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1. An Introduction of Polarography

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1.1 Introduction:

On February 10, 1922, Professor Jaroslav Heyrovsky carried out his pioneering experiment with a dropping mercury electrode from which polarography gradually evolved. Since then, polarography became a mature analytical method capable to adjust ever increasing demands on the sensitivity and selectivity and we believe that up to now mercury electrodes are among the best sensors for electroanalytical measurements[1,5]. Limits of determination gradually decreased from 10^{-5} M in the case of classical polarography[2], through 10^{-7} M for differential pulse polarography[3] to 10^{-11} M for adsorptive stripping voltammetry[4].

Development of mercury electrodes which proceeded from classical dropping mercury electrode[6] through mercury streaming electrode[7], hanging mercury drop electrode[8], static mercury drops electrode[9], mercury film electrode[10], mercury amalgam electrodes[11], mercury microelectrodes, chemically modified mercury electrodes[12], controlled growth mercury electrodes[13] and contractible mercury drop electrodes[14]. This process initiated by Professor Heyrovsky resulted in commercially available reliable mercury electrodes suitable for Nano molar and sub Nano molar concentrations. Further progress in this field can be documented by the above mentioned articles of Novotny and Kowalski and by papers of Gutz on versatile automatic mercury drop electrode[15-16].

Development of measuring techniques that proceeded from classical DC polarography[2], Through oscillopolarography[17], Kalousek's switcher[18], AC polarography[19], Tast polarography[20], Normal pulse polarography[21], Differential pulse polarography[22], Voltammetry[23], Cyclic voltammetry[24], Anodic stripping voltammetry[25], Adsorptive stripping voltammetry[26], Convolution techniques[27-28] and Elimination methods[29-30]. Development of preconcentration techniques on the surface of mercury electrodes enabling a substantial increase of sensitivity which proceeded from anodic stripping voltammetry and cathodic stripping voltammetry to adsorptive stripping voltammetry. The role of Professor Heyrovsky in the development of these methods cannot be underestimated. According to Zuman[31] the main contribution of Professor Heyrovsky consists in:

- Recognition of the importance of potential and its control;
- Recognition of analytical opportunities offered by measuring the limiting currents;
- The introduction of dropping mercury electrode as an invaluable tool of modern electroanalytical chemistry.

1.2 Principle of Technique:

Polarography is based on the unique characteristics of the current-voltage curves obtained with dropping mercury electrode, which was first introduced by Kucera[32] for electro capillary studies. In 1934 Ilkovic[33] derived an equation for the resulting constant. It deals with the measurement and interpretation of current-voltage curves when solution of electroactive substances is electrolyzed in a cell in which one electrode is polarisable i.e. mercury falling gravitationally drop wise from fine bore of capillary glass tube, while the other electrode remains non polarisable (saturated calomel electrode). Since the curves are graphical presentation of the dropping mercury electrodes, the apparatus is called ‘polarograph’ the curves as polarograms and technique is named as polarography. Thus, it is one of the most essential key to chemical analysis. The flow of current in the electrical circuit is observed only when the voltage is applied to electrodes changes at constant rate, raises the potential of a depolarizer present in the solution 10^{-5} moles/liter range. The current increases with the increasing negative potential of the electrode and during this time the concentration of the depolarizer on the surface of electrode decreases. When this concentration decreases to zero, current reaches to a constant value depending on the rate of depolarizer transport to the surface of electrode. In these conditions we have the maximum current which is often called limiting current.

Advantages of Dropping Mercury Electrode:

There are several advantages of the dropping mercury electrode.

- Each drop falling from the electrode exactly duplicates the behavior of the one that preceded it. This is because successive drops are born into solution of identical time, grow at a same rate and reach at the maximum size. Consequently, the currents are accurately reproducible from one drop to next.
- Solid products cannot accumulate on the electrode surface, changing its properties as it is possible with solid electrode.
- It is much less sensitive to mechanical disturbance than stationary electrode.
- High over potential of reduction of hydrogen ion or water on a mercury surface makes it to investigate processes that can occur only under strongly reducing conditions.

1.3 Applications of Polarography:

Polarography can be extensively applied in the field of inorganic analysis[34], organic chemistry[35], pharmacy[36], metallurgy, geology and archaeology[37], polymer chemistry[38], colloids and surface active substances[39], food chemistry[40], petroleum and fuel analysis[41], Trace analysis[42], rare earth analysis complex studies[43], trace determination of drugs[44-48], quantitative and qualitative analysis of organic compounds including drugs[49-54].

1.3.1 Analysis of Organic Compounds by Polarography:

Polarography has contributed significantly to the understanding of processes involved in the electrolysis of organic compounds. In organic chemistry, polarography can be used in the determination of equilibrium and rate constants, in studies of reaction mechanism, in the search of optimal conditions for some preparative reactions, in studies and comparisons of reactivity's of organic compounds and in correlations of structure with polarographic data.

From polarographic curves, identification of electrolysis with other methods may be used for elucidation of organic electrode process. Many organic functional groups undergo reduction or oxidation at dropping electrode and thus led themselves to polarographic determination. In general, the reactions of organic compounds at the dropping electrode are slower and are often more complex than those of inorganic ions; nevertheless, polarographic investigations can be useful for structure determination and for qualitative and quantitative analysis.

Reactions of organic substances at the dropping electrode usually involve hydrogen ions; a typical reaction can be represented by the equation.

$$R + nH^+ + ne^{\ominus} \rightleftharpoons RH_n$$

Where RH_n is the reduced form of the reducible compound R. As hydrogen ions (supplied from the solution) are involved in the reaction, the supporting electrolyte must be well buffered. Change in the pH of the supporting electrolyte may even lead to the formation of different reaction products. Thus, in slightly alkaline solution, benzaldehyde is reduced at -1.4 volts with formation of benzyl alcohol, but in acid solution (pH < 2), reduction takes place at –1.0 volts with formation of hydrobenzoin:

$$\boxed{2C_6H_5CHO + 2H^+ + 2e^{\ominus} \rightleftharpoons C_6H_5CH(OH)CH(OH)C_6H_5}$$

Some organic compounds can be investigated in aqueous solution. It is frequently necessary to add an organic solvent to improve the solubility. Suitable water miscible solvents include ethanol, methanol, ethane-1,2-diol, dioxane, acetonitrile and acetic acid. In some cases, a purely organic solvent must be used and anhydrous materials such as acetic acid, formamide and diethylamine have been employed. Suitable supporting electrolytes in these solvents include lithium perchlorate and tetra-alkyl ammonium salts R_4NX (R = ethyl or butyl; X = iodide or perchlorate).

The following functional groups can be expected to react at the dropping electrode.

C=C (When conjugated with another double bond or an aromatic ring), C≡C (when conjugated with an aromatic ring), C–X (X = halogen), C=O (aldehydes, ketones, quinones), dicarboxylic acids in which the carboxyl groups are conjugated with each other, Peroxides, epoxides, C=N, Nitro, nitroso, azo groups, heterocycles with two or more nitrogen atoms in the ring, C=S, S–S and S–H (mercaptans give an anodic wave).

1.3.2 Polar Graphic Study of Metal Complexes:

The chemistry of metal complexes is undergoing a period of a rapid development and engaging the attention of many researchers. Its progress has received an added impetus due to its several applications in chemical, industrial, agricultural, biological and technological fields. Metals that are essential for plant growth and animal nutrition have been found to form complexes with materials present in organisms. Metal-chelate formation also plays significant role in the functioning of enzymes and processes like moderate dyeing in the textile industry and the tanning process as in the leather industry. Their applications in inorganic analysis are of many folds and include detection, determination, purification and solvent extraction through complex formation. Complex forming reagents are extensively applied masking agents in various titrimetric, spectrophotometric, polarographic, chromatographic and electrophoresis methods.

Historically, credit to study inorganic complexes by polarography goes to the pioneering work of Stackelberg, Frey-hold[55] and Lingane[56]. The classical method of analysis was thoroughly discussed by Kolthoff and Lingane[57] in the monograph on polarography and related electrochemical techniques which resulted in remarkable progress and is now extensively used in the study of complexes in solutions. Some of the general developments are presented and discussed by Irving[58], Koryta[59], Westwood and Crow[60-62] in their publications. Excellent reviews have also been published by Vlcek[63-64] on relation between electrochemical reactivity and structure of inert complexes. A beautiful review has also been written by Tamamushi and Sato[65]. The contribution of Lingane, Deford and Hume[66], Ringbom and Erikson[67-68], Kacena and Matousek[69] Schwarzenbach[70-71], Buck[72], Butler[73], Macovsch[74] and Crow are there for study of metal complexes. Schapp and MacMasters[75] have extended Deford and Hume's treatment for study of mixed ligand complexes in solution.

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