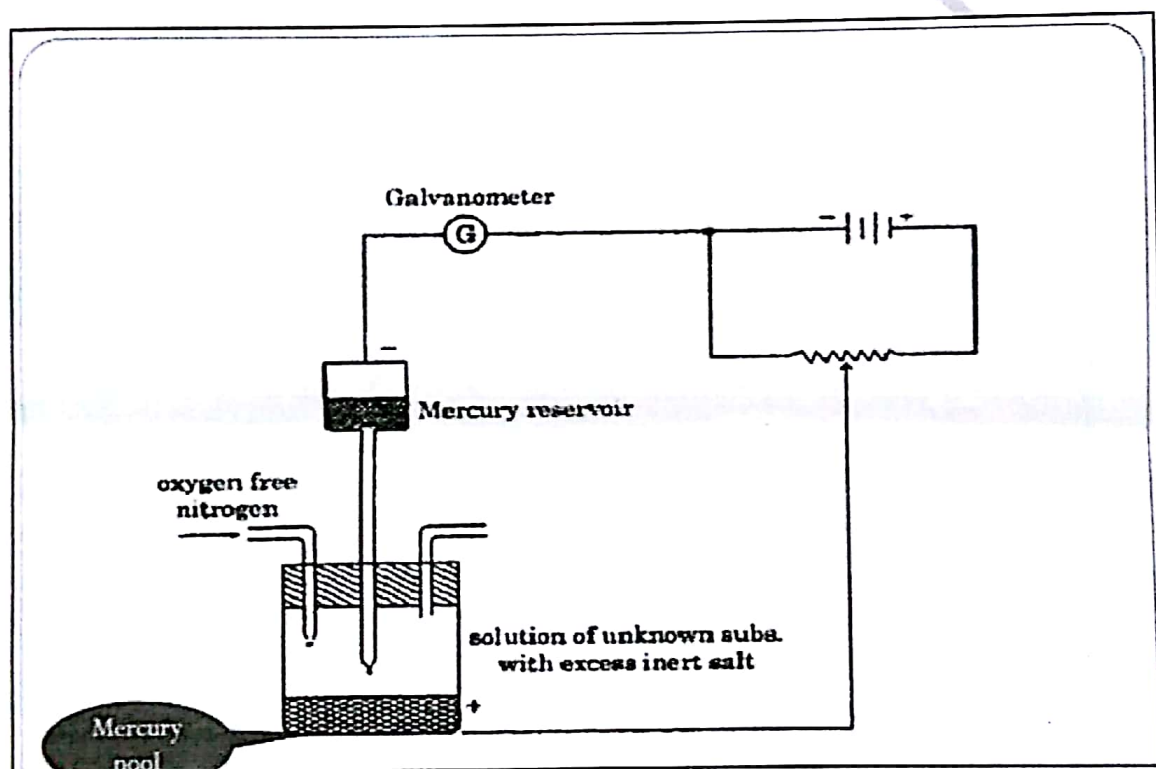


Fig1: Polarographic apparatus

The DME is fitted to the cell and the cell is mounted on a heavy stand on a platform free from vibrations.

The instrument part consists of standard power supply from battery, a variable potentiometer, EMF indicating Voltmeter, a Galvanometer for measuring the current.

Working of DME(POLAROGRAPHIC APPARATUS)

A solution to be analysed along with the solution of ground- inert electrolyte and maxima suppressor is placed in the cell. The anode and cathode are joined to positive and negative terminals of potentiometer.

This enables a variable potential difference to be applied between anode and cathode which is indicated by a voltmeter (V). the current flowing through the cell is indicated by Galvanometer(G).

Air is driven off by passing a current of nitrogen before the measurement of current –voltage.

The record of current- voltage is obtained by slowly increasing the applied voltage and measuring the current.

BASIC PRINCIPLE OF POLAROGRAPHY

Polarography is study of current voltage relationship using polarographic apparatus.

Let us consider a typical polarogram for a solution containing 10^{-3} M Pb^{2+} in 1 M KCl

(supporting electrolyte) and applying increasing negative potential.the polarographic wave is obtained as shown in following diagram:

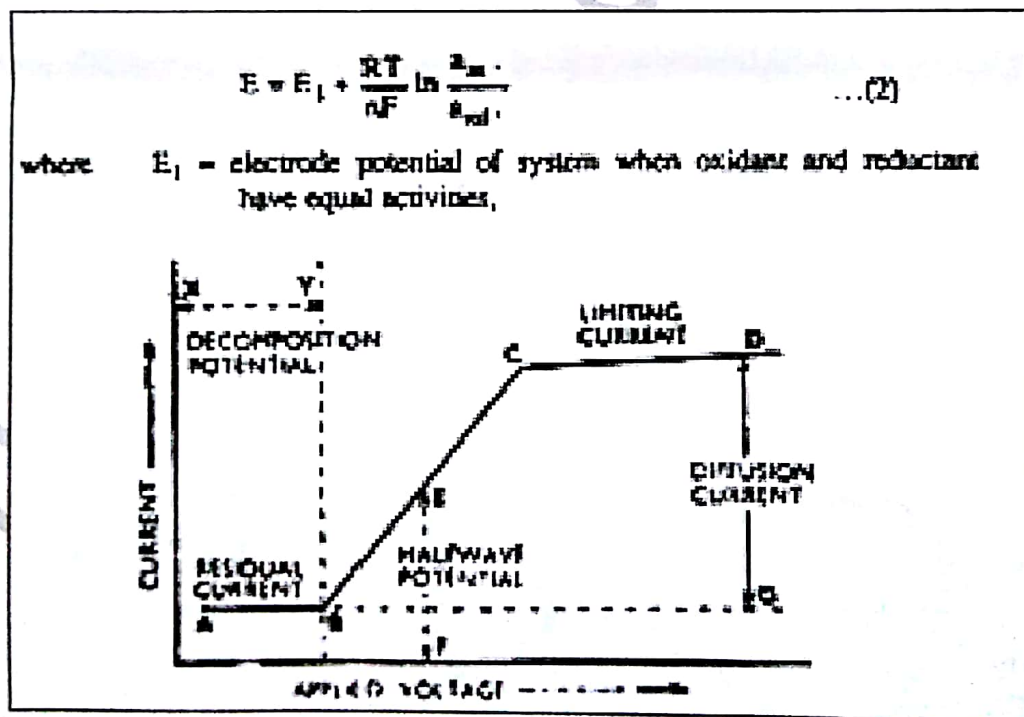


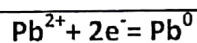
Fig 2 : polarographic wave

There is initially a small gradual rise in the current between A&B. it is known as residual current (i_r). as no electrolysis process takes place before the applied potential upto B, no current should flow through the galvanometer. This small background current is known as residual current. It sum of Faradic current (i_f) and condenser current (i_c).

The Faradic current is attributed to reducible impurities present in solution and the condenser current is because of the charge of each drop of mercury which carries the charge when it falls in the solution.

This background or residual current should be deducted for diffusion current measurements.

At point 'B' which correspond to the decomposition potential of electrolytes (Pb^{2+}). Electrolysis commences and ions (Pb^{2+}) move to the lectrode surface of DME an dget reduced.



At the potential between -0.3 and -0.5 V the current increases rapidly because of more lead ion from the solution carries the current. The ions get reduced to metal lead that forms amalgam with the mercury of DME. In this region of polarographic wave the electrode becomes depolarized. The current flows is the result of reduction of lead ion to give appropriate ratio of $[Pb \text{ amalgam}] / [Pb^{2+}]$ at lectrode surface.

At a point 'C' the corresponding voltage is **half-wave potential ($E_{1/2}$)**. At this point the concentration of oxidized and reduced forms at electrode surface is equal ($Pb^{2+} = Pb^0$). This potential is characteristics of nature of reducing substances and is used for identification of unknown substance.

The straight line DE is known as limiting current i_l reached.

The reducible ions are supplied to electrode surface by two independent forces:

1. A diffusion force which is proportional to the concentration gradient of electrode surface and bulk of solution (i_d).
2. Electrical force which is due to the opposite electrical charge of the ion. Thjis is also called as electrical migration (i_m).

$$i_l = i_d + i_m$$

if sufficient quantity of inert electrolyte (which is known as ground electrolyte or inert electrolyte) is added to the solution which reduces i_m to zero.

Thus, the current is limited to diffusion current. i.e. the substances reducing at electrode moves only due through thin diffusion layer because of concentration gradient.

THE ILKOVIC EQUATION

The diffusion current at the DME is given by Ilkovic equation:

$$I_d = 607 n D^{1/2} c m^{2/3} t^{1/6}$$

I_d = the average diffusion current during the life of drop, in amperes.

607 = a constant of various numerical factors including π , the faraday constant, density of mercury etc.

n = the number of electrons involved in the electrode reaction.

D = the diffusion coefficient of the substance in cm^2/sec

c = the concentration of substance in m.moles/litre.

m = the rate of mercury flowing through the capillary in mg/sec

t = the drop time in seconds.

The Ilkovic equation holds good for drop time of about 2 to 8 seconds.

For this the adjustment of capillary length and mercury pressure is made to bring the drop time within the range.

All factors are constant

$$I_d = k c$$

Where k is overall constant

Factors effecting variables in the Ilkovic equation:

1. The quantities m and t will vary with the capillary, its length and with the pressure of mercury.
2. It is important that the height of mercury column remains constant since the drop time depends upon the pressure exercised by the column of mercury at the tip of DME-solution interface.

3. Applied voltage causes changes in the surface tension, drop at the tip of electrode.
4. Temperature and viscosity changes should be minimum since it disturbs diffusion coefficient most.

ADVANTAGES OF DME:

1. It provides a smooth, fresh surface for the reaction.
2. Each drop remains unaffected and does not become contaminated by the deposited metal.
3. Mercury forms amalgam with most metals
4. Mercury has high hydrogen voltage.
5. Diffusion equilibrium is readily established at mercury solution interface.

DISADVANTAGES OF DME:

1. Surface area of mercury is never constant.
2. Applied voltage produces changes in surface tension and hence changes the droop size.
3. Mercury has limited applications in analysis of more positive potential range
4. Mercury is poisonous so care should be taken in its handling.

PRECAUTIONS:

1. The DME assembly should be mounted vertical on a heavy stand to be free from vibrations
2. Tip of DME should always be immersed in water when not in use.
3. Tip of DME should be cleaned by dipping in 50% nitric acid.
4. Pure and triple distilled mercury should be used in DME.
5. There should be sufficient mercury in reservoir so that pressure changes are negligible.

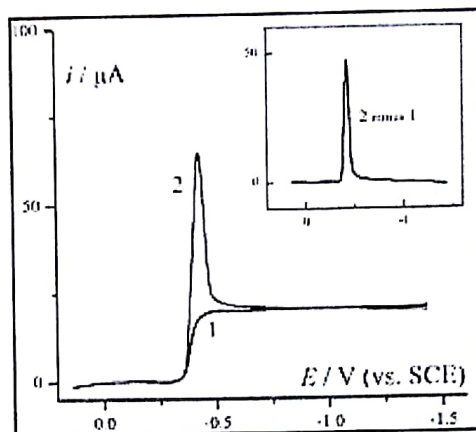
THE SUPPORTING ELECTROLYTE

The role of supporting electrolyte in polarographic analysis is to eliminate the influence of electrical migration on the reducing ions. The high concentration of inert supporting ions eliminates the attraction or repulsion forces between the electrode and the analyte. The inert electrolyte ions are not electrolysed at the applied potential range.

Potassium chloride, potassium nitrate or sodium chloride are often used for this purpose.

MAXIMA SUPPRESSORS:

In the polarographic studies, it is observed that instead of S-shaped polarographic wave there is a distortion. The wave shows a sharp peak or rounded hump.



- 1) 0.001 M lead nitrate solution with 0.01% gelatin as maxima suppressor.

The maxima suppressors form adsorbed layer on the aqueous side of mercury and prevents maxima. Care must be taken not to add too much of maxima suppressors otherwise diffusion current may be suppressed.

REMOVAL OF OXYGEN:

Dissolved oxygen is reduced in two steps, first to H₂O₂ and them to H₂O.



The interference of oxygen is eliminated by bubbling high-purity nitrogen through the solution for 5-10 min. A nitrogen atmosphere is maintained above the solution in cell while the polarogram is run.

QUANTITATIVE POLAROGRAPHIC METHODS:

1. Direct comparison method:

In the direct comparison method measurement of currents of standard solution of test ion with that of unknown or test ion is carried under the same condition of experiment. then using Ilkovic equation, the diffusion current quotient i_d/c can be found out.

2. Calibration curve method:

Various concentration of standard solutions are analysed for determining their diffusion current. A plot of diffusion current vs concentration is plotted. Diffusion current of unknown

sample is determined under the same conditions of experimentation of standard solution and concentration of unknown is found out.

3. Standard addition method

This is considered to be a very simple and reliable method in polarographic analysis. A polarogram of unknown solution with known volume is initially recorded. Then, an accurately measured quantity of standard solution of substance is added to another same quantity of test solution and second polarogram is run.

The concentration of unknown solution is found out from increase in the diffusion current using the formula.

$$C_1 = \frac{C_2 i_2 V_2}{V_1 (i_2 - i_1) + i_2 V_2}$$

Where C_1 , V and I are concentration, volume and diffusion current subscript 1 and 2 refers to test and standard solution respectively.

ANALYTICAL APPLICATIONS

Application of polarography is limited to those species both organic and inorganic that can be oxidized or reduced at electrode. Most of metal ions and many inorganic anions are readily determined alone as well as in mixture.

Polarographic method is applicable to several classes of organic compounds possessing:

1. Conjugated double bonds
2. Aromatic ring system
3. Carbonyl
4. Aldehyde
5. Nitro
6. Nitroso
7. Quaternary ammonium groups
8. Halogen groups

Many compounds which contain carbon-nitrogen, nitrogen-oxygen, sulphur-sulphur, carbon-sulphur bonds can be analysed polarographically. Drugs like acetazolamide, chlorthiazide, nitrofurantoin, chloramphenicol etc, are polarographically analysed.