CHAPTER - 1

Introduction, Review and Theoretical Aspects of Cyclic and Stripping Voltammetry
1.1 Introduction

Electrochemistry is a branch of chemistry which deals with the study of chemical reactions that take place in a solution at the interface of an electron conductor (the electrode, composed of a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involves electron transfer between the electrode and the electrolyte or species in solution. A process of this kind can always be represented as a chemical reaction and is known generally as an electrode process. Electrode processes take place within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions [1].

Voltammetry is a category of electroanalytical methods used in analytical chemistry and various industrial processes. In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied. The relationships between electrochemistry and molecules (molecular systems or materials, biomolecules) have expanded extensively, opening new opportunities to export concepts and techniques toward other sections of science such as photochemistry, the science of chemical reactivity and biochemistry. Elements of molecular and biomolecular electrochemistry provides a more complete coverage of these topics and advances than can currently be found in any other resource [2].

Cyclic voltammetry is the most versatile electro analytical technique for the study of electroactive species. It is used in all fields of chemistry as a means of studying redox
states. The electrode potential at which a drug, a metal ion or complex or some other compound undergoes reduction (acceptance of electrons) or oxidation (removal of electrons) can be rapidly located by cyclic voltammetry (CV). A very important aspect of CV is its ability to generate a new redox species during the first potential scan and then probe the species fate on the second and subsequent scans. CV is therefore a powerful kinetic probe monitoring reactive species. Since the rate of potential scan is variable, both fast and slow reaction can be followed [3]. Electron transfer plays fundamental role in governing the pathway of chemical reactions. Measurement of speed of the electron transfer process and the number of electrons involved are difficult in traditional experimental methods like spectroscopy [4].

Electrochemical studies of biologically active compounds serve to elucidate biological processes and their inter-relationships that are involved in living organisms [5-8]. An attempt has been made to study the electrochemical properties and of compounds, which plays an important role in biochemical redox reactions in various organisms. The primary objective of developing these cyclic voltammetric techniques was analytical, both qualitative as well as quantitative.

1.2 Basic principles

The most common experimental configuration for recording cyclic voltammograms consists of an electrochemical cell that has three electrodes, i.e., counter or auxiliary electrode (C), reference electrode (R), and working electrode (W), all immersed in a liquid and connected to a potentiostat. The potentiostat [9] allows the potential difference between the reference and working electrode to be controlled with minimal interference from IR (ohmic) drop. In this configuration, the current flowing
through the reference electrode also can be minimized thereby avoiding polarization of the reference electrode and hence keeping the applied potential distribution between the working and reference electrode stable.

Positioning the reference electrode (or Luggin probe [10]) close to the working electrode further helps to minimize the IR drop between the reference and working electrode due to the resistivity of the solution phase. Instrumental methods, based on positive feedback or other circuitry, for compensation of uncompensated resistance are also available [11-13].

1.2.1 Fundamentals of Cyclic Voltammetry

Voltammetry is the electrochemical technique in which the current at an electrode is measured as a function of the potential or voltage applied to the electrode. The potential is varied in some systematic manner and the resulting current-potential plot is called ‘voltammogram’. CV consists of cycling the potential of an electrode that is immersed in an unstirred solution and measuring the resulting current. The potential of this working electrode is controlled relative to a reference electrode such as saturated calomel electrode (SCE) or silver-silver chloride electrode (Ag/AgCl). The controlling potential can be considered as an excitation signal [14].

In cyclic voltammetry, the potential is scanned linearly from an initial value, $E_{\text{initial}}$, to a second value and then back to $E_{\text{initial}}$ (or some other final potential). This potential excitation signal is illustrated in Fig. 1.1, for a scan from +1.0 to +0.2 V versus the reference electrode, which in this case is a silver-silver chloride electrode (Ag/AgCl). At a potential of +0.2 V vs Ag/AgCl, the potential scan direction is reversed, returning back to the original potential of +1.0 V. One or more potential cycles can be performed, hence the term cyclic voltammetry [15]. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current ($i_{pa}$), the cathodic peak
current ($i_{pc}$), the anodic peak potential ($E_{pa}$) and the cathodic peak potential ($E_{pc}$). The voltammogram is a display of current (vertical axis) versus potential as shown in Fig 1.2.

The peak potentials supply information about the identity of the analyte and the kinetics of the oxidation/reduction process. The peak currents supply information about analyte concentration and the stability of the electro generated species.

1.2.2 Applications of Cyclic Voltammetry

CV has become a very popular technique for electrochemical studies of new systems, and has proved as a sensitive tool for obtaining information about fairly complicated electrode reactions [16, 17]. CV methods have found to have extensive applications for the evaluation of thermodynamic and kinetic parameters such as number of electrons change (n), heterogeneous rate constant ($k_0$), entropy (S), Gibb’s free energy (G) and diffusion coefficient ($D_0$) etc., of a number of redox reactions and associated chemical reactions. These methods are especially useful in both oxidation and reduction process and to study the multiple electron transfer in an electrochemical reaction [18].

Much intensive research is in progress with the additional regular analytical applications. CV studies in rat brain [19], in vivo studies in animals [20], bacteria [21] and even plants [22, 23] are picking up. With the introduction of newer electrode material of very small size [24], these methods of chemical analysis in living systems might grow even faster. CV studies of fused salts and solid electrolyte [25] might prove very useful for trace analysis. Voltammetric detectors may also find increasing applications in chromatography [26, 27]. This is an example of situation where an analytical tool of great importance also supplements the applicability of another analytical tool of great scope.
1.2.3 The working electrodes

The working electrodes are classified into four types; inert electrodes, reactive electrodes, photo excitable or semiconductor electrode and synthesized or chemically modified electrodes. Hg was the most popular working electrode [28]. Since it easily dissolves anodically, Hg is not suitable in anodic regions. For such processes Pt. is the electrode of first choice and it provides a very wide potential region. A few other metallic electrodes such as boron nitrides and some carbides were introduced into electrochemistry [29]. However, either because of poor reproducibility or high electrical resistivity, these electrodes were not very successful. A number of carbon electrodes have been introduced into voltammetric studies [30]. These electrodes have a very wide anodic as well as cathodic potential region, both in aqueous and non-aqueous solvents. Carbon paste made of graphite powder and mineral solvent was one of the earliest inert electrodes introduced into the electrochemistry [31]. The vitreous or glassy carbon electrode introduced into electrochemistry is the most widely used carbon electrode material today [32]. Its high mechanical stability, low porosity, inertness over a wide potential region and good conductivity and reproducibility are some of the reasons for its very wide applications.

Recently a variety of chemically modified electrodes (CME's) have been studied using cyclic voltammetry. Also, there are many premier laboratories using CV as a tool to help design biosensors. Glassy carbon was first used as an electrode material by Zittel and Miller [33] and many workers continue to use the electrode. The properties of glassy carbon have been described by Yamada and Sato [34].
1.2.4 Chemical Nature of Carbon Surfaces

Carbon is a natural field in which covalent bonds are planted for modification of electrodes. To understand this it is necessary to appreciate the basal plane-edge structure of carbon. Graphite carbon consists of giant sheets of fused aromatic rings, stacked coplanarly. An uninterrupted basal plane surface is nonionic, of low polarity, hydrophobic, and rich in pi-electron density. The population of chemical functionalities is low and probably concentrated along surface imperfections exposing edge plane. Without alterations the carbon basal plane is rendered barren to synthetic coupling reactions. On the other hand, the high pi-electron density is conductive to strong chemisorptive interactions, especially with unsaturated compounds, including aromatic types. This adsorptive property has been put to good use by Anson and colleagues [35 - 40] and Yeager and co-workers [41 - 43] on basal plane pyrolytic graphite surfaces for chemisorptive electrode modification.

Carbon as a material can be obtained in a wide variety of physical and chemical forms: graphite single crystal crystals, pyrolytic graphite, highly oriented pyrolytic graphite (HOPG), glassy (vitreous) carbon, compacted polycrystalline structures of varying porosity such as high density spectroscopic rods, powders, whiskers, fibers, yarn, cloth, fullerenes, carbon nanotubes and so on, each being available in different shapes and grades, and each with some elements of irreproducibility from sample to sample associated with the nature of its preparation and its supplier.

1.2.5. The auxiliary (counter) electrode

In voltammetric studies, the current flows between the working and counter electrode. Although the main interest is on the working electrode, it must be ensured that
the counter electrode does not complicate the matters. It must not dissolve in the medium. The reaction product at the counter electrode must reach or react at the working electrode. Platinum electrodes meet most of these requirements and this is the most widely used counter electrode in aqueous, non-aqueous as well as molten salt media. Platinum electrodes in the form of coils or thin foils are normally used. Carbon electrodes are also used in molten salts. The electrode area must be sufficiently larger than the working electrode area to ensure that the area of the counter electrode does not control the limiting current [44].

1.2.6 The reference electrode

The general requirement of a reference electrode is very simple. Its potential should not vary when the external potential is applied in the working electrode-reference electrode system of the cell. It must also be chemically stable. There is number of electrode reactions which possess these physicochemical properties [45 - 47].

The most popular reference electrodes, however, are the so-called electrodes of the second kind where the equilibrium electrode potential depends on an ion that does not directly involve in an electrode reaction. In the most widely used saturated calomel electrode (SCE), for example, the Hg is in contact with Hg2Cl2/KCl paste, which is in contact with a saturated KCl solution. The electrode reaction is Hg^+/Hg reaction but because of the low solubility of Hg2Cl2, the electrode potential depends on Cl^- concentration. The electrode potentials of such electrodes can very easily be maintained at a constant value. The Hg/Hg2SO4, Ag/AgCl and Hg/Hg2O electrodes also belong to this group [48, 49].
1.2.7 Chemically Modified Electrode

There has long been interest in electrochemistry in the occurrence and consequences of adsorption of ions and molecules on electrode surfaces. Adsorption can have both desirable and deleterious consequences, and adsorption research has been adjacent to numerous fundamental insights into the electrical double layer and the kinetics and mechanisms of electrochemical reaction. Adsorbed layers of molecule or ions can accelerate or retard electrode reaction rates can lead to passivation of electrodes to corrosion processes or promote them, as in the case of so called brighteners influence of the morphology of electro deposition reactions, can interfere with or be the basis of electro analytical measurements, among others. A great deal of information as accumulated on what species adsorbed on various electrodes, types of electrode materials, and from what solvents and electrolyte media. In some instances the adsorption phenomena are rationally explainable based on chemical reactivity or solubility grounds, adsorption of simple metal complexes on mercury electrodes being a case in point [50, 51]. However, to a substantial extent, the discovery of an adsorption phenomenon is an empirical event, and exploitation of it for useful purposes has had few systematic or fundamental origins.

Chemically modified electrodes diverge sharply from the traditional field of adsorption on electrode surfaces. The most essential difference is that one deliberately seeks [52-55] in some hopefully rational fashion to immobilize a chemical on an electrode surface so that the electrode thereafter displace the chemical, electrochemical, optical, and other properties of the immobilized molecule(s). The connotation flowing from this statement is that one selects immobilized chemicals on the basis of known and
desired properties, to be, for instance, fast outer-sphere electron transfer agents, chiral centers, electron transfer mediator- catalysts for a valuable substrate reaction, functionalities which scavenge trace molecules or ions from solutions for analysis in preconcentrated form, photosensitizers for a semiconductor electrode, corrosion inhibitors, and so on. That is, the electrode can be tailor-made to exhibit these properties. The electrochemical reactions of immobilized chemicals are also special; since these species are confined to the electrode surface, they provide an opportunity to study the basics of electrochemical reactions. These are the ideas and motivations associated with much of the recent and dubbed variously chemically modified such as derivatized, functionalized, electro statically trapped, and polymer coated.

STRIPPING VOLTAMMETRY

1.3. Introduction

The technique electrochemical stripping analysis is a combination of an effective accumulation step with an advanced measurement procedure results in a very low detection limit, and makes stripping analysis is one of the most important techniques in trace analysis [56].

The term anodic stripping voltammetry (ASV) was used first for the cathodic accumulation of metals as an amalgam followed by their anodic determination [57]. The term cathodic stripping voltammetry (CSV) was used first for the indirect determination of organics as mercury salts, involving anodic oxidation of mercury and subsequently cathodic reduction of the mercury ion [58]. The term 'stripping' used in naming the original technique, anodic stripping voltammetry, describes exactly the process that is occurring during the voltammetric scan [59].
1.3.1. Principles of Stripping Voltammetry

There are three important stages in a stripping experiment: Electrodeposition, rest period and stripping [60] as shown in Fig 1.3 and 1.4.

**Step 1. The electrodeposition step** - The metal ions $M^{n+}$ or electroactive species of interest are deposited (preconcentrated) electrochemically into or onto the surface of an electrode (usually a mercury film electrode or a hanging mercury-drop electrode, in the form of amalgam, $M$ (Hg): A short-time electrolysis (30 sec to 5 min) in a stirred solution and at a potential suitable for the reduction of the ions of interest ($E - E_{1/2}$ about -200 mV) may result under proper conditions in a fairly concentrated amalgam. This step is called the electrodeposition step. The concentration of the metal ion in the film depends on concentration of $M^{n+}$ in solution, time of electrolysis and rate of stirring. Since the electrodeposition is carried out on small electrodes, the amount of material deposited into it usually does not change significantly the concentration of the metal ions $M^{n+}$ in the solution.

**Step 2. Rest period** - After a predetermined time, the stirring of the solution is turned off. The solution is allowed to become quiescent and the concentration of the metal in the amalgam - to reach uniformity. The rest period extends for about 30 sec, during which the applied potential remains unchanged, thus ensuring that no re-oxidation of the metal by traces of oxygen takes place.

**Step 3. Stripping** - After the preconcentration step, the deposited metal $M$ is oxidized ("stripped") from the mercury or the working electrode back into the solution by oxidation to the ionic form under conditions of diffusion control, using one of the voltammetric methods.
1.4. Objective and Scope of the Thesis

The present thesis is aimed at investigating the electrochemical studies and elucidation of sequence of electron transfer and chemical reactions that occur at or near the electrode surface. The aspects investigated are: reversible/irreversible or coupled nature of electron transfer, number of electrons involved, effect of the concentration of the electroactive species on the redox pathway, effect of variation of supporting electrolytes, nature of the product formed, effect of pH, effect of surfactants on the electrochemical process of oxidation and reduction, etc.

In this thesis, more emphasis has been given not only to the redox behaviour of biologically relevant organic compounds but also to the versatile use of carbon paste and modified carbon paste electrodes. Modification of the electrodes successfully carried out by using fullerene and carbon nanotubes. Further, these electrodes exploited in the qualitative and quantitative detection of biologically important compounds.

This thesis addresses the electrochemical studies of dopamine at fullerene and carbon nanotubes modified carbon paste electrodes. The procedure for the simultaneous determination of adenine and guanine, dopamine and ascorbic acid were standardized.

The electrochemical behavior of theophylline at unmodified carbon paste electrode and multi-wall carbon nanotube paste electrodes has been studied. Oxidation of theophylline was carried out in different electrolytes viz., KCl, B-R buffer and phosphate buffer solution.

This thesis also aims at the simultaneous determination of trace metal ions at HMDE by stripping voltammetry. Trace metal ions like Cu, Pb, Cd, Zn, Co and Ni were
determined in medicinal plant leaves of Western Ghats and in Tunga river water using stripping voltammetry.

Fig. 1.1. Typical excitation signal for CV-triangular potential waveform with switching potential at 1.0 V to 0.2 V vs. Ag/AgCl.

Fig. 1.2. Typical cyclic voltammogram of 2.0 mM K₃Fe(CN)₆ with 1.0 M KNO₃.
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![Diagram](image)

**Fig. 1.3.** Principle of stripping voltammetry (anodic). Relation between stripping voltammograms and corresponding idealized polarogram.

**Fig. 1.4.** The sequence of steps of the stripping analysis.
1.4. References


