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PHARMACEUTICAL ANALYSIS I

UNIT 5

TOPIC :

- **Polarography –** Principle, Ilkovic equation, construction and working of dropping mercury electrode and rotating platinum electrode, application

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Polarography

- Polarography is an electroanalytical technique used to determine the concentration of reducible or oxidizable substances in a solution by measuring the current–voltage relationship during electrolysis using a dropping mercury electrode (DME).
- Polarography is an electrochemical analysis technique used to determine the concentration of reducible or oxidizable substances in a solution. It was developed by Jaroslav Heyrovský in 1922, for which he was awarded the Nobel Prize in Chemistry in 1959.
- In polarography, a voltage (potential) is applied to an electrochemical cell containing the analyte, and the resulting current is measured. This current changes with the applied voltage and provides information about the nature and concentration of the analyte.
- The method uses a dropping mercury electrode (DME) as the working electrode, which provides a renewable surface and high reproducibility.

Principle of Polarography

→ Polarography is based on the **Ilkovic equation**, and it involves applying a **linearly increasing voltage** to an electrochemical cell and measuring the resulting **current** due to **reduction or oxidation** of the analyte at the working electrode.

Basic Principle:

- A dropping mercury electrode (DME) is used as the working electrode.
- A reference electrode (usually calomel) is used for potential control.
- A potential is gradually increased between the electrodes.
- As the potential reaches a level where the analyte is reduced or oxidized, a current flows.
- The resulting current vs. voltage (polarogram) gives information about the analyte.

Ilkovic equation

→ The Ilkovic equation is used in polarography, a method for analyzing substances by measuring the current that flows during the electrolysis at a dropping mercury electrode (DME). It relates the diffusion current to the concentration of the substance.

Ilkovic Equation : $i_d = 607nD^{1/2}m^{2/3}t^{1/6}C$

Where:

i_d = Diffusion current (in microamperes, μA)

n = Number of electrons involved in the electrode reaction

D = Diffusion coefficient of the depolarizer (cm^2/s)

m = Rate of mercury flow (mg/s)

t = Drop time of mercury (s)

C = Concentration of the depolarizer (mmol/L)

Key Points:

1. **Applicable to DME (Dropping Mercury Electrode)**:
   The Ilkovič equation is specifically derived for polarographic measurements using a DME.
2. **Diffusion Current (id)**:
   It is the limiting current observed when mass transport occurs only by diffusion and is directly proportional to the analyte concentration.
3. **Constant (607)**:
   The value 607 is a theoretical constant that applies when the units used are specific (e.g., μA for current, cm^2/s for diffusion coefficient, mg/s for mercury flow rate, etc.).
4. **Nature of the Equation**:
   It shows that the diffusion current depends on:

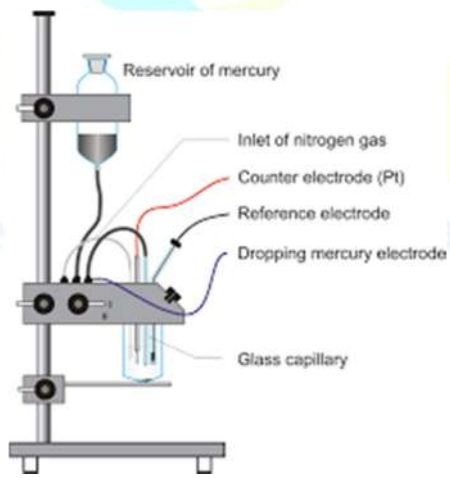
- The number of electrons (n) involved
- The diffusion coefficient (D)
- The concentration (C) of the species being analyzed
- The physical properties of the mercury drop (rate and time

Applications:

1. Quantitative analysis of metal ions.
2. Determination of drug concentration.
3. Used in research labs for studying electrochemical reactions.

Construction and working of dropping mercury electrode

→ A type of working electrode used in polarography, where mercury drops fall one by one into the electrolyte, providing a fresh surface for each measurement.



Construction of Dropping Mercury Electrode

→ The DME is designed to allow **mercury to drop slowly** through a fine capillary into the solution being analyzed. The construction includes the following parts:

1. Mercury Reservoir:

- A glass container filled with pure mercury (Hg).

- Mercury is used because it is liquid at room temperature, highly conductive, and chemically stable.

2. Fine Capillary Tube:

- A narrow glass capillary is attached at the bottom of the reservoir.
- The internal diameter of this capillary controls the size and frequency of mercury drops.
- Mercury flows drop by drop due to gravity.

3. Drop Tip / Outlet:

- The end of the capillary is submerged in the electrolyte solution.
- The mercury drop forms at regular intervals and falls into the solution.

4. Electrical Contact:

- A platinum wire or other conducting wire is inserted into the mercury reservoir.
- This connects the mercury to an external circuit (potentiostat or polarograph).

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Working of Dropping Mercury Electrode

Step-by-Step Process:

- ❖ Mercury drops fall continuously from the capillary into the solution.
- ❖ Each new drop provides a fresh, uncontaminated surface for the electrochemical reaction.
- ❖ A variable voltage is applied between the DME (working electrode) and a reference electrode (e.g., Saturated Calomel Electrode or SCE).
- ❖ As voltage increases, the electroactive substance in the solution (like metal ions) undergoes reduction at the mercury surface.

❖ This reaction causes a flow of electrons → current is produced.

❖ The current increases with voltage until it reaches a limiting value known as diffusion current (id).

❖ This current is recorded and plotted against the applied voltage to produce a graph called a polarogram.

Advantages of DME:

- ✓ **Fresh Surface for Every Drop** – prevents contamination and gives accurate results.
- ✓ **High Sensitivity** – suitable for detecting trace amounts of metals and drugs.
- ✓ **Smooth Polarograms** – due to regular and uniform drop formation.
- ✓ **Inexpensive and simple** setup compared to solid electrodes.

Limitations of DME:

- **Toxicity of Mercury** – Mercury is hazardous and requires careful handling.
- **Limited to aqueous media** – not suitable for many organic solvents.
- **Not suitable for oxidation reactions** – better suited for reduction reactions.
- **Short drop life** – each drop lasts only a few seconds, requiring continuous operation.

Applications of DME in Polarography:

- **Quantitative analysis** of metal ions like Zn^{2+}, Pb^{2+}, Cd^{2+}, etc.
- **Trace metal detection** in water, blood, or drug formulations.
- **Study of redox behavior** of organic and inorganic compounds.
- Used in **pharmaceutical quality control** and environmental analysis.

Construction and working of Rotating Platinum Electrode (RPE)

→A type of working electrode used in voltammetry to improve mass transport and provide a stable current during measurements.

Construction of Rotating Platinum Electrode

The Rotating Platinum Electrode is designed to rotate at a fixed speed, creating a controlled hydrodynamic environment. Its construction includes:

1. Platinum Disk:

- A small platinum disk (typically 1–5 mm in diameter) acts as the electrode surface.
- Platinum is chosen because it is:
    - Chemically inert
    - Good electrical conductor
    - Resistant to oxidation and corrosion

2. Electrode Body:

- The platinum disk is embedded in Teflon or glass insulation, forming a cylindrical electrode tip.
- The insulation prevents unwanted current from flowing except at the platinum surface.

3. Shaft or Rod:

- The electrode is attached to a metal or plastic shaft which allows it to rotate.
- The shaft provides a mechanical connection to the motor and an electrical connection to the circuit.

4. Motor Drive:

- A DC motor or AC motor rotates the electrode at a controlled speed (e.g., 100–3000 rpm).
- Speed control is essential to regulate mass transport to the electrode.

5. Electrical Connection:

- A wire runs through the shaft to connect the platinum surface to the potentiostat or measurement system.

Working of Rotating Platinum Electrode

Step-by-Step Explanation:

- The platinum disk is immersed in an electrolyte solution containing the electroactive substance.
- The electrode is connected to a voltage source (usually with a reference and counter electrode).
- As the electrode rotates, it creates a vortex in the solution, which pulls fresh analyte molecules continuously to the platinum surface.
- A redox reaction (oxidation or reduction) occurs at the platinum disk:

$$Ox + ne^- \leftrightarrow Red$$

- This movement enhances mass transport of ions, reducing concentration polarization and improving accuracy.
- The resulting current is measured — it is proportional to the concentration of the analyte.

Advantages of RPE:

- ✓ Stable and reproducible current due to controlled mass transport.
- ✓ Suitable for kinetic and mechanistic studies.
- ✓ Less affected by convection or random stirring.
- ✓ Ideal for electrocatalysis and enzyme-based sensors.

Limitations of RPE:

1. Requires motorized setup — more complex than static electrodes.
2. Surface cleaning of the platinum disk is necessary before use.
3. Not suitable for reactions involving mercury or unstable surfaces.

Applications of Rotating Platinum Electrode:

- Voltammetric analysis (e.g., linear sweep, cyclic voltammetry)
- Electrocatalysis studies
- Sensor development and enzyme kinetics
- Used in environmental, pharmaceutical, and biochemical analysis

Applications of Polarography

- **Pharmaceutical Applications:**
  - Used to determine drug concentration.
  - Detection of impurities in formulations.
  - Study of drug stability and degradation.
  - Analysis of vitamins, alkaloids, and antibiotics.
- **Environmental Analysis:**
  - Detection of heavy metals like Pb, Hg, Zn, Cd in water and soil.
  - Monitoring pollutants in industrial waste and river water.
  - Trace metal analysis in drinking water.
- **Biological and Clinical Use:**
  - Measurement of trace elements in blood, urine, and tissues.
  - Study of biochemical redox reactions.
  - Monitoring metal ion imbalance in metabolic disorders.
- **Industrial Applications:**

- Quality control in electroplating and metallurgy.
- Analysis of metal alloys and battery materials.
- Monitoring ion concentration in manufacturing processes.

- **Analytical and Research Use:**
  - Study of redox mechanisms and electrode reactions.
  - Used in kinetic and mechanistic studies of reactions.
  - Research on electrocatalysis and coordination compounds.
- **Food and Agriculture:**
  - Detection of metal contamination in food.
  - Analysis of pesticide residues.
  - Soil testing for micronutrient analysis.